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From Heterobimetallic Transition Metal Complexes to Linear Coordination Polymers Based on *cis*- and *trans*-$L_2Pt(C\equiv CPh)_2$

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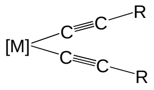
ABSTRACT: *The reaction of* cis-*(2,2′-bipyridine) $Pt(C\equiv CPh)_2$* cis-*(4,4′-dimethyl-2,2′-bipyridine) $Pt(C\equiv CPh)_2$ and* trans-*$(Ph_3P)_2Pt(C\equiv CPh)_2$ towards different group 11 transition-metal salts [M′X] (M′ = Cu, Ag; X = inorganic ligand) to give heterobimetallic or linear oligomeric and polymeric transition metal complexes is described. Different coordination modes for M′, $PhC\equiv C$, PPh_3, and X were found in these species. The structural aspects as well as the preference for one coordination mode over another is discussed.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:521–533, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10097

INTRODUCTION

Bis(alkynyl) transition metal complexes of type $[M](C\equiv CR)_2$ {$[M] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti, \ldots$; (bipy)-[Pt], …; $(Ph_3P)(CO)_3Re$; $(\eta^5\text{-}C_5H_5)Ru$; …; R = singly bound inorganic, organic, or organometallic group; bipy = 2,2′-bipyridine} (type **A** molecule) can successfully be used as organometallic chelates for the preparation of a high number of heterobimetallic complexes of structural type **B** and **C**, $\{[M](C\equiv CR)_2\}M'X$ (M′ = Cu, Ag, Fe, Ni, Co, …; X = singly or chelate-bound inorganic or organic ligand), in which the respective transition metals M and M′ are spanned by σ- and π-bound alkynyl groups [1,2].

In type **B** species the chelated metal center M′ and the $[M](C\equiv CR)_2$ unit are coplanar, while in structural type **C** molecules the M′ atom is displaced from the plane defined by M and the alkynyl ligands $RC\equiv C$ [1b]. These structural arrangements allow to study, for example, electron-transfer between the respective transition metals along the π-conjugated organic units [1b,3–5]. In addition, they possess considerable interest in organic and organometallic synthesis [1,2,6].



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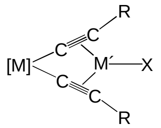

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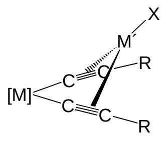

C

Since, the synthesis, reaction chemistry, structure and bonding, and physical properties of type **A–C** molecules have been reviewed lately [1b], herein we focus on recent developments made in the reaction behavior of cis- and trans-configurated bis(alkynyl) platinum complexes towards diverse group 11 transition-metal salts [M′X], producing heterobimetallic Pt-M′ (M′ = Cu, Ag) species or linear oligomers and polymers thereof.

Dedicated to Amaya del Villar.

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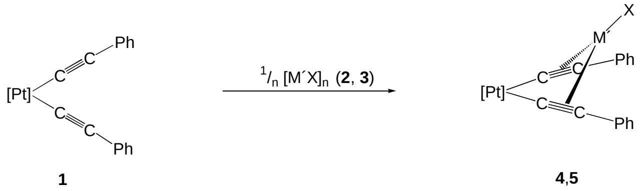
RESULTS AND DISCUSSION

For a better overall view this section is divided into two subsections:

1. Reaction chemistry of *cis*-[Pt](C≡CPh)$_2$ (synthesis of bimetallic–pentametallic coordination complexes).
2. Reaction behavior of *trans*-[Pt](C≡CPh)$_2$ (preparation of linear coordination polymers).

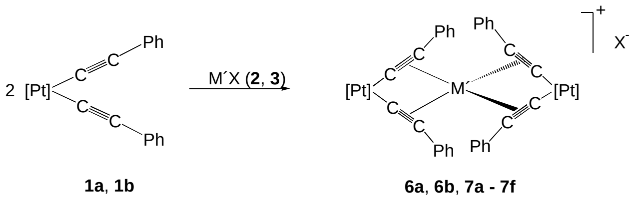
Reaction Chemistry of cis-[Pt](C≡CPh)$_2$

Based on heterobimetallic complexes of structural type **C** (complexes **4**, M′ = Cu, and **5**, M′ = Ag), which can be easily synthesized by the reaction of equimolar amounts of *cis*-[Pt](C≡CPh)$_2$ {**1a**: [Pt] = (bipy)Pt, bipy = 2,2′-bipyridine; **1b**: [Pt] = (bipy′)Pt, bipy′ = 4,4′-dimethyl-2,2′-bipyridine} with the copper(I) or silver(I) salts [M′X] (**2**: M′ = Cu, **3**: M′ = Ag; X = Cl, Br, NO_2, NO_3, OTf, BF_4, ClO_4, PF_6, . . . ; OTf = OSO_2CF_3),



diverse transition-metal complexes, featuring three, four, or even five metal atoms (ratio Pt/M′ = 2:1, 2:2, 3:2), are accessible by controlling both the stoichiometry and the reaction conditions [1,2,7–16].

When the molar ratio of **1** and **2** or **1** and **3** is changed from 1:1 to 2:1 then trimetallic complexes of type [{*cis*-[Pt](C≡CPh)$_2$}$_2$M′]X (M′ = Cu: **6a**, [Pt] = (bipy)Pt, X = BF_4; **6b**, [Pt] = (bipy′)Pt, X = BF_4. M′ = Ag, [Pt] = (bipy)Pt: **7a**, X = BF_4; **7b**, X = ClO_4; **7c**, X = PF_6. M = Ag, [Pt] = (bipy′)Pt: **7d**, X = BF_4; **7e**, X = ClO_4; **7f**, X = PF_6) are formed in which the respective group 11 metal centers M′ are chelate-bound by two *cis*-[Pt](C≡CPh)$_2$ units [12,14].



Selected species of the latter type were characterized by X-ray structural analysis [12,14]. The cation [{[Pt](C≡CPh)$_2$}$_2$M′]$^+$ is formed by two *cis*-[Pt](C≡CPh)$_2$ units that are nearly orthogonal positioned to each other and are connected through M′, which is π-bound by all four PhC≡C building blocks with a linear Pt—M′—Pt arrangement. The tendency that in heterobimetallic {*cis*-[Pt](C≡CPh)$_2$}M′X molecules of structural type **C** nonequivalent linkages of M′ to the C_α and C_β acetylide carbon atoms ($PtC_\alpha{\equiv}C_\beta$) are characteristic [1,7–11,14] is even more pronounced in **6** and **7** [12,14].

Compounds similar to **6** and **7** can be prepared, when $L_2Pt(C{\equiv}CR)_2$ (R = Ph: **1c**, L_2 = dppe, dppe = diphenylphosphinoethane; **1d**, L = PPh_3; **1e**, L = PEt_3; R = ^{t}Bu: **1f**, L_2 = dppe; **1g**, L = PPh_3) is reacted with **2** or **3** in a 2:1 molar ratio [1,7b,15]. The respective trinuclear species {[$L_2Pt(C{\equiv}CR)_2$]$_2$M′}X (M′ = Cu: **6c**, L_2 = dppe, R = Ph, X = BF_4; M′ = Ag: **7g**, L = PPh_3, R = Ph, X = ClO_4; **7h**, L = PEt_3, R = Ph, X = ClO_4; **7i**, L_2 = dppe, R = Ph, X = ClO_4; **7j**, L = PPh_3, R = ^{t}Bu, X = ClO_4; **7k**, L_2 = dppe, R = ^{t}Bu, X = ClO_4) were obtained in excellent yield.

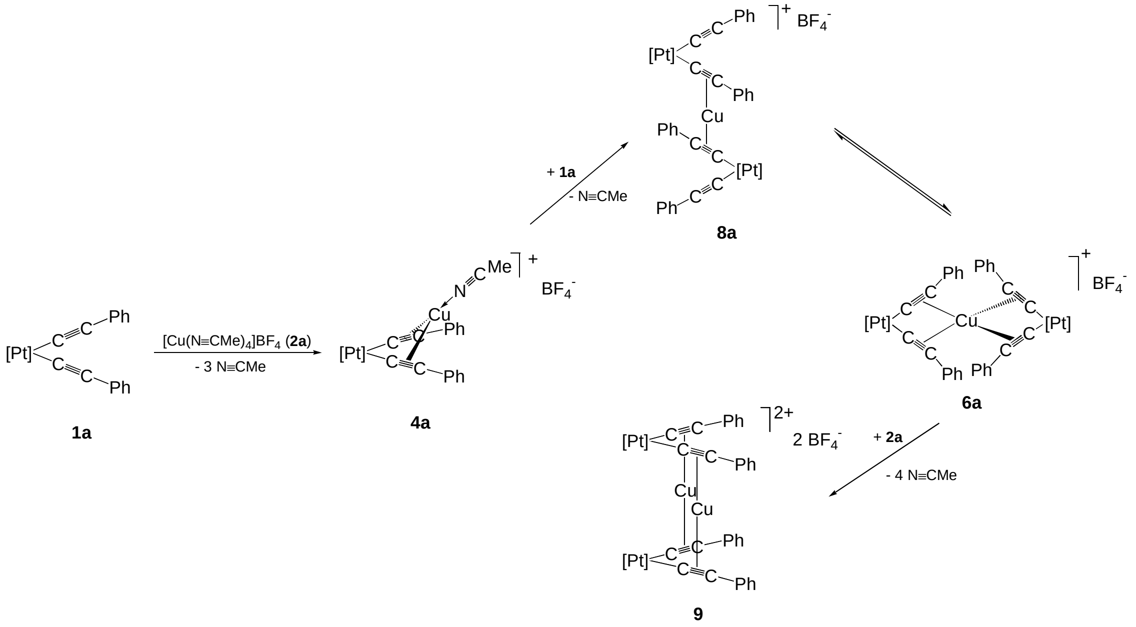
When **1c** is treated with [Cu(MeC≡N)$_4$]BF_4 (**2a**), ionic [{(dppe)Pt(C≡CPh]$_2$}Cu(MeC≡N)]BF_4 (**4c**) is initially formed, which rearranges in a mixture of acetone–acetonitrile to give trinuclear {[(dppe)Pt(C≡CPh)$_2$]$_2$Cu}BF_4 (**6c**) [7b,15].

A further possibility to synthesize complexes **6** and **7** is given by reacting **1** with **4** or **5**, respectively, in a 1:1 molar ratio [12,14]. Within these reactions two different mechanism take place (**6**: Scheme 1, **7**: Scheme 3). In the reaction of, for example, [{*cis*-[Pt](C≡CPh)$_2$}Cu(N≡CMe)]BF_4(**4a**) with *cis*-[Pt](C≡CPh)$_2$ (**1a**), first ionic **8a** is formed in which the copper(I) ion is π-bound by one PhC≡C ligand of each *cis*-[Pt](C≡CPh)$_2$ array, thus giving rise to the formation of a linear alkyne-copper-alkyne [(η^2-PhC≡C)$_2$Cu]$^+$ moiety (alkyne = midpoint of the C≡C triple bond) (Scheme 1).

Molecule **8a** can be considered as an intermediate in the formation of **6a** and hence, upon heating, it smoothly rearranges to afford **6a** (Scheme 1) [12,14].

Furthermore, it could be demonstrated that **6a** also represents a promising starting material for the synthesis of the tetrametallic Pt_2Cu_2 complex **9** as outlined in Scheme 1. In **9** two bis(alkynyl) platinum moieties are linked by copper ions in such a way that two PhC≡C units, one associated with each platinum atom, are η^2-coordinated to a copper(I) cation [12a,14]. Both platinum atoms are thereby orientated on the same side as it could be evidenced by X-ray single structure analysis [12a,14]. The copper ions are not interacting with each other.

A further possibility to synthesize [{*cis*-[Pt](C≡CPh)$_2$}$_2$Cu$_2$](BF_4)$_2$ (**9**) is given in Scheme 2.

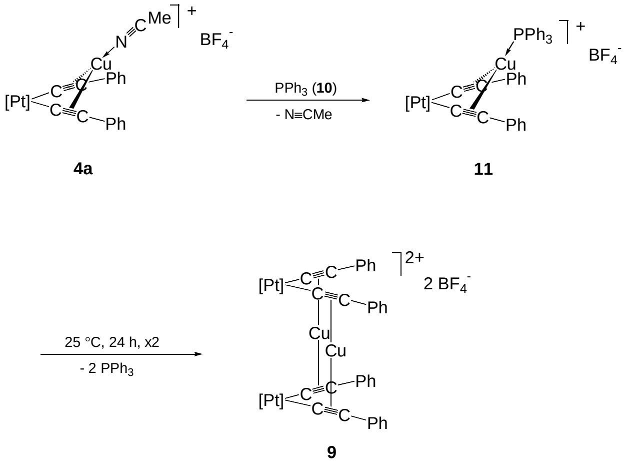


SCHEME 1 Synthesis of **6a** by the reaction of **4a** with **1a** [12,14].

Upon treatment of **4a** with PPh_3 (**10**) substitution of the weakly bound N≡CMe ligand in **4a** occurs and [{*cis*-[Pt](C≡CPh)$_2$}Cu(PPh_3)]BF_4 (**11**) is formed immediately, which on elimination of **10** produces by prolonged stirring tetrametallic **9** (Scheme 2) [12,14].

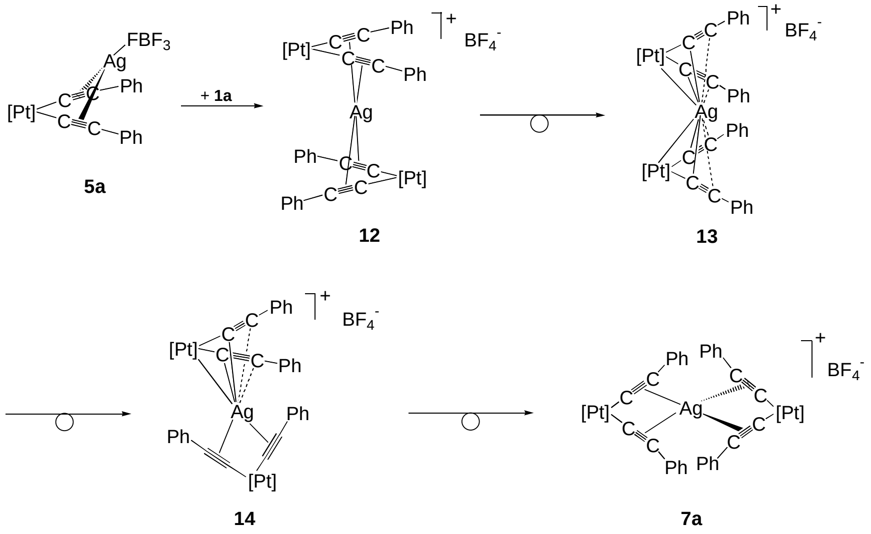
Isostructural complexes of **6a–6c** can be prepared by the reaction of {*cis*-[Pt](C≡CPh)$_2$}AgX (**5a**: X = FBF_3, **5b**: X = $OClO_3$, **5c**: X = FPF_5) with **1a** or **1b**, respectively [12b,14]. However, in the synthesis of **7a–7f** another mechanism was discovered (Scheme 3).

As shown in Scheme 3, the first step in the preparation of, for example **7a**, involves the elimination of BF_4 from **5a** by the addition of the organometallic chelate *cis*-[Pt](C≡CPh)$_2$ (**1a**). Initially formed [{*cis*-[Pt](C≡CPh)$_2$}$_2$Ag]BF_4 (**12**) contains, as result of a X-ray structural analysis, two *cis*-[Pt](C≡CPh)$_2$ units which are η^2-coordinated to a silver(I) cation *via* the PhC≡C groups; as counter ion BF_4^- is present [12b,14]. The two *cis*-[Pt](C≡CPh)$_2$ arrays are parallely orientated to each other with the platinum atoms on the opposite site [12b,14].



SCHEME 2 Synthesis of **9** by reacting **4a** with **10**.

Complex **12** isomerizes in solution to produce **13** and then **14**, which afterwards rearranges to form **7a** (Scheme 3). IR spectroscopic studies give the first hint for the different bonding modes of the respective alkynyl groups present in **5a, 7a**, and **12–14** [1,7b,10–15]. This finding could additionally be confirmed by single X-ray structure determinations [12,14]. For example, the silver atom in **13** is embedded between two cis-arranged [Pt](C≡CPh)$_2$ units. Within this structural arrangement, however, the silver(I) ion interacts with both platinum centers [Pt—Ag 2.8966(3) Å]. In addition, the silver atom preferentially binds to the α-atoms of the Pt($C_\alpha{\equiv}C_\beta$Ph)$_2$ building blocks, giving rise to a bonding situation that best can be explained by μ-bridging PhC≡C moieties. This bonding situation is favored by the Ag—C_α [2.443(6), 2.548(6) Å] and Ag—C_β distances [2.799(6), 3.042(6) Å] [12b,14]. A similar bonding situation is found in **14** [12b,14]. Half of the molecule corresponds to the latter bonding motif, while the other *cis*-[Pt](C≡CPh)$_2$Ag fragment resembles to a structural arrangement typical of **7** (Scheme 3) (vide



SCHEME 3 Synthesis of **7a** by the reaction of **1a** with **5a** [10].

supra) [7b,12,14]. In the latter unit the transition metals platinum and silver, the sp hybridized carbon atoms, and the C-ipso atom of the $Ph_{C\equiv C}$ ligands are thereby in-plane bound (r.m.s.d. 0.0196 Å] [12,14].

In trimetallic **7a–7c** the cation $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}_2Ag]^+$ is set-up by two nearly orthogonal positioned bidentate *cis*-$[Pt](C{\equiv}CPh)_2$ entities connected through silver(I) [12b,14]. The silver atom is thereby π-bound by all four PhC≡C building blocks of the two $[Pt](C{\equiv}CPh)_2$ arrays. Unlike heterobimetallic platinum–silver and platinum–copper complexes (type **C** molecules) (vide supra), the silver ion in structurally characterized **7a–7c** lies only slightly out of the best *cis*-$[Pt](C{\equiv}CPh)_2$ plane to minimize steric interactions. Similar observations were made for analogous complexes, featuring instead of bipy or bipy′ groups, phosphino ligands [1,7b,15]. It is common for all such systems to adopt a asymmetric structure in the solid state, as evidenced by the platinum–silver distances [e.g., **7g**: Ag···Pt(1) 3.384(1) Å, Ag···Pt(2) 3.513(1) Å]. The silver(I) center lies much closer to the platinum alkynyl plane for Pt(2) (0.01 Å) than that for Pt(1) (0.80 Å) [15].

Heteroatomic Pt_2Ag_2 assemblies featuring two $\{cis\text{-}[Pt](C{\equiv}CPh)_2\}AgX$ entities, which are connected *via* platinum–silver interactions, could recently be synthesized by the reaction of **1a** with $[AgO_2CCF_3]$ (**3d**) in a 1:1 molar ratio (Fig. 1) [11c,14]. Dimeric $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}Ag(O_2CCF_3)]_2$ (**15**) could be isolated in excellent yields.

A further possibility to synthesize an oligonuclear complex, for example, $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}_3Cu_2](BF_4)_2$ (**16**), is given by controlling the stoichiometry of the respective reactants [13,14]. Thus, treatment of 3 equiv. **1b** with two parts of **2a** produces pentametallic **16** (Scheme 4). In addition, **16** can also be synthesized by the reaction of $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}Cu(MeC{\equiv}N)]BF_4$ (**4b**) {[Pt] = (bipy′)Pt} with $[\{cis\text{-}[Pt](C{\equiv}CPh)_2\}_2Cu]BF_4$ (**8b**) in a 1:1 molar ratio [13]. In **16** three *cis*-$[Pt](C{\equiv}CPh)_2$ fragments are spanned by two copper(I) ions.

A possible mechanism for the formation of **16** is outlined in Scheme 5 and is based on the intermediate formation of **8b, 17b, 18b**, and **6b**; molecules of the latter type has been discussed in detail earlier (vide supra) [12,13].

The result of the X-ray structure determination of **16** is shown in Fig. 2 and demonstrates that **16** consists of three helically arranged bis(alkynyl) platinum building blocks [13].

The dicationic Pt_3Cu_2 unit of **16** is formed by three neutral *cis*-$[Pt](C{\equiv}CPh)_2$ fragments, which are spanned by two copper(I) ions, including all

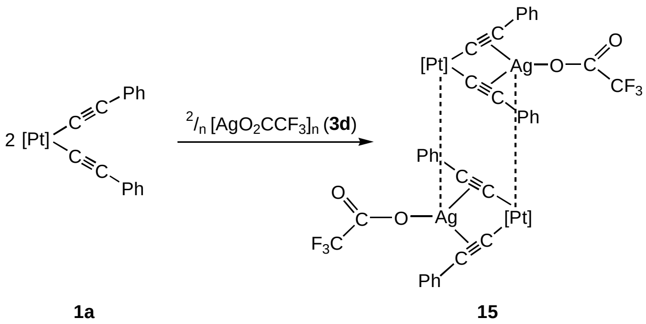
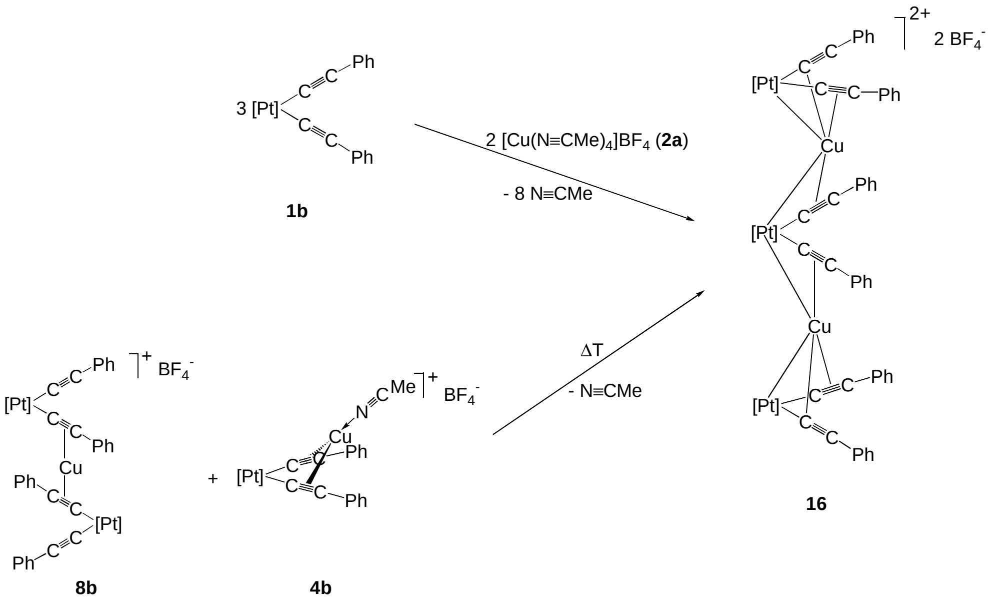
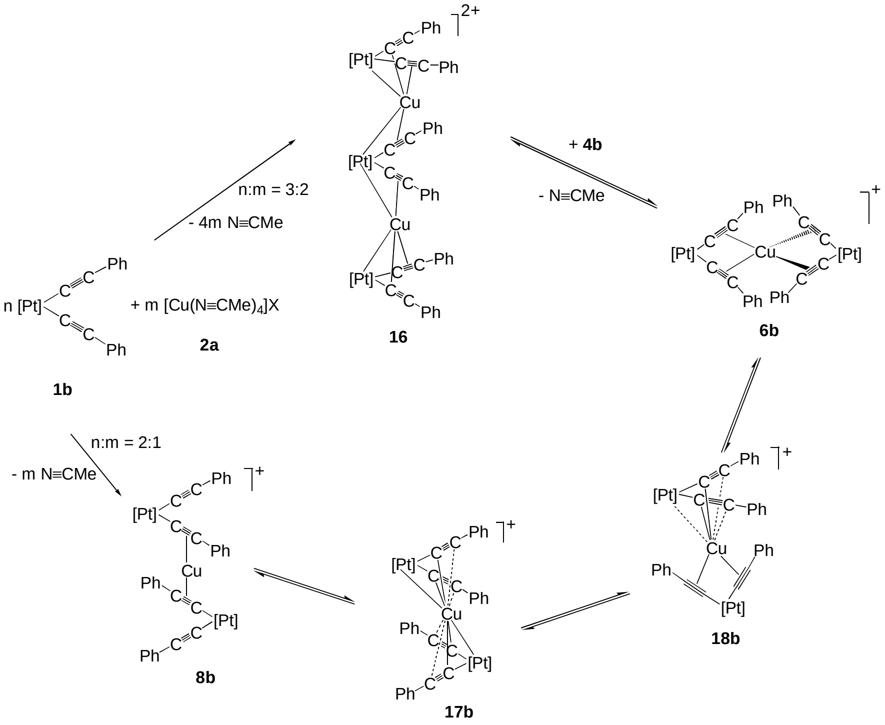


FIGURE 1 Synthesis of **15** by the reaction of **1a** with **3d** [11c, 14].



SCHEME 4 Synthesis of **16** by reaction of **1b** with **2a** or **8a** with **4b** {[Pt] = (bipy′)Pt}.

six acetylide ligands and the platinum(II) centers. As counterions noncoordinating BF_4^- units are present. Within the $[Pt_3Cu_2]^{2+}$ array the outer *cis*-[Pt](C≡CPh)$_2$ building blocks are bound to a Cu$^+$ ion in such way that one of the two PhC≡C ligands is η^2-coordinated, while the other one preferentially forms a σ-bond with the C_α atom of the Pt-C_α≡C_β fragment (Fig. 2). These two units are linked by a third *cis*-[Pt](C≡CPh)$_2$ entity of which the alkynyl ligands are unsymmetrically π-coordinated to the outer {[Pt](C≡CPh)$_2$}Cu$^+$ building blocks (vide supra). In addition, metal–metal interactions between the transition metals platinum and copper are found [13].



SCHEME 5 Possible mechanism for the formation of **16** {[Pt] = (bipy′)Pt}.

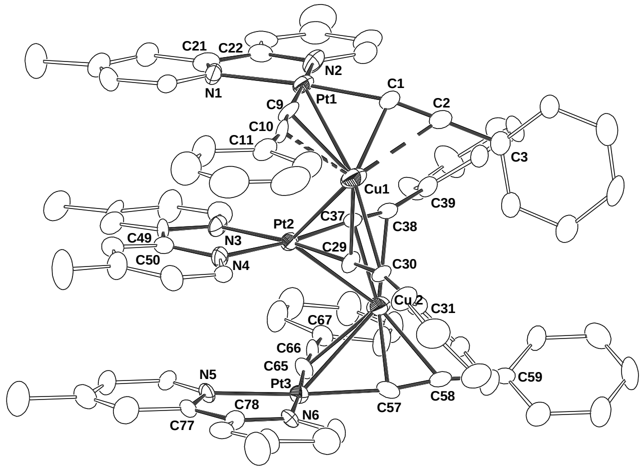
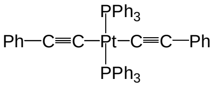


FIGURE 2 ZORTEP PLOT (50% probability level) of the molecular structure of **16** [13]. Selected interatomic distances (Å) and angles (°) are Pt(1)—N(1) 2.095(9), Pt(1)—N(2) 2.049(10), Pt(2)—N(3) 2.078(9), Pt(2)—N(4) 2.037(10), Pt(3)—N(5) 2.073(9), Pt(3)—N(6) 2.046(10), Pt(1)—C(1) 1.973(13), Pt(1)—C(9) 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); N(1)—Pt(1)—N(2) 79.8(4), N(3)—Pt(2)—N(4) 79.7(4), N(5)—Pt(3)—N(6) 78.6(4), N(1)—Pt(1)—C(1) 172.2(4), N(2)—Pt(1)—C(9) 175.1(5), N(1)—Pt(1)—C(9) 97.1(5), N(2)—Pt(1)—C(1) 94.6(5), N(3)—Pt(2)—C(29) 172.6(4), N(4)—Pt(2)—C(37) 174.3(4), N(3)—Pt(2)—C(37) 95.5(4), N(4)—Pt(2)—C(29) 93.3(4), N(5)—Pt(3)—C(57) 174.5(4), N(6)—Pt(3)—C(65) 176.8(5), N(5)—Pt(3)—C(65) 98.9(5), N(6)—Pt(3)—C(57) 98.6(5), N(1)—Pt(1)—C(9) 97.1(5), 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).

Reaction Behavior of trans-($Ph_3P)_2Pt(C\equiv CPh)_2$

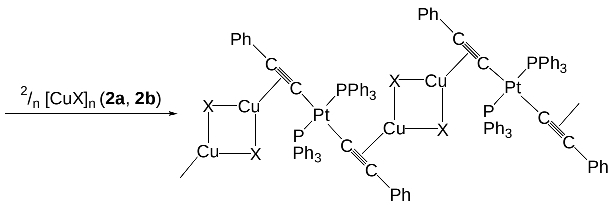
As shown in the preceding section, cis-configurated bis(alkynyl) platinum species can successfully be used as basic components for the construction of heterobimetallic and oligomeric complexes featuring up to five late transition-metal atoms. However, changing from *cis-* to *trans*-bis(alkynyl) platinum systems such as *trans*-$L_2Pt(C\equiv CR)_2$ (**19a**: L = PPh_3, R = Ph; **19b**: L = PMe_2Ph, R = ^tBu; **19c**: L = PMe_2Ph, R = H) novel linear coordination polymers are accessible, when **19a–19c** are reacted with various group 11 metal salts [M′X] (M′ = Cu, Ag; X = Cl, Br, OTf, BF_4, ClO_4, . . .) [1,7,14,17–23]. For other coordination polymers, featuring transition-metal centers other then platinum and copper or platinum and silver, see Ref. [23].

The reaction of *trans*-$(Ph_3P)_2Pt(C\equiv CPh)_2$ (**19a**) with the copper halides [CuX] (**2b**: X = Cl, **2c**: X = Br) in a 1:2 molar ratio affords the coordination polymers $(Ph_3P)_2Pt(C\equiv CPh)_2Cu_2X_2$ (**20a**: X = Cl, **20b**: X = Br) [14,19].



$$Ph-C\equiv C-\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pt}}-C\equiv C-Ph$$

19a



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In these species a linear polymeric structure is adopted by the fragments *trans*-Pt(μ-σ,η^2-$C\equiv CPh)_2$ and Cu(μ-X)$_2$Cu [19]. Exemplary, the solid-state structure of **20b** is shown in Fig. 3 [14,19].

In **20**, each copper atom is η^2-coordinated by an alkyne group, to give a *cis*oide arrangement of the Pt-C≡C-Ph unit, which is the reverse of the situation found for the respective cis-configurated heterobimetallic complexes as outlined in the preceding section (molecules of structural type **C**), where the Pt-C≡C-C_{Ph} units are trans-bent. In addition, the copper atoms in **20** are linked through double-halide bridges to each other to link the system into a linear polymeric chain. In the $Cu_2(\mu$-$X)_2$ cycles (X = Cl, Br) the respective metal atoms possess a trigonal planar environment, caused by the two halides X and the symmetrically side-on bound $C_{Ph}C\equiv C$ units. However, because of sterical effects, the Cu_2X_2 entities are divided from planarity. This differs from other well-known complexes of general type (η^2-alkyne)$_2Cu_2X_2$ [alkyne = organic or organometallic group, such as $Me_3SiC\equiv CSiMe_3$ [24], $C_{10}H_{16}S_2$ [25], $Me_3SiC\equiv CPh$ [26], (η^5-C_5H_5)(CO)$_2$Fe(C≡CPh) [27]; $C_{10}H_{16}S_2$ = 3,3,6,6-tetramethyl-1-thia-4-cycloheptene; X = Cl, Br] in which the Cu(μ-X)$_2$Cu linkages are in-plane orientated.

As typical for the structure in the solid-state, also in solution a trans-arrangement of the bis(alkynyl) platinum array is characteristic [14,19].

A similar polymer, *trans*-[{$(PhMe_2P)_2Pt(C\equiv C^tBu)_2$}$Cu_2(\mu$-$Cl)_2]_n$ (**20c**), is accessible by the linear copolymerization of *trans*-$(PhMe_2P)_2Pt(C\equiv C^tBu)_2$ (**1b**) with [CuCl] in presence of Et_2NH [7].

The polymeric structure of **20a** and **20b** can be broken down to trimetallic species, when they

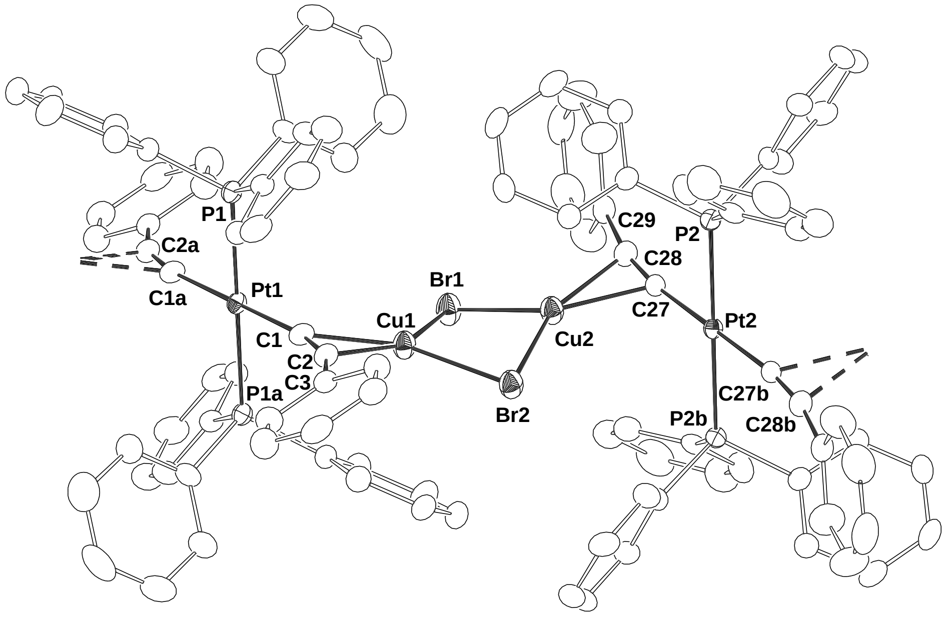
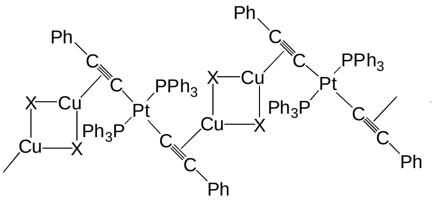
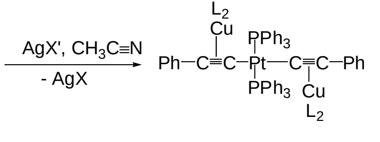


FIGURE 3 ZORTEP PLOT (50% probability level) of the molecular structure of **20b** (symmetry generated atoms are marked with the suffix a (symmetry code $-x + 1$, $-y$, $-z$) and b (symmetry code $-x + 1$, $-y - 1$, $-z + 1$)). [14,19] Selected interatomic distances (Å) and angles (°) are Pt(1)—C(1) 2.024(7), Pt(2)—C(27) 2.024(7), Cu(1)—C(1) 2.037(7), Cu(1)—C(2) 2.022(8); Cu(1)—Br(1) 2.4135(12), Cu(1)—Br(2) 2.4272(12), Cu(2)—Br(1) 2.4136(12), Cu(2)—Br(2) 2.4272(12), Cu(2)—C(27) 2.082(7), Cu(2)—C(28) 2.089(8), C(1)—C(2) 1.212(10), C(27)—C(28) 1.223(10); P(1)—Pt(1)—P(1a) 180.00(9), P(1)—Pt(1)—P(1a) 180.00(8), Cu(1)—Br(1)—Cu(2) 79.05(4), Cu(1)—Br(2)—Cu(2) 78.50(4), Cu(1)—C(1)—C(2) 72.0 (5), Cu(2)—C(27)—C(28) 73.3 (5), Pt(1)—C(1)—C(2) 164.7(7), Pt(2)—C(2)—C(28) 172.8(6).

are reacted with, e.g. the silver(I) salts [AgX′] (**3a**: X′ = BF_4, **3b**: X′ = ClO_4) in acetonitrile solutions [14,19]. Upon precipitation of AgX (X = Cl, Br) the $PtCu_2$ complexes {*trans*-$(Ph_3P)_2Pt[(\eta^2\text{-}C{\equiv}CPh)Cu(N{\equiv}CMe)_2]_2\}X_2$ (**21a**: X = BF_4, **21b**: X = ClO_4) are formed in quantitative yield [14,19].



20a: X = Cl
20b: X = Br

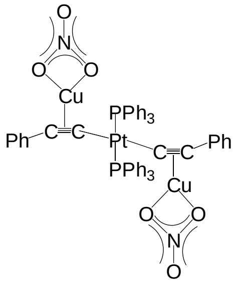


21a: X = BF_4
21b: X = ClO_4
L = N≡CMe

Molecules of structural type **21** can also be synthesized by treatment of *trans*-$(Ph_3P)_2Pt(C{\equiv}CPh)_2$ (**19a**) with two equivalents of $[Cu(N{\equiv}CMe)_4]X$ (**2a**: X = BF_4, **2d**: X = ClO_4), a reaction behavior which is typical for inorganic copper(I) species, except copper(I) halides [14,19,28].

Complexes **21a** and **21b** were characterized by spectroscopy (IR, NMR, MS) and single X-ray structure analysis [14,28].

The synthesis method for **21a** and **21b** can be transferred to other groups X, such as NO_2 and NO_3 [28]. However, in the so formed complexes *trans*-$(Ph_3P)_2Pt[(\eta^2\text{-}C{\equiv}CPh)CuX]_2$ (**22a**: X = O_2N, **22b**: X = O_2NO) the nitrite and nitrate ligands are chelate-bound via their oxygen atoms to the copper(I) center [28].



22b

Isostructural complexes to **22a** and **22b** are accessible when **19a** is reacted with the appropriate silver(I) salts AgX (**3d**: X = NO_2, **3e**: X = NO_3) [14,29].

In contrast, changing from X = NO_2 or NO_3 to X = OTf, BF_4, ClO_4 etc., novel coordination polymers can be obtained in which X as well as the PhC≡C and the Ph_3P moieties are responsible for the construction of the respective polymeric chain.

One of the first examples on that score was reported by Yamazaki et al., who obtained polymeric $\{[\textit{trans}\text{-}(PhMe_2P)_2Pt(C\equiv CH)_2]AgClO_4\}_n$ (**23**) by the reaction of **19c** with $[AgClO_4]$ (**3b**) in a 1:1 molar ratio [17]. This coordination polymer was structurally characterized by X-ray structural determination [17]. The polymeric chain is set-up by the η^2-coordination of PtC≡CH units to a $AgOClO_3$ building block as outlined in Fig. 4. The perchlorate is thereby σ-bound to the silver(I) center.

While in the reaction of **19c** with $[AgClO_4]$ (**3b**) selectively coordination polymer **23** is formed (vide supra), the reaction of **19a** with the same reagent leads to $\{[\textit{trans}\text{-}(PPh_3)_2Pt(C\equiv CPh)_2][Ag(\mu\text{-}OCl(O)_2O)Ag]\}_n$ (**24**) and $\{[\textit{trans}\text{-}(PPh_3)_2Pt(C\equiv CPh)AgOClO_3]_2\}_n$ (**25a, 25b**). These species differ in the bonding modes of the linking silver perchlorate units and contain two silver atoms per platinum element (Figs. 5–7) [20]. It must be noted that the formation of **24** and **25** strongly depends on the reaction conditions applied (temperature, solvent,. . .) [20].

From **24, 25a**, and **25b** single crystals could be obtained. The result of the X-ray structure analysis of these polymers is shown in Fig. 5 (**24**), Fig. 6 (**25a**), and Fig. 7 (**25b**) [14,20].

In **24** the linking of the $\textit{trans}\text{-}(Ph_3P)_2Pt(C\equiv CPh)_2$ fragments is achieved by $Ag[\mu\text{-}OCl(O_2)O]_2Ag$ cycles, which are η^2-coordinated by the PhC≡C groups of individual $Pt(C\equiv CPh)_2$ moieties. In addition, η^2-bonding of one phenyl group of a triphenylphosphine ligand results in the coordination number 4 at silver, thus giving rise to an 18-valence electron count around the group 11 metal (Fig. 5).

The parallel orientation of individual $Pt(C\equiv CPh)_2$ units in **24** also dominates the structure of **25a** (Fig. 6) [14,20].

In contrast to **24**, where perchlorate groups span the respective $[\textit{trans}\text{-}(PPh_3)_2Pt(C\equiv CPh)_2]Ag$ units, in **25a** (Fig. 6) the ClO_4 building blocks are terminal bound to the silver(I) center. To create a tetrahedral surrounding around silver and hence, to reach the 18-valence electron count, additional η^2-coordination of a phenyl group of the $(Ph_3P)_2Pt(C\equiv CPh)_2$ units must occur (Fig. 6) [14,20].

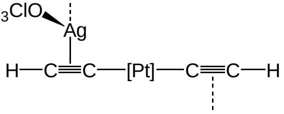


FIGURE 4 Schematic representation of the monomeric part of polymeric **23** {[Pt] = $(PhMe_2P)_2Pt$} [17].

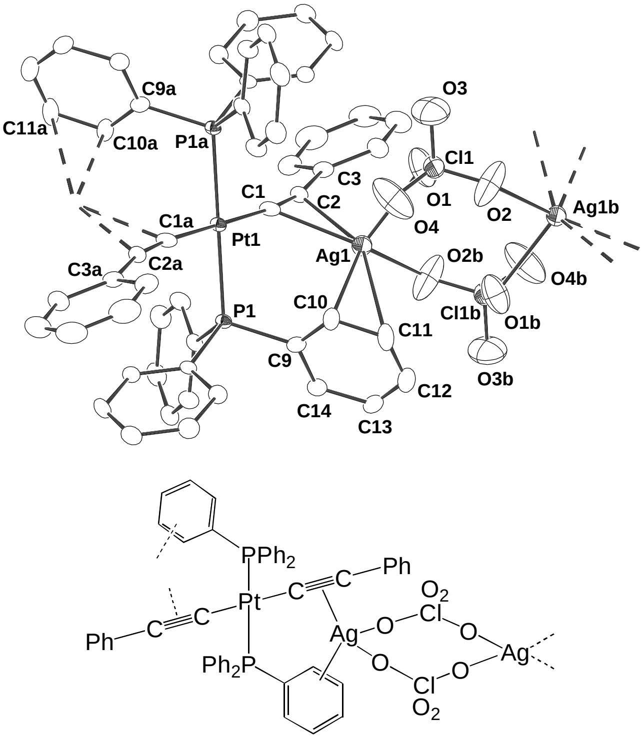


FIGURE 5 Molecular structure (top) and schematic representation (below) of **24**; selected bond lengths (Å) and angles (°) are as follows [14,20]: Pt(1)—C(1) 2.004(8), C(1)—C(2) 1.224(11), C(1)—Ag(1) 2.416(11), C(2)—Ag(1) 2.386(8), Ag(1)—O(1) 2.466(11), Pt(1)—P(1) 2.3213(18), O(1)—Cl(1) 1.466(10), Ag(1)—O(2a) 2.382(11); C(1)—Pt(1)—C(1a) 180.000(3), P(1)—Pt(1)—P(1a) 180.00(1), Pt(1)—C(1)—C(2) 174.2(7), C(1)—Ag(1)—C(2) 29.5(3), O(1)—Ag(1)—O(2a) 92.7(5), Ag(1)—O(1)—Cl(1) 114.1(6), O(1)—Cl(1)—O(2) 105.6(7).

Almost the same arrangement is found in **25b**, except that the silver(I) center is slipped along the surface of the phenyl ring and hence, an zigzag arrangement is characteristic (Fig. 7) [14,20].

The same structural motif (polymers **25a** and **25b**) is present in $\{[\textit{trans}\text{-}(PPh_3)_2Pt(C\equiv CPh)_2][AgFBF_3]_2\}_n$ (**26**), which selectively is produced by the addition of 2 equiv. of $[AgBF_4]$ (**3a**) to **19a** [14,22].

However, when $\textit{trans}\text{-}(PPh_3)_2Pt(C\equiv CPh)_2$ (**19a**) is reacted with 2 equiv. of [AgOTf] (**3f**) (OTf = OSO_2CF_3) polymeric $\{[\textit{trans}\text{-}(PPh_3)_2Pt(C\equiv CPh)_2][AgOTf]_2\}_n$ (**27**) is formed. In **27** the OTf moiety acts as a bridging unit between $[\textit{trans}\text{-}(PPh_3)_2Pt(C\equiv CPh)_2]Ag$ building blocks [14,21]. From elemental analysis it is obvious that polymeric **27**

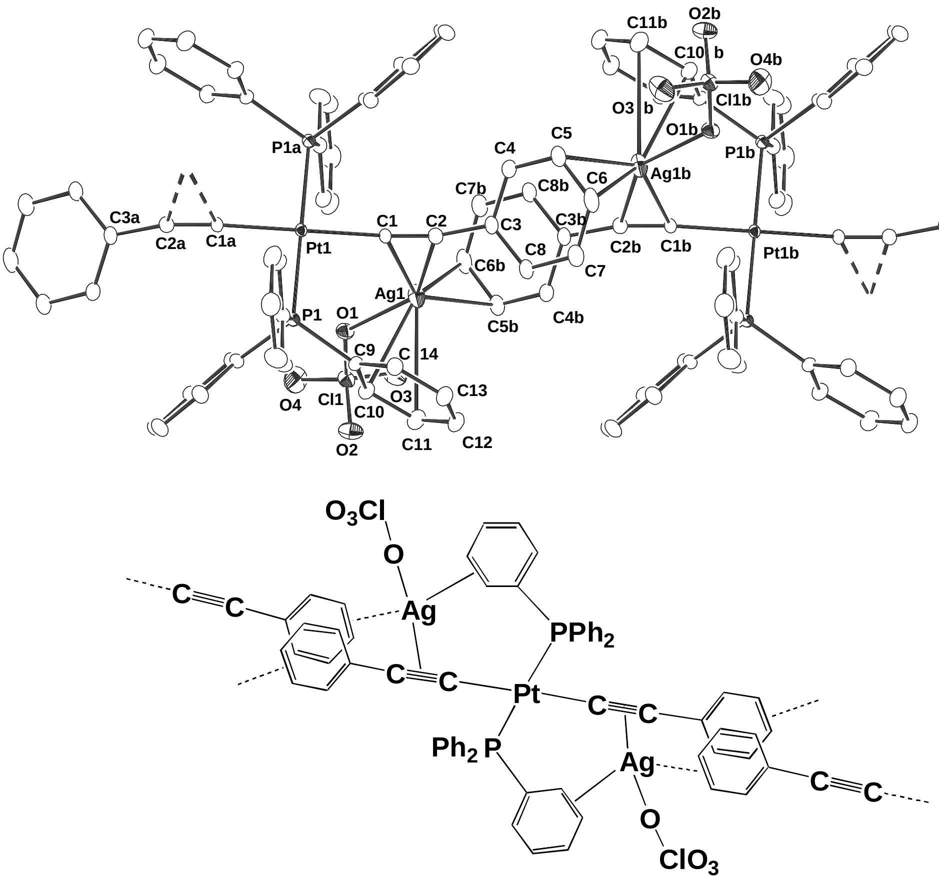


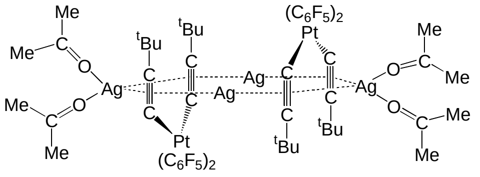
FIGURE 6 Molecular structure (top) and schematic representation (below) of **25a**; selected bond lengths (Å) and angles (°) are as follows [14,20]: Pt(1)—C(1) 2.009(3), C(1)—C(2) 1.209(5), C(1)—Ag(1) 2.345(3), C(2)—Ag(1) 2.377(4), Ag(1)—O(1) 2.458(3), Pt(1)—P(1) 2.3218(8), O(1)—Cl(1) 1.460(3), O(1)—Cl(2) 1.429(3), O(1)—Cl(3) 1.430(4), O(1)—Cl(4) 1.425(4); C(1)—Pt(1)—C(1a) 180.0, P(1)—Pt(1)—P(1a) 180.0, Pt(1)—C(1)—C(2) 172.6(3), C(1)—Ag(1)—C(2) 29.67(12), C(1)—Ag(1)—O(1) 116.73(11), C(2)—Ag(1)—O(2) 146.24(11), P(1)—Pt(1)—C(1) 91.11(9).

contains two silver atoms, being consistent with the formula $(Ph_3P)_2Pt(C_2Ph)_2Ag_2(OTf)_2$. IR spectroscopic studies reveal that in **27** a μ-bridging triflate is present, attributing to Ag[μ-OS(O)(CF_3)O]Ag eight-membered cycles.

The structural arrangement found in solution is also retained in the solid state and corresponds to the structural motif already discussed for **24** (vide supra) (Fig. 8) [14,21].

The polymeric structure of **27** is created by $(Ph_3P)_2Pt(\mu\text{-}\sigma,\eta^2\text{-}C{\equiv}CPh)_2$ and Ag[μ-OS(O)(CF_3)O]$_2$Ag units of which the latter moiety represents the linking group [14,21]. It is interesting to note that in **27** the eight-membered Ag[μ-OS(O)(CF_3)O]$_2$Ag cycles are "concave–convex" arranged and hence form a zigzag chain (Fig. 8). One should mention that the formation of such bridging entities is not common in group 11 triflate chemistry [30]. Similar orientations were found in, e.g. $\{[(R^1)(R^2)(PhC{\equiv}C)P]Ag(\mu\text{-}OSO_2CF_3)\}_2$ ($R^1 = OC_6H_2{}^tBu_3$-2,4,6; $R^2 = NEt_2$, Ph, PhC≡C) [30].

Recently, Fornies and co-workers demonstrated that polynuclear complexes of composition $[(C_6F_5)_2Pt(C{\equiv}CR)_2Ag_2]_n$ (**28a**: R = Ph; **28b**: R = ^{t}Bu) could be obtained by reacting either tetranuclear $(NBu_4)_2[(C_6F_5)_4Pt_2(C{\equiv}CR)_4Ag_2]$ (**29**) or $(NBu_4)_2[$*cis*-$Pt(C_6F_5)_4(C{\equiv}CR)_2]$ (**30**) with [$AgClO_4$] (**3b**), or *cis*-$Pt(C_6F_5)_2(Thf)_2$ with $[Ag(C{\equiv}CR)]_n$ (R = Ph, ^{t}Bu) (Pt/Ag ratio 1:2) in acetone [31]. Dissolving **28b** in acetone affords $[(C_6F_5)_2Pt(C{\equiv}C^tBu)_2Ag_2(CH_3COMe)_2]_2$ (**31**), which reverts to **28b** on air drying [18,31].



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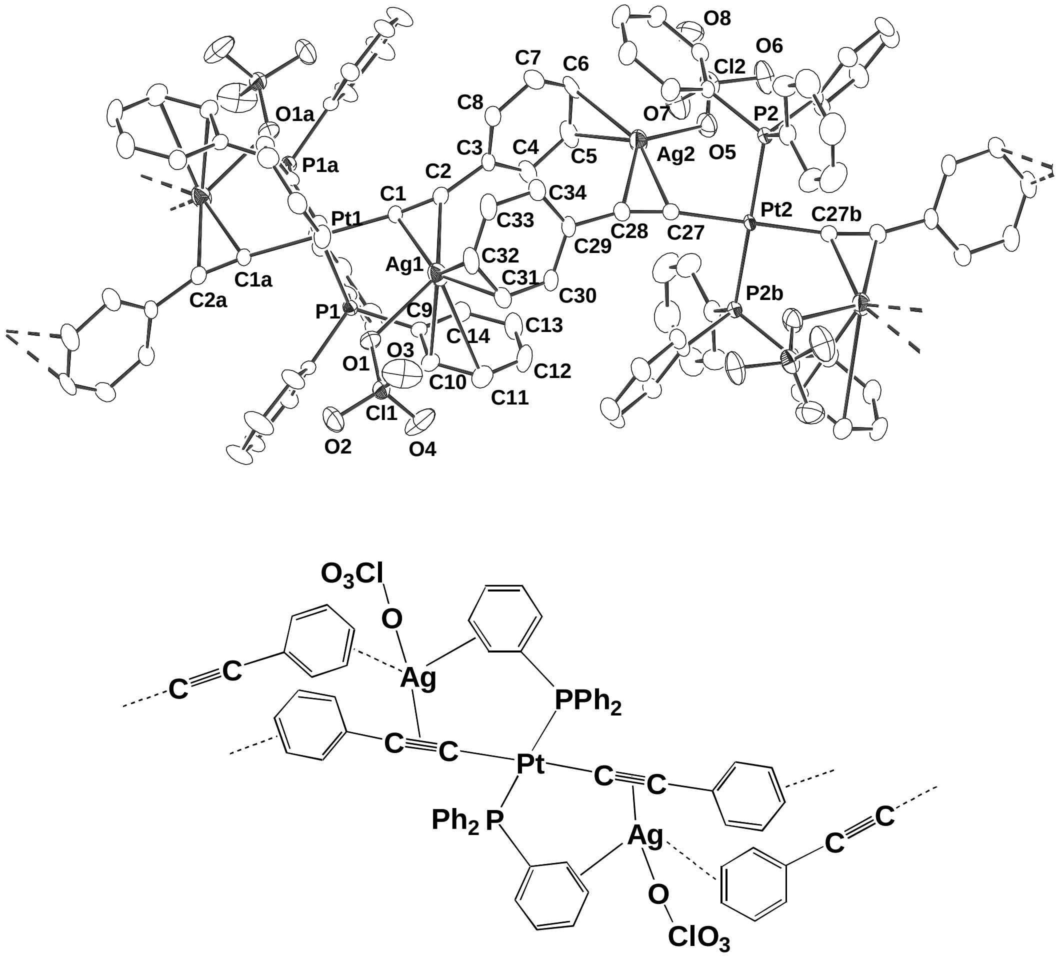


FIGURE 7 Molecular structure (top) and schematic representation (below) of **25b**; selected bond lengths (Å) and angles (°) are as follows [14,20]: Pt(1)—C(1) 2.000(4), C(1)—C(2) 1.220(6), C(1)—Ag(1) 2.346(4), C(2)—Ag(1) 2.367(5), Ag(1)—O(1) 2.579(3), Pt(1)—P(1) 2.3262(12), O(1)—Cl(1) 1.453(3), O(1)—Cl(2) 1.409(4), O(1)—Cl(3) 1.423(5), O(1)—Cl(4) 1.424(4); C(1)—Pt(1)—C(1a) 180.00(19), P(1)—Pt(1)—P(1a) 180.0, Pt(1)—C(1)—C(2) 171.0(4), C(1)—Ag(1)—C(2) 30.01(15), C(1)—Ag(1)—O(1) 111.51(13), C(2)—Ag(1)—O(2) 140.88(13), P(1)—Pt(1)—C(1) 89.93(13).

Complex **31** displays two identical $\{(C_6F_5)_2Pt(\mu\text{-}C{\equiv}C^tBu)_2\}Ag(Me_2CO)_2$ building blocks, which are linked by two silver atoms [18,31]. The polymeric structure of $[\{(C_6F_5)_2Pt(C{\equiv}CR)_2\}Ag_2]_n$ (**28a, 28b**) is thought to be based on square-planar *cis*-$(C_6F_5)_2Pt(C{\equiv}CR)_2$ entities, which are connected by silver atoms η^2-bound by the RC≡C ligands [18]. Moreover, it was found that on treatment of **28a** or **28b** with the 2-electron donors L (L = PPh_3, $P(C_2H_5)_3$, $C{\equiv}N^tBu$, $C_5H_5N, \ldots$) two new types of platinum–silver complexes are formed, depending on the silver-to-ligand molar ratio used. When 1 equiv. of L per silver atom is added, trimetallic $\{(C_6F_5)_2Pt(C{\equiv}CR)_2\}(AgL)_2$ [R = Ph: **32a**: L = PPh_3, **32b**: L = $P(C_2H_5)_3$, **32c**: L = $C{\equiv}N^tBu$, **32d**: L = C_5H_5N; R = ^{t}Bu: **32e**: L = PPh_3, **32f**: L = $P(C_2H_5)_3$, **32g**: L = $C{\equiv}N^tBu$, **32h**: L = C_5H_5N] is produced. However, when a 1:2 molar ratio is applied, hexametallic $\{(C_6F_5)_2Pt(C{\equiv}CR)_2\}Ag_2(AgL)_2$ (R = Ph: **31a**: L = PPh_3, **31b**: L = $P(C_2H_5)_3$, **31c**: L = $C{\equiv}N^tBu$, **31d**: L = C_5H_5N; R = ^{t}Bu: **31e**: L = PPh_3, **31f**: L = $P(C_2H_5)_3$, **31g**: L = $C{\equiv}N^tBu$, **31h**: L = C_5H_5N) is formed [18,31].

NMR spectroscopic studies show that the trans-configurated $Pt(C{\equiv}CPh)_2$ fragments in **20–27** are maintained in solution. However, when electron donating solvent molecules (also see reaction of **28** with neutral 2-electron donor ligands) are added, the polymeric arrangement in **20–27** is disrupted to form oligomeric or even monomeric structures. This also occurs, when, for example, **26** is reacted with chelating Lewis-bases such as bipy. Trimetallic

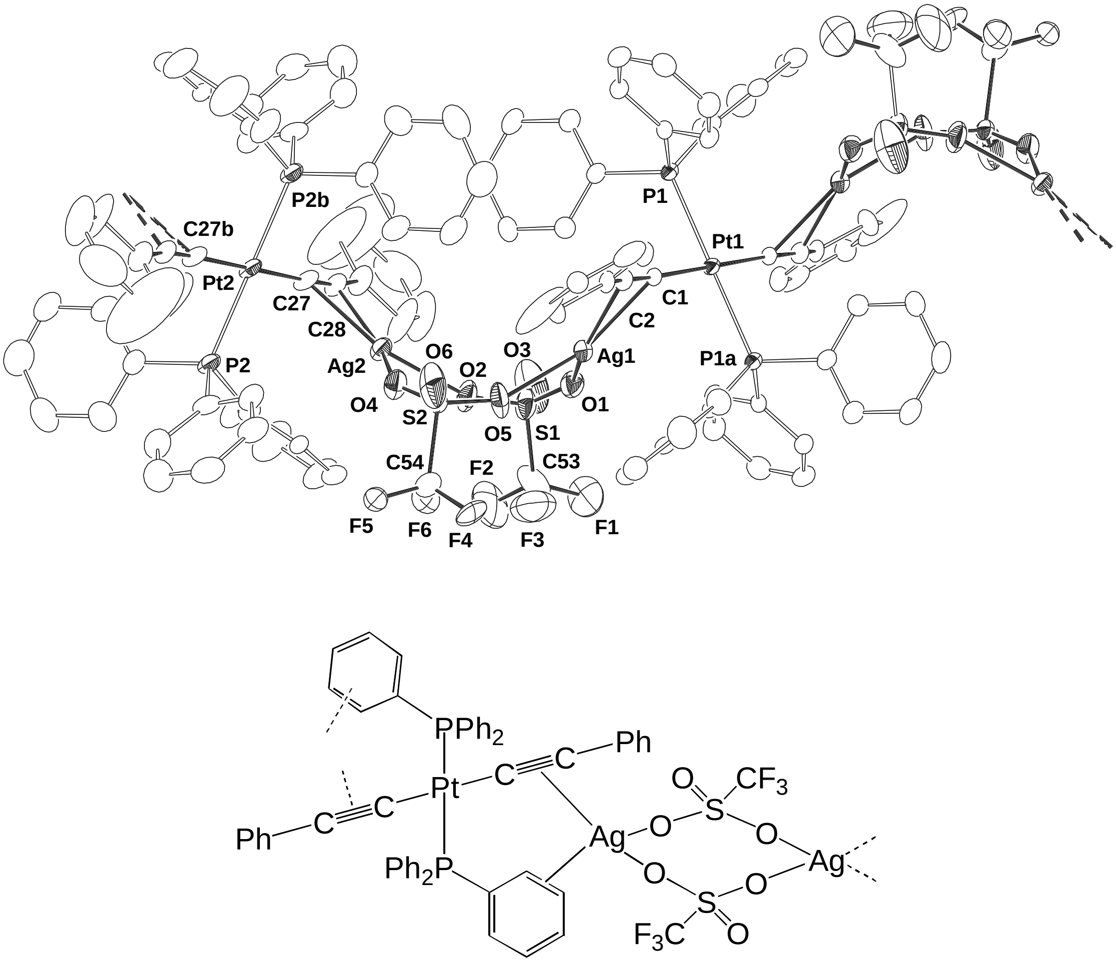
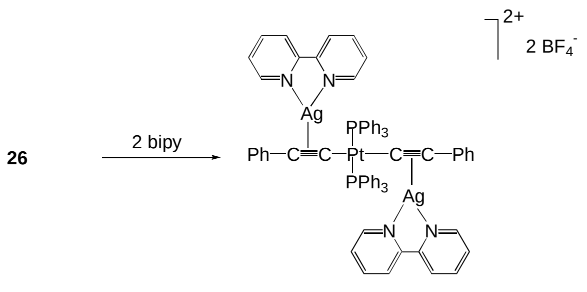


FIGURE 8 ZORTEP PLOT (30% probability level) of the molecular structure (top) and schematic representation (below) of **27** (symmetry generated atoms are labelled with the suffix a, (symmetry code $-x + 1$, $-y + 1$, $-z$) and b (symmetry code $-x + 1$, $-y + 1$, $-z + 1$)), selected bond lengths (Å) and angles (°) are as follows [14,21]: Pt(1)—C(1) 1.996(7), Pt(1)—C(27) 2.002(8), C(1)—C(2) 1.240(10), C(27)—C(28) 1.224(11), Ag(1)—C(1) 2.323(7), Ag(1)—C(2) 2.322(9), Ag(2)—C(27) 2.322(8), Ag(2)—C(28) 2.328(8), Ag(1)—O(1) 2.321(7), Ag(2)—O(2) 2.270(6), Ag(1)—O(5) 2.266(5), Ag(2)—O(4) 2.345(6), O(1)—S(1) 1.409(7), O(2)—S(1) 1.432(6), O(4)—S(2) 1.355, O(5)—S(2) 1.461(7); Pt(1)—C(1)—C(2) 172.0(7), Pt(2)—C(27)—C(28) 173.1(7), C(1)—Pt(1)—C(1a) 180.0(3), C(27)—Pt(2)—C(27a) 180.000(2), O(1)—Ag(1)—O(5) 92.6(3), O(2)—Ag(2)—O(4) 88.9(2), Ag(1)—O(1)—S(1) 137.3(4), Ag(1)—O(5)—S(2) 153.8(5).

33 is thereby produced in quantitative yield [14,22].



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