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Synthesis of di-, tri- and tetranuclear platinum(II) and copper(I) acetylide complexes

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Abstract

Heterobimetallic $\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)_2\}[Cu(N{\equiv}CMe)]BF_4$ (**3a**: $[Pt] = (bipy)Pt$, bipy = 2,2′-bipyridine; **3b**: $[Pt] = (bipy')Pt$, bipy′ = 4,4′-dimethyl-2,2′-bipyridine) is accessible by the reaction of $cis\text{-}[Pt](C{\equiv}CPh)_2$ (**1a**: $[Pt] = (bipy)Pt$, **1b**: $[Pt] = (bipy')Pt$) with $[Cu(N{\equiv}CMe)_4]BF_4$ (**2**). Substitution of $N{\equiv}CMe$ by PPh_3 (**4**) can be realized by the reaction of **3a** with **4**, whereby $[\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)_2\}Cu(PPh_3)]BF_4$ (**5**) is formed. On prolonged stirring of **3** and **5**, respectively, $N{\equiv}CMe$ and PPh_3 are eliminated and tetrametallic $\{[\{cis\text{-}[Pt](\eta^2\text{-}C{\equiv}CPh)_2\}Cu]_2\}(BF_4)_2$ (**6**) is produced. Addition of an excess of $N{\equiv}CMe$ to **6** gives heterobimetallic **3a**.

When instead of $N{\equiv}CMe$ or PPh_3 chelating molecules such as bipy (**7**) are reacted with **3a** then the heterobimetallic π-tweezer molecule $[\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)_2\}Cu(bipy)]BF_4$ (**8**) is formed. Treatment of **8** with another equivalent of **7** produced $[Cu(bipy_2)]BF_4$ (**9**) along with $[Pt](C{\equiv}CPh)_2$. However, when **3b** is reacted with **1b** in a 1:1 molar ratio then **10** and **11** of general composition $[\{[Pt](C{\equiv}CPh)_2\}_2Cu]BF_4$ are formed. These species are isomers and only differ in the binding of the $PhC{\equiv}C$ units to copper(I). A possible mechanism for the formation of **10** and **11** is presented.

The solid state structures of **6**, **10** and **11** are reported. In **11** the $[\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)_2\}_2Cu]^+$ building block is set-up by two nearly orthogonal positioned bis(alkynyl) platinum units which are connected by a Cu(I) ion, whereby the four carbon–carbon triple bonds are unsymmetrical coordinated to Cu(I). In trimetallic **10** two $cis\text{-}[Pt](C{\equiv}CPh)_2$ units are bridged by a copper(I) center, however, only one of the two $PhC{\equiv}C$ ligands of individual $cis\text{-}[Pt](C{\equiv}CPh)_2$ fragments is η^2-coordinated to Cu(I) giving rise to the formation of a $[(\eta^2\text{-}C{\equiv}CPh)_2Cu]^+$ moiety with a linear alkyne–copper–alkyne arrangement (alkyne = midpoint of the $C{\equiv}C$ triple bond). In **6** two almost parallel oriented $[Pt](C{\equiv}CPh)_2$ planes are linked by two copper(I) ions, whereby two individual $PhC{\equiv}C$ units, one associated with each Pt building block, are symmetrically π-coordinated to Cu.

Keywords: Platinum; Copper; Alkyne; Chelate; Multiheterometallic; X-ray structure; Mechanism

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1. Introduction

Recently, the reaction chemistry of organometallic chelating ligands, based on bis(alkynyl) titanocenes, toward different inorganic and organic copper(I) salts was reported [1–3]. In the thus formed heterobimetallic $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}CuX$ assemblies ($[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti, \ldots$; R = singly-bonded inorganic, organic or organometallic group; X = singly- or chelate-bonded inorganic or organic ligand) the bis(alkynyl) titanocene fragment acts as an organometallic chelating ligand (organometallic π-tweezer) to stabilize a low-valent CuX moiety. Such complexes allow to study intramolecular electron transfer, since the remote early (titanium) and late (copper) transition metals are spanned by σ- and π-coordinated alkynyls [4]. They also can be used as catalytic active species in homogeneous catalysis to study, for example, copper(I)-assisted organotransfer reactions and olefine-isomerizations [5].

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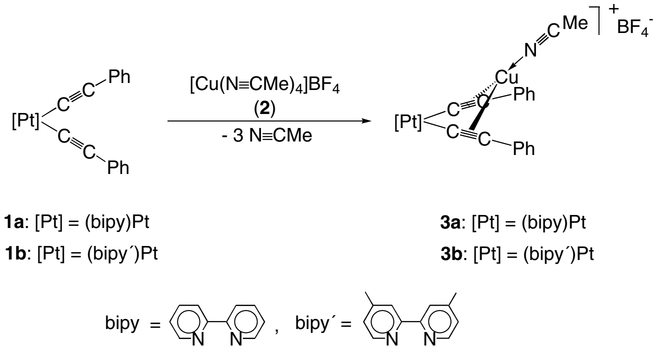
In contrast, the reaction chemistry of group-11 salts toward bis(alkynyl) transition metal complexes other than $[Ti](C\equiv CR)_2$ is only less studied [1,2,6]. Among them, bis(alkynyl) platinum complexes are of interest, since they feature a square-planar structure around the d^8-configurated group-10 metal which differs from the tetrahedral coordination sphere of the group-4 metal atoms titanium, zirconium and hafnium (d^0), respectively. This structural difference should significantly reflect on the chemistry of such species.

We here describe the synthesis and reaction chemistry of $[\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C\equiv CPh)_2\}Cu(N\equiv CMe)]BF_4$ and $[\{cis\text{-}[Pt](C\equiv CPh)_2Cu\}_2](BF_4)_2$ ([Pt] = (bipy)Pt, bipy = 2,2′-bipyridine; [Pt] = (bipy′)Pt, bipy′ = 4,4′-dimethyl-2,2′-bipyridine).

2. Results and discussion

A straightforward synthesis method to prepare heterobimetallic platinum(II)–copper(I) tweezer complexes of type $[\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C\equiv CPh)_2\}Cu(N\equiv CMe)]BF_4$ (**3a**, [Pt] = (bipy)Pt, bipy = 2,2′-bipyridine; **3b**, [Pt] = (bipy′)Pt, bipy′ = 4,4′-dimethyl-2,2′-bipyridine) is given by the reaction of $cis\text{-}[Pt](C\equiv CPh)_2$ (**1**) with $[Cu(N\equiv CMe)_4]BF_4$ (**2**) in a 1:1 molar ratio in dichloromethane as solvent at 25 °C (Eq. (1)) [6n].



(1)

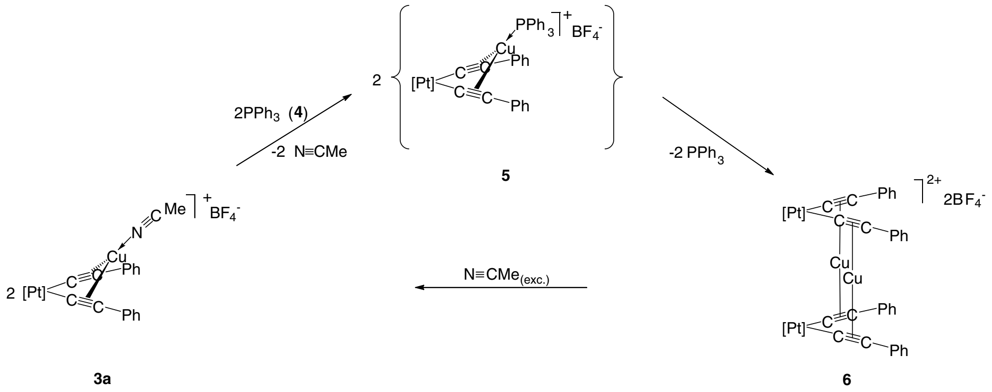
After appropriate work-up, **3a** and **3b** could be isolated as yellow solids which dissolve in polar organic solvents such as dichloromethane and tetrahydrofuran, whereby the bipy′ derivative **3b** shows a somewhat better solubility as **3a**. Complexes **3a** and **3b** are stable in the solid state and can be handled in air without significant decomposition. In contrast, the isostructural platinum(II)–silver(I) species $[\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C\equiv CPh)_2\}Ag(N\equiv CMe)]BF_4$ are more reactive, i.e. they decompose on exposure to sunlight and air on formation of metallic silver [7].

In heterobimetallic **3a** and **3b** the organometallic chelate $cis\text{-}[Pt](C\equiv CPh)_2$ stabilizes the low-valent $[Cu(N\equiv CMe)]^+$ fragment by the η^2-coordination of both $PhC\equiv C$ ligands to copper. As a result thereof, a 16-valence electron count of the $[(\eta^2\text{-}C\equiv CPh)_2Cu(N\equiv CMe)]^+$ unit is most likely, a most favoured structural motif in organometallic π-tweezer chemistry [1].

In **3a** or **3b** the acetonitrile ligand is only weakly-coordinated to copper(I) as it could be shown by addition of Lewis-bases L (L = PPh_3, bipy, $cis\text{-}[Pt](C\equiv CPh)_2$). For example, when equimolar amounts of PPh_3 (**4**) were added to **3a** a color change from yellow over orange to orange-brown took place. After appropriate work-up, tetrametallic $\{cis\text{-}[Pt](\eta^2\text{-}C\equiv CPh)_2Cu\}_2(BF_4)_2$ (**6**) could be isolated in good yield (Section 4, Scheme 1).

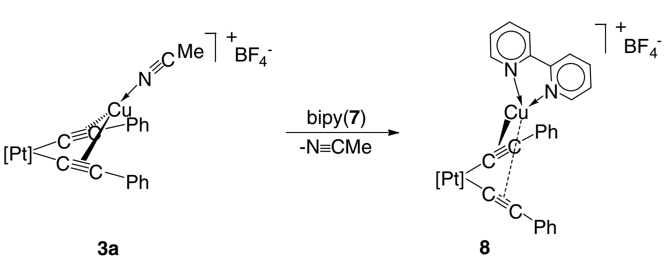
Within the reaction of **3a** with **4** presumably the heterobimetallc organometallic π-tweezer $[\{cis\text{-}[Pt](\mu\text{-}\sigma,\pi\text{-}C\equiv CPh)_2\}Cu(PPh_3)]BF_4$ (**5**) is formed at first in which PPh_3 is datively-bonded to Cu(I). However, it appeared that this species is not stable in solution and dimerizes on elimination of PPh_3 to give tetrametallic **6** (Scheme 1). Complexes similar to **5** could lately be isolated in titanium(IV)–copper(I) and titanium(IV)–silver(I) π-tweezer chemistry. [1] There it was found that depending on the donor–acceptor capacity of the Lewis-base L, reversible coordination adducts of type $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CR)_2\}M(L)]X/\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CR)_2\}MX$ are formed ($[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; M = Cu, Ag; R = singly-bonded inorganic, organic or organometallic ligand; X = BF_4, PF_6, ClO_4; L = NR'_3, PR'_3, $P(OR')_3$, …) [1,8]. Complex **6** can be transferred to the starting material **3a** on its reaction with an 5-fold excess of $N\equiv CMe$ (Scheme 1).

The copper(I) ion in **3a** and **3b** possesses coordination number 3. Thus, it should be possible to reach coordination number four at copper by adding, for example, organic or organometallic chelating molecules such as bipy



Scheme 1. Synthesis of **6** from **3a** and **4**.

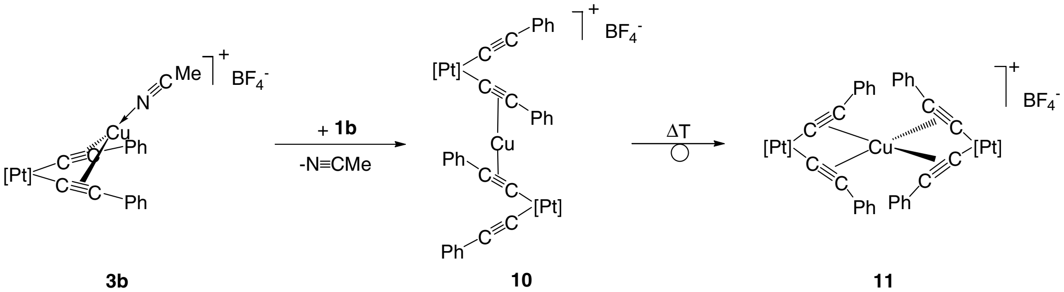
and *cis*-[*Pt*](C≡CPh)$_2$, respectively. Treatment of **3a** with one equivalent of bipy (**7**) produced the platinum(II)–copper(I) complex [{*cis*-[Pt](μ-σ,π-C≡CPh)$_2$}Cu(bipy)]BF$_4$ (**8**) in dichlormethane at 25 °C (Eq. (2)). In **8** the copper(I) ion possesses a pseudo-tetrahedral surrounding, set up by the chelating ligands bipy and *cis*-[Pt](C≡CPh)$_2$ (Eq. (2)).



(2)

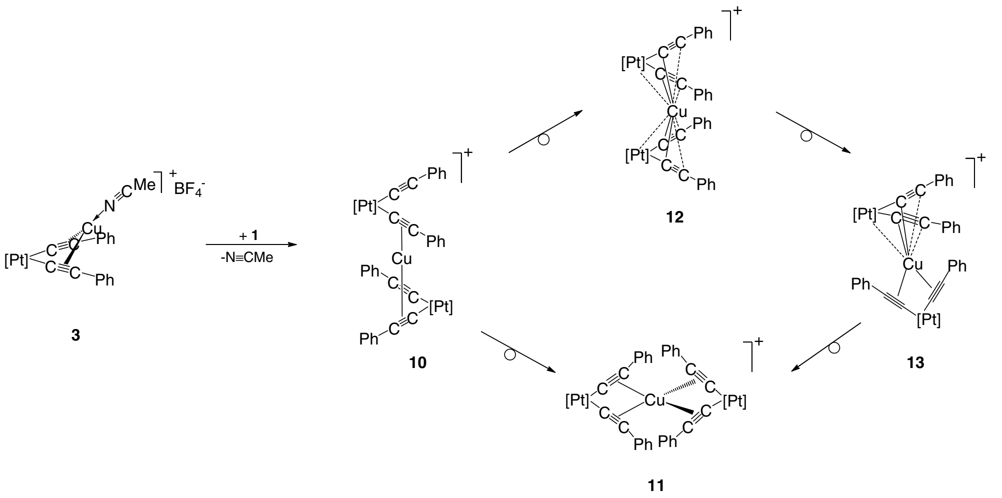
Heterobimetallic red **8** only dissolves in polar organic solvents and is not stable for a longer period of time, either in the solid state nor in solution. On elimination of *cis*-[Pt](C≡CPh)$_2$ (**1a**) the bipy-copper complex [Cu(bipy)$_2$]BF$_4$ (**9**) is formed. This clearly shows that bipy is a better chelating ligand for copper(I) then **1a**. The formation of **1a** and **9** from **8** can be enhanced, when **8** is reacted with a further equivalent of bipy (**7**). The separation of **9** from **1a** can be carried out by crystallization from dichloromethane-*n*-pentane mixtures at 0 °C. Due to its lower solubility, complex **9** precipitates at first. Both complexes were characterized by IR and ^{1}H NMR spectroscopy, ESI-TOF mass spectrometry and elemental analysis.

In attempt to synthesize a coordination complex in which a copper(I) ion is embedded between two *cis*-[Pt](C≡CPh)$_2$ entities, a structural motif which is typical for **11**, we reacted **3b** with **1b** in a 1:1 molar ratio (Eq. (3)). Within this reaction, the acetonitrile ligand is replaced by the organometallic chelate *cis*-[Pt](C≡CPh)$_2$ to give [{*cis*-[Pt](C≡CPh)(η^2-C≡CPh)}$_2$Cu]BF$_4$ (**10**) (Eq. (3)). After appropriate work-up, complex **10** could be isolated as an orange solid in quantitative yield.



(3)

In **10** two *cis*-oriented [Pt](C≡CPh)$_2$ building blocks are connected by a copper(I) ion, whereby one of the two phenylethynyl ligands of individual *cis*-[Pt](C≡CPh)$_2$ units is η^2-coordinated to Cu(I). A linear C$_2$–Cu–C$_2$ entity (C$_2$ = midpoint of the C≡C units) is formed. The respective [(η^2-C≡CPh)$_2$Cu]$^+$ moieties count to 18-valence electrons.



Scheme 2. Possible mechanism for the formation of **11** by treatment of **1** with **3**.

In the synthesis of **10** it is necessary to keep the reaction time below 3 h, and to run the reaction between 0 and 20 °C. Otherwise **10** starts to isomerize to give **11** (Eq. (3)). On prolonged stirring of **10** at 25 °C (12 h), complex **11** is formed in quantitative yield and can be isolated in form of bright orange crystals. These studies show that **10** can be considered as an intermediate in the formation of **11**. In **11** all PhC≡C units are η^2-coordinated to copper(I), a structural motif, which is characteristic in titanium-, palladium- and platinum-π-tweezer chemistry [1,2].

A possible reaction sequence for the formation of **11** by starting from **1** and **3** is presented in Scheme 2.

Complex **10**, produced by the reaction of **1** with **3** (vide supra), rearranges in solution to give most probably **12**, a compound in which the platinum and copper metal atoms are connected by μ,σ-bridged phenylethynyl ligands (Scheme 2). Complexes similar to **12** could be isolated and characterized, i.e. [{(*cis*-[Pt](μ-σ-C≡CPh)$_2$)$_2$}Ag]X (X = ClO$_4$, BF$_6$) [1,6,7]. From platinum–silver chemistry it is known that such molecules rearrange in solution to give complexes of structural type **13** (Scheme 2) [1,6,7]. In **13**, one of the two [*cis*-Pt(C≡CPh)$_2$Cu] units possess, as typical for **12**, μ,σ-bridging PhC≡C ligands, while the second [*cis*-Pt(C≡CPh)$_2$Cu] moiety shows a tweezer-type arrangement with μ-σ,π-coordinating phenylacetylides. Trimetallic **13** isomerizes at 25 °C to produce **11** (Scheme 2) [1a,1c]. The proposed mechanism and hence, the formation of **11** from **10** via intermediates **12** and **13**, relates to isostructural platinum–silver complexes, which could be isolated and characterized by single X-ray structure analysis [1,6,7]. The formation of the appropriate isostructural Pt–Ag complexes can be realized by controlling the temperature and the reaction time, respectively. That such a mechanism may also play a key role in platinum–copper chemistry is related to the observation that during the reaction of **1b** with **3b** different colors (yellow-orange-red-orange) appear. However, no further species could be isolated, except **10** and **11**, even not, when the reaction temperature and the reaction time were systematically varied.

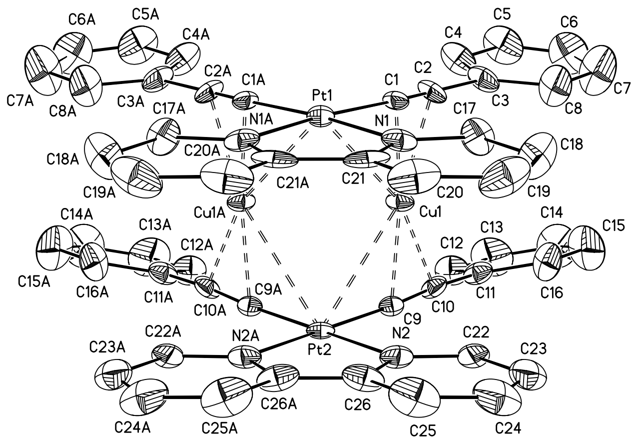


Fig. 1. ORTEP plot (30% probability level) of the molecular structure of **6** with the atom numbering scheme. The counter-ions BF$_4^-$, the molecule CH$_2$Cl$_2$ and the hydrogen atoms are omitted for clarity.

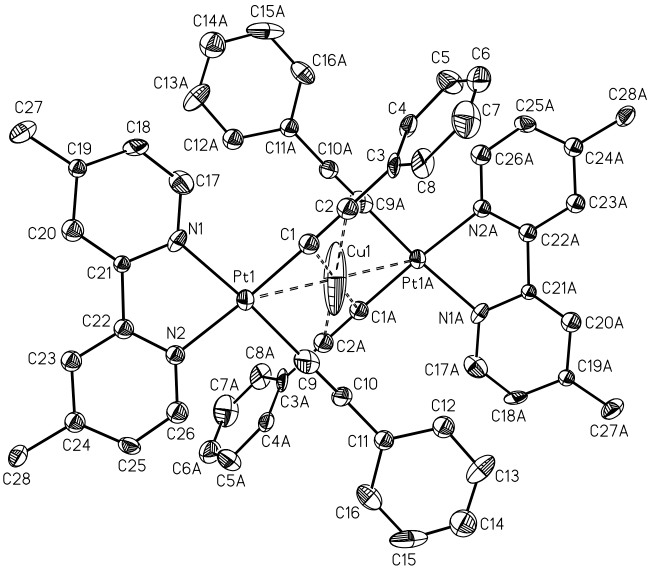


Fig. 2. ORTEP plot (50% probability level) of the molecular structure of **10** with the atom numbering scheme. The counter-ion BF$_4^-$ and the hydrogen atoms are omitted for clarity. Cu(1)–Pt(1) 2.7642(6), Cu(1)–C(1) 2.066(16), Cu(1)–C(2) 2.494(15), Pt(1)–N(1) 2.073(14), Pt(1)–N(2) 2.055(11), Pt(1)–C(1) 1.960(14), Pt(1)–C(9) 2.01(2), C(1)–C(2) 1.201(18), C(2)–C(3) 1.477(19), C(9)–C(10) 1.15(2), C(10)–C(11) 1.43(2); Pt(1)–C(1)–C(2) 177.4(15), Pt(1)–C(9)–C(10) 177.8(19), N(1)–Pt(1)–N(2) 79.1(5), C(1)–Pt(1)–C(9) 86.5(6), C(1)–Cu(1)–C(2) 28.6(5), N(1)–Pt(1)–C(9) 175.8(6), N(2)–Pt(1)–C(1) 176.7(6), C(1)–C(2)–C(3) 168.7(18), C(9)–C(10)–C(11) 176(2), N(1)–Pt(1)–C(1) 97.7(6), N(1)–Pt(1)–Cu(1) 118.2(3), Pt(1)–Cu(1)–C(1) 45.1(4), Pt(1)–Cu(1)–C(2) 73.7(3), Cu(1)–Pt(1)–C(9) 65.0(5), Cu(1)–Pt(1)–C(1) 48.3(5), N(2)–Pt(1)–C(9) 96.7(5), N(2)–Pt(1)–Cu(1) 134.2(3).

Complexes **3**, **6** and **8–11** were characterized by elemental analysis and spectroscopy (IR, ^{1}H NMR) (Section 4). From **6**, **10** and **11** the solid state structure was determined by single X-ray structure determination.

Single crystals of **6**, **10** and **11** could be grown by diffusion of *n*-pentane into a dichloromethane solution containing **6**, **10** or **11** at 25 °C (**6**) or 0 °C (**10**, **11**). The molecular structures of **6**, **10** and **11** are shown in Figs. 1 (**6**), 2 (**10**) and 3 (**11**). Geometric details for **6** and **11** are listed in Tables 1 and 2. The crystal and intensity collection data for complexes **6**, **10** and **11** are summarized in Table 3 (Section 4).

Complex **6** crystallizes in the monoclinic space group *C*2/*m* (Fig. 1). The half molecule is symmetry generated by a mirror plane (x, $-y$, z; $-x+1/2$) passing through the Pt1 and Pt2 atoms; symmetry generated atoms are indicated with the suffix A (Fig. 1).

Two almost parallel oriented *cis*-[Pt](C≡CPh)$_2$ planes are linked by the copper(I) ions Cu(1) and Cu(1a) with the platinum atoms Pt(1) and Pt(2) on the same site (the bond distances are Pt1–Cu1 2.969(3) and Pt2–Cu1 2.934(2) Å), whereby two individual PhC≡C ligands, one associated with each platinum fragment, are symmetrical η^2-coordinated to Cu(1). The bond distances are Cu(1)–C(1) 1.992(19), Cu(1)–C(9) 1.993(19) Å for the C$_\alpha$ carbons

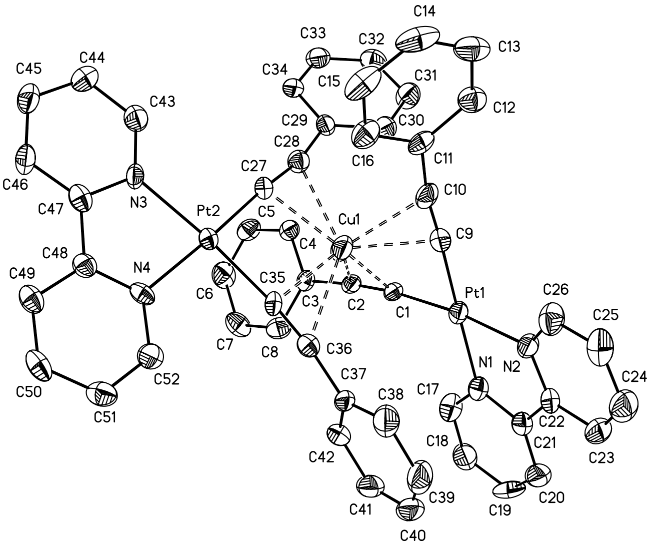


Fig. 3. ORTEP plot (50% probability level) of the molecular structure of **11** with the atom numbering scheme. BF$_4^-$ as counter-ion, the hydrogen atoms and the CH_2Cl_2 molecule are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **6**[a]

Bond distances			
Pt(1)–N(1)	2.055(18)	Pt(2)–Cu(1)	2.934(2)
Pt(1)–C(1)	1.951(17)	Cu(1)–C(9)	1.993(19)
C(1)–C(2)	1.225(10)	Cu(1)–C(10)	2.15(2)
Cu(1)–C(1)	1.992(19)	Pt(2)–N(2)	2.051(18)
Cu(1)–C(2)	2.15(2)	Pt(2)–C(9)	1.93(2)
Pt(1)–Cu(1)	2.969(3)	C(9)–C(10)	1.26(3)
Angles			
Pt(1)–C(1)–C(2)	173(2)	C(1)–Cu(1)–C(10)	158.9(9)
C(1)–C(2)–C(3)	173(3)	Pt(1)–Cu(1)–Pt(2)	83.82(7)
Pt(2)–C(9)–C(10)	176.5(18)	N(1)–Pt(1)–C(1)	96.5(8)
C(9)–C(10)–C(11)	174(2)	N(1)–Pt(1)–Cu(1)	97.2(8)
C(1)–Cu(1)–C(2)	33.2(8)	N(2)–Pt(2)–C(9)	95.8(5)
C(1)–Cu(1)–C(9)	165.5(8)	N(2)–Pt(2)–Cu(1)	94.2(5)
C(9)–Cu(1)–C(10)	34.9(8)	C(1)–Pt(1)–C(1A)	89.4(12)
C(2)–Cu(1)–C(9)	160.9(9)	C(9)–Pt(1)–C(9A)	85.5(12)
C(2)–Cu(1)–C(10)	126.0(9)		

[a] The estimated standard deviations of the last significant digit(s) are shown in parenthesis.

and Cu(1)–C(2)/Cu(1)–C(10) 2.15(2) Å for the C_β atoms ($PtC_\alpha{\equiv}C_\beta Ph$) (Table 1). Similar structural arrangements are found, for example, in silver(I) transition metal chemistry [9]. The dihedral angle formed by the calculated mean planes I (Pt(1), C(1), C(2) and N(1)) and II (Pt(2), C(9), C(10) and N(2)) is 5.03(1)° (r.m.s. deviation of fitted atoms = 0.0075 (plane I) and 0.0187 Å (plane II)). The Pt–C and Pt–N bond distances and angles are typical for this type of complexes [1,2,6]. All other bond distances and angles (Table 1) are in the range of expected values and are characteristic for such groups.

Complex **10** crystallizes in the monoclinic space group $C2/c$ and possesses a centre of inversion at Cu(1) ($1 - x + 1/2, -y + 1/2, -z$) (Fig. 2). The symmetry generated atoms are indicated with the suffix A (Fig. 2).

Table 2
Selected bond distances (Å) and angles (°) for **11**[a]

Bond distances			
Pt(1)–Cu(1)	3.0405(11)	C(1)–C(2)	1.227(11)
Pt(2)–Cu(1)	3.1824(11)	C(2)–C(3)	1.450(11)
Pt(1)–C(1)	1.971(8)	C(9)–C(10)	1.222(12)
Pt(1)–C(9)	1.960(9)	C(10)–C(11)	1.448(12)
Pt(2)–C(27)	1.987(8)	C(27)–C(28)	1.228(11)
Pt(2)–C(35)	1.991(8)	C(28)–C(29)	1.456(11)
Pt(1)–N(1)	2.059(7)	C(35)–C(36)	1.204(11)
Pt(1)–N(2)	2.075(7)	C(36)–C(37)	1.450(11)
Pt(2)–N(3)	2.078(7)	Cu(1)–C(27)	2.208(7)
Pt(2)–N(4)	2.071(6)	Cu(1)–C(28)	2.282(8)
Cu(1)–C(1)	2.296(8)	Cu(1)–C(35)	2.224(8)
Cu(1)–C(2)	2.549(8)	Cu(1)–C(36)	2.457(8)
Cu(1)–C(9)	2.263(8)		
Cu(1)–C(10)	2.509(9)		
Angles			
N(1)–Pt(1)–N(2)	79.4(3)	N(3)–Pt(2)–C(27)	98.5(3)
N(3)–Pt(2)–N(4)	78.9(3)	N(3)–Pt(2)–C(35)	174.6(3)
C(1)–Pt(1)–C(9)	88.0(3)	N(4)–Pt(2)–C(27)	176.0(3)
C(27)–Pt(2)–C(35)	86.9(3)	N(4)–Pt(2)–C(35)	95.7(3)
N(1)–Pt(1)–C(1)	96.0(3)	Pt(1)–C(1)–C(2)	173.0(7)
N(1)–Pt(1)–C(9)	175.2(3)	Pt(1)–C(9)–C(10)	174.9(8)
N(2)–Pt(1)–C(1)	173.8(3)	Pt(2)–C(27)–C(28)	175.8(7)
N(2)–Pt(1)–C(9)	96.5(3)	Pt(2)–C(35)–C(36)	175.1(7)
C(9)–C(10)–C(11)	169.1(9)	C(1)–C(2)–C(3)	173.4(8)

[a] The estimated standard deviations of the last significant digit(s) are shown in parenthesis.

However, due to the crystal quality (thin plates) the molecular structure of **10** is only presented for comparison and selected bond distances and angles are given for a rough estimate.

The molecular structure of **10** involves two *cis*-oriented (bipy′)Pt($C{\equiv}CPh$)$_2$ units which are spanned by Cu(1). Each of the two *cis*-[Pt]($C{\equiv}CPh$)$_2$ entities coordinate with one alkynyl group (C(1)–C(2), C(1a)–C(2a)) toward Cu1, thus Cu1 acts as a connecting ion. The phenylethynyl ligands are thereby unsymmetrically η^2-coordinated to Cu(1) (Cu(1)–C(1) 2.066(16), Cu(1)–C(2) 2.494(15) Å) (Fig. 2). The two platinum atoms are opposite positioned to each other, whereby the Pt(1)–Cu(1)–Pt(1a) atoms are linear oriented (Fig. 2). Following trends are found: (i) the η^2-coordinated carbon–carbon triple bonds C(1)–C(2) are somewhat longer than the respective *non*-coordinated acetylides C(9)–C(10), (ii) the Pt(1)–C(1)–C(2) and Pt(1)–C(9)–C(10) angles are almost identical, and (iii) through the π-bonding of C(1)–C(2) to Cu(1) the Pt(1)–C(1)–C(2) unit is almost not affected (177.4(15)°), while the C(1)–C(2)–C(3) moiety is *cis*-bent by 168.7(18)°.

The solid state structure of **11** is illustrated in Fig. 3. Complex **11** crystallizes in yellow blocks in the triclinic space group $P\bar{1}$. In **11**, the copper(I) ion Cu(1) unsymmetrically spans two almost orthogonal positioned *cis*-[Pt]($C{\equiv}CPh$)$_2$ units, thus reaching coordination number 4 at copper and hence, following an 18-valence electron-count.

Two coordination modes of the *cis*-[Pt]($C{\equiv}CPh$)$_2$ units toward Cu1 in **11** are observed. The Pt2-containing Pt(2),

Table 3
Crystal and intensity collection data for **6**, **10** and **11**

Compound	**6**	**10**	**11**
Formula weight	1492.65	656.74	1342.30
Empirical formula	$C_{53}H_{38}B_2Cl_2\,Cu_2F_8N_4Pt_2$	$C_{28}H_{22}B_{0.50}Cu_{0.50}F_2N_2Pt$	$C_{53}H_{38}BCl_2CuF_4N_4Pt_2$
Chemical formula	$[C_{52}H_{36}Cu_2N_4Pt_2](BF_4)_2 \cdot CH_2Cl_2$	$[C_{56}H_{44}CuN_4Pt_2](BF_4)$	$[C_{52}H_{36}CuN_4Pt_2](BF_4)^{\cdot}\,CH_2Cl_2$
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*m*	*C*2/*c*	$P\bar{1}$
a (Å)	14.3164(5)	20.8525(9)	11.04910(10)
b (Å)	24.6301(9)	9.4531(5)	12.6557(2)
c (Å)	15.8504(5)	23.2561(12)	18.1036(2)
V (Å^3)	5286.4(3)	4583.1(4)	2497.37(5)
α (°)	–	–	89.8340(10)
β (°)	108.942(2)	91.3100(10)	80.6930(10)
γ (°)	–	–	88.5420(10)
ρ_{calc} (g cm^{-3})	1.875	1.904	1.785
Crystal dimension (mm)	0.50 × 0.10 × 0.05	0.08 × 0.06 × 0.02	0.3 × 0.2 × 0.1
Z	4	8	2
Diffractometer model	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD
Radiation (λ, Å)	0.71073	0.71073	0.71073
Max., min. transmission	0.7456, 0.1465	0.681298, 0.534729	0.424224, 0.221867
Absorption coefficient (μ, mm^{-1})	6.239	6.611	6.171
Temperature (K)	173(2)	173(2)	173(2)
Scan mode	ω-scans	ω-scans	ω-scans
Scan range (°)	1.65–25.00	1.75–26.00	1.61–26.00
Index ranges	$-14 \leqslant h \leqslant 17$, $-28 \leqslant k \leqslant 29$, $-18 \leqslant l \leqslant 13$	$-22 \leqslant h \leqslant 25$, $-8 \leqslant k \leqslant 11$, $-13 \leqslant l \leqslant 28$	$-13 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $-16 \leqslant l \leqslant 22$
Total reflections	13634	7352	14585
Unique reflections	4590	3771	9641
Observed reflections [$I \geqslant {}^32\sigma(I)$]	2546	2213	7132
Refined parameters	336	243	604
R_1^{a}, wR^{2a} [$I \geqslant 2\sigma(I)$]	0.0965, 0.1978	0.0774, 0.1078	0.0478, 0.1179
R_1^{a}, wR_2^{a} (all data)	0.1791, 0.2398	0.1586, 0.1296	0.0684, 0.1269
Weighted schematic parameters (*a*/*b*)	0.1086/12.6701	0.0/0.0	0.0715/0.0
R_{int}	0.1144	0.1158	0.0346
Max., min. peak in final Fourier map (e Å^{-3})	5.827, −3.310[b]	1.181, −1.963	8.010, −2.400[b]
Goodness-of-fit on F^{2b}	1.113	0.964	0.995

[a] $R_1 = [\sum(||F_o| - |F_c|)/\sum|F_o|]$; $wR_2 = [\sum(w(F_o{}^2 - F_c{}^2)^2)/\sum(wF_o{}^4)]^{1/2}$; $P = [F_o{}^2 + 2F_c{}^2]/3c$; $S = [\sum w(F_o{}^2 - F_c{}^2)^2]/(n-p)^{1/2}$; n = number of reflections, p = parameters used; $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$.

[b] The highest unrefined electron density peaks (Q peaks) for **6** are located at distances below 131 pm around Pt: (*d*(Pt(1)–Q(1)) = 115.5 pm; 5.83 e Å^{-3}; *d*(Pt(2)–Q(2)) = 130.2 pm; 3.87 e Å^{-3}) and for **11** below 100 pm around Pt: (*d*(Pt(1)–Q(1)) = 99.6 pm; 8.01 e Å^{-3}; *d*(Pt(2)–Q(2)) = 92.4 pm; 1.70 e Å^{-3}). According to Refs. [13,14], this might be observed for heavy atoms for which remaining electron density peaks with ca. 10% of the electron density of the heavy atom are expected to be observed at distances between 60 and 120 pm.

C(27), C(28), C(35) and C(36) unit coordinates Cu1 in plane, while the Pt1-containing Pt(1), C(1), C(2), C(9) and C(10) entity coordinates Cu1 out-of-plane. Thus, the highest deviation from a calculated mean plane (plane II) of all *non*-hydrogen atoms for the Pt2-containing unit (including Cu1, but excluding the two Ph groups; r.m.s. deviation of fitted atoms = 0.0150 Å) is observed for C35 (0.0266(7) Å). Above a calculated mean plane (plane I) of all *non*-hydrogen atoms for the Pt1-containing unit (excluding Cu and the two Ph groups, r.m.s. deviation of fitted atoms = 0.0390 Å) Cu1 is located at a distance of 1.0637(7) Å. The dihedral angle formed by planes I and II is 88.33(2)°.

Both bis(alkynyl) platinum building blocks Pt(C≡CPh)$_2$ are acting as organometallic chelates toward Cu(1) (Fig. 3, Table 2), whereby the carbon–carbon triple bonds are asymmetric η^2-coordinated. Typical copper–carbon distances are Cu(1)–C(1) 2.296(8), Cu(1)–C(9) 2.263(8), Cu(1)–C(27) 2.208(7), and Cu(1)–C(35) 2.224 (8) Å for the C$_α$ carbons as well as Cu(1)–C(2) 2.549(8), Cu(1)–C(10) 2.509(9), Cu(1)–C(28) 2.282(8) and Cu(1)–C(36) 2.457(8) Å for the C$_β$ atoms (PtC$_α$≡C$_β$Ph) (Table 2). Within the Pt$_2$Cu segment Cu(1) is more symmetrically bound to Pt(1) than to Pt(2) (Table 2). The same phenomenum is observed in trimetallic {[(PPh$_3$)$_2$Pt(μ-σ,π-C≡CPh)$_2$]$_2$Ag}ClO$_4$, [{[Ti](μ-σ,π-C≡CR)$_2$}$_2$M]X (M = Cu, Ag; X = BF$_4$, PF$_6$, ClO$_4$; R = Ph, Fc) [1,2,6]. If one compares the bond distances of the copper–carbon acetylides with the data typical in heterobimetallic platinum–copper tweezer chemistry, it is most obvious that in **11** longer bonds are found. This indicates that in **11** the interaction of the four acetylides with Cu(1) is weaker, when compared with {*cis*-[Pt](μ-σ,π-C≡CPh)$_2$}CuX [1,6].

Through the η^2-coordination of the PhC≡C ligands to Cu(1), a bond-lengthening of the C≡C triple bonds from 1.201(6) and 1.211(6) Å in **1a** [9] to 1.227(11) (C(1)–C(2)), 1.222(12) (C(9)–C(10)), 1.228(11) (C(27)–C(28)) and 1.204(11) Å (C(35)–C(36)) in **11** is found (Table 2). This corresponds to the observation generally made in transition metal chemistry by changing from free, *non*-coordinated alkynes to η^2-coordinated acetylides. Due to the π-bonding of C$\equiv$C to Cu(1), the linear Pt–C$\equiv$C–C_{Ph} units in **1a** are *cis*-bent, which is evidenced by considering the corresponding Pt–C$\equiv$C and C$\equiv$C–C_{Ph} angles (Table 2). Due to steric reasons and, due to the tweezer effect of the bis(alkynyl) platinum units, the angles at Pt(1) and Pt(2) differ from those ones typical for square-planar Pt complexes and are in the range of 78–99° (Table 2). The Pt–C and Pt–N bond distances are typical for this type of complexes [1].

Furthermore, it is found that copper(1) is only displaced by 1.0637(7) Å from the Pt(1) coordination plane, while it is with 0.2565(7) Å above the ideal Pt(2) plane oriented (Fig. 3). The platinum–copper distances with 3.0405(11) and 3.1824(11) Å show that no Pt–Cu interactions exist.

3. Conclusion

Within this study the synthesis and properties of [{*cis*-[Pt](μ-σ,π-C$\equiv$CPh)$_2$}Cu(N$\equiv$CMe)]BF_4 ([Pt] = (bipy)Pt, (bipy′)Pt; bipy = 2,2′-bipyridine, bipy′ = 4,4′-dimethyl-2,2′-bipyridine) is discussed. The reaction chemistry of the latter molecule toward diverse 2- and 4-electron donor molecules L such as PPh_3, bipy and [Pt](C$\equiv$CPh)$_2$ is reported. Depending on L different (isomeric) complexes are formed. Typical species are {*cis*-[Pt][(μ-σ,π-C$\equiv$CPh)Cu]$_2$}$(BF_4)_2$, [{*cis*-[Pt](μ-σ,π-C$\equiv$CPh)$_2$}Cu(bipy)]BF_4, [{*cis*-[Pt](C$\equiv$CPh)(η^2-C$\equiv$CPh)}$_2$Cu]BF_4 and [{*cis*-[Pt](μ-σ,π-C$\equiv$CPh)$_2$}$_2$Cu]BF_4. Furthermore, it could be shown that depending on the temperature [{*cis*-[Pt](C$\equiv$CPh)(η^2-C$\equiv$CPh)}$_2$Cu]BF_4 isomerizes in solution via the intermediate formation of [{*cis*-[Pt](μ-σ-C$\equiv$CPh)$_2$}$_2$Cu]BF_4 and [{*cis*-[Pt](μ-σ-C$\equiv$CPh)$_2$}Cu{[Pt](μ-σ,π-C$\equiv$CPh)$_2$}]BF_4 to give trimetallic Pt_2Cu [{*cis*-[Pt](μ-σ,π-C$\equiv$CPh)$_2$}$_2$Cu]BF_4.

4. Experimental

4.1. General methods

All reactions were carried out in an atmosphere of purified nitrogen (O_2 traces: CuO catalyst, BASF AG, Ludwigshafen, Germany; H_2O traces: molecular sieve, 4 Å, Roth company) using standard Schlenk techniques. Solvents were purified by distillation (*n*-hexane/*n*-pentane and dichloromethane: calcium hydride; benzene and toluene: sodium; tetrahydrofuran: sodium/benzophenone ketyl). FT-IR spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer (KBr or as film between NaCl plates). NMR spectra were recorded with a Bruker Avance 250 spectrometer operating in the Fourier transform mode. ^1H NMR spectra were recorded at 250.123 MHz (internal standard, relative to $CDCl_3$, δ 7.26 and CD_2Cl_2, δ 5.32). $^{13}C\{^1H\}$ NMR spectra were recorded at 67.890 MHz (internal standard, relative to $CDCl_3$, δ 77.16 and CD_2Cl_2, δ 53.50); $^{31}P\{^1H\}$ NMR were recorded at 101.202 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard (δ 139.0, relative to 85% H_3PO_4, δ 0.00). Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane with the solvent signal as reference. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries with a Gallenkamp MFB 595 010 melting point apparatus. Microanalyses were performed by the Organic Department at Chemnitz, University of Technology and the Institute of Organic Chemistry at the University of Heidelberg.

4.2. General remarks

Compounds **1a**, **1b** [9] and [Cu(N$\equiv$CMe)$_4$]BF_4 [10] were prepared by published procedures. All other chemicals were purchased by commercial suppliers and were used as received.

4.3. Synthesis of ***3a***

To 225 mg (0.406 mmol) of **1a** dissolved in dichloromethane (125 mL), molecule **2** (127 mg, 0.406 mmol) was added in a single portion at 25 °C, whereby a color change from yellow to orange and again to yellow was observed. After 12 h of stirring at this temperature the solvent was decanted from the yellow precipitate and was washed with *n*-pentane (2 × 10 mL). The remaining residue was tried in *oil-pump vacuum* affording a yellow solid. Yield: 300 mg (0.404 mmol, 99% based on **1a**).

M.p. (°C): 240 (decomp.). IR (KBr) [cm^{-1}]: $\nu_{N\equiv C}$ 2289 (m), 2282 (w); $\nu_{C\equiv C}$ 2028 (s), 1990 (sh); ν_{B-F} 1056 (vs). ^1H NMR (d_6-dmso): [δ] 2.05 (s, 3H, CH_3C$\equiv$N), 7.1–7.3 (m, 6H, ^{m}H, ^{p}H/Ph), 7.46 (d, $^3J_{HH} = 7.2$ Hz, 4H, ^{o}H/Ph), 7.84 (dd, $^3J_{H^5H^6} = 5.9$ Hz, $^3J_{H^5H^4} = 7.1$ Hz, 2H, H^5/bipy), 8.40 (dd, $^3J_{H^4H^3} = 8.1$ Hz, $^3J_{H^4H^5} = 7.1$ Hz, 2H, H^4/bipy) 8.63 (d, $^3J_{H^3H^4} = 8.1$ Hz, 2H, H^3/bipy), 9.28 (d, $^3J_{H^6H^5} = 5.9$ Hz, 2H, H^6/bipy). Anal. Calc. for $C_{28}H_{21}N_3PtCuBF_4$ (744.76): C, 45.16; H, 2.84; N, 5.63. Found: C, 44.96; H, 2.87; N, 5.24%.

4.4. Synthesis of ***3b***

Complex **3b** was prepared as described for the synthesis of **3a** (see above). Thus, 200 mg (0.349 mmol) of **1b** were reacted with **2** (109 mg, 0.349 mmol) in tetrahydrofuran (125 mL). After appropriate work-up, complex **3b** could be isolated as a yellow solid in 270 mg (0.349 mmol, 100% based on **1b**) yield.

M.p. (°C): 220 (decomp.). IR (KBr) [cm^{-1}]: $\nu_{N\equiv C}$ 2322 (m), 2291 (w); $\nu_{C\equiv C}$ 2042 (s), 2027 (s), 1992 (sh); ν_{B-F} 1056 (vs). ^1H NMR[1] (d_6-dmso): [δ] 2.05 (s, 3H, CH_3C$\equiv$N),

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[1] The resonance signal for the $CH_{3(bipy)}$ protons is covered by the signal of the d_6-dmso solvent molecule.

7.2–7.3 (m, 6H, ^{m}H, ^{p}H/Ph), 7.44 (d, $^{3}J_{HH} = 7.2$ Hz, 4H, ^{o}H/Ph), 7.62 (d, $^{3}J_{H^5H^6} = 6.3$ Hz, 2H, H^{5}/bipy′), 8.44 (s, 2H, H^{3}/bipy′), 9.04 (d, $^{3}J_{H^6H^5} = 6.3$ Hz, 2H, H^{6}/bipy′). Anal. Calc. for $C_{30}H_{25}N_3PtCuBF_4$ (773.00): C, 46.61; H, 3.26; N, 5.43. Found: C, 46.36; H, 3.27; N, 5.15%.

*4.5. Synthesis of **5** and **6***

200 mg (0.286 mmol) of **3a** were reacted with equimolar amounts of PPh_3 (**4**) in diethyl ether at 25 °C. During the course of the reaction the color of the reaction solution turned from yellow to orange (formation of **5**) and then to orange-brown. After 24 h of stirring at this temperature all volatiles were removed in *oil-pump vacuum* and the residue was extracted with dichloromethane (20 mL). Evaporation of the solvent in *oil-pump vacuum* gave 186 mg (0.127 mmol, 95% based on **3a**) of **6**. Single crystals of **6** could be obtained by slow diffusion of *n*-pentane into a dichloromethane solution containing **6** at 25 °C.

*4.6. Synthesis of **8** and **9***

200 mg (0.286 mmol) of **3a** were reacted with one equivalent of **7** in dichloromethane at 25 °C. The reaction mixture changed its color from yellow to orange (formation of **8**). Further addition of another equivalent of bipy produced a red solution. Evaporation of all volatiles in *oil-pump vacuum* yielded a red solid. Crystallization from a 1:1 dichloromethane-*n*-pentane mixture at 25 °C gave red **9**. On subsequent cooling the remaining solution to 0 °C pale yellow crystals of **1a** formed. Yield: **1a**: 148 mg (0.286 mmol, 100% based on **3a**). **9**: 124 mg (0.286 mmol, 100%).

*4.7. Synthesis of **10***

To **3b** (22 mg, 0.028 mmol) suspended in dichloromethane (25 mL) complex **1b** (17 mg, 0.028 mmol) was added in a single portion at 25 °C, whereby a color change from red to yellow was observed. After 3 h of stirring at this temperature all volatiles were removed in *oil-pump vacuum*. The orange residue was washed with *n*-pentane (2 × 5 mL). Yield of **10**: 36 mg (0.028 mmol, 100% based on **1b**). Orange single crystals could be grown from a saturated 10:1 dichloromethane-*n*-pentane mixture at 0 °C.

M.p. (°C): 228 (decomp.). IR (KBr) [cm^{-1}]: $\nu_{C\equiv C}$ 2118 (s), 2033 (s); ν_{B-F} 1056 (vs). ^{1}H NMR (d$_6$-dmso)[1]: [δ] 7.1–7.3 (m, 6H, ^{m}H, ^{p}H/ Ph), 7.41 (d, $^{3}J_{HH} = 7.8$ Hz, 4H, ^{o}H/Ph), 7.58 (d, $^{3}J_{H^5H^4} = 5.4$ Hz, 2H, H^{5}/bipy′), 8.40 (s, 2H, H^{3}/bipy′), 9.03 (d, $^{3}J_{H^6H^5} = 5.4$ Hz, 2H, H^{6}/bipy′). Anal. Calc. for $C_{56}H_{44}N_4Pt_2CuBF_4$ (1313.52): C, 51.20; H, 3.37; N, 4.26. Found: C, 50.97; H, 3.44; N, 4.45%.

*4.8. Synthesis of **11***

*Reaction of **1a** with **3a***: 100 mg (0.180 mmol) of **1a** was dissolved in dichloromethane (50 mL) and 134 mg (0.180 mmol) of **3a** was added in a single portion at 25 °C. After 12 h of stirring at this temperature all volatiles were removed in *oil-pump vacuum*. Yield of **11**: 221 mg (0.176 mmol, 98% based on **1a**).

*From **10***: Compound **1a** (233 mg, 0.42 mmol) was dissolved in dichloromethane (50 mL) and 77 mg (0.35 mmol) of **2** was added at 25 °C. The reaction solution was stirred for 12 h, whereas the color changed from yellow to brown. 75 mL of *n*-pentane were added and a greenish precipitate formed. The thus obtained solid was dissolved in 10 mL of dichloromethane. By a slow diffusion of *n*-pentane into this solution gave yellow to orange colored crystals of **11**. Yield: 85 mg (0.064 mmol, 56% based on **1a**).

M.p. (°C): 229 (decomp.). IR (KBr) [cm^{-1}]: $\nu_{C\equiv C}$ 2085, 2057; ν_{B-F} 1060. ^{1}H NMR (CD_3CN): [δ] 7.2–7.3 (m, 6H, ^{m}H, ^{p}H/Ph), 7.4–7.5 (m, 4H, ^{o}H/Ph), 7.61 (pt, $^{3}J_{HH} = 6.5$ Hz, 2H, H^{5}/bipy), 8.1–8.2 (m, 4H, H^{4}, H^{3}/bipy), 9.48 (d, $^{3}J_{H^6H^5} = 6.9$ Hz, 2H, H^{6}/bipy). Anal. Calc. for $C_{52}H_{36}N_4Pt_2CuBF_4 \cdot CH_2Cl_2$ (1342.44): C, 47.42; H, 2.86 N, 4.17. Found: C, 45.51; H, 3.30; N, 4.17%.

*4.9. Single X-ray structure analysis of **6**, **10** and **11***

The solid state structures of **6**, **10** and **11** were determined by single crystal X-ray diffraction. Data collection was performed on a Bruker axs SMART 1k with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Crystallographic data of **6** and **11** are given in Table 3, while the data for **10**, due to the crystal quality, are only given for comparison in Fig. 2. The structures were solved by direct methods using SHELXS-97 [11]. An empirical absorption correction was applied. The structures were refined by full-matrix least-square procedures on F^2 using SHELXL-97 [12]. All *non*-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions.

5. Supplementary material

CCDC 645853, 645856 and 645854 contain the supplementary crystallographic data for **6**, **10** and **11**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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