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Journal of Organometallic Chemistry 670 (2003) 45–55

Journal of Organometallic Chemistry

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Heterobimetallic platinum–copper and platinum–silver transition metal complexes based on *cis*-[Pt](C≡CPh)$_2$: an overview

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Received 13 September 2002; accepted 28 October 2002

Abstract

The reaction of *cis*-[Pt](C≡CPh)$_2$ {[Pt] = (bipy)Pt, (bipy′)Pt; bipy = 2,2′-bipyridine, bipy′ = 4,4′-dimethyl-2,2′-bipyridine} with different copper(I) and silver(I) salts [M′X] (M′ = Cu, Ag; X = inorganic or organic ligand) produces alkynyl-bridged (hetero)bi-, tri-, tetra- or pentametallic transition metal complexes. The structural aspects and reaction chemistry of such species and the preference for one coordination mode over another is discussed. The interconversion and mechanistical aspects in the formation of the latter complexes is also reported.

Keywords: Alkynyl; Platinum; Copper; Silver; π-Tweezer; Heterometallic; Oligometallic

1. Introduction

Recent developments made in bis(alkynyl) transition metal chemistry [M](C≡CR)$_2$ {[M] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti, [NBu$_4$]$_2$[Pt(C$_6$F$_5$)$_2$], [NBu$_4$]$_2$[Pt(C≡CR)$_2$], Ir(PPh$_3$)$_2$(C≡CC$_6$F$_5$)$_2$, Re(PPh$_3$)(CO)$_3$, ...; R = singly-bound organic or organometallic ligand} (type **A** molecule), led to diverse alkynyl-bridged species (type **B**–**G** molecules) (Scheme 1) [1–3].

In type **B**–**G** molecules a number of different structures, depending upon steric ([M′], R) and electronic ([M], [M′], R) properties of the respective transition metals M and/or M′ and organic or organometallic ligands R involved, are generated. Since, the two alkynyl ligands in type **B**–**G** molecules hold the metals M and M′ in close proximity to each other, synergistic and cooperative effects between the appropriate metal atoms are observed and hence, these complexes can be used, for example, as model compounds to study electron transfer between the metals along the μ–σ,π-bound alkynyls [4,5]. Also, they can be utilised as active components in homogeneous catalysis [6].

While, among type **A**–**G** molecules the bis(alkynyl) titanocene-based systems are well-studied including their reaction chemistry, structure, bonding and physical properties, and have been reviewed lately [1b], only less is known about the use of *cis*-orientated bis(alkynyl) platinum-based coordination complexes as organometallic π-tweezers [1,7–11].

Out of this reason, we here focus on recent developments made in the synthesis and reaction behaviour of *cis*-[Pt](C≡CPh)$_2$ {[Pt] = (bipy)Pt, (bipy′)Pt; bipy = 2,2′-bipyridine, bipy′ = 4,4′-dimethyl-2,2′-bipyridine} towards diverse Group-11 transition metal salts [M′X] (M′ = Cu, Ag; X = inorganic or organic ligand) producing (hetero)bi-, tri-, tetra- or even pentametallic complexes.

For the reaction behaviour of other bis(alkynyl) platinum compounds see, for example Refs. [1,7,11–14,17].

2. Results and discussion

Coordination complexes of type **B** (Scheme 1) can be considered as bidentate organometallic chelating ligands

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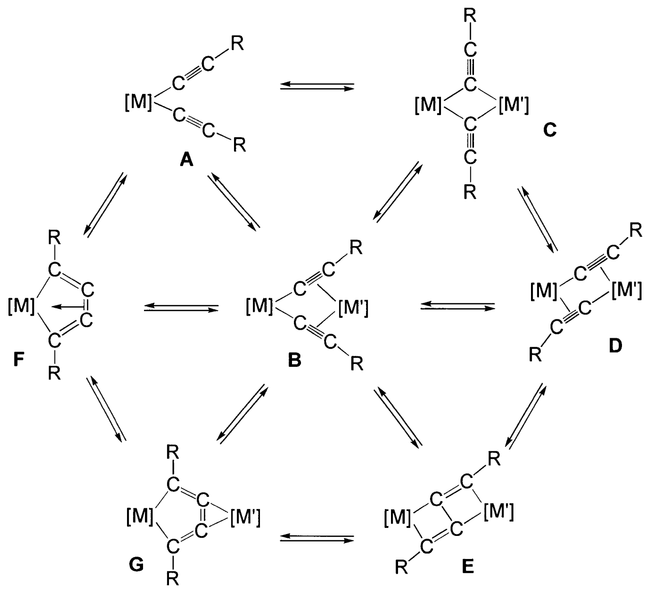
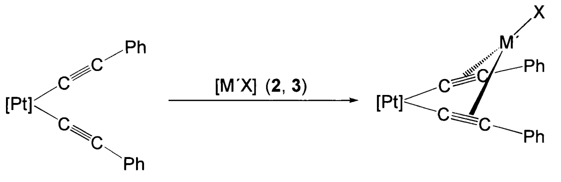
PII: S0022-328X(02)02105-8



Scheme 1. Potential interconversion and possible structures of alkynyl coordination modes in heterobimetallic π-tweezer chemistry [1].

and hence, can be used to stabilise, for example, Group-11 metal salts [M′X] (M′ = Cu, Ag; X = inorganic or organic ligand) [1]. In the so formed heterobimetallic late–late {*cis*-[Pt](C≡CPh)$_2$}M′X tweezer complexes (type **B** molecule) (**4**: M′ = Cu, **5**: M′ = Ag) the M′ atoms are displaced from the plane defined by the platinum(II) ion and the phenylethynyl ligands (see below). This differs from the structure of the respective titanium(IV)–copper(I) or titanium(IV)–silver(I) tweezer systems {[Ti](C≡CR)$_2$}M′X {[Ti] = (η^5-C$_5$H$_5$)$_2$Ti, (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti, ...; R = singly-bound organic or organometallic ligand} in which the Group-11 metal M′ and the [Ti](C≡CR)$_2$ fragment are coplanar [1].

The synthesis of complexes **4** and **5** can be achieved by reacting *cis*-[Pt](C≡CPh)$_2$ {**1a**: [Pt] = (bipy)Pt, **1b**: [Pt] = (bipy′)Pt; bipy = 2,2′-bipyridine; bipy′ = 4,4′-dimethyl-2,2′-bipyridine} with diverse [M′X] salts (**2**: M′ = Cu, **3**: M′ = Ag) in dichloromethane or tetrahydrofuran solutions in a 1:1 M ratio (Eq. (1)) (Table 1).



1a, **1b** **4**, **5**

(1)

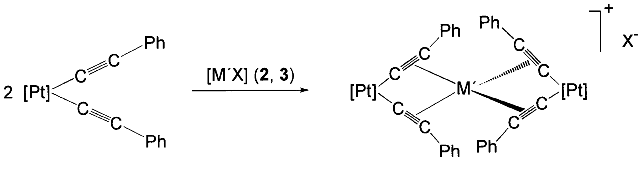
Yellow coloured **1**, **4** and **5** can be used for the preparation of transition metal complexes which feature three, four or even five transition metals. The latter molecules are accessible by controlling the stoichiometry (ratio of Pt:M′ = 2:1, 2:2 or 3:2, respectively) and/or the reaction conditions [11,12].

Table 1
Synthesis of heterobimetallic **4** and **5** [11,12]

Compound	[Pt]	M′	X
4a	(bipy)Pt	Cu	Cl
4b	(bipy′)Pt	Cu	Cl
4c	(bipy)Pt	Cu	Br
4d	(bipy′)Pt	Cu	Br
4e	(bipy)Pt	Cu	I
4f	(bipy′)Pt	Cu	I
4g	(bipy)Pt	Cu(N≡CMe) [a]	BF$_4$
4h	(bipy′)Pt	Cu(N≡CMe) [a]	BF$_4$
4i	(bipy′)Pt	Cu(N≡CMe) [a]	ClO$_4$
4j	(bipy′)Pt	Cu	NO$_3$
4k	(bipy′)Pt	Cu	OTf [b]
4l	(dppe)Pt	Cu(N≡CMe) [a]	BF$_4$
4m	(bipy)Pt	Cu(PPh$_3$) [a]	BF$_4$
5a	(bipy′)Pt	Ag	Cl
5b	(bipy′)Pt	Ag	Br
5c	(bipy′)Pt	Ag(N≡CMe) [a]	BF$_4$
5d	(bipy′)Pt	Ag(CH$_2$Cl$_2$) [a]	BF$_4$
5e	(bipy′)Pt	Ag	BPh$_4$
5f	(bipy′)Pt	Ag(N≡CMe) [a]	ClO$_4$
5g	(bipy′)Pt	Ag(N≡CMe) [a]	PF$_6$
5h	(bipy′)Pt	Ag	NO$_2$
5i	(bipy′)Pt	Ag	NO$_3$
5j	(bipy)Pt	Ag	OTf [b]
5k	(bipy)Pt	Ag	OC(O)CF$_3$
5l	(bipy′)Pt	Ag	OC(O)Me
5m	(bipy′)Pt	Ag(PPh$_3$) [a]	BF$_4$
5n	(bipy′)Pt	Ag	acac [c,d]
5o	(bipy′)Pt	Ag	C$_3$HO$_2$-1,3-^{t}Bu$_2$ [c]
5p	(bipy′)Pt	Ag	hfac [c,e]
5q	(bipy′)Pt	Ag	C$_3$HO$_2$-1,3-Ph$_2$ [c]
5r	(bipy′)Pt	Ag	trop [c,f]

[a] Datively-bound (solvent) molecule.
[b] OTf, triflate, OSO$_2$CF$_3$.
[c] Chelate-bound.
[d] acac, acetylacetonate.
[e] hfac, hexafluoro-acetylacetonate.
[f] trop, troponolate.

Although, the reaction of *cis*-[Pt](C≡CPh)$_2$ (**1a**, **1b**) with [M′X] in a 1:1 M ratio results in the formation of heterobimetallic structural type **B** molecules, an interesting class of Pt$_2$M′ complexes is produced, when two equivalents of **1** are allowed to react with a M′ source such as [M′X] (X = BF$_4$, ClO$_4$, PF$_6$) to form species of general type [{*cis*-[Pt](C≡CPh)$_2$}$_2$M′]X (**6**, **7**) (Eq. (2)) (Table 2) [11c,13].



1a, **1b** **6a**, **6b**, **7a - 7f**

(2)

In **6** and **7** the metals M′ are chelate-bound and hence, tetrahedrally coordinated by two *cis*-[Pt](C≡CPh)$_2$ π-

Table 2
Synthesis of complexes **6** and **7** [11c,13]

Compound	[Pt]	M′	X
6a	(bipy)Pt	Cu	BF_4
6b	(bipy′)Pt	Cu	BF_4
7a	(bipy)Pt	Ag	BF_4
7b	(bipy)Pt	Ag	ClO_4
7c	(bipy)Pt	Ag	PF_6
7d	(bipy′)Pt	Ag	BF_4
7e	(bipy′)Pt	Ag	ClO_4
7f	(bipy′)Pt	Ag	PF_6

tweezer units, which are orthogonal positioned to each other [1,11c,13].

In these Pt_2M' complexes the counter-ion X^- must be a poor ligand, e.g. BF_4^-, PF_6^-, ClO_4^- to prevent the formation of type **B** molecules and free *cis*-[Pt]$(C{\equiv}CPh)_2$ (**1**). Also, such compounds are only formed, when a phenyl or ferrocenyl group is present at the alkynyl ligands. Larger groups ($R = SiMe_3$, ^{t}Bu) will give without exception structural type **B** molecules (Scheme 1). Similar Pt_2M' complexes (**8**, **9**), derived from other Pt-containing tweezers as **1a** and **1b**, are accessible, when $L_2Pt(C{\equiv}CR)_2$ (R = Ph: **1c**, L_2 = dppe; **1d**, L = PPh_3; **1e**, L = PEt_3. R = ^{t}Bu: **1f**, L_2 = dppe; **1g**, L = PPh_3; dppe = diphenylphosphinoethane) is treated with [M′X] in a 2:1 M ratio (Table 3) [1,8b,14]. Similar results are obtained, when instead of bis(alkynyl) platinum coordination complexes, bis(alkynyl) titanocenes of type [Ti]$(C{\equiv}CR)_2$ {[Ti] = $(\eta^5\text{-}C_5H_5)_2Ti$, $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; R = Ph, Fc, ...; Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$} are used as organometallic π-tweezers [1,15,16].

The solid-state structure of selected species of the latter type (complexes **6**–**9**) was determined by using X-ray structure analysis [1,8,11c,13,14]. In all species the cationic part $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}_2M']^+$ (**6**, **7**)/$\{[cis\text{-}L_2Pt(C{\equiv}CR)_2]_2M'\}^+$ (**8**, **9**) is set-up by two almost orthogonal positioned bis(alkynyl) platinum parts, which are spanned by the Group-11 metal ion M'^+. M'^+ is thereby η^2-coordinated by all four $RC{\equiv}C$ ligands of the *cis*-$Pt(C{\equiv}CR)_2$ units, forming a linear Pt–M′–Pt array. A very characteristic feature of **6**–**9** is the non-equivalent linkages of C_α and C_β to M′ ($Pt\text{-}C_\alpha{\equiv}C_\beta$), which is even more pronounced as it is the case in type **B** molecules [1,7,11].

Table 3
Synthesis of complexes **8** and **9** [1,8b,11c,14]

Compound	L_2/L	R	M′	X
8	dppe [a]	Ph	Cu	BF_4
9a	PPh_3	Ph	Ag	ClO_4
9b	PEt_3	Ph	Ag	ClO_4
9c	dppe [a]	Ph	Ag	ClO_4
9d	PPh_3	^{t}Bu	Ag	ClO_4
9e	dppe [a]	^{t}Bu	Ag	ClO_4

[a] Chelate-bound; dppe, diphenylphosphinoethane.

While in **8** the transition metal atom copper lies only slightly out of the $Pt(C{\equiv}CC_{Ph})_2$ plane, to presumably minimise steric interactions between the phenylethynyl ligands and the dppe chelate, in **9a** a asymmetric structure is typical, which means that the silver(I) ion is closer situated to one $Pt(C{\equiv}CC_{Ph})_2$ fragment than to the other one [Pt(1)···Ag 3.384 Å, Pt(2)···Ag 3.513 Å] [1,8b,14].

Complexes **6**–**9** can also be prepared by starting out from type **B** molecules. When, for example, *cis*-(dppe)-$Pt(C{\equiv}CPh)_2$ (**1c**) is treated with $[Cu(N{\equiv}CMe)_4]BF_4$ (**2d**) heterobimetallic $\{[cis\text{-}(dppe)Pt(C{\equiv}CPh)_2]Cu(N{\equiv}CMe)\}BF_4$ (**4l**), a type **B** molecule, is formed, which rearranges in a mixture of acetone–acetonitrile to afford the Pt_2Cu complex **8** (Table 3) [8b,14].

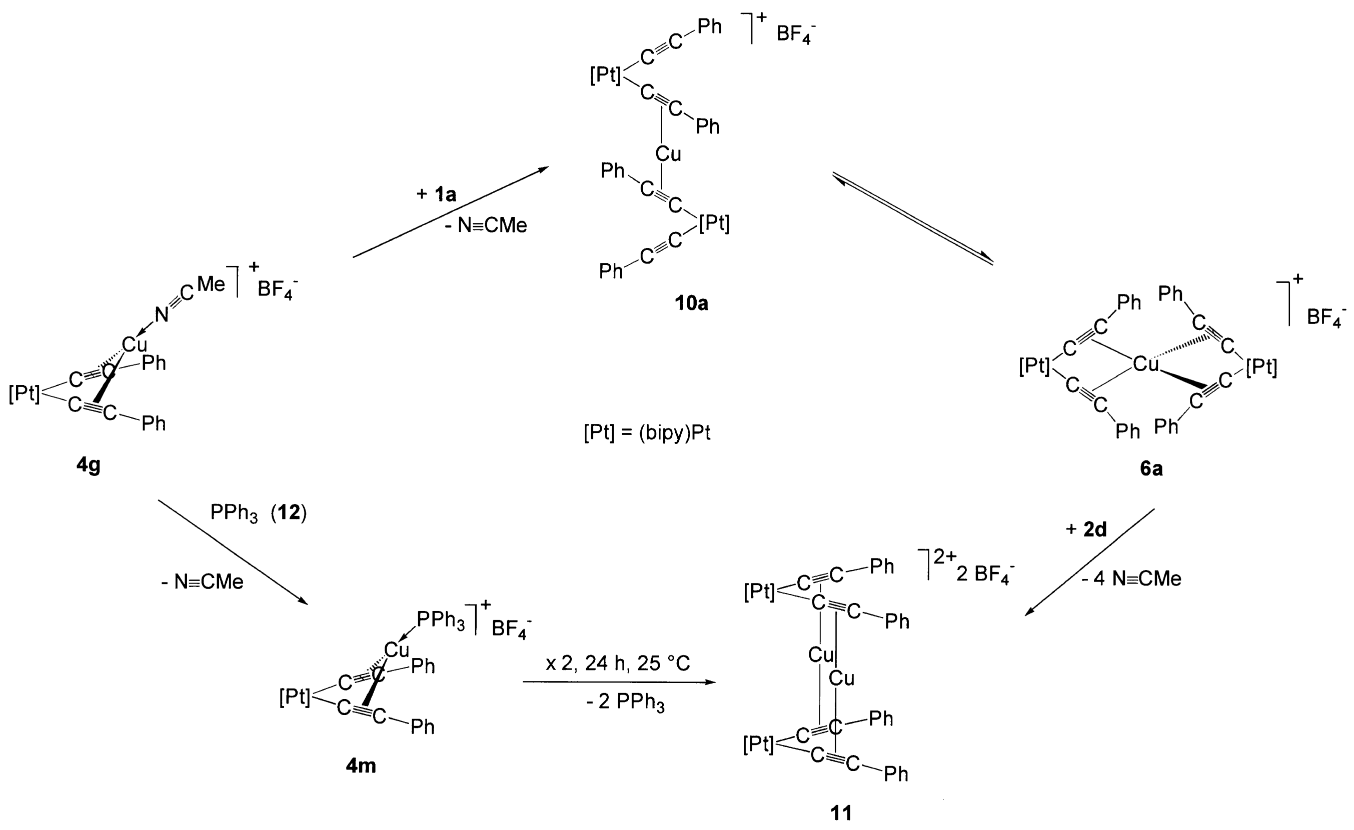
Another possibility to synthesise complexes of the latter type is given by reacting complexes **6** and **7**, respectively, with a type **A** π-tweezer molecule. However, within these reactions two different mechanism take place (**6**: Scheme 2, **7**: Scheme 4) [11c,13].

When, for example, heterobimetallic **4g** is reacted with *cis*-[Pt]$(C{\equiv}CPh)_2$ (**1a**) the weakly-bound acetonitrile is replaced by **1a**, thus forming trimetallic **10a** (Scheme 2). In **10a** two *cis*-[Pt]$(C{\equiv}CPh)_2$ units are spanned by a copper(I) ion in such a way that one $PhC{\equiv}C$ ligand of each individual *cis*-[Pt]$(C{\equiv}CPh)_2$ array is π-coordinated to Cu(I), thus giving rise to the formation of a linear alkyne–copper–alkyne moiety, $[[(\eta^2\text{-}C{\equiv}CPh)_2Cu]^+$ (alkyne = midpoint of the C≡C triple bond) (Scheme 2) [11c,13]. Upon warming **10a** it rearranges to give **6a** (Scheme 2).

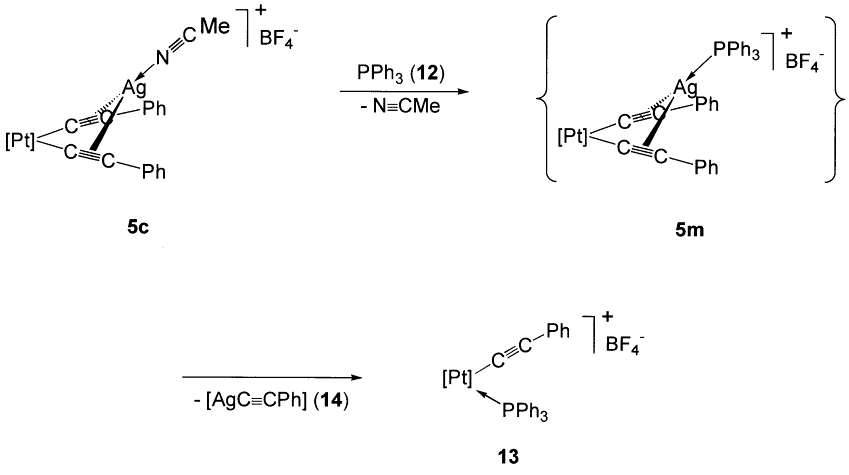
Complexes **6a** and **10a** contain also the information to act as suitable starting material for the synthesis of the tetrametallic Pt_2Cu_2 complex **11** (Scheme 2). On treatment of **6a** with **2d** complex **11** is formed upon loss of $N{\equiv}CMe$ [11c,13]. This molecule is also available, when **4g** is reacted with one equivalent of PPh_3 (**12**). At first $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}CuPPh_3]BF_4$ (**4m**) is formed, which produces on prolonged stirring on elimination of **12** tetrametallic **11** (Scheme 2) [11c].

In an attempt to synthesise isostructural $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}AgPPh_3]BF_4$ (**5m**) {[Pt] = (bipy′)Pt}, however, as stable species only the ionic monoalkynyl platinum triphenylphosphane $\{cis\text{-}[Pt](C{\equiv}CPh)(PPh_3)\}BF_4$ (**13**) along with $[AgC{\equiv}CPh]$ (**14**) could be isolated (Eq. (3)) [17]. Presumably **13** is formed via the intermediate formation of **5m** in which as Lewis-base PPh_3 (**12**) is datively-bound to the silver(I) ion.

A possible mechanism for the formation of **13** and **14** is outlined in Scheme 3, and includes the rearrangement

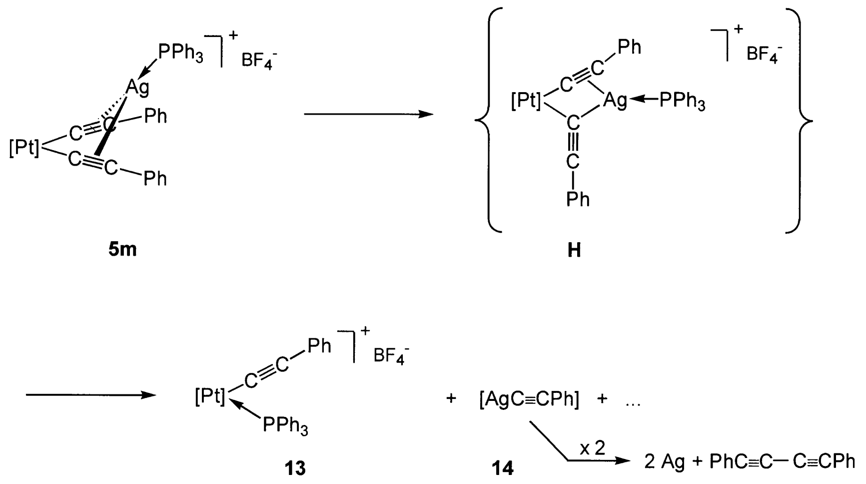


Scheme 2. Synthesis and reaction chemistry of **6a** [11c,13].



(3)

of **5m** to give as intermediate a structural type **H** molecule. In **H** one of the two PhC≡C ligands occupies a μ–σ-bridging position between platinum and silver, while the other one, as in the starting material, acts as σ,μ–π-ligand. Molecules of type **H** could recently be isolated in titanocene–tweezer chemistry [1]. From molecule **H** the elimination of [AgC≡CPh] (**14**) occurs yielding **13**. Finally, [AgC≡CPh] undergoes a redox



Scheme 3. Possible mechanism for the synthesis of **13** [17].

reaction to give elemental silver along with the butadiyne PhC≡C–C≡CPh [17]. Mechanistic studies were carried out [17].

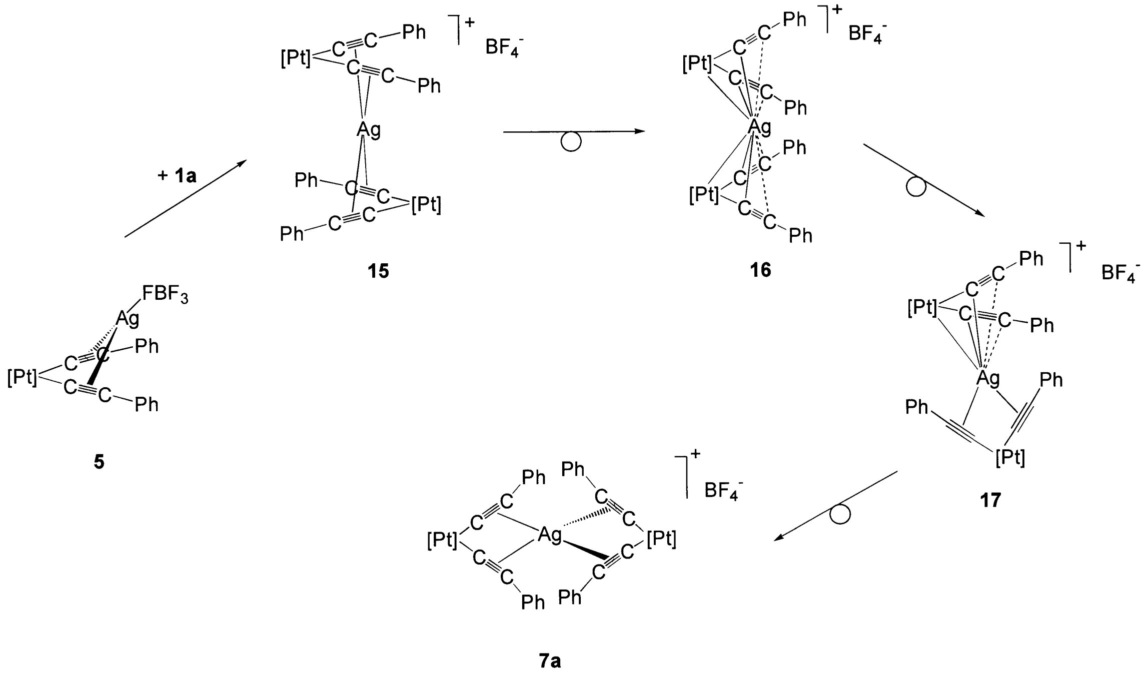
As mentioned earlier, in the synthesis of **7a**–**7f** another mechanism came about (Scheme 4) [11c]. This could be demonstrated by the reaction of {*cis*-[Pt](C≡CPh)$_2$}AgFBF$_3$ with **1a**.

As shown in Scheme 4, the first step in the preparation of **7a** involves the elimination of BF$_4$ from **5** by addition of the organometallic chelate **1a**. Initially formed [{*cis*-[Pt](C≡CPh)$_2$}$_2$Ag]BF$_4$ (**15**) contains two *cis*-[Pt](C≡CPh)$_2$ units which are η^2-coordinated to a silver(I) ion via the four PhC≡C groups [11c]. The two *cis*-[Pt](C≡CPh)$_2$ moieties are thereby parallel orientated to each other with the platinum atoms laying on the opposite site [11c].

Complex **15** isomerises in solution to produce **16** and then **17**, which finally rearranges to form **7a** (Scheme 4).

IR spectroscopic studies give the first hint for the different bonding modes of the alkynyl groups present in **5**, **7a** and **15**–**17** [1,8b,11c].

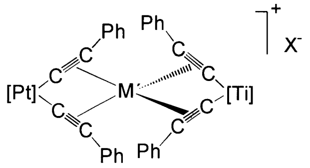
This could also be confirmed by single X-ray structure determinations [11c]. In **15** a silver(I) ion spans two *cis*-[Pt](C≡CPh)$_2$ moieties with all four PhC≡C units η^2-coordinated to Ag(I), resulting in a pseudo-tetrahedrally coordination sphere at the Group-11 transition metal ion [11c]. The two d^8-configurated platinum ions are thereby positioned on opposite sites. This molecule



Scheme 4. Synthesis of **7a** by the reaction of **5** with **1a** [11c].

rearranges to give **16** in which the silver atom is again embedded between two *cis*-arranged $[Pt](C{\equiv}CPh)_2$ entities. Within this structural arrangement, however, the silver(I) ion interacts with both platinum centres [Pt–Ag 2.8966(3) Å]. In addition, the silver atom preferentially binds to the C_α-atoms of the $Pt(C_\alpha{\equiv}C_\beta Ph)_2$ building blocks, giving rise to a bonding situation which best can be explained by μ–σ-bridging phenylacetylide moieties. This structural arrangement is favoured by the Ag–C_α [2.443(6), 2.548(6) Å] and Ag–C_β distances [2.799(6), 3.042(6) Å] [11c]. A similar bonding situation is found in **17** [11c]. Half of the molecule corresponds to the latter bonding motif, while the other $\{[Pt](C{\equiv}CPh)_2\}Ag$ fragment resembles to a bonding situation as typical for **7** (Scheme 4) [8b,11c]. In the latter unit the transition metals platinum and silver, the sp-hybridised carbon atoms and the C-*ipso* atom of the $Ph_{C{\equiv}C}$ ligands are thereby in-plane bound (rms deviation 0.0196 Å) [11c].

First attempts to synthesise mixed titanium(IV)–platinum(II)–copper(I) or titanium(IV)–platinum(II)–silver(I) complexes of molecules of type **6** or **7**, respectively, have not been successful (complex **18**) [11c]. In all reactions the appropriate $[\{[Ti](C{\equiv}C\text{-}Ph)_2\}_2M']X$ (**19**) $\{[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; $M' = Cu$, Ag; $X = BF_4$, $ClO_4\}$ and $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}_2M']X$ $\{[Pt] = (bipy)Pt$, (bipy′)Pt; **6**: $M' = Cu$, **7**: $M' = Ag$; $X = BF_4$, $ClO_4\}$ were formed [1,11c,14–16].



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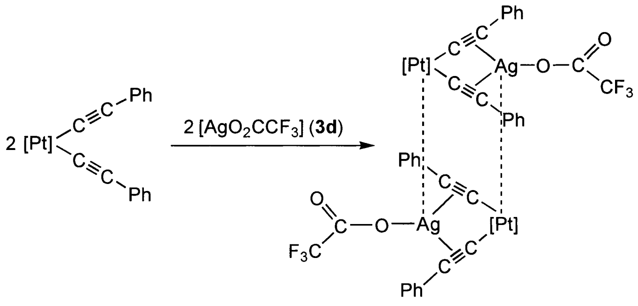
Nevertheless, changing from [AgX] (X = inorganic ligand) to [AgR] (R = organic group) as given in, for example, $[AgO_2CCF_3]$ (**3j**) a different product is obtained, when **1a** is treated with **3j** in a 1:1 M ratio. Complex **20** is formed in excellent yields (Eq. (4)) [11c].



1a **20**

(4)

In the solid-state two heterobimetallic $\{cis\text{-}[Pt](C{\equiv}C\text{-}Ph)_2\}AgOC(O)CF_3$ π-tweezer moieties are hold together by the formation of platinum–silver interactions [Pt···Ag distance: 2.8674(15) Å] [11c]. The F_3CCO_2 group is thereby σ-bound by one oxygen atom to silver(I), which is typical in organometallic π-tweezer chemistry [1].

Not only the preparation of (hetero)bi-, tri- and tetrametallic transition metal complexes, based on *cis*-$[Pt](C{\equiv}CPh)_2$ is possible, also the synthesis of a pentametallic Pt_3Cu_2 species, by controlling the stoichiometry of the reactants succeeds. Treatment of three equivalents of **1b** with two parts of $[Cu(N{\equiv}CMe)_4]BF_4$ (**2d**) affords $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}_3Cu_2][BF_4]_2$ (**21**) in high yield (Scheme 5). Complex **21** is also accessible, when $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}Cu(N{\equiv}CMe)]BF_4$ (**4h**) is reacted with $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}Cu]BF_4$ (**10b**) in a 1:1 M ratio [11c]. In **21** three *cis*-$[Pt](C{\equiv}CPh)_2$ fragments are spanned by two copper(I) ions, including all six acetylides (Scheme 5) [11c].

A possible mechanism for the formation of **21** is presented in reference [11c].

3. Structure and bonding

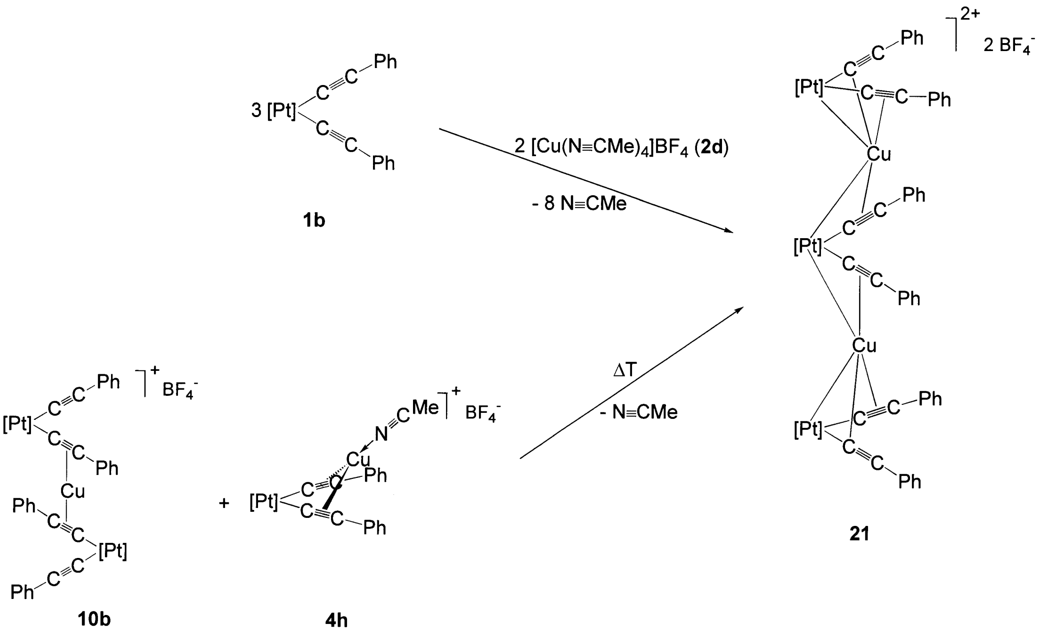
As shown above, *cis*-$[Pt](C{\equiv}CPh)_2$ (**1a**, **1b**) can be used as organometallic π-tweezer for the stabilisation of monomeric, low-valent copper(I) and silver(I) salts [M′X]. In the so assembled heterobimetallic Pt–M′ species $\{cis\text{-}[Pt](C{\equiv}CPh)_2\}M'X$ (complexes **4** and **5**, Table 1) the *cis*-$[Pt](C{\equiv}CPh)_2$ fragment is η^2-coordinated to the respective M′ transition metal, which means that *cis*-$[Pt](C{\equiv}CPh)_2$ acts as chelating ligand for the M′X entities. In complexes **4** and **5** the $\{cis\text{-}[Pt](C{\equiv}C\text{-}Ph)_2\}M'$ unit is distorted from planarity at which M′ is displaced from the *cis*-$[Pt](C{\equiv}CPh)_2$ plane {[Pt] = (bipy)Pt, (bipy′)Pt} [1,11].

The solid-state structure of selected examples of **4** and **5** were determined by X-ray structure analysis [1,11c]. Significant observations with respect to the η^2-alkyne-to-M′ interactions are:

i) bond-weakening of the carbon–carbon triple bonds,
ii) bending of the $Pt{-}C{\equiv}C{-}C_{Ph}$ units upon their side-on coordination to M′ (whereby the $C{\equiv}C{-}C_{Ph}$ entity is more effected than the $Pt{-}C{\equiv}C$ part), and
iii) diminution of the $C_\alpha{-}Pt{-}C_{\alpha'}$ angle ($Pt{-}C_\alpha{\equiv}CPh$).

Since, topics (i)–(iii) have already been discussed in detail earlier [1], this section focuses on some more general aspects.

In addition to X-ray structure analysis, IR spectroscopy is a much better guide to observe the change in bonding by going from free to η^2-coordinated copper(I) or silver(I) alkynes, respectively, since type **B** molecules display a very characteristic shift of the C≡C stretching vibrations to lower wavenumbers, when compared with



Scheme 5. Synthesis of **21** {[Pt] = (bipy′)Pt} [11c].

the non-coordinated starting materials **1a** or **1b** (type **A** molecule) [1,11].

From the obtained $\nu_{C\equiv C}$ data one can conclude that in the platinum(II)–silver(I) complexes weaker alkyne-to-metal interactions are present than in the analogous platinum(II)–copper(I) species, since the $\nu_{C\equiv C}$ absorptions of the latter compounds appear at lower frequencies [1,11].

A similar trend for titanium(IV)–silver(I) and titanium(IV)–copper(I) tweezer coordination complexes came across [1b].

Another characteristic feature of structural type **B** molecules is that the Pt···M′ distances with values between 2.9 and 3.5 Å indicate the absence of direct metal–metal interactions. The close proximity of platinum and copper as well as platinum and silver must be, however, regarded simply as an effect of the σ–μ,π-bridging of both phenylethynyl ligands [1].

Due to the η^2-coordination of the PhC≡C units to M′, a deformation of these ligands is observed and the Pt–C≡C–C_{Ph} angles are bent from linearity, to allow the alkynyl β-carbon atom to approach the copper or silver transition metal. The $C_\alpha \equiv C_\beta - C_{Ph}$ angle is more effected than the Pt–$C_\alpha \equiv C_\beta$ one, with the phenyl groups bent away from the M′ ion (vide supra) [1,11].

Also, the solid-state structure confirms that the Group-11 metals M′ lie out of the Pt(C≡C_{Ph})$_2$ plane. Complex {*cis*-[Pt](C≡C_{Ph})$_2$}CuBr (**4d**) is exemplary shown for all complexes **4** and **5** in Fig. 1 [1,11a].

In addition to complexes **4** and **5**, also the solid-state structure of molecules **6**, **7**, **10**, **11**, **13**, **15**–**17**, **20** and **21** was established. Since, these coordination complexes show similar trends in the solid-state only **6a**, **17** and **21** will be discussed to some extent in the following.

In trimetallic **6a** (Fig. 2) the two square-planar platinum coordination planes are almost orthogonal positioned to each other, with Cu(1) as bridging ion [1a,11c]. This structural arrangement makes it possible that both pairs of phenylethynyl ligands {*cis*-[Pt](C≡C-Ph)$_2$} adopt a bidentate coordination to copper(I) and hence, form a [(η^2-C≡CPh)$_4$Cu]$^+$ building block in which copper is embedded within the alkynyl ligands and possesses an approximately tetrahedral environment involving only carbon atoms. A striking feature of **6a** is, however, the unsymmetrically side-on binding of the four PhC≡C ligands to Cu$^+$ [Cu–C_α: 2.297(7), 2.260(7), 2.222(7), 2.206(7); Cu–C_β: 2.550(7), 2.510(8), 2.456(7), 2.278(7) Å; Pt–$C_\alpha \equiv C_\beta$] (Fig. 2). In conclusion, in **6a** the four acetylides are more weakly-bound to Cu(1) than in, for example, type **B** tweezer molecules [1a,11c].

A interesting feature of trimetallic Pt$_2$Ag (**17**) in which a silver(I) ion spans two *cis*-[Pt](C≡CPh)$_2$ planes is the presence of two sets of different bound platinum–silver-acetylide units. One [Pt](C≡CPh)$_2$Ag entity contains μ–σ,π-coordinating PhC≡C units as typical, for example, for structural type **B** π-tweezer molecules, while the other one holds σ,μ-bridging PhC≡C units between the platinum(II) and silver(I) ions (Fig. 3) [11c]. In addition, the latter building block includes a metal–metal interaction [2.9964(7) Å].

While the silver atom is almost in-plane-bound with Pt(2), C(27), C(28), C(35) and C(36) [maximum deviation from this plane: 0.074(4) Å] it is clearly out-of the

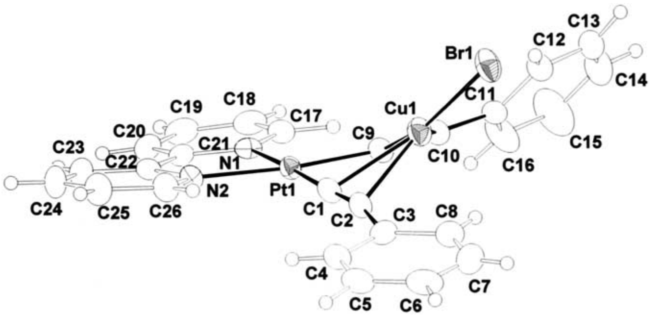


Fig. 1. X-ray structure analysis of **4d** [1,11a]. Selected interatomic bond distances (Å) and bond angles (°) are as fellows: Pt(1)–Cu(1) 3.0343(6), Pt(1)–C(1) 1.966(5), Pt(1)–C(9) 1.936(5), C(1)–C(2) 1.207(6), C(9)–C(10) 1.221(7), Cu(1)–Br(1) 2.3129(8), Cu(1)–C(1) 2.193(5), Cu(1)–C(2) 2.328(5), Cu(1)–C(9) 2.100(5), Cu(1)–C(10) 2.227(5); C(1)–Pt(1)–C(9) 84.8(2), Pt(1)–Cu(1)–Br(1) 154.74(3), Pt(1)–C(1)–C(2) 172.2(5), Pt(1)–C(9)–C(10) 173.1(4), C(1)–C(2)–C(3) 166.1(5), C(9)–C(10)–C(11) 162.3(5).

Pt(1), C(1), C(2), C(9) and C(10) plane orientated [maximum deviation from this plane: 1.719(6) Å]. All other distances and angles are in agreement with the data usually observed for platinum- and copper-alkynyls.

The result of the X-ray structure determination of **21** is shown in Fig. 4, and demonstrates that **21** consists of three helically arranged bis(alkynyl) platinum building blocks [1a,11c].

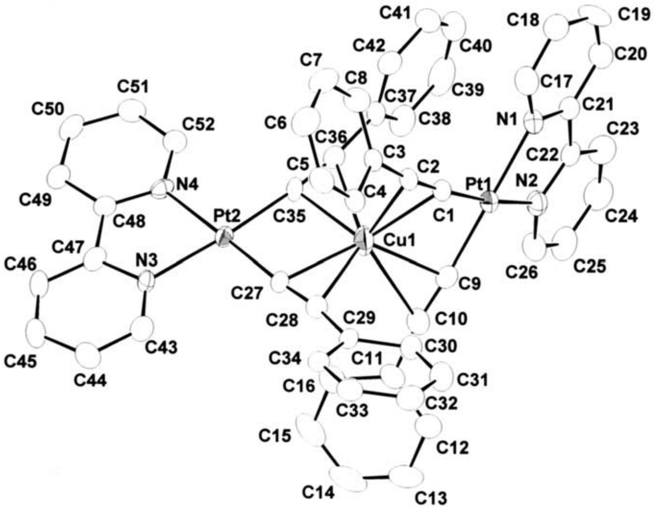


Fig. 2. X-ray structure analysis of **6a** with the atom numbering scheme [1a,11c]. Selected interatomic distances (Å) and bond angles (°) are: Pt(1)–Cu(1) 3.0397(10), Pt(1)–C(1) 1.971(7), Pt(1)–C(9) 1.961(8), Pt(2)–C(27) 1.988(7), Pt(2)–C(35) 1.995(7), Cu(1)–C(1) 2.297(7), Cu(1)–C(2) 2.550(7), Cu(1)–C(9) 2.260(7), Cu(1)–C(10) 2.510(8), Cu(1)–C(27) 2.206(7), Cu(1)–C(28) 2.278(7), Cu(1)–C(35) 2.222(7), Cu(1)–C(36) 2.456(7), C(1)–C(2) 1.229(10), C(9)–C(10) 1.221(10), C(27)–C(28) 1.226(10), C(35)–C(36) 1.199(10); Pt(1)–C(1)–C(2) 172.7(6), Pt(1)–C(9)–C(10) 175.0(7), Pt(2)–C(27)–C(28) 175.9(6), Pt(2)–C(35)–C(36) 174.9(7), C(1)–C(2)–C(3) 173.5(7), C(9)–C(10)–C(11) 169.5(8), C(27)–C(28)–C(29) 166.4(8), C(35)–C(36)–C(37) 172.8(8), C(1)–Pt(1)–C(9) 87.9(3), C(27)–Pt(2)–C(35) 86.7(3).

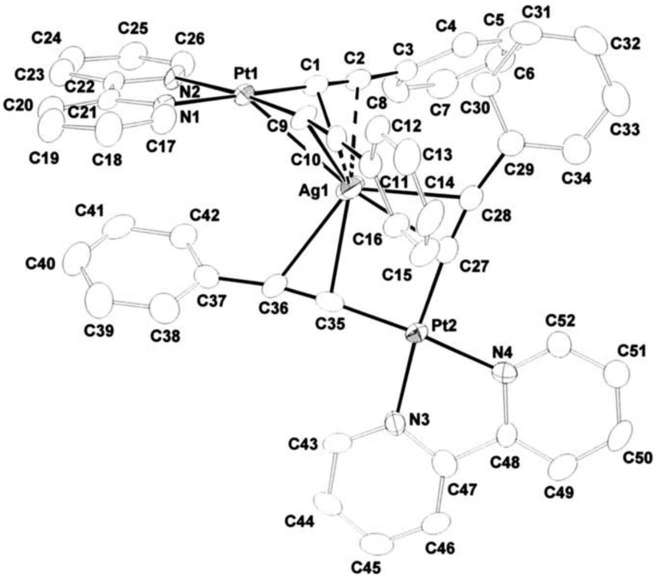


Fig. 3. X-ray structure analysis of **17** with the atom labelling scheme [11c]. Selected interatomic bond distances (Å) and bond angles (°) are as fellows: Pt(1)–Ag(1) 2.9964(7), Pt(1)–C(1) 1.986(9), Pt(1)–C(9) 1.979(8), Pt(2)–Ag(1) 3.3909(7), Pt(2)–C(27) 1.937(9), Pt(2)–C(35) 1.957(9), C(1)–C(2) 1.205(11), C(9)–C(10) 1.202(11), C(27)–C(28) 1.238(12), C(35)–C(36) 1.216(11), Ag(1)–C(1) 2.477(8), Ag(1)–C(2) 2.885(9), Ag(1)–C(9) 2.497(8), Ag(1)–C(10) 2.843(9), Ag(1)–C(27) 2.427(8), Ag(1)–C(28) 2.601(8), Ag(1)–C(35) 2.469(8), Ag(1)–C(36) 2.656(9); Pt(1)–C(1)–C(2) 178.5(8), Pt(1)–C(9)–C810) 171.9(8), Pt(2)–C(27)–C(28) 173.5(7), Pt(2)–C(35)–C(36) 174.9(8), C(1)–C(2)–C(3) 176.2(9), C(9)–C(10)–C(11) 175.0(9), C(27)–C(28)–C(29) 169.1(9), C(35)–C(36)–C(37) 171.8(9), C(1)–Pt(1)–C(9) 90.3(3), C(27)–Pt(2)–C(35) 90.1(3).

The dicationic Pt_3Cu_2 unit of **21** is formed by three neutral *cis*-$[Pt](C\equiv CPh)_2$ fragments, which are spanned by two copper(I) ions, including all six acetylide ligands and the platinum(II) centres. As counter-ions non-coordinating BF_4^- units are present (Fig. 4). Within the $[Pt_3Cu_2]^{2+}$ array the outer *cis*-$[Pt](C\equiv CPh)_2$ building blocks are bound to a Cu^+ ion in such way that one of the two $PhC\equiv C$ ligands is η^2-coordinated, while the other one preferentially forms a σ-bond with the C_α atom of the $Pt-C_\alpha\equiv C_\beta$ fragment and hence, corresponds to a μ-bridging $PhC\equiv C$ unit (Fig. 4). These two outer *cis*-$[Pt](C\equiv CPh)_2$ units are linked by a third bis(phenylethynyl) platinum entity of which the alkynyl ligands are unsymmetrically π-coordinated to the outer $\{[Pt](C\equiv C\text{-}Ph)_2\}Cu^+$ building blocks (vide supra). In addition, metal–metal interactions between the transition metals platinum and copper are found [1a,11c].

4. Conclusion

The synthesis of structural type **B** molecules and their reaction chemistry to form (hetero)bi-, tri-, tetra- or even pentametallic coordination complexes by control-

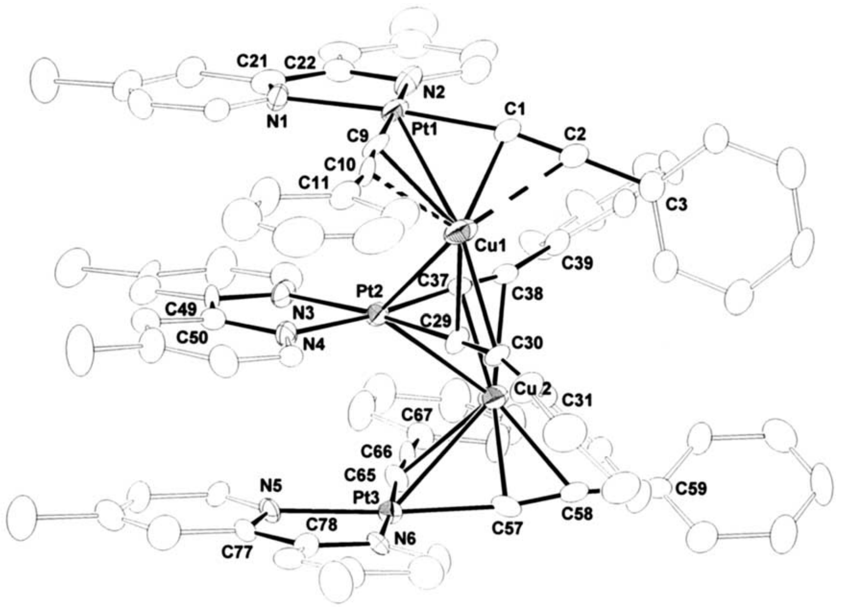
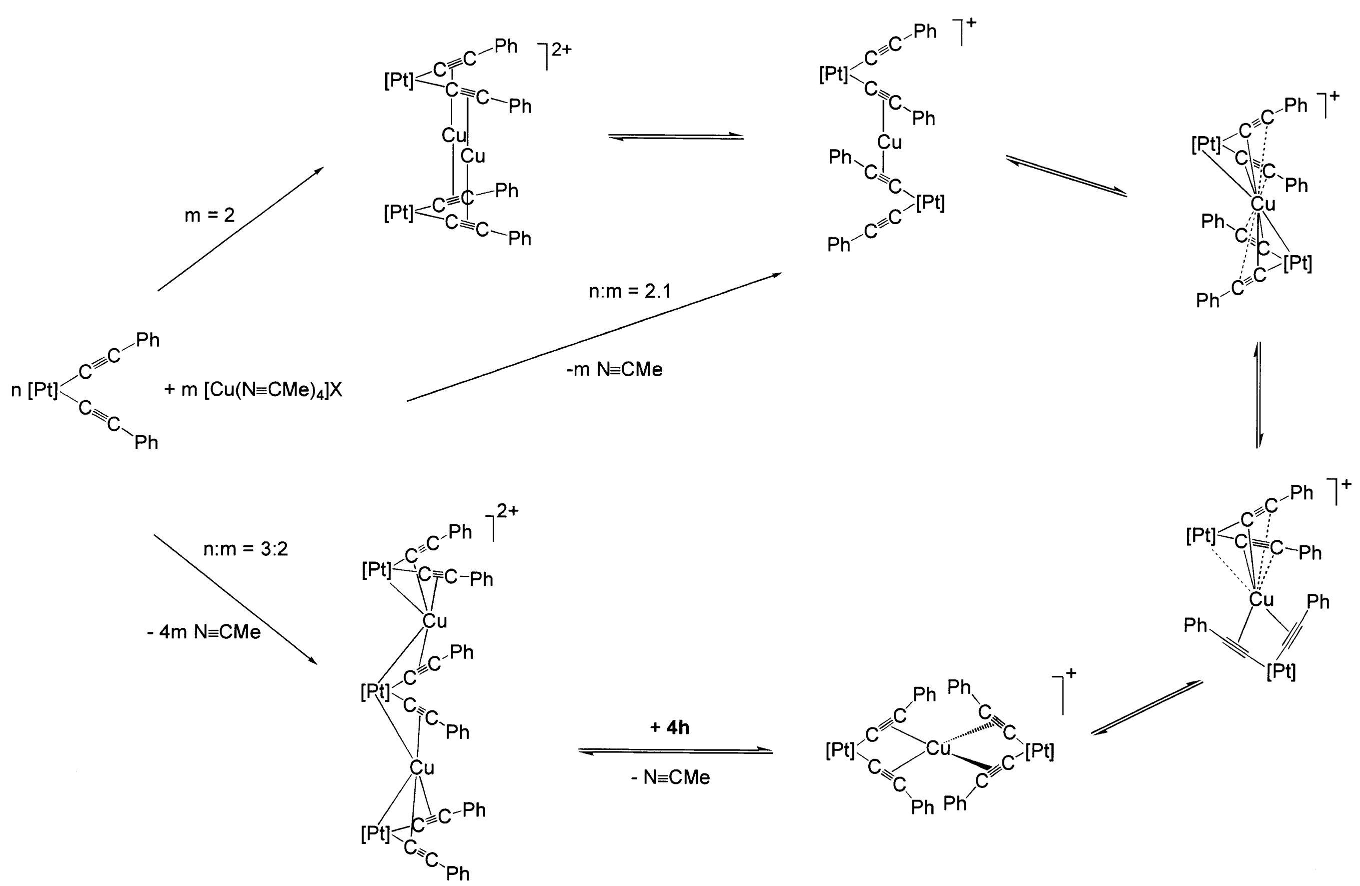


Fig. 4. ZORTEP PLOT (50% probability level) of the molecular structure of **21** [1a,11c]. Selected interatomic distances (Å) and angles (°) are: Pt(1)–C(1) 1.973(13), Pt(1)–C(9) 1.983(13), Pt(3)–C(57) 1.991(14), Pt(3)–C(65) 1.956(14), Cu(1)–Pt(1) 2.7856(16), Cu(1)–Pt(2) 2.9742(16), Cu(2)–Pt(2) 2.9981(16), Cu(2)–Pt(3) 2.7625(17), Cu(1)–C(1) 2.238(13), Cu(1)–C(9) 2.092(11), Cu(1)–C(10) 2.414(13), Cu(2)–C(57) 2.013(12), Cu(2)–C(65) 2.369(12), C(1)–C(2) 1.218(16), C(1)–C(2) 1.225(16), C(57)–C(58) 1.188(16), C(65)–C(66) 1.192(16); Pt(1)–C(1)–C(2) 169.1(11), Pt(1)–C(9)–C(10) 175.9(11), Pt(2)–C(29)–C(30) 171.4(9), Pt(2)–C(37)–C(38) 173.6(11), Pt(3)–C(57)–C(58) 171.3(11), Pt(3)–C(65)–C(66) 174.0(11), C(1)–Pt(1)–C(9) 88.0(5), C(29)–Pt(2)–C(37) 91.6(4), C(57)–Pt(3)–C(65) 83.8(5).



Scheme 6. Interconversion of alkynyl coordination modes in (hetero)bi-, tri-, tetra- and pentametallic platinum(II)–copper(I) and platinum(II)–silver(I) species.

ling the stoichiometry of the reactants is discussed. Possible structures of these complexes and their potential interconversion are depicted in Scheme 6.

Despite the quantity of experimental work done in this relatively young field of organometallic platinum–π-tweezer chemistry, based on *cis*-[Pt](C≡CPh)$_2$ {[Pt] = (bipy)Pt, (bipy′)Pt; bipy = 2,2′-bipyridine, bipy′ = 4,4′-dimethyl-2,2′-bipyridine} the factors which control and influence the interconversion of such structures (Scheme 6) in the above shown systems is still an open question and will continue to stimulate fruitful and innovative work in this field of chemistry.

Acknowledgements

The authors are grateful for the financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and Degussa AG, Hanau. Also, we are thankful to Mrs. Ute Stöß for preparing the drawings.

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