Heterometallic Pt–Ag and Pt2Ag transition metal complexes

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Abstract

Complexes of type {*cis*-[Pt](μ-σ,π-C≡CPh)2}AgX (**3a**, [Pt] = (bipy′)Pt, X = FBF3; **3b**, [Pt] = (bipy′)Pt, X = FPF5; **3c**, [Pt] = (bipy)Pt, X = OClO3; **3d**, [Pt] = (bipy′)Pt, X = BPh4; bipy′ = 4,4′-dimethyl-2,2′-bipyridine; bipy = 2,2′-bipyridine) are accessible by combining *cis*-[Pt](C≡CPh)2 (**1a**, [Pt] = (bipy′)Pt; **1b**, [Pt] = (bipy)Pt) with equimolar amounts of [AgX] (**2a**, X = BF4; **2b**, X = PF6; **2c**, X = ClO4; **2d**, X = BPh4). In **3a**–**3d** the platinum(II) and silver(I) ions are connected by σ- and π-bonded phenyl acetylide ligands. When the molar ratio of **1** and **2** is changed to 2:1 then trimetallic [{*cis*-[Pt](μ-C≡CPh)2}2Ag]X (**8a**, [Pt] = (bipy)Pt, X = BF4; **8b**, [Pt] = (bipy′)Pt, X = PF6; **8c**, [Pt] = (bipy)Pt, X = BF4) is produced. The solid state structure of **8a** was determined by single X-ray crystal structure analysis. In **8a** the silver(I) ion is embedded between two parallel oriented *cis*-[Pt](C≡CPh)2 units. Within this structural arrangement the phenyl acetylides of individual [Pt](C≡CPh)2 entities possess a μ-bridging position between Pt(II) and Ag(I). In addition, a very weak dative Pt → Ag interaction is found (Pt–Ag 2.8965(3) Å). The respective silver carbon distances Ag–C$_\alpha$ (2.548(7), 2.447(7) Å) and Ag–C$_\beta$ (3.042(7), 2.799(8) Å)(PtC$_\alpha$≡C$_\beta$Ph) confirm this structural motif.

Complexes **8a**–**8c** isomerize in solution to form trimetallic [{*cis*-[Pt](μ-σ,π-C≡CPh)2}2Ag]X (**9a**, [Pt] = (bipy)Pt, X = BF4; **9b**, [Pt] = (bipy′)Pt, X = PF6; **9c**, [Pt] = (bipy)Pt, X = ClO4). In the latter molecules the organometallic cation [{*cis*-[Pt](μ-σ,π-C≡CPh)2}2Ag]$^+$ is set-up by two nearly orthogonal positioned [Pt](C≡CPh)2 entities which are hold in close proximity by the group-11 metal ion. Within this assembly all four PhC≡C units are η^2-coordinated to silver(I). A possible mechanism for the formation of **9** is presented.

1. Introduction

Early–late and late–late heterobimetallic transition metal complexes in which two remote metal atoms are separated by alkynyl ligands are of interest because of their potential application in supramolecular chemistry and material science [1–3]. Within this field, platinum(II) acetylide and alkynyl-titanocene, -zirconocene and -hafnocene complexes have attracted much attention. In these compounds the acetylide ligands RC≡C can act as 3–5 electron

ligands to the appropriate metal atoms including μ–σ and μ-σ,π coordination and hence, the chemistry of such transition metal alkynyl complexes has been intensively studied, due to their structural diversity and chemical reactivity [1–3]. Among such complexes, molecules of general composition {[M](μ-σ,π-C≡CR)2}M′X ([M] = (η^5-C5H4SiMe3)2M, (η^5-C5H5)2M; R = singly-bonded organic or organometallic group; M = Ti, Zr, Hf; M′X = 10–12 valence electron complex fragment, such as CuR, AgR and AuR or Ni(CO) and Co(CO)) have been studied in detail [1]. In these heterobimetallic early–late transition metal compounds the two metals M and M′ are hold in close proximity by the chelating effect of the organometallic π-tweezer molecule [M](C≡CR)2, whereby the RC≡C

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ligands are μ-σ,π-bridging M and M', respectively [1]. In contrast, only less is known about {*cis*-[Pt](μ-σ,π-C≡CR)$_2$}MX ([Pt] = (bipy)Pt, bipy = 2,2'-bipyridine) systems in which two late metal atoms are bridged by acetylide ligands [2,4].

We here discuss the reaction chemistry of *cis*-[Pt](C≡CPh)$_2$ ([Pt] = (4,4'-dimethyl-2,2'-bipyridine)Pt, (bipy')Pt; [Pt] = (2,2'-bipyridine)Pt, (bipy)Pt) towards diverse silver(I) salts [AgX] (X = BF$_4$, PF$_6$, ClO$_4$, BPh$_4$) in the ratios of 1:1 and 2:1, respectively.

2. Results and discussion

Treatment of *cis*-[Pt](C≡CPh)$_2$ (**1a**, [Pt] = (4,4'-dimethyl-2,2'-bipyridine)Pt, (bipy')Pt; **1b**, [Pt] = (2,2'-bipyridine)Pt, (bipy)Pt) [5] with the silver(I) salts [AgX] (**2a**, X = BF$_4$; **2b**, X = PF$_6$; **2c**, X = ClO$_4$; **2d**, X = BPh$_4$) in a 1:1 molar ratio produced the heterobimetallic transition metal π-tweezer complexes {*cis*-[Pt](μ-σ,π-C≡CPh)$_2$}-AgX (**3a**, [Pt] = (bipy')Pt, X = FBF$_3$; **3b**, [Pt] = (bipy')Pt, X = FPF$_5$; **3c**, [Pt] = (bipy)Pt, X = OClO$_3$; **3d**, [Pt] = (bipy')Pt, X = BPh$_4$) in dichloromethane at 25 °C (Eq. (1)) (Table 1). It is advisable to run these reactions in the dark, since otherwise slow decomposition of **3a–3d** may occur to give [Pt](C≡CPh)$_2$ along with elemental silver implying redox processes. After appropriate work-up, complexes **3a–3d** could be isolated as yellow solids in 75–85% yield (Section 4). They readily dissolve in polar organic solvents such as tetrahydrofuran, dimethylsulfoxide and acetonitrile.

$$ (1) $$
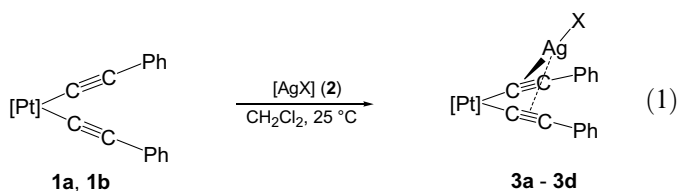
In **3a–3d** the platinum(II) and silver(I) ions are μ-bridged by two σ,π-bonded phenyl acetylides and hence, the 3-platina-penta-1,4-diyne fragment behaves as an organometallic bidentate chelating ligand toward the low-valent AgX building block [1,4].

If the ratio of the reactands **1** and **2** is changed to 2:1 then trimetallic yellow colored Pt$_2$Ag complexes of composition [{*cis*-[Pt](μ-C≡CPh)$_2$}$_2$Ag]X (**8a**, [Pt] = (bipy)Pt, X = BF$_4$; **8b**, [Pt] = (bipy')Pt, X = PF$_6$; **8c**, [Pt] = (bipy)Pt,

X = BF$_4$) were formed under similar reaction conditions (Scheme 1). Complexes **8a–8c** could be isolated in 98% (**8a**), 76% (**8b**) or 60% (**8c**) yield. In **8a–8c** two *cis*-oriented [Pt](C≡CPh)$_2$ units are parallel positioned to each other and are connected by a silver(I) ion (Fig. 1). The respective groups X are of non-coordinating character which differs from heterobimetallic **3a–3c**, where X is datively-bonded to the silver(I) ion *via* one fluoride (FBF$_3$, FPF$_5$) or oxygen atom (OClO$_3$).

When dichloromethane solutions containing **8a–8c** were stirred for 7 days in the dark at 25 °C complexes **8a–8c** isomerize to give **9a–9c** (Scheme 1). Complexes **8** and **9** possess the same elemental composition, however, they show a different structural arrangement concerning the bonding mode of the alkynyl ligands. In **9a–9c** the two *cis*-[Pt]-(C≡CPh)$_2$ coordination planes are orthogonal positioned to each other and are linked by a pseudo-tetrahedrally coordinated silver(I) ion involving only carbon atoms. Similar complexes to **9a–9c** could recently be synthesized [1,6]. This nicely demonstrates that depending on the stoichiometry of **1** and **2** bi- (**3a–3d**) or trimetallic (**8a–8c**, **9a–9c**) complexes are formed (Eq. (1) and Scheme 1). Depending on the reaction time complexes **8a–8c** rearrange to produce **9a–9c** and hence, can be considered as intermediates in the formation of **9a–9c** (for a detailed discussion see below).

Complexes **8** and **9** were also formed, when **3a–3c** were treated with the bis(phenylethynyl)platinum species **1a** and **1b**, respectively, in dichloromethane at room temperature (Eq. (2)). Within this reaction the weakly coordinated groups X in **3a–3c** are replaced by the organometallic chelate [Pt](C≡CPh)$_2$. After appropriate work-up, complexes **9a–9c** could be isolated in excellent yield (4).

$$ (2) $$
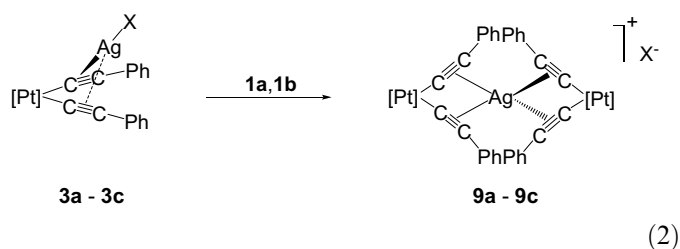
Elemental analyses of **3a–3d**, **8a–8c** and **9a–9c** confirm that next to a silver atom one (complex **3a–3d**) or two platinum atoms (**8a–8c** and **9a–9c**) are present which corresponds to the composition [(bipy'/bipy)Pt(C$_2$Ph)$_2$]AgX (**3**) and [(bipy'/bipy)Pt(C$_2$Ph)$_2$]$_2$AgX (**8, 9**), respectively.

Complexes **3a–3d**, **8a–8c** and **9a–9c** show their $v_{C≡C}$ absorptions at lower frequencies (2060–2120 cm^{-1}), when compared with the starting materials **1a** (2124 and 2114 cm^{-1}) and **1b** (2122 and 2112 cm^{-1}) [1,4,5], pointing to a μ/π-bridging of the phenylethynyl ligands. In addition, the IR spectra of **3a–3c** show the typical absorptions for datively-bonded groups X (X = FBF$_3$, FPF$_5$, OClO$_3$) [7,8]. In contrast, for **8a–8c** and **9a–9c** characteristic absorptions are found for non-coordinated X$^-$ entities (4) [1,7,8].

Table 1
Synthesis of **3a–3d**

Compound	[Pt]	X	Yield[a] (%)	Refs.
3a	(bipy')Pt[b]	FBF$_3$	85	[4a]
3b	(bipy')Pt	FPF$_5$	75	This work
3c	(bipy)Pt[c]	OClO$_3$	84	This work
3d	(bipy')Pt	BPh$_4$	80	This work

[a] Based on **1a** or **1b**.
[b] bipy' = 4,4-dimethyl-2,2'-bipyridine.
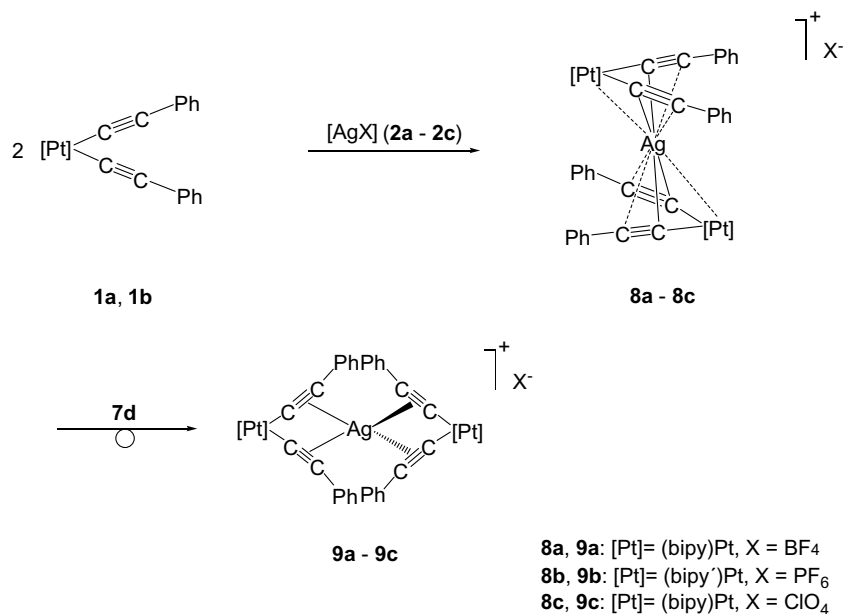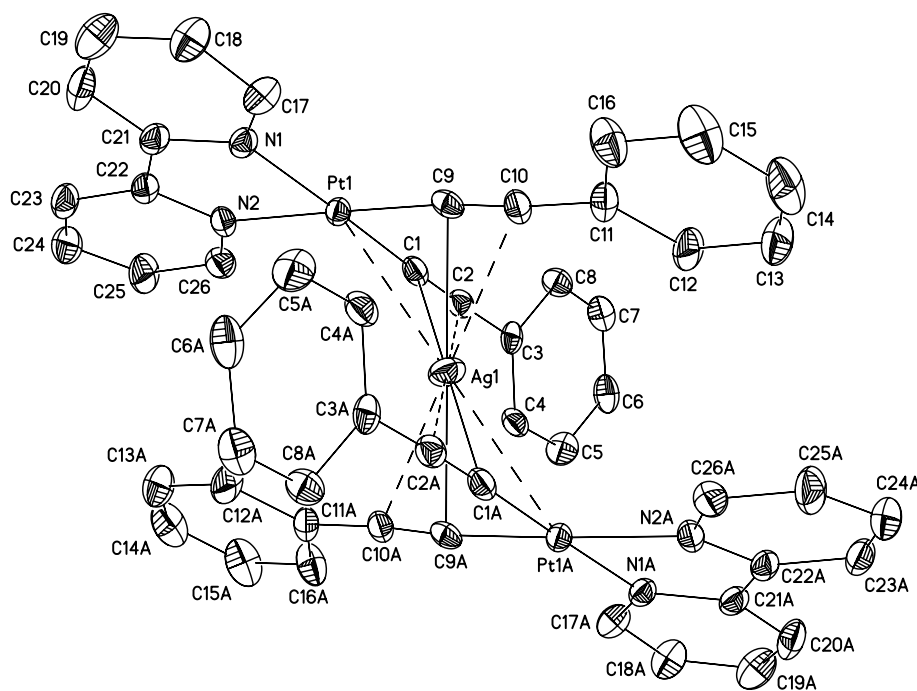[c] bipy = 2,2'-bipyridine.

Scheme 1. Synthesis of **8** and **9** from **1** with **2**.

Fig. 1. ORTEP plot (30 % probability level) of the solid state structure of **8a** with the molecular geometry and atom numbering scheme (the anion BF_4^- and the hydrogen atoms are omitted for clarity). Symmetry transformations used to generate equivalent atoms: $-x + 1/2, -y + 3/2, -z$ and $-x + 1, y, -z + 1/2$.

The counter-ion PF_6^- in **3b**, **8b** and **9b** appears in the $^{31}P\{^1H\}$ NMR spectrum at -142.9 ppm as a heptet with $J_{PF} = 710$ Hz, typical for PF_6^- counter ions.

In the ^1H NMR spectra of all new complexes character-istic resonance signals are observed for the phenyl groups and the chelated bipy and bipy′ ligands in the expected region with the corresponding coupling pattern (4). The resonance signals for the CH_3 groups of the bipy′ entities are overlapping with the d^6-dmso solvent signal, which must be used as solvent for **3a**–**3d**, **8a**–**8c** and **9a**–**9c**, since these complexes are only soluble in polar organic solvents (vide supra).

Complexes similar to **3** and **9** have already been charac-terized by single X-ray crystal structure analysis [1,4,6,9]. In **3a**–**3d** a low-valent mononuclear [AgX] entity is chelate-bonded by the [Pt](C≡CPh)₂ fragment. The AgX

building block is thereby oriented out of the best [Pt](C≡C–C$_{Ph}$)$_2$ plane [1,4]. Trimetallic **9** consists of the cationic transition metal moiety [{[Pt](C≡CPh)$_2$}$_2$Ag]$^+$ in which two almost orthogonally positioned *cis*-[Pt](C≡CPh)$_2$ moieties are spanned by a pseudo-tetrahedrally coordinated silver(I) ion through all four C≡C triple bonds [1,6]. The tweezer moieties are thereby unsymmetrically π-coordinated by the PhC≡C ligands. This structural behavior was also concluded from the IR spectra of these species (**4**, vide supra).

Yellow crystals of [{*cis*-(bipy)Pt(C≡CPh)$_2$}$_2$Ag]BF$_4$ (**8a**) could be obtained by cooling a dichloromethane/*n*-pentane mixture of ratio 20:1 containing **8a** to −0 °C. A view of the molecular solid state structure of **8a** is given in Fig. 1. Selected bond distances (Å) and angles (°) are presented in Table 2. The crystal and intensity collection data are summarized in Table 3 (**4**).

Trimetallic **8a** crystallizes in the monoclinic space group $C2/c$ and contains a centre of inversion at Ag1; the symmetry-generated atoms are indicated with the suffix A. The most striking feature of **8a** is the presence of two parallel oriented *cis*-(bipy)Pt(C≡CPh)$_2$ units (r.m.s. deviation of fitted atoms 0.128 Å (C1, C2, C9, C10, C17–C26, N1, N2, and Pt1); highest deviation: −0.315(6) Å, C10). These planes are connected by Ag1, whereby the group-11 metal ion interacts with Pt, C$_\alpha$ and C$_\beta$ of the PtC$_\alpha$≡C$_\beta$Ph fragment. Within this arrangement the Ag1–C1 (2.548(7) Å) and Ag1–C9 (2.447(7) Å) distances are remarkably shorter, when compared with the Ag1–C2 (3.042(7) Å) and Ag1–C10 (2.799(8) Å) separations. Thus the silver(I) ion is coordinated stronger by the C$_\alpha$ atoms than the C$_\beta$ carbons [10]. Considering that the C$_\alpha$ atoms (C1/C1A and C9/C9A) are preferentially coordinated to Ag1, a planar Ag1, C1/C1A, C9/C9A entity is formed. Due to long Ag1–C2 and Ag1–

Table 3
Crystal and Intensity Collection data for **8a**

Formula weight	1301.71
Chemical formula	C$_{52}$H$_{36}$AgBF$_4$N$_4$Pt$_2$
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	19.4059(11)
b (Å)	9.0795(5)
c (Å)	24.9277(13)
β (°)	99.3320(10)
V (Å^3)	4334.0(4)
$\delta_{calcd.}$ (g cm^{-3})	1.995
Crystal dimension (mm)	0.22 × 0.08 × 0.06
Z	4
Radiation (λ, Å)	0.71073
Maximum, mininum transmission	0.444262/0.316732
Absorption coefficient (μ, mm^{-1})	6.947
Scan mode	ω-Scans
Scan range (°)	1.66–26.00
Index range	$-23 \leqslant h \leqslant 23$, $-9 \leqslant k \leqslant 11$, $-30 \leqslant l \leqslant 30$
Total reflections	13089
Unique reflections	4263
Observed reflections [$I \geqslant 3\sigma(I)$]	3116
Refined parameters	291
R_1^a, wR_2^a [$I \geqslant 3\sigma(I)$]	0.0371, 0.0733
R_1^a, wR_2^a (all data)	0.0664, 0.0800
Weighting scheme paramater (a/b) R(int)	0.0597
Maximum, minimum peak in final Fourier map (e Å^{-3})	1.495, −1.450
Goodness-of-fit on F^2	0.979

[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; $w = 1/[2(F_o^2) + (aP)^2 + bP]$.

C10 distances (Table 2) the Pt–C≡C–C$_{Ph}$ units are almost linear oriented (Pt1–C1–C2 178.5(6), C1–C2–C3 176.9(8)°; Pt1–C9–C10 175.0(7), C9–C10–C11 175.4(9)°) (Table 2).

Comparing **8a** with chemically related [Pt$_2$Ag(C≡CPh)$_4$(PPh$_3$)$_4$]$^+$ [11] in which the chelating bipy unit is replaced by Ph$_3$P ligands, a significant different coordination geometry around Ag1 (Fig. 2) is found.

While in [Pt$_2$Ag(C≡CPh)$_4$(PPh$_3$)$_4$]$^+$ [11] the alkynyl ligands (C$_\alpha$,C$_\beta$) are π-coordinated to Ag (2.367(7)–2.709(7) Å), in molecule **8a** the PhC≡C moieties are preferentially bonded via the C$_\alpha$ carbon atoms (vide supra). This is most probably attributed to the formation of a very weak Pt → Ag dative bond (Pt1–Ag1 2.8965(3) Å) [12,13]. Typical unsupported Pt → Ag separations are ranging up to 2.7659(6) Å [12,13]. This value is at the upper end of the sum of $r_{(Ag^+)}$ and the van-der-Waals radius of Pt
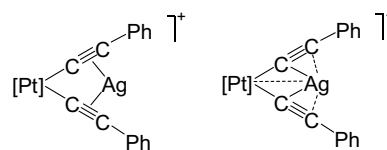
Table 2
Selected bond distances (Å) and angles (°) for **8a**[a]

Bond distances

Pt(1)–N(1)	2.056(5)	Ag(1)–C(9)	2.447(7)
Pt(1)–N(2)	2.058(5)	Ag(1)–C(10)	2.799(8)
Pt(1)–C(1)	1.958(8)	C(1)–C(2)	1.203(9)
Pt(1)–C(9)	1.964(7)	C(2)–C(3)	1.455(10)
Pt(1)–Ag(1)	2.8965(3)	C(9)–C(10)	1.205(9)
Ag(1)–C(1)	2.548(7)	C(10)–C(11)	1.440(9)
Ag(1)–C(2)	3.042(7)		

Angles

N(1)–Pt(1)–N(2)	79.2(2)	C(1)–Ag(1)–C(2)	22.7(2)
N(1)–Pt(1)–C(1)	175.3(2)	C(9)–Ag(1)–C(10)	25.4(2)
N(1)–Pt(1)–C(9)	97.1(2)	Pt(1)–C(1)–C(2)	178.5(6)
N(2)–Pt(1)–C(1)	96.3(3)	Pt(1)–C(9)–C(10)	175.0(7)
N(2)–Pt(1)–C(9)	175.0(2)	C(1)–C(2)–C(3)	176.9(8)
C(1)–Pt(1)–C(9)	87.5(3)	C(9)–C(10)–C(11)	175.4(9)
Pt(1)–Ag(1)–Pt(1A)[b]	180.00(10)	C(1)–Pt(1)–Ag(1)	59.7(2)
C(1)–Ag(1)–C(9)	65.7(2)	C(9)–Pt(1)–Ag(1)	56.6(2)
C(2)–Ag(1)–C(10)	96.13(19)		

[a] The estimated standard deviation(s) of the last significant digit(s) are shown in parantheses.
[b] Symmetry transformations used to generate equivalent atoms: $-x + 1/2$, $-y + 3/2$, $-z$ and $-x + 1$, y, $-z + 1/2$.

Fig. 2. Schematic representation of **8a** (planar Ag coordination) (right) and [Pt$_2$Ag(C≡CPh)$_4$(PPh$_3$)$_4$]$^+$ [11] (distorted tetrahedral Ag surrounding) (left).

(2.77–2.87 Å). The different Pt → Ag interaction (Fig. 2) of **8a** versus [Pt$_2$Ag(C≡CPh)$_4$(PPh$_3$)$_4$]$^+$ can be explained by the different electron household at platinum, due to the bipy versus PPh$_3$ ligands.

As typical for d^8-configurated transition metals, the platinum(II) ion in **8a** possesses a square-planar environment, caused by the atoms N1, N2, C1–C3 and C9–C11 (rms deviation of fitted atoms 0.0521 Å). The two pyridine rings of the bipy moieties are tilted by 7.8° (Fig. 1). The Pt1–N1 and Pt1–N2 separations correspond with 2.056(5) and 2.058(5) Å to well-known distances typical for this type of units [9]. The Pt1–C1 and Pt1–C9 bond lengths are 1.958(8) and 1.964(7) Å and are shortened, when compared with platinum(II) compounds containing σ-bonded sp^3- or sp^2-hybridized carbon atoms which can be explained with a higher s-orbital contribution at C1 and C9 in **8a** [14–18].

3. Conclusion

An efficient synthesis route for the preparation of heterobi- and heterotrimetallic complexes of type {cis-[Pt](μ-σ,π-C≡CPh)$_2$}AgX (**3a**–**3d**), [{cis-[Pt](μ-C≡CPh)$_2$}$_2$Ag]X (**8a**–**8c**), and [{cis-[Pt](μ-σ,π-C≡CPh)$_2$}$_2$Ag]X (**9a**–**9c**) by reacting cis-[Pt](C≡CPh)$_2$ ([Pt] = (bipy′)Pt, (bipy)Pt) with diverse silver(I) salts [AgX] (X = BF$_4$, PF$_6$, ClO$_4$, BPh$_4$) in the molar ratios of 1:1 and 2:1, respectively, is reported. Complexes {cis-[Pt](μ-σ,π-C≡CPh)$_2$}$_2$AgX ([Pt] = (bipy)Pt, (bipy′)Pt; X = BF$_4$, ClO$_4$, PF$_6$) are also formed by treatment of **3** with cis-[Pt](C≡CPh)$_2$. Complexes **8** and **9** possess the same elemental composition, but are, as demonstrated by single crystal X-ray structure analyses and IR spectroscopic studies, different structured. Complexes **9a**–**9c** contain two orthogonal positioned cis-bis(alkynyl) platinum(II) coordination planes and each of the four phenyl acetylides is π-bonded to a silver(I) ion in a pseudo-tetrahedral environment involving only carbon atoms [1,6]. This is the most stable conformation for such species. In **8a**–**8c**,

the less stable isomer, the platinum atoms of the two parallel oriented cis-[Pt](C≡CPh)$_2$ entities and the C$_\alpha$ carbon atoms (PtC$_\alpha$≡C$_\beta$Ph) are preferentially interacting with the silver(I) ion. On prolonged stirring or heating complexes **8a**–**8c** smoothly isomerize to produce more stable **9a**–**9c**. Nevertheless, it was not possible to systematically study this rearrange process by, for example, NMR spectroscopy, since the signals are found in a very narrow chemical shift window, so no assignment could be carried out.

Thus **8a**–**8c** can be considered as intermediates in the formation of trimetallic **9a**–**9c**. It would be of interest to show, if there would even be a further step (formation of **8′**) in the synthesis of **9** (Fig. 3). Such complexes could recently be synthesized in platinum(II)–copper(I) organometallic π-tweezer chemistry [1,19].

4. Experimental

All reactions were carried out under an atmosphere of purified nitrogen (O$_2$ traces: Cu catalyst, BASF-AG, Ludwigshafen; H$_2$O: molecular sieve, Merck) using standard Schlenk techniques. Solvents were purified by distillation prior to use; n-pentane and dichloromethane:calciumhydride; diethyl ether: sodium/benzophenone ketyl; ethanol: sodium. FT-IR spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer (KBr). ^{1}H NMR spectra were recorded with a Bruker Avance 250 spectrometer, operating in the Fourier transform mode at 250.130 MHz (internal standard relative to CDCl$_3$, δ = 7.27). Chemical shifts are reported in δ units (ppm) downfield from SiMe$_4$ with the solvent as reference signal. Melting points were determined using analytically pure samples, sealed off in nitrogen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Organic Department, Chemnitz Technical University and the Institute of Organic Chemistry at the University of Heidelberg.
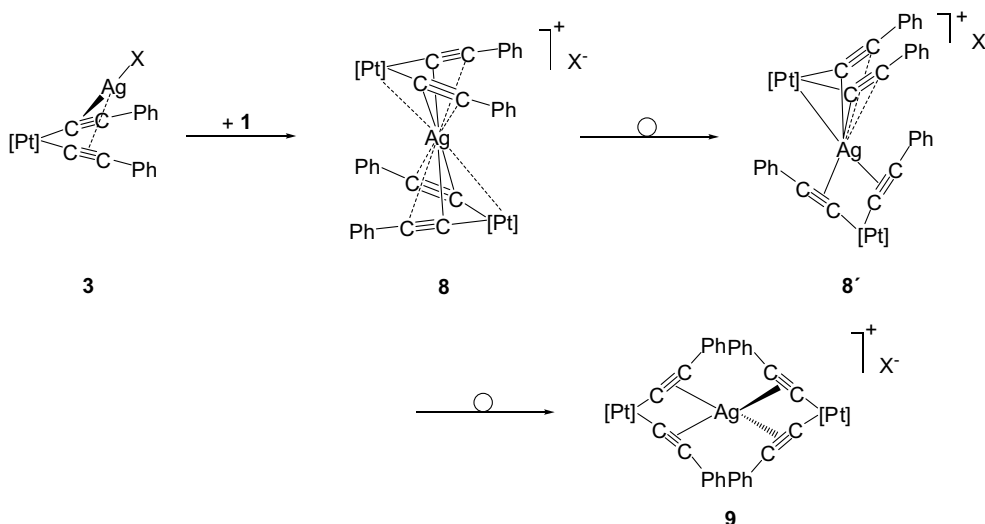

Fig. 3. Possible mechanism for the formation of **9** via in situ generated **8** and **8′**, respectively, by reacting **1** with **3**.

General remarks. cis-(bipy′)Pt(C≡CPh)$_2$ (**1a**), cis-(bipy)-Pt(C≡CPh)$_2$ (**1b**) and [cis-(bipy′)Pt(μ-σ,π-C≡CPh)$_2$]-AgFBF$_3$ (**3a**) were prepared by published procedures [1,4,5]. All other chemicals were purchased by commercial suppliers and were used as received.

4.1. Synthesis of 3b

To 100 mg (0.17 mmol) of cis-[Pt](C≡CPh)$_2$ (**1a**) dissolved in 35 mL of dichloromethane the silver(I) salt [AgPF$_6$] (**2b**) (43 mg, 0.17 mmol) was added at 25 °C. The reaction mixture was stirred for 12 h in the dark. Heterobimetallic **3b** precipitated as a yellow solid during the course of the reaction. The reaction mixture was filtered through a glass filter and the remaining solid was washed twice with 20 mL portions of dichloromethane and then with *n*-pentane. All volatiles were removed in oil-pump vacuum. Complex **3b** remained as a yellow solid. Yield: 110 mg (0.13 mmol, 76 % based on **1a**).

M.p. [°C]: 240 (decomp.). IR (KBr) [cm^{-1}]: $v_{C≡C}$ 2104, 2057; v_{P-F} 840. ^{1}H NMR (d^6-dmso)[1]: [δ] 7.2–7.3 (m, 6H, ^{m}H, ^{p}H/Ph), 7.4–7.5 (m, 4H, ^{o}H/Ph), 7.57 (d, $^3J_{H^5H^6}$ = 5.6 Hz, 2H, H^5/bipy′), 8.31 (s, 2H, H^3/bipy′), 8.95 (d, $^3J_{H^6H^5}$ = 5.6 Hz, 2H, H^6/bipy′). ^{31}P{^{1}H} NMR (dmso-d^6): [δ] −142.9 (h, $^1J_{PF}$ = 710 Hz). Anal. Calc. for C$_{28}$H$_{22}$AgF$_6$N$_2$PPt (834.44): C, 40.30; H, 2.66; N, 3.36. Found: C, 40.16; H, 3.14; N, 3.14%.

4.2. Synthesis of 3c

The title compound was synthesized according to the preparation of **3b**. To 200 mg (0.36 mmol) of **1b** dissolved in a mixture of 125 mL of dichloromethane and 25 mL of tetrahydrofuran, 75 mg (0.36 mmol) of [AgClO$_4$] (**2c**) were added in a single portion. After appropriate work-up, **3c** could be isolated as a yellow solid in 230 mg (0.303 mmol, 84% based on **1b**) yield.

M.p. [°C]: 234 (decomp.). IR (KBr) [cm^{-1}]: $v_{C≡C}$ 2060 (s), v_{Cl-O} 1090 (vs). ^{1}H NMR (d^6-dmso)[1]: [δ] 7.1–7.2 (m, 6H, ^{m}H, ^{p}H/Ph), 7.4–7.5 (m, 4H, ^{o}H/Ph), 7.76 (pt, $^3J_{H^5H^6}$ = 5.7 Hz, $^3J_{H^5H^4}$ = 7.5 Hz, 2H, H^5/bipy), 8.30 (pt, $^3J_{H^4H^3}$ = 8.1 Hz, $^3J_{H^4H^5}$ = 7.5 Hz 2 H, H^4/bipy), 8.47 (d, $^3J_{H^3H^4}$ = 8.1 Hz, 2H, H^3/bipy), 9.15 (d, $^3J_{H^6H^5}$ = 5.7 Hz, 2 H, H^6/bipy). Anal. Calc. for C$_{26}$H$_{18}$AgClN$_2$O$_4$Pt (760.77): C, 41.40; H, 2.38; N, 3.67. Found: C, 39.24; H, 2.44; N, 3.27%.

4.3. Synthesis of 3d

Complex **3d** was prepared in the same manner as described for the synthesis of **3b** (vide supra). In this respect, 100 mg (0.171 mmol) of **1a** were reacted with 73 mg (0.17 mmol) of [AgBPh$_4$] (**2d**) in 35 mL of dichloromethane

at 25 °C. After appropriate work-up, 140 mg (0.137 mmol, 80 % based on **1a**) of yellow **3d** could be isolated.

M.p. [°C]: 166 (decomp.). IR (KBr) [cm^{-1}]: $v_{C≡C}$ 2108 (s), 2087 (s). ^{1}H NMR (d^6-dmso)[1]: [δ] 6.81 (d, $^3J_{HH}$ = 7.2 Hz, 4H, BPh$_4$), 6.93 (t, $^3J_{HH}$ = 7.2 Hz, 8H, BPh$_4$), 7.1–7.3 (m, 14 H, Ph/BPh$_4$)), 7.4–7.5 (m, 4H, Ph), 7.57 (d, $^3J_{H^5H^6}$ = 5.5 Hz, 2H, H^5/bipy′), 8.30 (s, 2H, H^3/bipy′), 8.96 (d, $^3J_{H^6H^5}$ = 5.5 Hz, 2H, H^6/bipy′). Anal. Calc. for C$_{52}$H$_{42}$AgBN$_2$Pt (1008.72): C, 61.91; H, 4.21; N, 2.78. Found: C, 61.92; H, 4.12; N, 2.98%.

4.4. Synthesis of 8a

To 100 mg (0.180 mmol) of **1b** dissolved in dichloromethane (50 mL), 17 mg (0.090 mmol) of [AgBF$_4$] (**2a**) were added in one portion at 25 °C. After 12 h of stirring in the dark, all volatiles were removed in oil-pump vacuum to leave a yellow solid. Single crystals of **8a** could be obtained by cooling a concentrated dichloromethane/*n*-pentane solution containing **8a** to 0 °C. Yield: 115 mg (0.176 mmol, 98 % based on **1b**). It is advisable to store **8a** in the dark, otherwise decomposition on precipitation of elemental silver may occur.

M.p. [°C]: 146 (decomp.). IR (KBr) [cm^{-1}]: $v_{C≡C}$ 2116 (s), 2097 (s), 2079 (w); v_{B-F} 1060 (vs). ^{1}H NMR (d^6-dmso): [δ] 7.1–7.2 (m, 6H, ^{m}H, ^{p}H/Ph), 7.3–7.5 (m, 4H, ^{o}H/Ph), 7.82 (pt, $^3J_{H^5H^6}$ = 5.6 Hz, $^3J_{H^5H^4}$ = 7.2 Hz 2H, H^5/bipy), 8.36 (pt, $^3J_{H^4H^3}$ = 8.2 Hz, $^3J_{H^4H^5}$ = 7.2 Hz 2H, H^4/bipy), 8.56 (d, $^3J_{H^3H^4}$ = 8.2 Hz, 2H, H^3/bipy), 9.31 (d, $^3J_{H^6H^5}$ = 5.6 Hz, 2H, H^6/bipy). Anal. Calc. for C$_{52}$H$_{36}$AgBF$_4$N$_4$Pt$_2$ (1301.76): C, 47.98; H, 3.79; N, 4.30. Found: C, 47.59; H, 3.67; N, 3.95%.

4.5. Single X-ray structure analysis of 8a

The solid state structure of **8a** was determined from single crystal X-ray diffraction. Data collections were performed on a Bruker axs SMART 1 K area detector using Mo Kα radiation at 173(2) K. Crystallographic data of **8a** are given in Table 3. The structure was solved by direct methods (SHELXS 97) [20]. An empirical absorption correction was applied. The structure was refined by the least square method based on F^2 with all reflections [21]. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were placed in calculated positions. The molecule shown in Fig. 1 was plotted by using XShell.

4.6. Synthesis of 8b

In regard to the preparation of **8a**, complex **8b** was synthesized by treatment of 100 mg (0.17 mmol) of **1a** with [AgPF$_6$] (**2b**) (21 mg, 0.085 mmol) in dichloromethane (50 mL) at 25 °C in the dark. After appropriate work-up, **8b** could be isolated as a yellow solid in 95 mg yield (0.067 mmol, 76 % based on **1a**).

M.p. [°C]: 199 (decomp.). IR (KBr) [cm^{-1}]: $v_{C≡C}$ 2102 (s), 2095 (ss); v_{P-F} 837 (vs). ^{1}H NMR (d^6-dmso)[1]: [δ] 7.1–

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[1] The CH$_3$ resonance signal of the bipy′ ligand is overlapping with the respective d^6-dmso signal.

7.2 (m, 6H, mH, ^{p}H/Ph), 7.4–7.5 (m, 4H, ^{o}H/Ph), 7.58 (d, $^3J_{H^5H^6}$ = 5.5 Hz, 2H, H^5/bipy′), 8.40 (s, 2H, H^3/bipy′), 9.01 (d, $^3J_{H^6H^5}$ = 5.5 Hz, 2H, H^6/bipy′). ^{31}P{^{1}H} NMR (d^6-dmso): [δ] −142.94 (h, $^1J_{PF}$ = 710 Hz). Anal. Calc. for C$_{56}$H$_{44}$AgF$_6$N$_4$PPt$_2$ (1416.04): C, 47.50; H, 3.14; N, 3.96. Found: C, 47.03; H, 3.42; N, 4.07%.

4.7. Synthesis of 8c

In analogy to the synthesis of **8a**, 100 mg (0.180 mmol) of **1b** were reacted with 18 mg (0.090 mmol) of [AgClO$_4$] (**2c**) in dichloromethane (50 mL). After appropriate work-up, 70 mg (0.05 mmol, 60% based on **1b**) of **8c** could be isolated as a yellow solid.

M.p. [°C]: 225 (decomp.). IR (KBr) [cm^{-1}]: $v_{C\equiv C}$ 2112 (sh), 2076 (s); v_{Cl-O} 1090 (vs). ^{1}H NMR (d^6-dmso): [δ] 7.2–7.3 (m, 6H, ^{m}H, ^{p}H/Ph), 7.45 (d, $^3J_{HH}$ = 7.2 Hz, 4H, ^{o}H/Ph), 7.78 (pt, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 6.3 Hz, 2H, H^5/bipy), 8.40 (pt, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.9 Hz, 2H, H^4/bipy), 8.62 (d, $^3J_{H^3H^4}$ = 7.9 Hz, 2H, H^3/bipy), 9.41 (d, $^3J_{H^6H^5}$ = 6.4 Hz, 2 H, H6/bipy). Anal. Calc. for C$_{52}$H$_{36}$AgClN$_4$O$_4$Pt$_2$ (1314.40): C, 47.51; H, 2.77; N, 4.26. Found: C, 47.32; H, 2.59; N, 4.20%.

4.8. Synthesis of 9a

Similar to the preparation of **8a**, 100 mg (0.180 mmol) of **1b** were reacted with 17 mg (0.090 mmol) of [AgBF$_4$] (**2a**) in dichloromethane (50 mL). After 7 days of stirring in the dark and appropriate work-up (see Section 4.4), complex **9a** could be isolated as a yellow solid. Yield: 100 mg (0.077 mmol, 43 % based on **1b**). It is advisable to store **9a** in the dark, otherwise decomposition upon formation of elemental silver may take place.

M.p. [°C]: 236 (decomp.). IR (KBr) [cm^{-1}]: $v_{C\equiv C}$ 2087 (s), 2074 (s); v_{B-F} 1059 (vs). ^{1}H NMR (d^6-dmso): δ 7.1–7.2 (m, 6H, mH, ^{p}H/Ph), 7.3–7.4 (m, 4H, ^{o}H/ Ph), 7.70 (t, $^3J_{H^5H^6}$/$^3J_{H^5H^4}$ = 6.8 Hz, 2H, H^5/bipy), 8.32 (t, $^3J_{H^4H^3}$ = $^3J_{H^4H^5}$ = 7.9 Hz 2H, H^4/bipy), 8.49 (d, $^3J_{H^3H^4}$ = 8.2 Hz, 2H, H^3/bipy), 9.22 (d, $^3J_{H^6H^5}$ = 5.4 Hz, 2H, H^6/bipy). Anal. Calc. for C$_{52}$H$_{36}$N$_4$Pt$_2$AgBF$_4$ (1301.76): C, 47.98; H, 2.79; N, 4.30. Found: C, 48.06; H, 3.02; N, 4.44%.

4.9. Synthesis of 9b

Complex **9b** was prepared in accordance to **9a** by treatment of 42 mg (0.075 mmol) of **1a** with 9 mg (0.035 mmol) of [AgPF$_6$] (**2b**) in 50 mL of dichloromethane. After appropriate work-up, and crystallization at −30 °C from a saturated 1:1 dichloromethane/n-pentane mixture containing **9b**, 13 mg (0.009 mmol, 25 % based on **1a**) of **9b** could be isolated.

M.p. [°C]: 160 (decomp.). IR (KBr) [cm^{-1}]: $v_{C\equiv C}$ 2097 (sh), 2078 (s); v_{P-F} 837 (vs). ^{1}H NMR (d^6-dmso)[1]: [δ] 7.1–7.2 (m, 6H, ^{m}H, ^{p}H/Ph), 7.4–7.5 (m, 4H, ^{o}H/Ph), 7.82 (pt, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 6.3 Hz, 2H, H^5/bipy′), 8.36 (dt, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.4 Hz,

$^4J_{HH}$ = 1.2 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, H^4/bipy′), 8.55 (d, $^3J_{H^3H^4}$ = 8.03 Hz, 2H, H^3/bipy′), 9.28 (d, $^3J_{H^6H^5}$ = 5.6 Hz, 2H, H^6/bipy′). ^{31}P{^{1}H} NMR (d^6-dmso): [δ] −142.94 (h, $^1J_{PF}$ = 710 Hz). Anal. Calc. for C$_{52}$H$_{36}$AgF$_6$N$_4$PPt$_2$ (1359.92): C, 45.92; H, 2.67; N, 4.12 %. Found: C, 45.87; H, 2.49; N, 3.80.

4.10. Synthesis of 9c

In a similar manner to the preparation of **9a**, 100 mg (0.180 mmol) of **1b** were reacted with 18 mg (0.090 mmol) of [AgClO$_4$] (**2c**) in dichloromethane (50 mL). After appropriate work-up, 50 mg (0.038 mmol, 4 % based on **1b**) of **8c** could be isolated in form of a yellow solid.

M.p. [°C]: 199 (decomp.). IR (KBr) [cm^{-1}]: $v_{C\equiv C}$ 2111 (sh), 2075 (s); v_{Cl-O} 1090 (vs). ^{1}H NMR (d^6-dmso): [δ] 7.1–7.2 (m, 6H, ^{m}H, ^{p}H/Ph), 7.4–7.5 (m, 4H, ^{o}H/Ph), 7.75 (pt, $^3J_{HH}$ = 6.6 Hz, 2H, H^5/bipy), 8.30 (pt, $^3J_{H^4H^3}$ = 8.1 Hz, $^3J_{H^4H^5}$ = 7.8 Hz, 2H, H^4/bipy), 8.46 (d, $^3J_{H^3H^4}$ = 8.1 Hz, 2H, H^3/bipy), 9.18 (d, $^3J_{H^6H^5}$ = 5.4 Hz, 2H, H^6/bipy). Anal. Calc. for C$_{52}$H$_{36}$N$_4$Pt$_2$AgClO$_4$ (1314.40): C, 47.51; H, 2.77; N, 4.26. Found: C, 47.18; H, 2.61; N, 4.21%.

4.11. Synthesis of 9a–9c from 3a–3c

Complexes **3a**–**3c** (50 mg; **3a**, 0.064 mmol; **3b**, 0.060 mmol; **3c**, 0.066 mmol) were reacted with equimolar amounts of **1a** and **1b**, respectively, in dichloromethane at room temperature for 7 days. After appropriate work-up (see above, synthesis of **9a**–**9c** from **1** and **2**), the title complexes **9a**–**9c** were isolated in 67 % (55 mg, 0.043 mmol; **9a**), 73 % (62 mg, 0.044 mmol; **9b**) and 71 % (62 mg, 0.047 mmol; **9c**) yield, respectively.

5. Supplementary material

CCDC 626848 contains the supplementary crystallographic data for **8a**. 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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