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Synthesis, structure and reactivity of homo- and hetero-polynuclear complexes of platinum bearing C≡CR groups as unique bridging ligands

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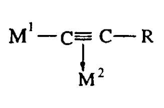
Recent advances in the preparation of bi- or poly-nuclear platinum complexes bridged only by alkynyl ligands are described. Emphasis is placed not only on the co-ordination modes of alkynyl ligands but also on their migration and chemical activation.

The chemistry of organometallic complexes containing two or more transition metals has progressed rapidly over the last years.[1] The interest in such complexes stems not only from their intriguing structural diversity but also from their potential catalytic activity.[2] Complexes incorporating unsaturated hydrocarbon ligands as bridges between metal atoms are particularly interesting[3] because of the enhanced and possibly unique activation of the organic substrates which cannot be achieved by a monometallic centre. Although this metal–metal co-operativity has elicited most interest in this area, little is known of the functions of the different metals involved. Consequently, studies on even the simplest dinuclear systems can improve our understanding of concepts that range from the nature of the metal–metal or the different metal–ligand interactions to ligand mobilities around the bimetallic core.

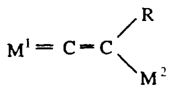
Among the unsaturated hydrocarbons used to bridge metal centres increasing attention has been paid to alkynyl ligands in recent years. This interest mainly arises from the favourable electronic and structural features of C≡CR ligands *via* σ or σ–π networks which can be modulated by varying both or either of the R substituents and the metal centres, and from a wish to gain better knowledge of the frequently observed ligand-based coupling and oligomerization reactions.[4] Complexes with bridging alkynyl ligands are also of interest as possible models for reactive intermediates on heterogeneous catalyst surfaces[5] and for the unusual material properties of designed ynyl-based oligomers and polymers.[3d,e,6] Several reviews dealing with aspects related to the chemistry of alkynylmetal complexes have recently been published.[3e,f,7]

The chemistry of σ-alkynyl mononuclear platinum complexes has long been the subject of intensive study[7a] and recently there has been growing interest in the preparation of polymetallic derivatives based on linear or cross-conjugated σ,σ-bis(alkynyl)- and σ-alkynyl-substituted (bipyridyl, terpyridyl, ferrocenyl) building blocks as possible candidates for non-linear optical, low-dimensional, conducting, luminiscent and liquid-crystalline materials.[3e,6c,7a,8] However, the chemistry of homo- and hetero-polynuclear platinum compounds containing monoanionic μ-C≡CR bridging ligands has been developed to a relatively lesser extent. In addition, while complexes containing additional bridging ancillary ligands [bis(diphenylphosphino)-methane, 2-(diphenylphosphino)pyridine] are relatively common,[3f,9] derivatives bearing μ-C_2R groups as unique bridging ligands are quite rare.[10]

In this article we will describe the chemistry recently developed in our group in order to prepare di- or poly-nuclear platinum complexes containing only bridging alkynyl ligands between the metal centres. Complexes with bridging alkynyl ligands can be formed when alkynyl substrates containing linear M^1–C≡CR arrangements are combined with adequate electrophilic metal centres or derivatives containing potential leaving ligands (M^2). This is the case in several of the reactions discussed here. In the final products the structural features of the μ-C_2R ligands can be explained in terms of a resonance hybrid of three canonical structures, *i.e.* the metal-substituted η^2-alkyne form (μ-$\eta^1:\eta^2$, **A**), metal-substituted η^1-vinylidene structure (**B**) and the symmetrically bridging structure (μ-$\eta^1:\eta^1$, **C**).



A



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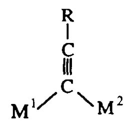

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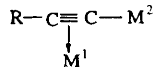


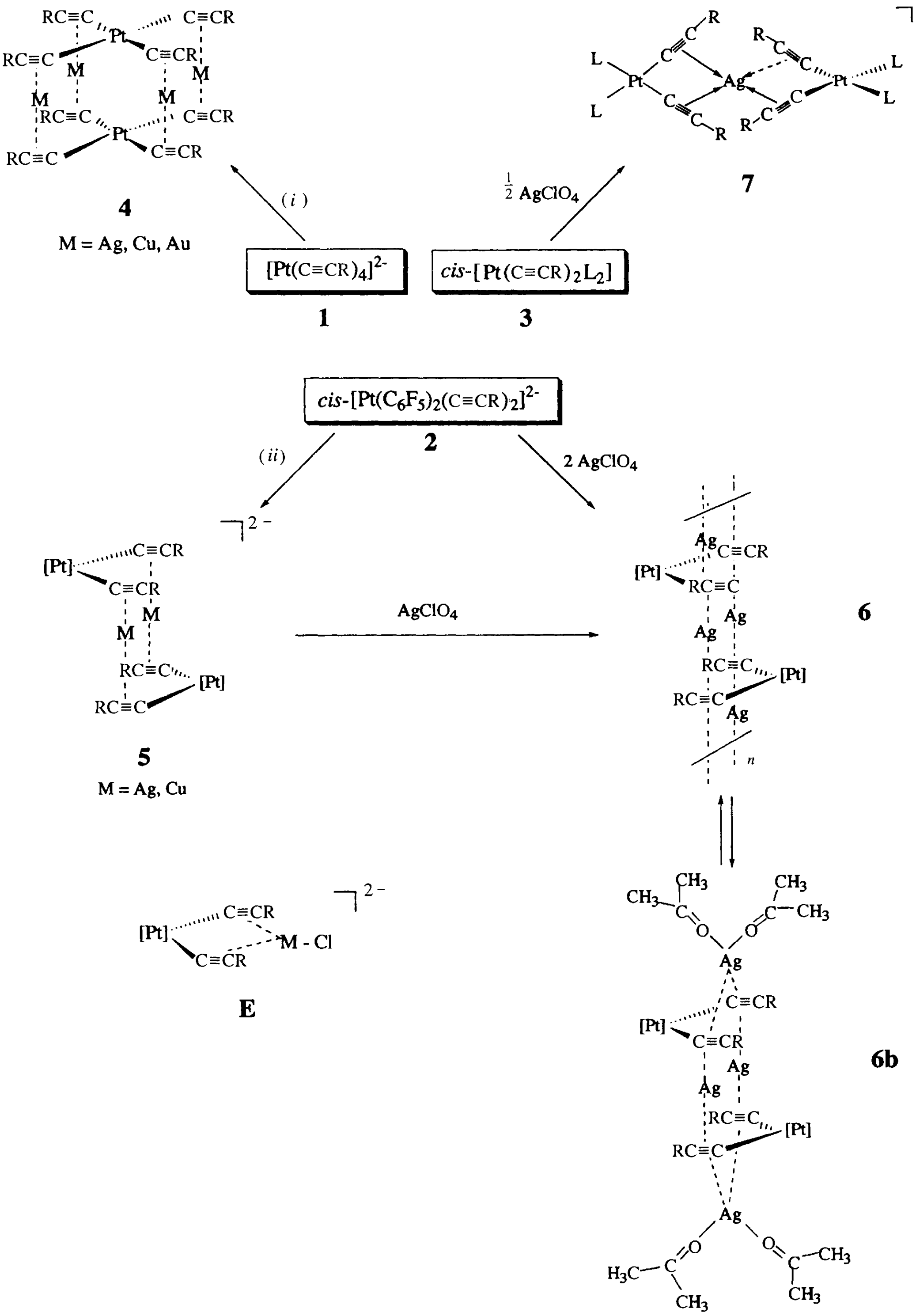
D

The structures lie, in most of cases, between the extremes **A** and **C** or **A** and **B** but closer to **A**. Electronic features of the metal centres and/or steric requirements of the R substituents can, however, in some instances, determine a site preference with respect to σ and π co-ordination modes of the C≡CR groups and during the course of the reaction a σ-alkynyl migration can take place (**D**). Thus, in the following discussion emphasis will be placed on the nature of the metal–alkyne interactions and on the alkynyl migration reactions. This latter feature seems to play a key role in some surprising results found with the electrophilic fragment '*cis*-$Pt(C_6F_5)_2(CO)$' which provides a new entry into the chemistry of μ-ethynediyl and μ-vinylidene diplatinum complexes. Most of the complexes described have been prepared starting from alkynyl mononuclear platinum precursors (anionic or neutral) either with cationic or neutral electrophilic metal fragments.

Heteropolynuclear Pt–Ag, Pt–Cu or Pt–Au Complexes

(*a*) Examples with only alkynyl fragments bonded to Group 11 metal centres

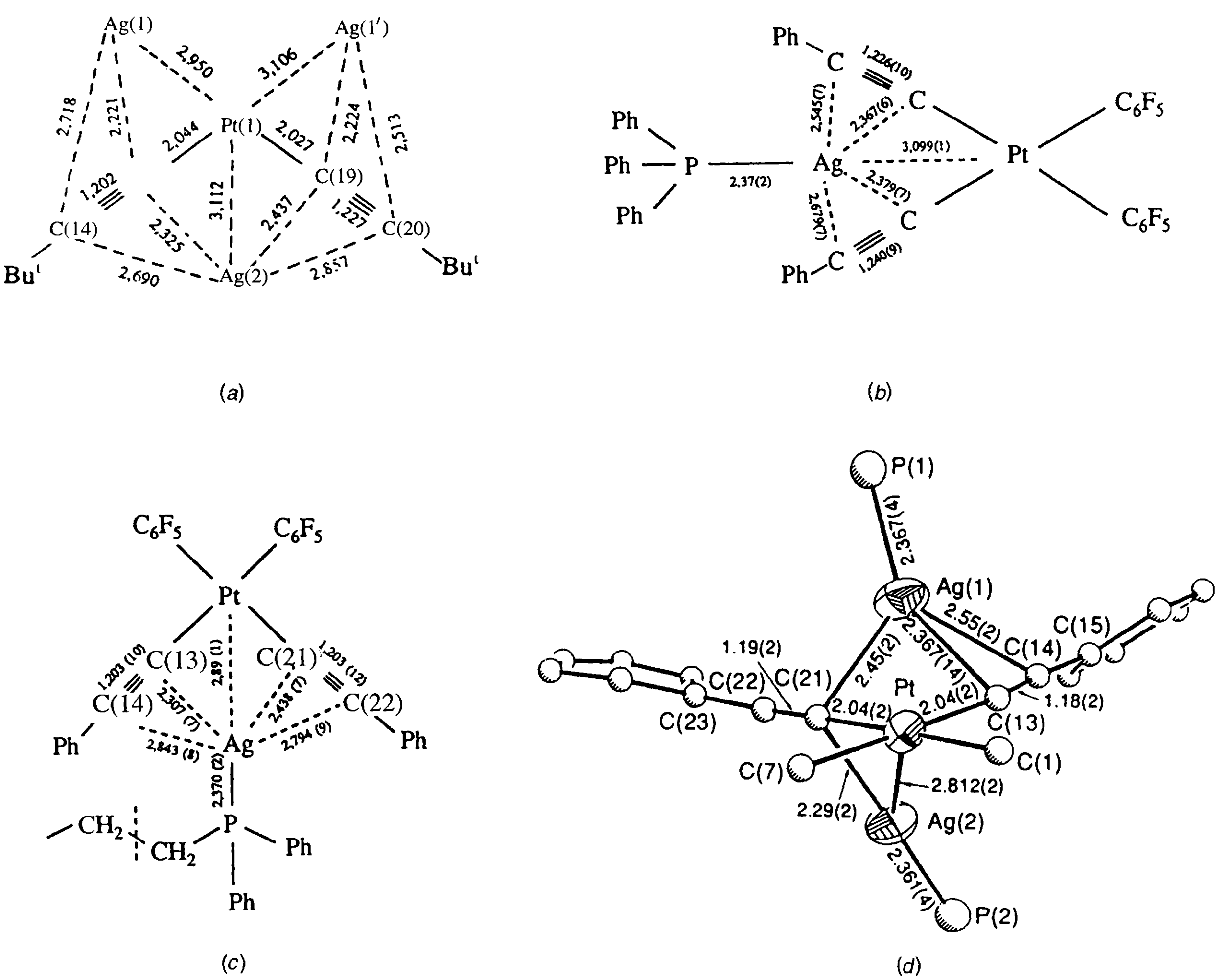
Encouraged by the discovery of a convenient method for the synthesis of homoleptic $[NBu_4]_2[Pt(C{\equiv}CR)_4]{\cdot}nH_2O$ **1** (R =



Scheme 1 [Pt] = $Pt(C_6F_5)_2$; R = Ph or Bu^t; L = PPh_3, PEt_3 or dppe. (*i*) M = Ag, 2 $AgClO_4$, diethyl ether; M = Cu or Au, 2 CuCl or 2 [AuCl(tht)]–2 $NaClO_4$, acetone; (*ii*) $AgClO_4$, AgCl (M = Ag), CuCl (M = Cu)

Ph,[11] *n* = 0; R = Bu^t, *n* = 2)[12] and mixed-ligand $Q_2[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ **2** (Q = $PMePh_3$, R = Ph; Q = NBu_4, R = Bu^t)[13] alkynylplatinate(II) complexes, we have investigated their behaviour towards suitable electrophilic silver-, copper- or gold-(I) complexes in detail. This has led to the isolation of four types of heteropolynuclear platinum complexes depending on the nature of the platinum starting material and on the molar ratio of the reactants (Scheme 1). Thus, treatment of the homoleptic tetraalkynylplatinate(II) ions **1** with $AgClO_4$, or with CuCl or [AuCl(tht)] (tht = tetrahydrothiophene) in the presence of a halide abstractor ($NaClO_4$), in 1 : 2 molar ratio resulted in the formation of neutral hexanuclear complexes $[Pt_2M_4(C{\equiv}CR)_8]$ **4** [Scheme 1(*i*)] in which two $Pt(C{\equiv}CR)_4$ fragments are connected by four metal centres M in such a way that each is asymmetrically η^2 bonded (Ag–C_α bond lengths slightly shorter than Ag–C_β ones) to two alkynyl fragments.[12] Recently, Sonogashira and co-workers[14] have also obtained $[Pt_2Cu_4(C{\equiv}CPh)_8]$ by treating the ferrocenylplatinum complex $[Pt\{C_5H_4Fe(C_5H_5)\}Cl(cod)]$ (cod = cycloocta-1,5-diene) with an excess of phenylacetylene and CuI.

On the other hand, treatment of the mixed-ligand *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ **2** with $AgClO_4$, AgCl or CuCl in a 1 : 1 molar ratio affords anionic tetranuclear complexes $[Pt_2M_2(C_6F_5)_4(C{\equiv}CR)_4]^{2-}$ **5** [Scheme 1(*ii*)] in which, once

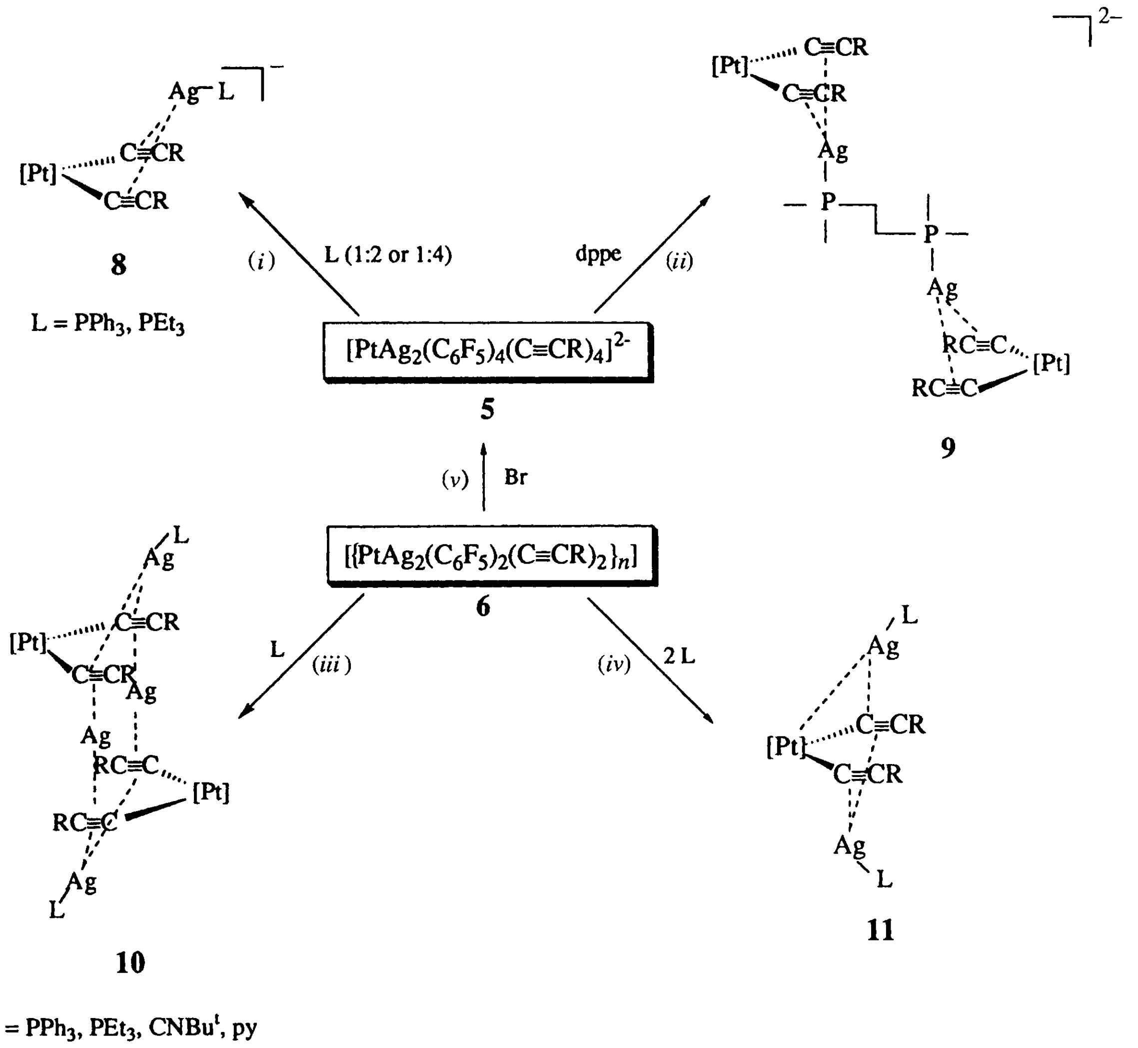


Scheme 2 Alkynyl bonding modes for (*a*) $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CBu^t)_4(Me_2CO)_4]$ **6b**, (*b*) $[NBu_4][PtAg(C_6F_5)_2(C{\equiv}CPh)_2(PPh_3)]$ **8**, (*c*) $[NBu_4]_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CPh)_4(dppe)]$ **9** and (*d*) $[PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(PPh_3)_2]$ **11**. Distances in Å

again, two square-planar *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ units are linked by two silver or copper centres which are two-co-ordinated by two η^2-alkynyl fragments each one associated with each platinum atom.[13] It should be noted that these complexes are formed by the displacement of the Cl ligand suggesting that in these systems the η^2-alkyne fragments have a higher co-ordinating ability towards the silvers or copper centres than the chloride ion. Surprisingly, and in contrast to the behaviour of other bis(alkynyl)metal species $LnM(C{\equiv}CR)_2$ which act as didentate chelating 1,4-metallodiyne ligands towards unsaturated M'Ln fragments (including AgCl or CuCl),[3f,15] in these systems each of the two *cis*-$Pt(C_6F_5)_2$-$(C{\equiv}CR)_2$ units behaves as a didentate bridging diyne ligand. Their formation is noteworthy since dinuclear dianionic systems of type **E** (Scheme 1) would have been expected.

Taking into account the anionic nature of the tetranuclear complexes $Q_2[Pt_2M_2(C_6F_5)_4(C{\equiv}CR)_4]$ **5** and the fact that the alkynyl ligands are co-ordinating *via* only one of their two orthogonal π C–C bonds, these anionic species are potential synthons for higher-nuclearity complexes. Thus, when pale yellow solutions of **5** (M = Ag) are treated with $AgClO_4$ (1 : 2 molar ratio) or alternatively, from $[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ **2** and 2 equivalents of $AgClO_4$, deep yellow solids of general formulae $[\{PtAg_2(C_6F_5)_2(C{\equiv}CR)_2\}_n]$ **6** are obtained.[16] A polymeric structure of the type shown in Scheme 1 has been proposed for these complexes. Although the phenylacetylide derivative (R = Ph) is insoluble in common organic solvents, we observed that the *tert*-butylacetylide compound is soluble in acetone and colourless crystals of the hexanuclear species $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CBu^t)_4(Me_2CO)_4]$ **6b** have been obtained from this solution. A schematic view of its molecular structure determined by X-ray diffraction is shown in Scheme 1. The polynuclear compound displays two bridging silver atoms exclusively bonded to alkynyl fragments and two terminal ones bonded to alkynyl units and to two acetone molecules, although the latter seem to be weakly bonded since when this complex is air-dried it changes to bright yellow producing the polymer **6**. It is noteworthy that in **6b** each '*cis*-$Pt(C_6F_5)_2(C{\equiv}CBu^t)_2$' fragment behaves as a tridentate bridging ligand and the alkynyl groups adopt an asymmetric μ_3-η^2 bonding mode forming a σ bond with a Pt atom and two very assymmetric π bonds with two structurally different silver atoms [2 Ag^1 and Ag^2, see Scheme 2(*a*)].

As part of these studies we were also interested to know whether similar polynuclear species were also achievable from neutral *cis*-$[Pt(C{\equiv}CR)_2L_2]$ **3** complexes (Scheme 1). Starting from **3** and $AgClO_4$, not only was it straightforward to carry out the synthesis of the 1 : 1 adducts $[Pt_2Ag_2(C{\equiv}CR)_4L_4]$-$[ClO_4]_2$ which are believed to be structurally similar to complexes **5**, but the formation of 2 : 1 adducts $[Pt_2Ag$-$(C{\equiv}CR)_4L_4]ClO_4$ **7** (Scheme 1), containing a silver centre tetrahedrally co-ordinated by four acetylenic fragments also posed no problems.[17] Yamazaki and Deeming[15h] have also reported a similar platinum–copper complex $[\{(dppe)Pt$-$(C{\equiv}CPh)_2\}_2Cu]BF_4$ (dppe = $Ph_2PCH_2CH_2PPh_2$) which was obtained by recrystallization (acetone–acetonitrile) of $[(dppe)Pt(\mu$-$\eta^1{:}\eta^2$-$C{\equiv}CPh)_2Cu(NCMe)]BF_4$. As expected, the molecular structures of both $[Pt_2Ag(C{\equiv}CPh)_4(PPh_3)_4]ClO_4$ and $[PtCu_2(C{\equiv}CPh)_4(dppe)_2]BF_4$ reveal that the organometallic platinum fragments $L_2Pt(C{\equiv}CR)_2$ are acting as didentate



Scheme 3

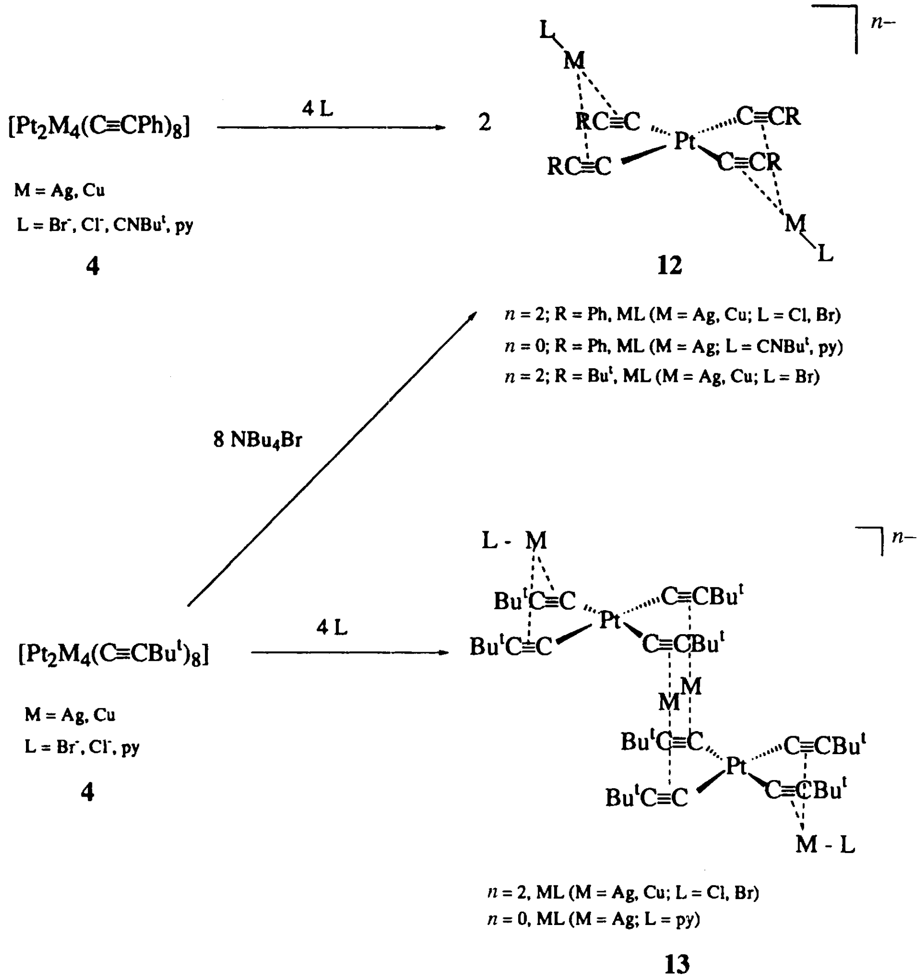
chelate diyne ligands. In the silver complex the very long Ag–C (alkynyl) bond lengths observed suggest that the η^2-alkyne interactions are very weak.

(*b*) Complexes with alkynyl fragments and other groups acting as ligands

The facility with which acetone produces a partial depolymerization of the polymeric species **6** (R = Bu^t) yielding **6b** contrasts with the remarkable stability of the tetranuclear complexes **5** towards chloride ions. We therefore considered it of interest to explore the reactivity of some of the above-mentioned derivatives towards other proligands. As we will discuss later, these complexes are excellent precursors for the synthesis of new polynuclear derivatives. Thus, as already mentioned, chloride ligands do not cleave the metal–alkyne interactions in the tetranuclear anionic compounds **5** to yield dinuclear complexes of type **E** (Scheme 1). This type of compound (**8**)[18] however is easily obtained when phosphine ligands (PPh$_3$ or PEt$_3$) are used [Scheme 3(*i*)]. On the other hand, by treating $[NBu_4]_2[Pt_2Ag_2(C_6F_5)_4(C{\equiv}CR)_4]$ **5** with dppe new tetranuclear dianionic complexes **9** [Scheme 3(*ii*)] are formed. Complexes **8** (R = Ph, L = PPh$_3$) and **9** (R = Ph) have been fully characterized by X-ray crystallography.[18] In both derivatives the 3-platinapenta-1,4-diyne fragment *cis*-$Pt(C_6F_5)_2(C{\equiv}CPh)_2$ behaves as a didentate chelating ligand towards the silver centre which completes its trigonal co-ordination with a phosphine group. The details of the bridging alkynyl ligands schematically drawn in Scheme 2(*b*) and (*c*) clearly suggest that the silver centres prefer to bond to the C_α atoms, the bonding mode of the alkynyl groups being approximately halfway between the μ-η^2 and the μ-η^1 bridging modes (**A** and **C**).

On the other hand, as expected, treatment of the polymeric complexes **6** with phosphines, *tert*-butyl isocyamide or pyridine in a Ag:L molar ratio of 2:1 [Scheme 3(*iii*)] produces only a partial depolymerization giving hexanuclear $[Pt_2Ag_4(C_6F_5)_4(C{\equiv}CR)_4L_2]$ complexes **10** structurally related to the acetone complex **6b**.[19a] An X-ray analysis on the complex with R = Ph and L = PPh$_3$ reveals that once again the two *cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2$ fragments act as tridentate bridging ligands towards structurally different silver centres (two bridging and one terminal) and the alkynyl ligands exhibit a very unsymmetrical μ_3-η^2 bonding mode. Once again, attempts to obtain anionic complexes related to **10** but with anionic ligands (such as Br$^-$) by treating **6** with NBu$_4$Br [1 equivalent, Scheme 3(*v*)] failed due to the precipitation of AgBr. The tetranuclear complexes **5** were isolated from the mother-liquors.

In contrast to the above, total depolymerization takes place when a higher proportion of proligand L is used (Scheme 3(*iv*)] yielding trinuclear $[PtAg_2(C_6F_5)_2(C{\equiv}CR)_2L_2]$ **11** derivatives.[19] The X-ray analysis of $[PtAg_2(C_6F_5)_2(C{\equiv}CPh)_2(PPh_3)_2]$ [see skeletal view in Scheme 2(*d*)][19b] has shown that the co-ordination of the two $Ag(PPh_3)^+$ fragments to the anion *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)]^{2-}$ is rather different. One Ag(1)PPh$_3$ unit is bonded to both alkynyl groups while the other is only bonded to the C_α atom of one alkynyl function and seems to be also bonded to the platinum atom [Ag–Pt 2.812 (2) Å]. As a result,



Scheme 4

one alkynyl acts as a μ-η^2 ligand and the other bridges the three metal atoms in a predominantly σ manner (μ$_3$-η^1).

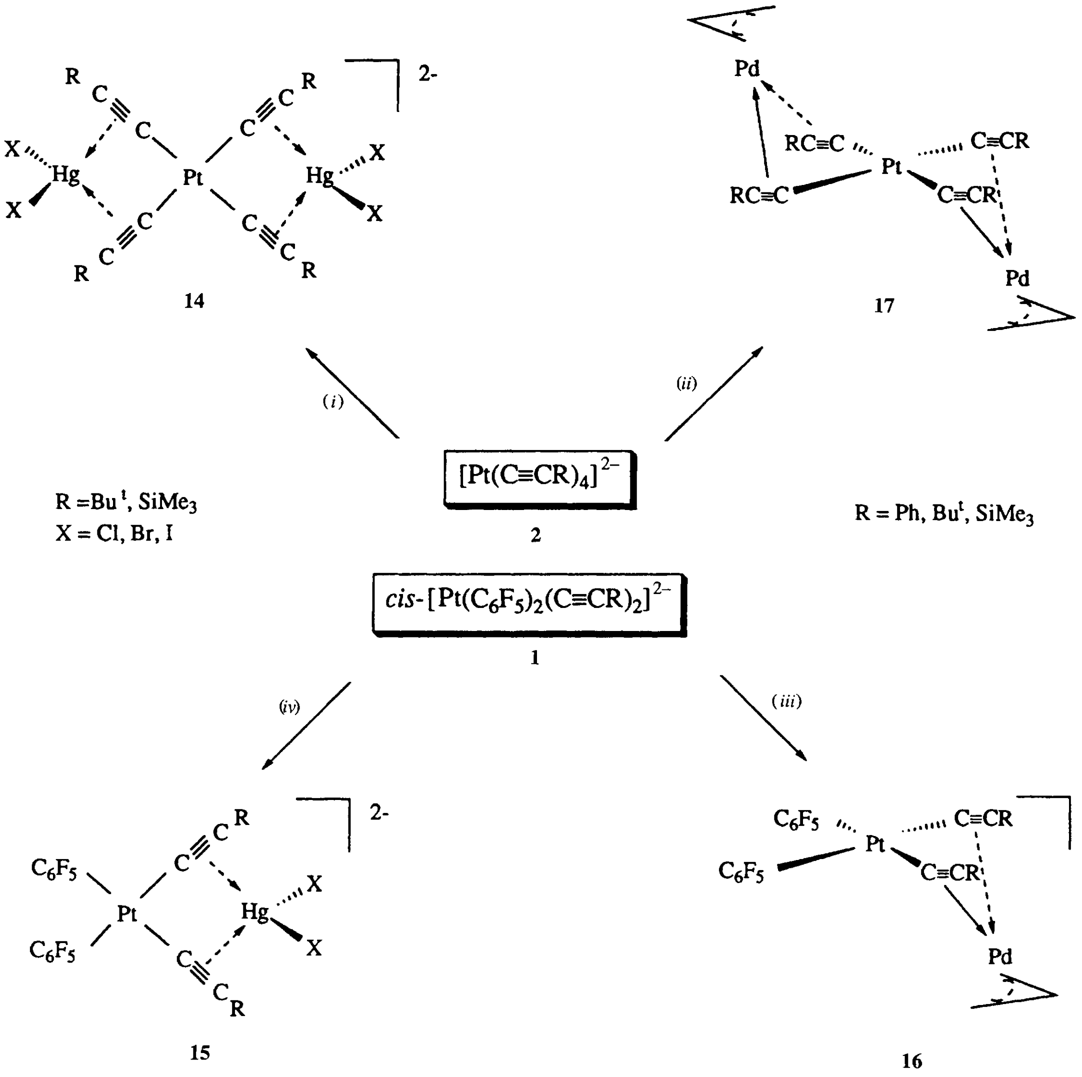
When we extended the reactivity to the $[Pt_2M_4]$ hexanuclear complexes **4** with only alkynyl ligands we found that the resulting products depended not only on the ligand used but also on the nature of the alkynyl ligand[20] (see Scheme 4). Thus, treatment of the phenylacetylide derivatives **4** (M = Cu or Ag) with anionic X^- (X = Cl or Br) or neutral donors [L = CNBu^t or pyridine (py)] resulted in the formation of trinuclear anionic or neutral complexes **12** in which the $Pt(C{\equiv}CPh)_4$ fragment chelates two neutral MX or cationic $[ML]^+$ units as is confirmed by an X-ray analysis of $[NBu_4]_2[Pt(C{\equiv}CPh)_4(CuBr)_2]$. However, similar reactions with $[Pt_2M_4(C{\equiv}CBu^t)_8]$ afford hexanuclear complexes **13** (Scheme 4) structurally related to the acetone complex **6b** (Scheme 1) and **10** (Scheme 3) and only by using an excess of ligand (such as Br^-, 8 equivalents) can the analogous trinuclear complexes be obtained.[20] In contrast, attempts to prepare similar complexes with phosphines L (PPh_3 or PEt_3) failed. The corresponding reactions produce a partial displacement of the alkynyl ligands from the platinum forming the neutral *trans*-$[Pt(C{\equiv}CPh)_2L_2]$ complexes and the polymeric $[\{M(C{\equiv}CR)\}_n]$ (M = Ag or Cu) derivatives. This result, which implies formal alkynylation of the Ag and Cu, is rather surprising because both silver and copper alkynyl derivatives have proved to be very useful alkynylating reagents[21] and, in fact, some of the compounds described in this section have also been prepared using the polymeric $[\{Ag(C{\equiv}CR)\}_n]$ species.[12,13,16] It seems logical to assume that the presence of the C_6F_5 groups plays a key role in the final stability of the aforementioned polynuclear phosphine complexes **8**–**11** (Scheme 3). It is likely that the enhanced acidity of the platinum centre, brought about by the electron-withdrawing nature of the C_6F_5 ligands, prevents the alkynylation processes of the electrophilic silver centres from occurring.

Synthesis of Homo- and Hetero-di- and -tri-nuclear Platinum Complexes with Double (μ-C≡CR)$_2$ Bridging Systems

Bis(alkynyl) complexes $L_nM(C{\equiv}CR)_2$ are excellent building blocks for the synthesis of bimetallic systems because they can act as a didentate chelating ligand *via* η^2 co-ordination to a second metal fragment L_nM'. This synthetic strategy has recently been employed by Lang *et al.*[15a,22] using bis(alkynyl)-titanocene species as precursors. The homoleptic and mixed-ligand platinum complexes **1** and **2** are potential synthons not only for dinuclear doubly bridged alkynyl complexes but also for trinuclear bis(doubly bridged) ones. The bonding mode of the μ-C≡CR ligands can however be widely varied depending on the different metal centres, ligands and substituents. As previously mentioned, electronic factors and/or steric requirements seem to exert a notable influence on the preference of the metal centres for the σ- or π-electron density of the alkynyl groups. Owing to that the reactions between $L_nPt(C{\equiv}CR)_2$ and $M'L_n$ not only produce dimetallic species *via* π co-ordination of the platinum complex to the $M'L_n$ fragment but also mono- or di-alkynylation processes of the $M'L_n$ fragment have been observed.

(*a*) Reactions without σ-alkynyl migration

The results presented in Scheme 5 illustrate that the platinum mononuclear complexes **1** and **2** have a great potential as



Scheme 5 (*i*) $2HgX_2$; (*ii*) $[\{Pd(\eta^3-C_3H_5)Cl\}_2]$; (*iii*) $\frac{1}{2}[\{Pd(\eta^3-C_3H_5)Cl\}_2]$; (*iv*) HgX_2

precursors for the synthesis of di- and tri-nuclear complexes containing doubly bridged alkynyl systems of the chelating type. Thus, the reactions of **1** and **2** with mercury halides in adequate molar ratios afford bis(η^2-alkyne) 1 : 2 or 1 : 1 adducts **14** and **15** respectively.[23] This contrast with previous reported reactions between neutral *cis*-$[Pt(C{\equiv}CR)(C{\equiv}CR')L(CO)]$[24a] or *cis*-$[Pt(C{\equiv}CPh)_2L_2]$[24b] and $HgCl_2$ which result in the transfer of the alkynyl groups but not the formation of bimetallic Pt–Hg complexes. Their formation is also noteworthy since although adducts with mercury salts have been postulated as intermediates in solvomercuriation processes of alkynes, none of these proposed η^2 complexes had, however, been reported to date.[25]

On the other hand, the peculiar ability of these anionic substrates **1** or **2** to stabilize unusual η^2-alkyne–metal interactions is also demonstrated by the formation of the heterodinuclear Pt–Pd anionic complexes $Q[(C_6F_5)_2Pt(C{\equiv}CR)_2Pd(\eta^3-C_3H_5)]$ **16** and neutral trinuclear derivatives $[(\eta^3-C_3H_5)Pd\{Pt(C{\equiv}CR)_4\}Pd(\eta^3-C_3H_5)]$ **17** containing the very electrophilic cationic $Pd(\eta^3-C_3H_5)^+$ unit[26] (Scheme 5). It is also interesting that although these complexes are formally zwitterionic, no alkynylation processes, which would formally result in neutralization of the charges, take place. Only a few palladium(II) complexes containing η^2-coordinated alkynes have been reported[27] and none has been characterized by X-ray diffraction. X-Ray analyses have been carried out to clarify the structures of these new Pt ··· Hg and Pt ··· Pd complexes by using single crystals of **15** (R = $SiMe_3$) and **16** (R = $SiMe_3$) and these are presented in Fig. 1. The most remarkable difference is that the platinum–mercury complex exhibits a tweezer-like structure with the Hg atom well embedded in the platinadiyne fragment, resulting in an almost planar central PtC_4Hg core (maximum deviation 0.076 Å for the Hg atom). However, in the platinum–palladium derivative the Pd atom is not embedded in the bis(alkynyl)platinum fragment but sandwiched between the acetylenic fragments and the allylic ligand. Consequently the central PtC_4Pd core of the resulting metallacycle is bent. It is rather surprising that the bite angle C(13)–Pt–C(18) in the mercury compound is notably smaller [63.1(8)°] than that in the palladium complex [81.8(7)°] due, probably, to the tweezer effect of the $[Pt](C{\equiv}CSiMe_3)_2$ moiety.[15a,22a] It is also interesting that the η^2-mercury–alkynide linkages are clearly asymmetric and the Hg–C_β distances are shorter than the corresponding Hg–C_α ones. This is in contrast to the symmetrical η^2-palladium linkages and implies some participation of a normal carbene-like structure of type **B**.

(*b*) Reactions in which σ-alkynyl migration processes are involved

With the aim of preparing di- and tri-platinum complexes we have examined the reactivity of alkynyl mononuclear platinum compounds towards *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pt or Pd) in which both tetrahydrofuran (thf) molecules can be readily displaced by a great variety of donors.[27b,28] The results of this study are shown in Scheme 6. Only the reactions with neutral *cis*-bis(alkynyl)platinum complexes **3** (1 : 1 molar ratio) produce the expected diplatinum complexes **18** with a doubly alkynyl-bridged system of the chelating type as has been confirmed by an X-ray analysis of **18** (L = ½ dppe, R = Ph).[29] The reactions with the dianionic mixed-ligand species **2** afford the symmetric double-bridging alkynide bimetallic complexes $[(C_6F_5)_2Pt(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CR)(\mu\text{-}\eta^2:\eta^1\text{-}C{\equiv}CR)Pt(C_6F_5)_2]^{2-}$ **19**. The crystal structure of one derivative (R = Ph) shows that two identical $(C_6F_5)_2Pt\text{-}C{\equiv}CPh$ units are joined together by symmetrical η^2 bonding of C≡CR, thus indicating that the complex is formed *via* migration of one σ-alkynyl group between the two platinum centres.[29] It seems reasonable to suggest that alkynylation takes place because of the difference in the formal charges between the platinum starting materials. Such migration could occur *via* initial formation of a chelating type species (**F**, Scheme 7), such as **18** in Scheme 6, which evolves through an intermediate such as **G** with symmetrical $\mu\text{-}\eta^1:\eta^1$-alkynyl bridges to yield the final less-polar complex. Although type **G** compounds are in general characteristic of electrophilic metal centres (main group element[30] or f-orbital centres[31]), the reaction between $[Ti(\eta\text{-}C_5H_5)_2(C{\equiv}CBu^t)_2]$ and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ yields the titanium–platinum complex **20** (Scheme 6) which has been shown by X-ray crystallography to contain two asymmetric $\mu\text{-}\eta^1$-alkynyl ligands.[32] It should be noted that in solution complexes **19** are highly fluxional involving a rapid intramolecular σ-C≡CR migration, probably through an intermediate such as **G** (Scheme 7), between the platinum atoms.

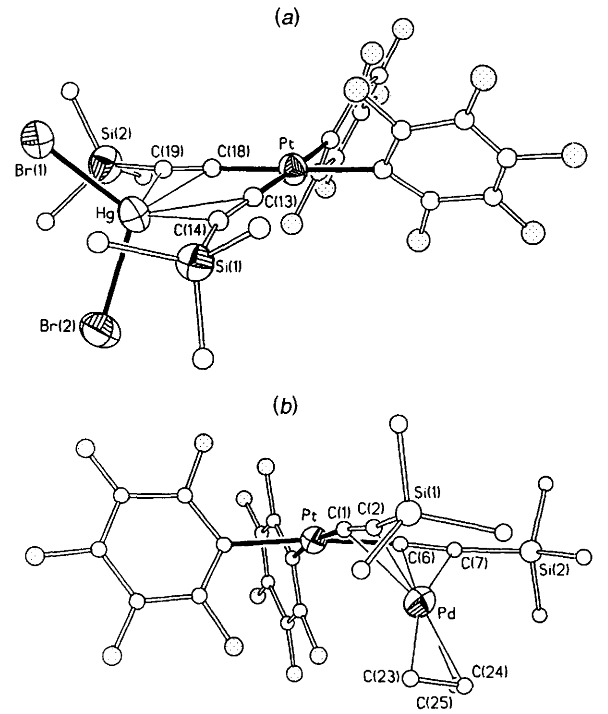
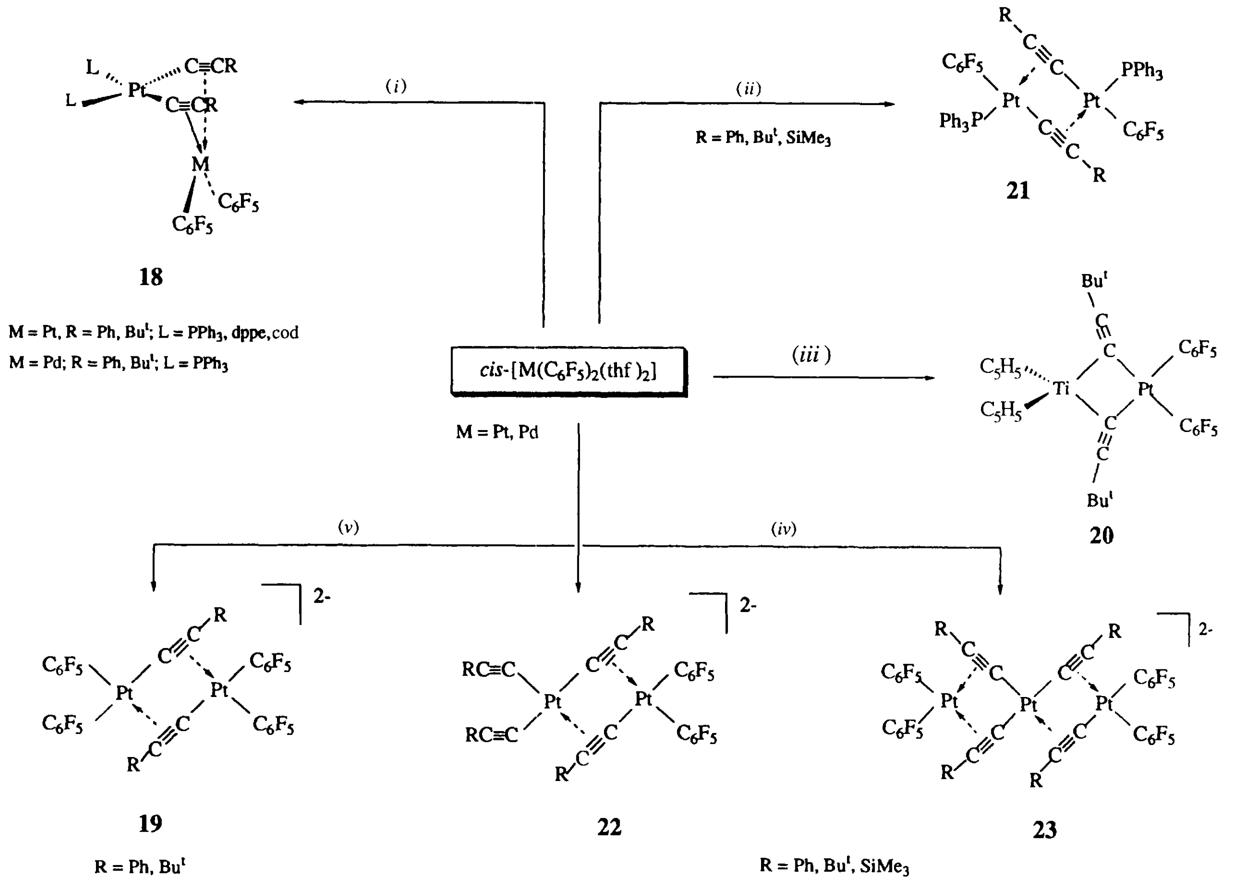


Fig. 1 Structures of the anions (*a*) $[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2HgBr_2]^{2-}$ and (*b*) $[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CSiMe_3)_2Pd(C_3H_5)]^-$

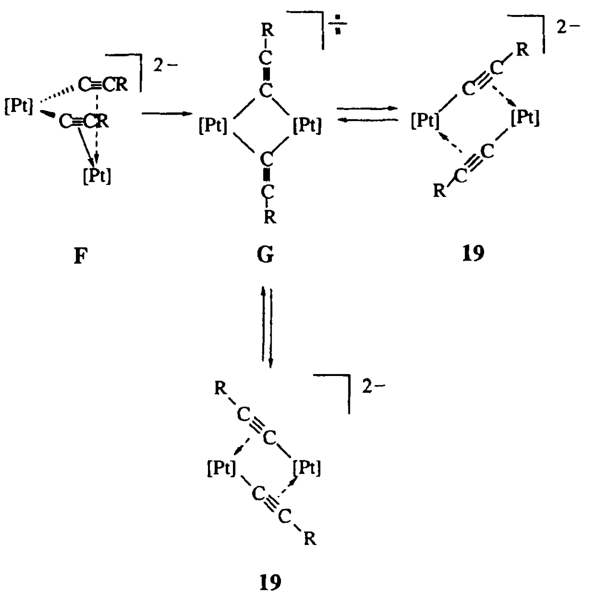
Similar bimetallic neutral complexes $[\{Pt(C_6F_5)(C{\equiv}CR)(PPh_3)\}_2]$ **21** (Scheme 6) with a symmetric doubly alkynyl bridging system are obtained from *trans*-$[Pt(C{\equiv}CR)_2(PPh_3)_2]$ and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ the formation of which requires a redistribution of the ligands.[33] Finally the homoleptic compounds **1** react with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ either in a 1 : 1 or in a 1 : 2 molar ratio yielding the expected bi- and tri-metallic anionic complexes **22** and **23**, respectively.[34] The crystal structure of the trinuclear complex with R = Ph reveals that only one of the expected σ-alkynyl migrations has taken place and, consequently, the simultaneous presence of both chelating and σ/π double alkynyl bridging systems is observed.



Scheme 6 (*i*) *cis*-$[Pt(C{\equiv}CR)_2L_2]$ **3**; (*ii*) *trans*-$[Pt(C{\equiv}CR)_2(PPh_3)_2]$; (*iii*) $[Ti(\eta\text{-}C_5H_5)_2(C{\equiv}CBu^t)_2]$; (*iv*) $[Pt(C{\equiv}CR)_4]^{2-}$ **1**; (*v*) *cis*-$[Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ **2**

Surprisingly no evidence of further rearrangement under thermal conditions (CHCl$_3$, reflux, 12 h) has been found in spite of the facts that (*a*) these species are highly fluxional in solution (formal D_{2h} symmetry at room temperature) and (*b*) they have formally two negatively charged adjacent platinum fragments.[3f]

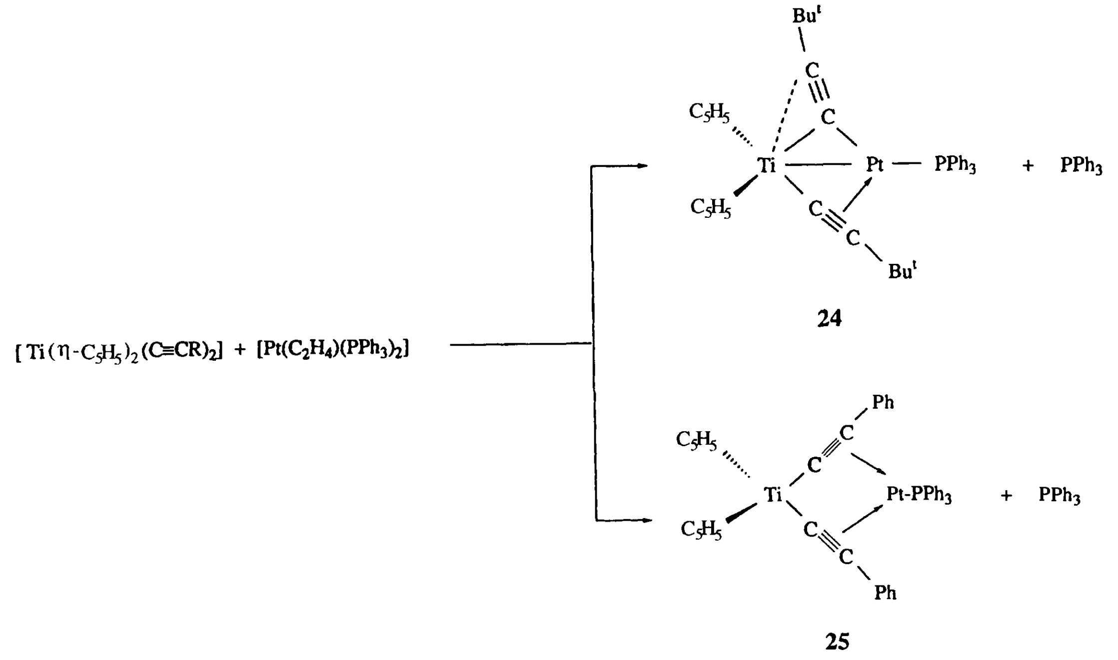
Interestingly, a very asymmetric σ,π doubly bridging alkynyl system is observed (X-ray analysis) in the binuclear $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-}\eta^1:\eta^1\text{-C}{\equiv}\text{Bu}^t)(\mu\text{-}\eta^2:\eta^1\text{-C}{\equiv}\text{CBu}^t)\text{Pt}(\text{PPh}_3)]$ **24** (see Fig. 2) synthetized by the reaction of $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{C}{\equiv}\text{CBu}^t)_2]$ and $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$[35] (Scheme 8). The co-ordination of the Pt atom to the alkynyl moiety is almost symmetrical with very short Pt–C bond distances [Pt–C(7) 2.054(13) and Pt–C(8) 2.191(15) Å] suggesting a very strong η^2-alkynide interaction while the titanium–alkynyl interaction is much weaker with longer and very dissimilar Ti–C distances [Ti–C(1) 2.435(14) and Ti–C(2) 2.795(14) Å], suggesting that this bond has predominant σ character. The formation of **24**, which can be formally considered to be the result of the oxidative addition of a Ti^{IV}–C bond to a platinum(0) substrate yielding a dinuclear Ti^{III}–Pt^{I} compound with a metal–metal bond (Ti–Pt 2.789 Å), is especially surprising given that the analogous phenylacetylide complex $[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{C}{\equiv}\text{CPh})_2]$ only acts as a chelating ligand towards the Pt(PPh$_3$) unit.[35,36] As previously pointed out,[4e] these results clearly suggest that steric or electronic factors of the substituents at the alkynyl units also affect the σ/π bonding preferences of the metal centres.



Scheme 7 [Pt] = Pt(C$_6$F$_5$)$_2$

Finally, we have also studied the reactions between platinum alkynyl complexes and some electrophilic species of rhodium and iridium with the aim of preparing dinuclear Pt–Rh and Pt–Ir complexes with a doubly alkynyl bridging system. Some of the results obtained, which are presented in Scheme 9, have been communicated[37] and a full study will be reported in the future. Binuclear anionic Pt^{II}–Rh^{I} complexes **26** containing two bridging alkynyl ligands can easily be obtained by treating the mixed-ligand alkynylplatinum complexes **2** with the cationic solvento species $[\text{Rh(cod)(OEt}_2)_x]^+$ prepared '*in situ*' [Scheme 9(*i*)]. The reaction of **2** (R = SiMe$_3$) with $[\{\text{IrCl(cod)}\}_2]$ (2:1 molar ratio) gives an analogous mixed platinum(II)–iridium(I) complex which has been shown by X-ray crystallography to contain a σ/π doubly alkynyl bridged system (**H**, Scheme 9) related to those found in the diplatinum anion **19** (R = Ph) and in $[\{\text{Ir}(\text{C}{\equiv}\text{CPh})(\text{cod})\}_2]$.[38] Once again the σ migration of one of the alkynyl ligands produces a less-polar end complex.

Similarly, neutralization reactions between the dicationic rhodium(III) and iridium(III) solvento species $[\text{M}(\eta\text{-C}_5\text{Me}_5)(\text{PEt}_3)(\text{Me}_2\text{CO})_x][\text{ClO}_4]_2$ and the dianionic **2** (R = Ph or SiMe$_3$) complexes result in formation of the corresponding mixed dinuclear neutral complexes. X-Ray analysis[37] of the dinuclear iridium–platinum complex with R = Ph has shown that the formation of the dinuclear complex takes place through an unexpected double alkynylation process and that the resulting neutral unit '$\text{Ir}(\eta\text{-C}_5\text{Me}_5)(\eta^1\text{-C}{\equiv}\text{CPh})_2(\text{PEt}_3)$' acts as a chelating metalloligand towards the '$\text{Pt}(\text{C}_6\text{F}_5)_2$' fragment (**I**, Scheme 9). In contrast, the structure of the analogous dinuclear platinum–rhodium derivative with R = SiMe$_3$ determined by us quite recently reveals that only one of the expected σ-alkynyl migrations has occurred yielding a zwitterionic neutral complex $[(\text{Et}_3\text{P})(\eta\text{-C}_5\text{Me}_5)\text{Rh}^+(\mu\text{-}\eta^1:\eta^2\text{-C}{\equiv}\text{CSiMe}_3)(\mu\text{-}\eta^2:\eta^1\text{-C}{\equiv}\text{CSiMe}_3)\text{Pt}^-(\text{C}_6\text{F}_5)_2]$ with a σ/π doubly alkynyl bridging system (**J**, Scheme 9). This result once more shows the influence



Scheme 8

of several factors in the final preference of the metals towards σ or π co-ordination with the alkynyl ligands.

A Single Alkynyl Ligand connecting Platinum Centres: Unusual Behaviour

The recent synthesis of mono η^2-alkyne platinum(II) complexes *cis*-[Pt(C_6F_5)$_2$(CO)(RC≡CR)] carried out by some of us by treating alkynes and *cis*-[Pt(C_6F_5)$_2$(CO)(thf)][28d] prompted us to investigate whether the corresponding metallalkyne derivatives *cis*-[Pt(C_6F_5)$_2$(CO)(RC≡CML$_n$)] were also obtainable in a similar way. Initial attempts to use monoalkynylplatinum derivatives such as *trans*-[PtX(C≡CR)(PPh$_3$)$_2$] (X = C_6F_5, R = Ph, Bu^t or SiMe$_3$; X = Cl, R = Ph) were however unsuccessful. We therefore turned our attention towards neutral bis(alkynyl) derivatives [Pt(C≡CR)$_2$L$_2$] and some of the processes studied as well as the results are summarized in Scheme 10. All the reactions between *cis*-[Pt(C_6F_5)$_2$(CO)(thf)] and [Pt(C≡CR)$_2$L$_2$] afford the corresponding dinuclear monoalkynyl bridging complexes **28**–**30**. Both the spectroscopic data (IR, NMR) and the crystal structure of **28** (R = Ph, L = PPh$_3$) provide evidence that the reactions take place with stereoretention and an unexpected alkynylation of the fragment '*cis*-Pt(C_6F_5)$_2$(CO)' occurs, thus producing the formally zwitterionic dinuclear complexes [(OC)(C_6F_5)$_2$Pt$^-$(μ,η^1 : η^2-C≡CR)Pt$^+$(η^1-C≡CR)L$_2$].[39] This result is noteworthy since once again less-polar complexes would have been expected. The enhanced electrophilic character of the platinum centre in '*cis*-Pt(C_6F_5)$_2$(CO)' caused by the electron-withdrawing nature of the C_6F_5 groups and the π-acceptor properties of the CO ligand is probably the reason for its preference for co-ordination to the C_α atom of the alkynyl ligand (alkynylation process). It is worth mentioning that, at least, in the *cis,trans*-[(OC)(C_6F_5)$_2$Pt(μ,η^1 : η^2-C≡CPh)Pt(η^1-C≡CPh)(PPh$_3$)$_2$] complex the η^2-acetylenic interaction is quite stable and no reaction takes place when the complex is treated with PhC≡CPh, py, PPh$_3$, CO or HBF$_4$.

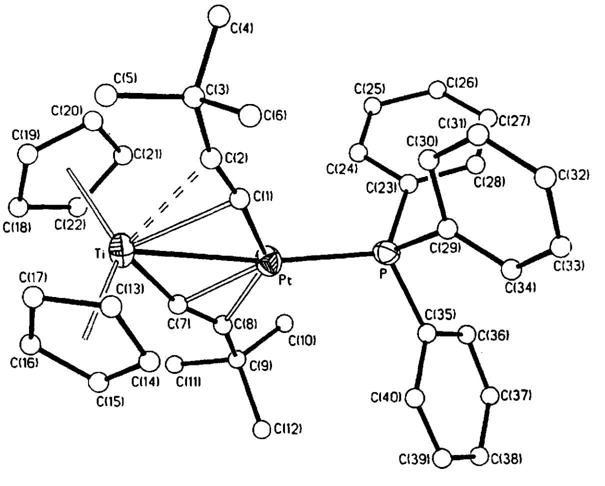
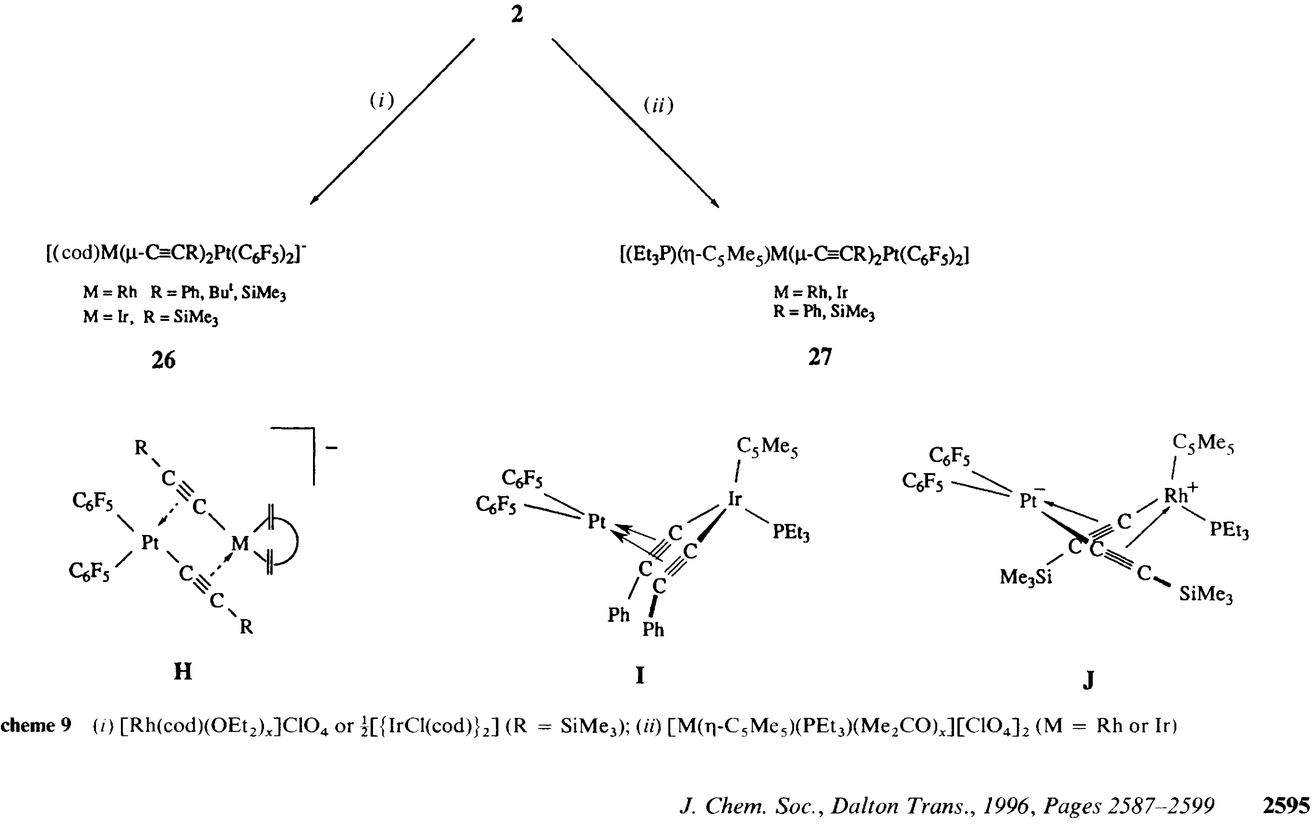


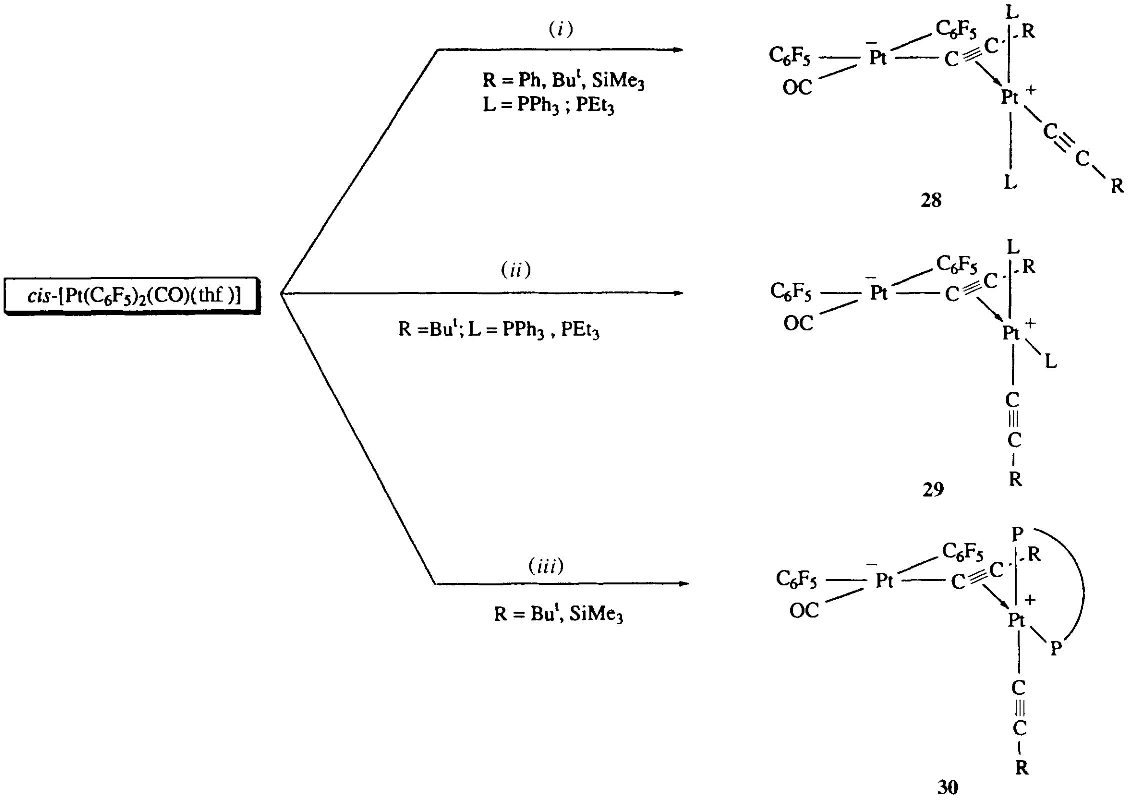
Fig. 2 Molecular structure of [(η-C_5H_5)$_2$Ti(μ-C≡CBu^t)$_2$Pt(PPh$_3$)]·0.5thf. Reprinted from *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2083 with kind permission from the editor

In contrast to the aforesaid, the analogous complex **28** with trimethylsilylacetylide reacts easily with alcohols (EtOH, MeOH) rendering the (μ-ethynediyl)(alkoxymethylcarbene) diplatinum complexes **31**, as a result of unexpected rearrangement chemistry involving both bridging and terminal trimethylsilylalkynyl groups[40] (Scheme 11). The X-ray analysis (R = OEt, L = PEt$_3$) reveals that the two co-ordination planes around the platinum atoms are almost coplanar (dihedral angle 6.7°), contrasting with the staggered geometry found in the only other two (μ-C$_2$) diplatinum compounds structurally characterized.[41] A plausible mechanism proposed for the formation of **31** is shown in Scheme 11. The initial step (*i*) would be desilylation of μ,η^1 : η^2-C≡CSiMe$_3$, promoted by the addition of alcohol to **28**, yielding similar derivatives containing μ-ethynyl bridges (**K**). These intermediates could undergo a sequence of two successive steps, deprotonation (*ii*)/protonation (*iii*), yielding the zwitterionic μ-ethynediyl vinylidene species **M**. Finally, nucleophilic addition of ROH across the vinylidene C=C bond, which is quite a common process,[7f,g] could produce the resulting complexes **31**.

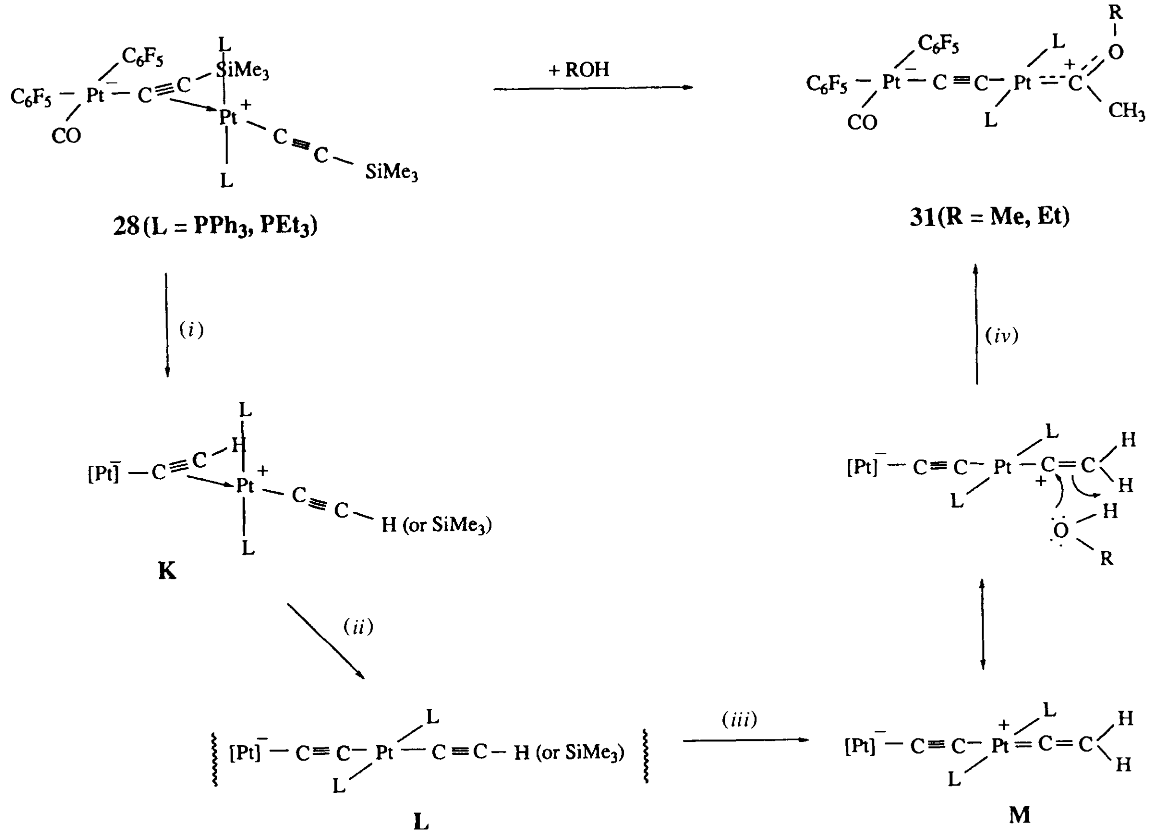
Interestingly, when *trans*-[PtH(C≡CPh)(PPh$_3$)$_2$] was used as



Scheme 9 (*i*) [Rh(cod)(OEt$_2$)$_x$]ClO$_4$ or $\frac{1}{2}$[{IrCl(cod)}$_2$] (R = SiMe$_3$); (*ii*) [M(η-C_5Me_5)(PEt$_3$)(Me$_2$CO)$_x$][ClO$_4$]$_2$ (M = Rh or Ir)

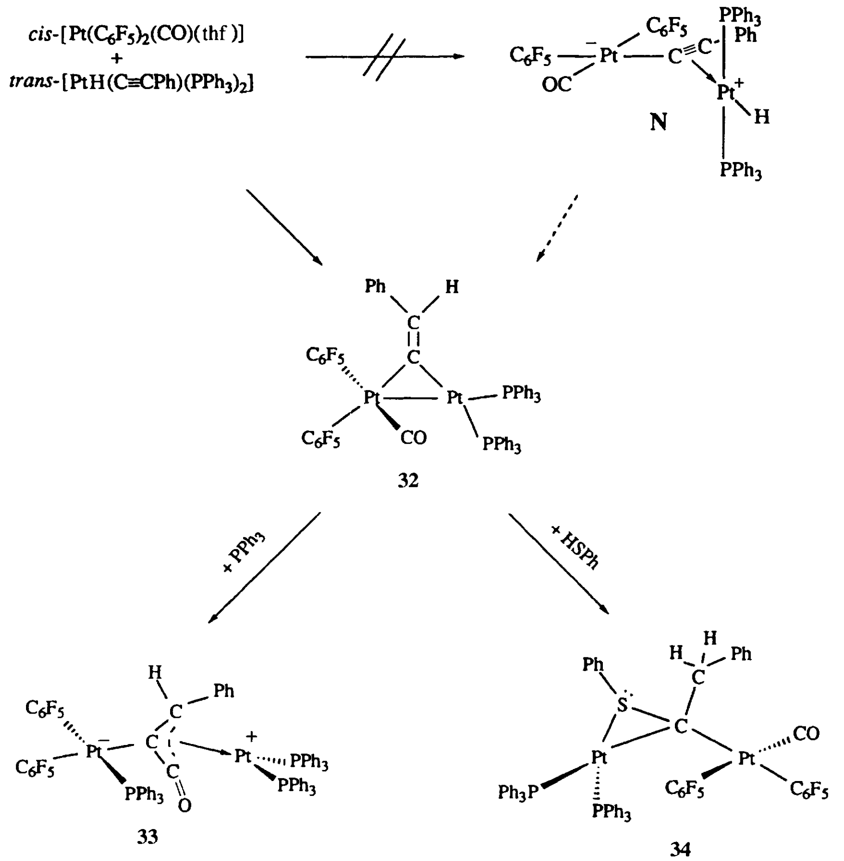


Scheme 10 (*i*) *trans*-[Pt(C≡CR)$_2$L$_2$]; (*ii*) *cis*-[Pt(C≡CR)$_2$L$_2$]; (*iii*) [Pt(C≡CR)$_2$(dppe)]



Scheme 11

the metalloligand a quite different reaction occurred (Scheme 12). The expected dinuclear zwitterionic complex **N** was not obtained upon treatment of *trans*-[PtH(C≡CPh)(PPh$_3$)$_2$] with *cis*-[Pt(C$_6$F$_5$)$_2$(CO)(thf)], but instead unexpected coupling of hydride and phenylacetylide ligands proceeded to yield the new μ-phenylethenylidene-bridged diplatinum complex **32**.[42] Lukehart and co-workers[43] have reported that the Pt–H bond of *trans*-[PtH(PEt$_3$)$_2$(Me$_2$CO)]$^+$ adds regioselectively across the C≡C triple bond of a terminal alkynyl ligand affording homo- or hetero-dinuclear complexes containing bridging alkenylidene ligands. Thus, the formation of **32** could be the result of an initial alkynylation of the '*cis*-Pt(C$_6$F$_5$)$_2$(CO)' fragment and simultaneous formation of the expected *cis,trans* μ-acetylide hydride intermediate **N**, followed by isomerization



Scheme 12

to the *cis,cis* isomer and *cis*-1,2 addition of the Pt–H bond across the C–C triple bond. Both the NMR spectroscopic data and the remarkable reactivity of complex **32** (Scheme 12) are evidence of the presence of the μ-vinylidene ligand in **32**. Thus, the reaction of **32** with PPh$_3$ (1 : 1 molar ratio) results in an unprecedented reductive coupling of the CO ligand and the vinylidene bridging group to give **33** which has been shown by X-ray analysis[42] to contain an expanded, unsaturated μ-η^1:η^3-benzylidene ketene bridging ligand connecting the platinum centres. This unsaturated bridging ligand is very unusual.

On the other hand, treatment of compound **32** with benzenethiol generates the new diplatinum complex **34** which is the result of a formal addition of the PhSH to the carbon–carbon double bond of the vinylidene group in **32**. The presence of a μ,η^2(C,S):η^1(C)-benzyl(phenylsulfanyl)methylene bridging group has been unequivocally confirmed by X-ray analysis.[42] These reactions add to a growing body of evidence suggesting that μ-alkenylidene in di- and poly-nuclear complexes is a versatile reactive ligand for which a rich chemistry can be anticipated.[7f]

In summary, the work presented in this perspective indicates that anionic acetylide platinate complexes are excellent precursors for the synthesis of polynuclear (homo- and hetero-metallic) complexes with only alkynyl fragments bridging the metal centres. The bonding features of the bridging alkynyl groups (**A**–**D**), their reactivity or stability are strongly dependent not only on the steric and/or electronic factors of the different alkynyl ligands but also on the metal fragments. Thus, the following conclusions can be drawn from this work. (*i*) The bis(alkyne)platinate substrates which usually act as chelating ligands co-ordinate to [AgL]$^+$ fragments (complexes **8**–**11**, Schemes 2 and 3) in such a way that the silver centre is closer to the C$_\alpha$ atom of the alkynylide ligand (**A** and **C**). However, in none of the cases is the [AgL]$^+$ fragment well embedded in the platinadiyne fragments, in contrast to other similar species in which the unsaturated M′L$_n$ (M = Ag or Cu) fragments are well embedded between the two arms of the acetylide ligands.[15a] (*ii*) On the other hand ML$_2$ fragments (M = Pd or Pt) η^2 co-ordinated to the metallodiyne fragment form more symmetrical acetylide bridging ligands and the tendency of the metal centres M to square-planar co-ordination clearly forces the location of the palladium or the platinum centres outside the MC$_4$ metallodiyne plane [complexes **16**–**18**, **23**, **27** (M = Ir, R = Ph), Schemes 5, 6, 9]. (*iii*) Another interesting question which still remains open is that in some of the reactions studied alkynylation processes take place. Although one may think that these processes are provoked because of the difference in the formal charges of the metal centres involved (complexes **19**, **22**, **23**, **26**, **27**, Schemes 6, 9), obviously this is not the only reason why such processes occur. No alkynylation has been observed in the formation of complexes **16** and **17** (Scheme 5) while unexpected alkynylation takes place in the synthesis of complexes **28**–**30** (Scheme 10) giving rise to the formation of zwitterionic derivatives. Moreover, R substituents on the alkynyl ligand and/or the metal centre also play a decisive role in the concurrence of alkynylation processes. This can easily be seen when comparing the structures of the dinuclear platinum–iridium and –rhodium complexes (**27**, Scheme 9, **I** and **J**). Obviously, further efforts have to be made in order to clarify all of these points.

Acknowledgements

Grateful thanks go to our dedicated and enthusiastic co-workers whose names appear in the Reference list and who made this work possible. In this regard particular acknowledgement must go to Drs. M^a. Teresa Moreno and J. Ruben Berenguer. The Comisión Interministerial de Ciencia y Tecnologia (CICYT) of Spain is also gratefully acknowledged for its continuous support of our work (Projects PB 89-0057 and PB 92-0364).

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Received 9*th February* 1996; *Paper* 6/00971I