2,2′-Bipyrimidine transition metal complexes: Synthesis, reaction chemistry and solid state structures

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ABSTRACT

2,2′-Bipyrimidine metal complexes with Ti, Mo, Fe, Ru, Pt, Ag, and Cu transition metal atoms have been synthesized and structurally characterized. These molecules were prepared by following synthesis methodologies. The reaction of 2,2′-bipyrimidine (**1**; bipym) with $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}AgOTf$ ([Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$, OTf = OSO_2CF_3) (**2**) in a 1:1 molar ratio gave $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}Ag(bipym)]OTf$ (**3**) which on further treatment with another equivalent of **2** produced $[(\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}Ag)_2(\mu\text{-}1,2,3,4\text{-}bipym)](OTf)_2$ (**4**). As consequence thereof, the coordination number of Ag(I) was changed from 3 to 4. A platinum–bipym complex with two acetylide substituents was accessible by the gradual reaction of **1** with $K_2[PtCl_4]$ (**5**) and two equivalents of $HC\equiv CR$ (**7a**, R = $SiMe_3$; **7b**, R = Fc; **7c**, R = Rc; Fc = $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe$; Rc = $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Ru$) in di-*iso*-propylamine and in presence of [CuI]. Originating from *cis*-$[(bipym)Pt(C\equiv CR)_2]$ (**8a**, R = $SiMe_3$; **8b**, R = Fc; **8c**, R = Rc) diverse multinuclear complexes with two, three or four different transition metals could be obtained. These are: $[((CO)_4Mo)(\mu\text{-}1,2,3,4\text{-}bipym)Pt(C\equiv CFc)_2]$ (**10**), $[(AgClO_4)(\mu\text{-}1,2,3,4\text{-}bipym)\{[Pt(\mu\text{-}\sigma,\pi\text{-}C\equiv CFc)_2]AgOClO_3\}]$ (**12**), $[(McC\equiv C)_2Pt(\mu\text{-}1,2,3,4\text{-}bipym)(\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}M)]X$ (**15a**, Mc = Fc, M = Cu, X = PF_6; **15b**, Mc = Rc, M = Cu, X = PF_6; **15c**, Mc = Fc, M = Ag, X = ClO_4), and $[(McC\equiv C)_2Pt(\mu\text{-}1,2,3,4\text{-}bipym)PtCl_2]$ (**17**). Like other organometallic Pt–Ag tweezer complexes, compound **12** decomposed to give $FcC\equiv C\text{-}C\equiv CFc$ (**13**). During prolonged stirring of **15a** and **15b**, respectively, $[(McC\equiv C)_2Pt(\mu\text{-}1,2,3,4\text{-}bipym)(\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)(\mu\text{-}\sigma,\pi\text{-}C\equiv CH)\}M)]X$ (**15′a**, M = Cu, X = PF_6; **15′b**, M = Cu, X = PF_6) was formed.

The structures of **8b**, **8c**, **15a′**, and **15b′** in the solid state are reported. All complexes exhibit the anticipated planar dinuclear Pt–M structure (M = Pt, Cu, Ag) with the 2,2′-bipyrimidine unit in a μ-1,2,3,4-bridging mode.

Electrochemical investigations were carried out with **8a**, **8b**, and **8c** and show that no significant influence of R on the bipym redox potentials exists. The typical redox behavior for the bipym, ferrocene, ruthenocene units and platinum were observed.

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1. Introduction

Recently, the synthesis, solid state structure and the photophysical properties of mono- and dinuclear (d–f) transition metal complexes based on the 2,2′-bipyrimidine (bipym) ligand have received increasing attention because bipym can act as a doubly bidentate bridging unit for the preparation of homobimetallic (e.g., $[OsCl(\eta^6\text{-}C_6H_4\text{-}1\text{-}^iC_3H_7\text{-}4\text{-}CH_3)]$, $[Cu(AsPh_3)_2]^+$, $[Cu(PPh_3)_2]^+$, $[Cu(\mu\text{-}Ph_2P(CH_2)_mPPh_2)]^+$ (m = 6, 8), $[Mo(CO)_4]$, $[Mo(CO)_2(P^nBu_3)_2]$, $[Re(CO)_3Cl]$, $[Re(CO)_4]$,…) [1] or heterobimetallic compounds $([Ru(bipy)_2]^{2+}$, $[Cu(PPh_3)_2]^+$; $[Ru(bipy)_2]^{2+}$, $[Mo(CO)_4]$;…) [2]. Bipym shows a delocalized π-bonding combining the chelating properties of molecules such as 2,2′-bipyridine and 1,4-diazines,

respectively [3]. For the synthesis of platinum-containing bipym complexes the kinetically inert d-block species *cis*-$[(bipym)ML_n]$ (ML_n = $PtCl_2$, $Pt(C\equiv C\text{-}1\text{-}C_6H_4\text{-}4\text{-}R)_2$; R = H, CH_3, CF_3) were used as starting materials [2g]. These molecules possess a peripheral vacant *N,N′*-bidentate binding site and on their reaction with a further transition metal complex fragment such as lanthanide tris(β-diketonate) dihydrate $[Ln(dik)_3(H_2O)_2]$ (Ln = Yb, Nd, Er, Gd; dik = $^tBuC(O)CH_2C(O)^nC_3F_7$,…) gave by complexation of the free *N,N′*-coordination site to $Ln(dik)_3$ the heterobimetallic d–f molecules of type $[L_nM(\mu\text{-}1,2,3,4\text{-}bipym)Ln(dik)_3]$ [2g]. The syntheses are facile and high-yielding. In these complexes a $Ln(dik)_3$ unit is attached to the secondary 2,2′-bipyrimidine unit to evaluate the ability of d-block chromophores to act as antennae for causing sensitized near-infrared luminescence from adjacent Ln(III) ions [2g].

cis-$[(bipym)PtCl_2]$ [4] possesses both a vacant *N,N′*-bidentate coordination site and a platinum-chloride functionality and hence, it should act as precursor for the synthesis of complexes of higher

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nuclearity. However, to the best of our knowledge, no further reactions with this mononuclear species to platinum bis(acetylides), except *cis*-[(bipym)Pt(C≡C-1-C_6H_4-4-R)$_2$] (R = H, CH_3, CF_3) and their respective Ln(dik)$_3$ complexes [2g], were carried out. This prompted us to study in more detail the reaction chemistry of *cis*-[(bipym)PtCl$_2$] toward diverse transition metal fragments.

We report here on the development of straightforward synthesis methodologies to prepare heteromultimetallic di(alkynyl)Pt–M (M = Fe, Ru), Pt–Fe–M′ (M′ = Mo, Cu, Ag), Ti$_2$Ag$_2$ and Pt–M–M′–Ti (M = Fe, Ru; M′ = Cu, Ag) complexes.

2. Results and discussion

Our studies focused on demonstrating the feasibility of the use of 2,2′-bipyrimidine (bipym) (**1**) as (doubly) chelating ligand for the synthesis of higher nuclear bipym transition metal complexes. In the beginning of our work we selected as transition metal building block the heterobimetallic Ti–Ag organometallic π-tweezer molecule {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}AgOTf ([Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti, OTf = OSO$_2$CF$_3$) (**2**) as starting material because we have experience in using such compounds for the preparation of multiheterometallic systems in which different metal atoms are bridged by carbon-rich organic and/or inorganic connecting moieties [5,6].

When **1** was reacted with stoichiometric amounts of **2** in tetrahydrofuran at room temperature for 3 hours then [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Ag(bipym)]OTf (**3**) could be isolated as an orange solid in 98% yield (Scheme 1) (Section 4). Further treatment of **3** with another equivalent of **2** or reacting **1** with **2** in a 1:2 molar ratio gave tetrametallic [({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Ag)$_2$(μ-1,2,3,4-bipym)](OTf)$_2$ (**4**) as a dark orange solid. In **4** two heterobimetallic Ti–Ag tweezer units are bridged by a planar bipym connectivity. In **3** and **4** the coordination number at silver(I) is four and hence, silver(I) possesses a pseudo-tetrahedral coordination sphere. This differs from **2**, where Ag(I) have coordination number 3 and is within the {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}AgOTf building block in a planar surrounding [7].
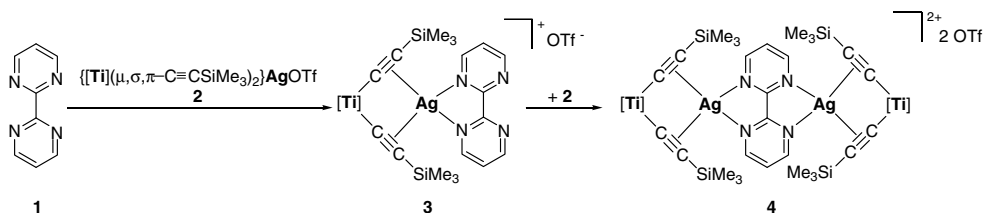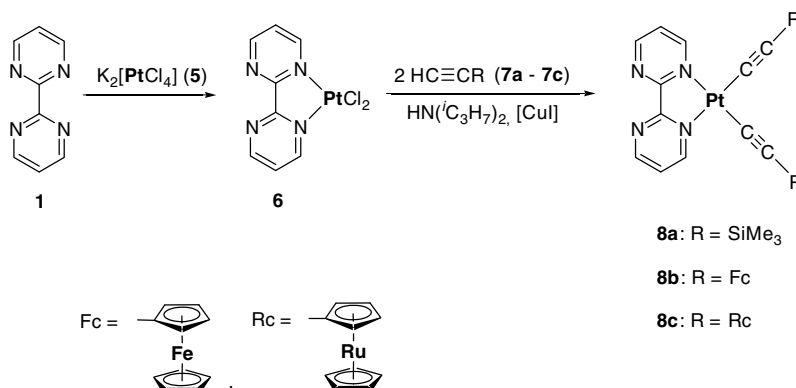
Complexes **3** and **4** were characterized by elemental analysis and were assayed by NMR spectroscopy (^{1}H, ^{13}C{^{1}H}) (Section 4). The NMR spectra of **3** and **4** are in agreement with the formulation of compounds in which the bipym moiety acts as a terminal capping ligand (**3**) or as a μ-1,2,3,4-bridging unit (**4**) (Section 4).

A bis(alkynyl)platinum-containing bipym system, which can be used as starting material for the synthesis of molecules of higher nuclearity (vide infra), was synthesized as depicted in Scheme 2.

Gradual reaction of bipym (**1**) with K$_2$[PtCl$_4$] (**5**) gave *cis*-[(bipym)PtCl$_2$] (**6**) [8] which on further treatment with 2.5 equivalents of HC≡CR (**7a**, R = SiMe$_3$; **7b**, R = Fc; **7c**, R = Rc; Fc = (η^5-C$_5$H$_4$)(η^5-C$_5$H$_5$)Fe; Rc = (η^5-C$_5$H$_4$)(η^5-C$_5$H$_5$)Ru) in a di-*iso*-propylamine-dichloromethane mixture of ratio 1:3 in presence of catalytic amounts of [CuI] produced *cis*-[(bipym)Pt(C≡CR)$_2$] (**8a**, R = SiMe$_3$; **8b**, R = Fc; **8c**, R = Rc) (Scheme 2). After appropriate work-up, the bis(alkynyl)platinum complexes **8a**–**8c** could be isolated as yellow (**8a**) or red-brown (**8b**, **8c**) solids in yields between 35% and 96% (Section 4). Complexes **8a**–**8c**, which are stable to air and moisture, are soluble in dichloromethane and tetrahydrofuran, while in *n*-hexane and other unpolar organic solvents they are insoluble. These compounds with their kinetically inert *cis*-[(bipym)PtCl$_2$] building block possess a vacant diimine N,N′-binding site and hence, should react with other transition metal systems to produce multimetallic complexes in which at least two different metal complex fragments are separated by a bipym unit. Thus, we reacted **8b** and **8c** with different reagents such as [(CO)$_4$(nbd)Mo] (nbd = *nor*bornadiene) (**9**), [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M]X (**14a**, M = Cu(N≡CMe), X = PF$_6$; **14b**, M = Ag, X = OClO$_3$) and [(PhC≡N)$_2$PtCl$_2$] (**16**) in a 1:1 molar ratio and with [AgClO$_4$] (**11**) in a 1:2 stoichiometry, in tetrahydrofuran or dichloromethane as solvent (Scheme 3) (Section 4).

Treatment of **8b** with [(CO)$_4$(nbd)Mo] (**9**) in tetrahydrofuran produced on elimination of nbd, dark green [((CO)$_4$Mo)(μ-1,2,3,4-bipym)(Pt(C≡CFc)$_2$)] (**10**) (Scheme 3, reaction (i)). In heterotrimetallic **10** a octahedral coordinated molybdenum atom is connected with a square-planar surrounded platinum(II) ion by the μ-1,2,3,4-bipym unit.

Scheme 1. Synthesis of **3** and **4** from **1** and **2**, respectively.

Scheme 2. Synthesis of **8a**–**8c** from **1**, **5** and **7a**–**7c**.
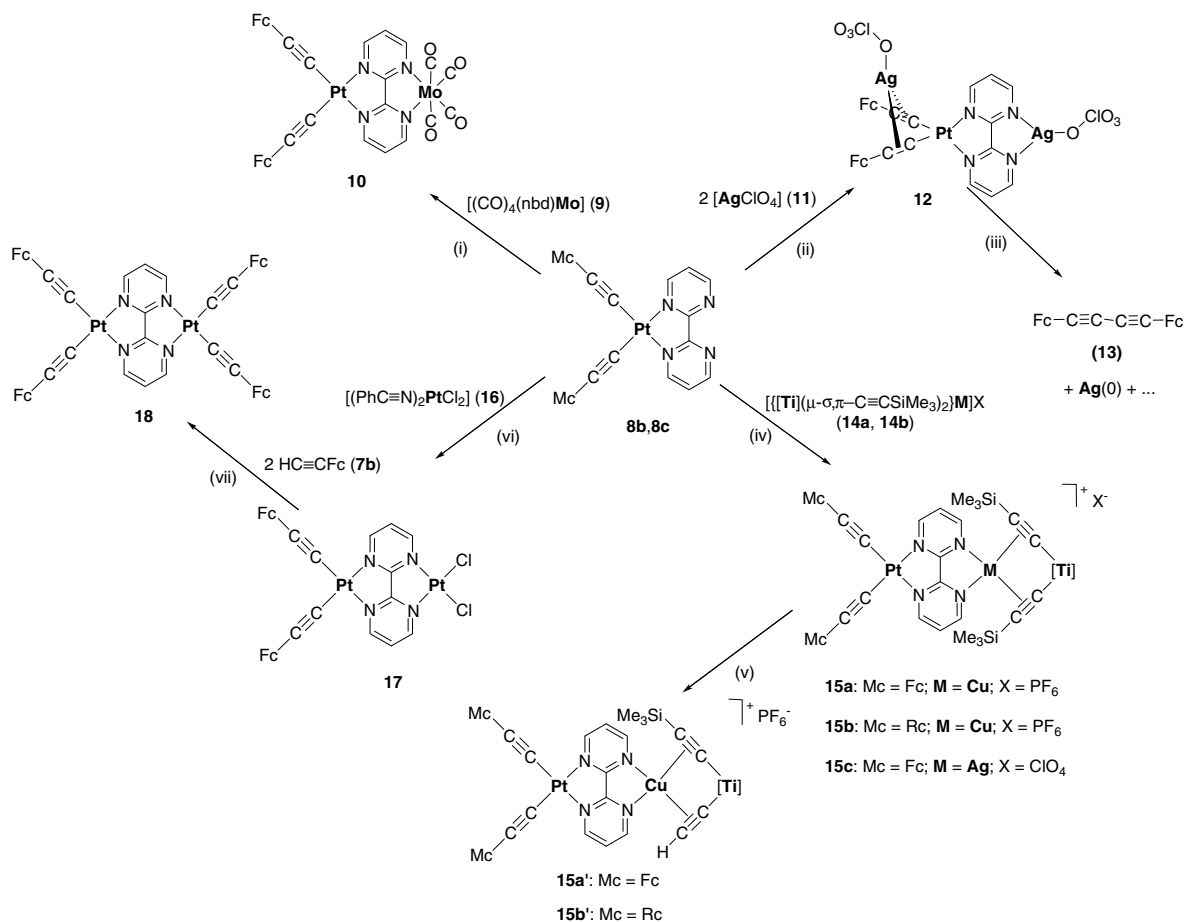
Scheme 3. Synthesis of multinuclear complexes **10**, **12**, **15a–15c**, **15a'**, **15b'**, **17** and **18** from **8b** and **8c**, respectively. (i) tetrahydrofuran, 16 h, 25 °C; (ii) tetrahydrofuran, 5 min, 25 °C; (iii) acetonitrile, 2 days, 25 °C; (iv) tetrahydrofuran, 2.5 h, 25 °C; (v) tetrahydrofuran, 2.5 h, 25 °C; (vi) tetrahydrofuran, 8 hours, 60 °C; (vii) tetrahydrofuran/HN^{i}Pr$_2$ (1:1, vs/vs), [CuI], 7 days.

A pentametallic PtFe$_2$Ag$_2$ transition metal compound is [(AgO-ClO$_3$)(μ-1,2,3,4-bipym)((Pt(μ-σ,π-C≡CFc)$_2$)AgOClO$_3$)] (**12**), which is accessible by the reaction of **8b** with [AgClO$_4$] (**11**) in a 1:2 molar ratio in tetrahydrofuran at ambient temperature (Scheme 3, reaction route (ii)). This reaction is accomplished by an precipitation of the organometallic π-tweezer complex **12** which exclusively dissolves in acetonitrile. Due to this, no further purification of the latter molecule was necessary. When an acetonitrile solution containing **12** was stirred over 14 days at room temperature a redox reaction occurred and the all-carbon 1,4-bis(ferrocenyl)but-adi-1,3-yne (**13**) along with elemental silver was formed (Scheme 3, reaction route (iii)). C$_4$-bridged **13** can be considered as coupling product of two ethynyl ferrocene moieties. This reaction behavior is typical for this type of molecules and was lately reported for similar compounds including free organometallic π-tweezers such as [(η^5-C$_5$H$_4$R)$_2$Ti(C≡CMc)$_2$] (Mc = Fc, Rc; R = H, SiMe$_3$) [9].

A possibility to prepare a complex in which four different metal atoms M–Pt–M'–Ti (M = Fe, Ru; M' = Cu, Ag) are present is given by reaction (iv) (Scheme 3). Complex [((McC≡C)$_2$Pt)(μ-1,2,3,4-bi-pym)({[Ti](μ-σ,π-C≡CSi Me$_3$)$_2$}M)]X (**15a**, Mc = Fc, M = Cu, X = PF$_6$; **15b**, Mc = Rc, M = Cu, X = PF$_6$; **15c**, Mc = Fc, M = Ag, X = ClO$_4$) was available by the addition of [{[Ti](μ-σ,π-C≡CSi Me$_3$)$_2$}M]X (**14a**, M = Cu(N≡CMe), X = PF$_6$; **14b**, M = Ag, X = ClO$_4$) to **8b** or **8c** in tetrahydrofuran. Heterotetrametallic **15a–15c** were formed in high yield (Section 4). After appropriate work-up, these compounds could be isolated as red-brown to dark brown solids which are stable toward air and moisture. However, tetrahydrofuran solutions containing **15a** or **15b** produced upon prolonged

stirring at room temperature unsymmetrical tetrametallic [(((McC≡C)$_2$Pt)(μ-1,2,3,4-bipym)({[Ti](μ-σ,π-C≡CSiMe$_3$)(μ-σ,π-C≡CH)}M)]X (**15a'**, Mc = Fc, M = Cu, X = PF$_6$; **15b'**, Mc = Rc, M = Cu, X = PF$_6$) (Scheme 3) in which one of the two Me$_3$SiC≡C ligands in **15a** and **15b** is replaced by a HC≡C unit. The exchange of both alkynyl-bonded Me$_3$Si units was, however, never observed. This result is astonishing because molecules such as [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M(LL)]$^+$ (LL = bipy, phen,…) and **15c** in which a perchlorate counter-ion is present are stable under identical reaction conditions. Most probably the PF$_6^-$ ion in combination with electronic effects resulting from the *cis*-[(bipym)Pt(McC≡C)$_2$] unit is involved in Si–C activation and hence, results in the cleavage of this bond, which shows a similar influence as the [^{n}Bu$_4$N]F reagent.

Although treatment of **8b** with [(PhC≡N)$_2$PtCl$_2$] (**16**) gave very dark brown [(((McC≡C)$_2$Pt)(μ-1,2,3-bipym)(PtCl$_2$)] (**17**), alkylation with **7b** resulted in the formation of tetranuclear [(((McC≡C)$_2$Pt)(μ-1,2,3,4-bipym)(Pt(C≡CMc)$_2$)] (**18**). However, this molecule could not be separated in pure form from the appropriate mono-substituted system, the respective starting materials and [H$_2$N^{i}Pr$_2$]Cl either by column chromatography nor by crystallization.

Elemental analysis, IR and ^{1}H NMR spectroscopy as well as ESI-TOF mass spectrometry support the structural formulation of **8a–8c**, **10**, **12**, **13**, **15**, and **17** as bipym-terminated or bipym-bridged heterometallic transition metal complexes (vide supra, Section 4).

Structural information concerning the presence of bis(alky-nyl)platinum and bis(alkynyl)titanocene moieties was obtained from IR spectroscopic investigations (Section 4). Most informative

are the respective vibrations typical for the C≡C, CO and PF_6^-, ClO_4^-, and OTf^- units. For the free FcC≡CPt building block in **8b** absorption bands are found at 2115 and 2122 cm^{-1}, while η^2-coordination leads, as expected, to a shift to lower wavenumbers (**12**: 2061, 2103 cm^{-1}). The η^2-coordinated Me$_3$SiC≡CTi units in **15a**–**15c** are observed between 1924 and 1959 cm^{-1}. The carbonyl ligands in **10** give rise to a very characteristic vibration pattern at 2022 (s), 1919 (vs), 1881 (vs) and 1831 (vs) cm^{-1} which is representative for [(CO)$_4$M] groups (M = Cr, Mo, W) with C$_{2v}$ symmetry [10] containing a *cis*-coordinated chelating ligand [11].

Also the NMR spectroscopic properties of **8a**–**8c**, **10**, **12**, **13**, **15**, and **17** correlate with their formulations as mono-, di-, tri- or tetrametallic complexes. The Mc (Mc = Fc, Rc) cyclopentadienyl protons in all compounds show a AA′XX′ pattern for the C$_5$H$_4$ ligand with centers lying at 4.15 and 4.51 ppm (C$_5$H$_4$/Fc), 4.49 and 4.87 ppm (C$_5$H$_4$/Rc) and a singlet for the C$_5$H$_5$ annulenes at 4.24 ppm (C$_5$H$_5$/Fc) or 4.60 ppm (C$_5$H$_5$/Rc). In contrast, the appropriate C$_5$H$_4$ protons of the titanocene moieties in **15a**–**15c** are observed as broad signals at 6.5 ppm, deepfield-shifted, when compared with Mc. The bipym ligands give rise to three signals found between 7.7 and 10.0 ppm with the characteristic coupling pattern [2g]. In addition, representative Pt–H couplings with J_{PtH} = 28 Hz are observed for H^6 in **8a**–**8c**.

The molecular structures of **8b** (Fig. 1), **8c** (Fig. 2), **15a**′ and **15b**′ (Fig. 3) in the solid state were confirmed using single crystal X-ray crystallography. Table 1 lists selected geometric parameters for **8b** and **8c**, while Table 2 contains the appropriate bond lengths (Å) and angles (°) of **15a**′ and **15b**′. Selected crystal data, and refinement parameters are summarized in Table 3 (Section 4).

The structures of **8b** and **8c** in the solid state show that these molecules are similar with a square-planar geometry around Pt1. The alkynyl ligands RC≡C (R = Fc, Rc) are σ-bonded and the bipym building block is chelate-coordinated to the group-10 metal atom. Apparent differences between **8b** and **8c** are the positions of the metallocene units as shown in Figs. 1 and 2. In **8b** the two ferrocene entities are out of the best bipym-Pt–C$_4$ plane bonded (18.0(2)° for ferrocene with Fe1 and 80.6(1)° with Fe2), while the ruthenocene fragments in **8c** are almost in-plane oriented
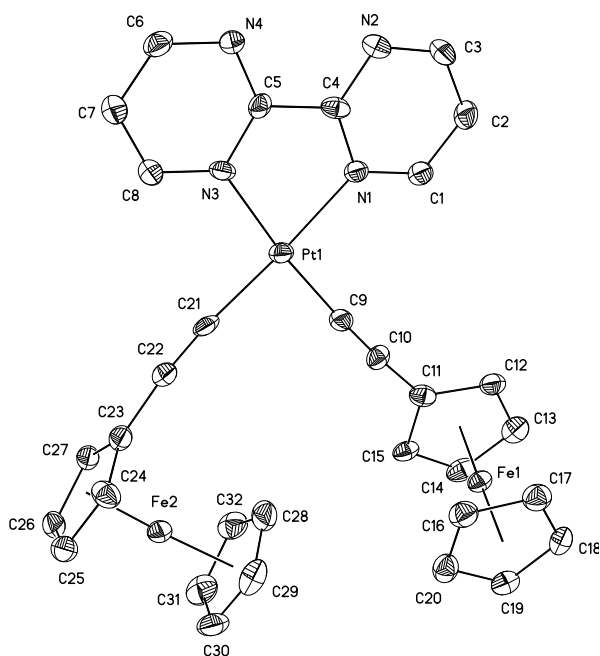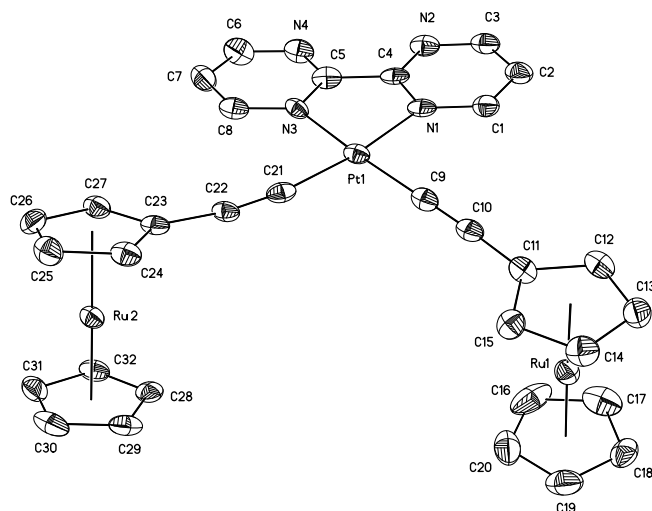

Fig. 2. ORTEP diagram (50% probability level) and atom labeling scheme of **8c**. The three solvent molecules dichloromethane are omitted for clarity.

(2.5(2)° for ruthenocene with Ru1 and 17.2(1)° with Ru2). No significant differences were observed in the bond distances and the bond angles between **8b** and **8c** (Table 1). For **8b** and **8c** the metallocene units show a nearly ecliptic conformation (2.6(4), 6.9(5)° **8b**; 2.6(1), 10.57(4)° **8c**). In both cases the cyclopentadienyl rings are nearly parallel oriented as expressed by their inter-planar angles of the calculated mean planes (**8b**: 2.2(4), 2.9(4)° and **8c**: 1.4(4), 0.9(1)°).

Although the solid state structures of heterotetrametallic **15a**′ and **15b**′ are very similar, both complexes are not iso-structural. They crystallize in the monoclinic or triclinic space group $P2_1/a$ (**15a**′) or $P\bar{1}$ (**15b**′). In both complexes the bipym moiety acts as a bis-chelating bridging connectivity between the two heterobimetallic building blocks [{[Ti](μ-σ,π-C≡CSiMe$_3$)(μ-σ,π-C≡CH)}Cu]$^+$ and Pt(C≡CFc)$_2$ (Fig. 3). The two metal atoms Pt1 and Cu1 are with 5.643 Å (**15a**′) as well as 5.719 Å (**15b**′) well separated (Table 2). The inter-ring distances are 1.462(9) (**15a**′) and 1.498(9) Å (**15b**′) (Table 2) and are similar as those ones found in other bipym coordination complexes [1h,12]. Worthy of mention is the somewhat shorter inter-ring separation found in both structures which can be explained either by some back-donation from the two metal-containing fragments or the formation of a dimer set-up by intermolecular Pt–Pt and π–π interactions as depicted in Fig. 4.

In the dimeric structures of **15a**′ and **15b**′ π–π contacts exist between the Pt(C≡CFc)$_2$ alkynyl fragments and individual aromatic rings of the bipym bridging moiety. Due to steric reasons the two bulky terminal organometallic π-tweezer groups are thereby facing each other, a bonding situation which is justified by the geometrical compatible planarity of the Cu(bipym)(Pt(C≡CC$_{Fc}$)$_2$) units and the non-stackable organometallic π-tweezer part because this fragments are perpendicular oriented to the Cu(bipym)(Pt(C≡CC$_{Fc}$)$_2$) plane (r.m.s. deviation of fitted atoms 0.0265 (**15a**′) and 0.0489 (**15b**′) Å). The latter structural motif is substantiated to the pseudo-tetrahedral coordination sphere at copper(I) allowing the π-tweezer fragment only being vertical positioned to the planar bipym connecting building block. The planarity of the Cu(bipym)(Pt(C≡CC$_{Fc}$)$_2$) arrangement is based on the d^8-electron configuration inducing a square-planar coordination at Pt(II).

The copper-nitrogen bond distances are 2.087(5) and 2.216(5) Å in **15a**′ and 2.047(5) and 2.385(5) Å in **15b**′ showing a somewhat unsymmetrical binding of the bipym ligand to Cu1 explainable by the packing effect of the dimer and in addition to the position of the PF_6^- anion. All other bond distances and bond angles are in

Fig. 1. ORTEP diagram (50% probability level) and atom labeling scheme of **8b**. The two solvent molecules dichloromethane are omitted for clarity.
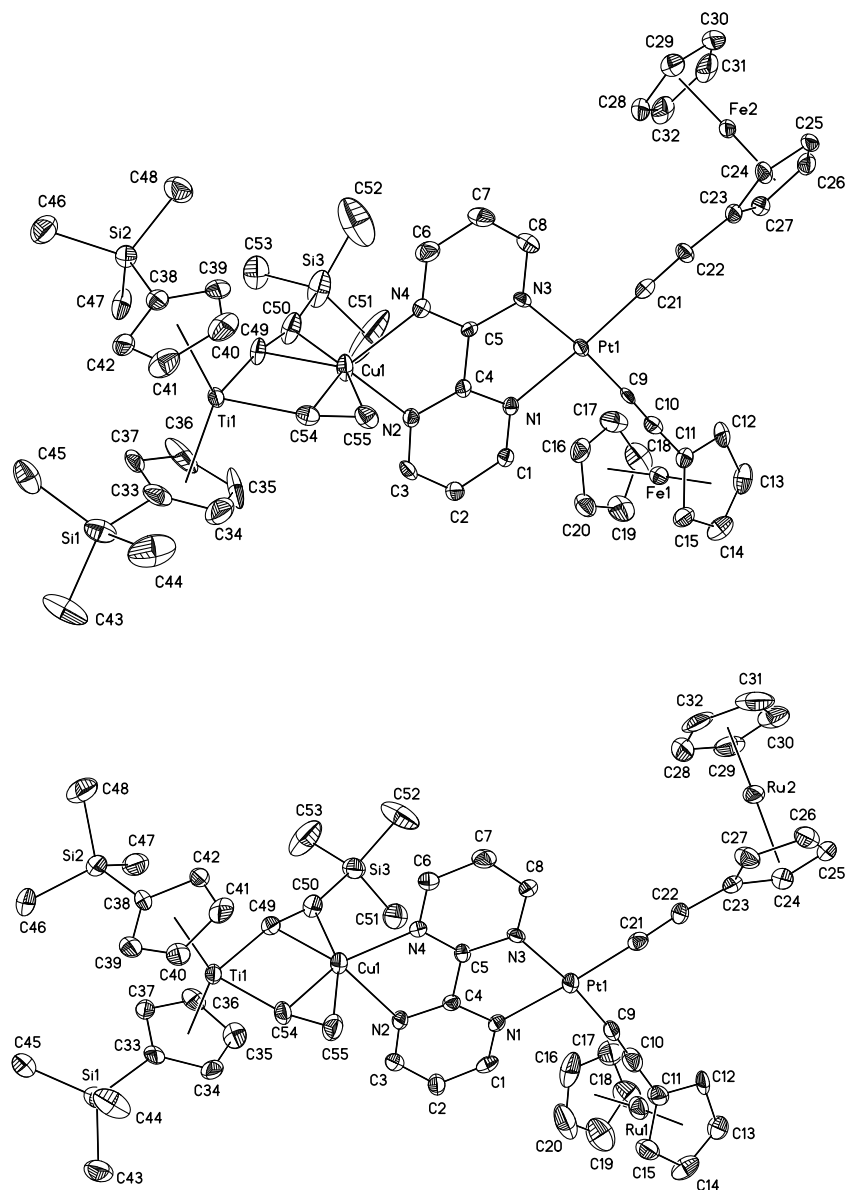
Fig. 3. Molecular structure and atom labeling scheme of **15a'** (top) and **15b'** (bottom) with thermal ellipsoids at 50% probability level. The five solvent molecules trichloromethane and the PF_6^- ion in **15a'** as well as the two solvent molecules tetrahydrofuran and the PF_6^- ion in **15b'** are omitted for clarity.

agreement with similar organometallic or metal-organic building block systems [5,13].

Solely the cyclic voltammograms of **8a–8c** were measured in tetrahydrofuran as solvent because all other complexes are very badly soluble in common organic solvents. The potentials of these molecules and bipym for comparison are summarized in Table 3.

The reductions found for **8a–8c** (Table 3 and Fig. 5) show for the bipym connecting unit two reversible one-electron processes [1a,1b,1d,1f,2a,2b] which are observed at more positive potentials than those of the corresponding free ligand but particularly more negative than the values of bipym-homobimetallic complexes containing $PtMe_2$ or $PtMes_2$ fragments (Mes = C_6H_2-2,4,6-Me_3) [1f]. This result shows that **8a–8c** are more difficult to reduce than [$(Me_2Pt)_2(\mu$-1,2,3,4-bipym)] and [$(Mes_2Pt)_2(\mu$-1,2,3,4-bipym)]. Furthermore, it can be concluded that bimetallic-bipym complexes [1,2] are considerably easier to reduce than mononuclear molecules, which can be explained by the fact that two electron-withdrawing Lewis-acids are bonded to one bipym unit. In the anodic region complexes **8b–8c** show a irreversible oxidation for **8a** at

+0.67 V which can be assigned to platinum (Fig. 5) [1f,15]. For **8b** and **8c** two oxidations are observed (Fig. 5). The cyclic voltammetric response of **8b** in the anodic region demonstrates one reversible wave for the [Fe(II)/Fe(III)] redox couple (E_0 = 0.11 V, ΔE = 0.12 V) of the Fc units and one irreversible potential at E_{pa} = 0.42 V for the platinum(II) oxidation. Obviously there is no detectable communication between the HOMOs of the metal centers through the organic π-system. This differs, however, from cis-[$L_2Pt(C\equiv CFc)_2$] (L_2 = 3,8-di-n-pentyl-4,7-di(phenylethynyl)-1, 10-phenanthroline, 2 Ph_3P), where two cyclovoltammetrically reversible one-electron processes for the Mc units were found [16]. Complex **8c** shows, as expected and most typical for ruthenocene sandwich structures, one irreversible oxidation at E_{pa} = 0.29 V. Additionally, a second oxidation is found at E_{pa} = 0.36 V, which can be assigned to the platinum oxidation (vide supra) [1f]. For the platinum oxidations of **8b–8c** it is apparent that the Fc and Rc units facilitate this oxidation, when compared with the trimethylsilyl substituted derivative **8a**. Square wave voltammetric experiments displayed no significant separation of the oxi-

Table 1
Selected bond distances (Å) and bond angles (°) for **8a** and **8c**[a]

	8b	8c
Bond distances		
Pt1–N1	2.064(5)	2.066(5)
Pt1–N3	2.061(5)	2.060(5)
Pt1–C9	1.955(6)	1.964(6)
Pt1–C21	1.957(7)	1.945(6)
C9–C10	1.200(8)	1.196(8)
C21–C22	1.193(9)	1.212(8)
Bond angles		
D1–Mc1–D2[b,c]	1.643(3)	1.816(2)
D3–Mc2–D4[b,c]	1.636(2)	1.815(2)
N1–Pt1–N3	79.34(19)	79.03(18)
N1–Pt1–C9	95.5(2)	96.0(2)
N3–Pt1–C21	96.4(2)	92.4(2)
C9–Pt1–C21	88.8(3)	92.6(2)
N1–Pt1–C21	175.5(2)	171.4(2)
N3–Pt1–C9	174.8(2)	174.66(19)
Pt1–C9–C10	176.9(6)	176.3(5)
Pt1–C21–C22	174.1(5)	169.2(5)
C9–C10–C11	175.9(7)	176.1(6)
C21–C22–C23	173.6(7)	172.1(6)

[a] Standard uncertainties of the last significant digit(s) are shown in parenthesis.
[b] D1 = centroid of C16–C20, D2 = centroid of C11–C15, D3 = centroid of C28–C32, D4 = centroid of C23–C27.
[c] Mc = Fc in **8b**, Mc = Rc in **8c**.

dation potentials in **8c**, indicating that the oxidation of both metals is very similar which corresponds to related ruthenium and platinum complexes [17].

Due to the acceptor character of the organic ligands at platinum the appropriate oxidations are found at almost the same potentials as typical for bis(aryl)–bipym–platinum molecules, however, they appear somewhat positive shifted in comparison to the anodic peak potentials of alkyl-platinum(II) complexes [1f].

3. Conclusion

A straightforward synthesis methodology to prepare mono-, tri-, tetra-, and pentanuclear transition metal complexes with up to four different metal atoms is described. The appropriate metals are connected *via* carbon-rich organic groups including the 2,2'-bipyrimidine (bipym) connecting unit. Through the bipym connectivity planar molecules are formed with the Pt(II)-containing fragments [PtCl$_2$], [Pt(C≡CR)$_2$] (R = SiMe$_3$, Fc, Rc; Fc = (η^5-C$_5$H$_4$)(η^5-C$_5$H$_5$)Fe; Rc = (η^5-C$_5$H$_4$)(η^5-C$_5$H$_5$)Ru) and [Mo(CO)$_4$], respectively. In these compounds the bipym chelating moiety, the respective metal ions, the C≡C units, and/or chloride ligands are in-plane bound. However, in [({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Ag)$_2$(μ-1,2,3,4-bipym)](OTf)$_2$, [((McC≡C)$_2$Pt)(μ-1,2,3,4-bipym)({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M)]X and [((McC≡C)$_2$Pt)(μ-1,2,3,4-bipym)({[Ti](μ-σ,π-C≡CSiMe$_3$)(μ-σ,π-C≡CH)}M)]X (M = Cu, Ag) the organometallic π-tweezer molecules {[Ti](C≡CSiMe$_3$)$_2$} are perpendicular oriented to the bipym or M(μ-1,2,3,4-bipym)Pt (C≡CC$_{Mc}$)$_2$ moieties. From cyclic voltammetric studies it can be concluded that organometallic **8a**–**8c** are in general easier to reduce than a *non*-coordinated free bipym molecule, explainable by the fact that a electron-withdrawing Lewis-acid is bonded to the bipym unit.

4. Experimental

4.1. General data

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, petroleum ether and *n*-hexane were purified by distillation from sodium/ben-

Table 2
Selected bond distances (Å) and bond angles (°) for **15a'** and **15b'**[a]

	15a'	15b'
Bond distances		
Pt1–N1	2.059(5)	2.081(5)
Pt1–N3	2.073(5)	2.085(5)
Pt1–C9	1.954(7)	1.967(7)
Pt1–C21	1.957(7)	1.952(7)
C9–C10	1.199(9)	1.203(10)
C21–C22	1.206(9)	1.215(9)
C49–C50	1.229(10)	1.243(9)
C54–C55	1.226(10)	1.231(10)
Cu1–N2	2.216(5)	2.385(5)
Cu1–N4	2.087(5)	2.047(5)
Cu1–C49	2.059(7)	2.083(7)
Cu1–C50	2.177(7)	2.144(7)
Cu1–C54	2.089(7)	2.093(7)
Cu1–C55	2.137(7)	2.136(8)
Ti1–C49	2.102(7)	2.106(7)
Ti1–C54	2.097(7)	2.091(7)
M1–D1[b,c]	1.640(4)	1.818(5)
M1–D2[b,c]	1.637(4)	1.813(4)
M2–D3[b,c]	1.638(4)	1.803(5)
M2–D4[b,c]	1.631(3)	1.807(4)
Ti1–D5[b]	2.044(4)	2.060(4)
Ti1–D6[b]	2.040(3)	2.053(4)
Bond angles		
D1–M1–D2[b,c]	178.5(2)	176.9(2)
D3–M2–D4[b,c]	178.34(18)	177.0(2)
N1–Pt1–N3	79.9(2)	79.8(2)
N1–Pt1–C9	94.7(2)	93.3(2)
N3–Pt1–C21	97.1(2)	95.3(2)
C9–Pt1–C21	88.2(2)	91.6(3)
N1–Pt1–C21	176.9(2)	175.0(2)
N3–Pt1–C9	174.5(2)	173.1(3)
Pt1–C9–C10	177.3(6)	174.8(6)
Pt1–C21–C22	177.5(6)	178.0(6)
C9–C10–C11	177.8(7)	176.0(9)
C21–C22–C23	176.0(7)	173.2(9)
Ti1–C49–C50	168.0(6)	164.9(6)
Ti1–C54–C55	164.1(6)	164.6(6)
C49–Ti1–C54	90.1(3)	90.2(3)
C49–Ti1–D5[b]	106.4(2)	103.2(2)
C49–Ti1–D6[b]	104.3(2)	105.8(2)
C54–Ti1–D5[b]	105.2(2)	104.4(3)
C54–Ti1–D6[b]	105.2(2)	105.3(3)

[a] Standard uncertainties of the last significant digit(s) are shown in parenthesis.
[b] D1 = centroid of C16–C20, D2 = centroid of C11–C15, D3 = centroid of C28–C32, D4 = centroid of C23–C27, D5 = centroid of C33–C37, D6 = centroid of C38–C42.
[c] M = Fe in **15a'**, M = Ru in **15b'**.

zophenone ketyl; dichloromethane was purified by distillation from calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations.

4.2. Instruments

Infrared spectra were recorded with a Thermo Electron Corporation FT-IR spectrometer Nicolet IR 200. ^{1}H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; ^{13}C{^{1}H} NMR spectra were recorded at 62.860 MHz; ^{31}P{^{1}H} NMR spectra were recorded at 101.249 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^{1}H NMR: CDCl$_3$ (99.8%), δ = 7.26; (CD$_3$)$_2$CO (99.9%), δ = 2.05; CD$_3$CN (99.8%), δ = 1.94. ^{13}C{^{1}H} NMR: CDCl$_3$ (99.8%), δ = 77.16; (CD$_3$)$_2$CO (99.9%), δ = 29.84, 206.26. ^{31}P{^{1}H} NMR: rel. H$_3$PO$_4$ (85%), δ = 0.0; rel. P(OMe)$_3$, δ = 139.0; external). The abbreviation pt in the ^{1}H NMR spectra corresponds to pseudo-triplet. ESI-TOF mass spectra were recorded using a Mariner biospectrometry workstation 4.0 (Applied Biosystems). Cyclic voltammograms were recorded in a dried cell purged with purified argon. Platinum

Table 3
Electrochemical data of **8a–8c**, and bipym for comparison[a]

Compound	1st reduction E_0/V (ΔE_p/V)	2nd reduction E_0/V (ΔE_p/V)	Oxidation	
			[M(II)/M(III)][b] E_0/V (ΔE_p/V)	[Pt(II)] E_{pa}/V (irr.)
Bipym	−2.31(0.08)[b]	−2.77 (irr.) [c,d]	–	–
8a	−1.47 (0.19)	−2.16 (0.26)	–	0.67
8b	−1.52 (0.10)	−2.20 (0.12)	0.11 (0.12)	0.42
8c	−1.47 (0.10)	−2.18 (0.10)	0.29 (irr.) [d]	0.36

[a] Cyclic voltammograms from 10^{-3} M solutions in tetrahydrofuran at 25 °C with [^{n}Bu$_4$N]PF$_6$ (0.1 M) as supporting electrolyte, scan rate = 0.10 V s^{-1}. All potentials are given in V and are referenced to the [FcH/FcH$^+$] redox couple (FcH = (η^5-C$_5$H$_5$)$_2$Fe) with E_0 = 0.00 V, ΔE_p = 0.15 V) [14].
[b] M = Fe in **8b**, M = Ru in **8c**.
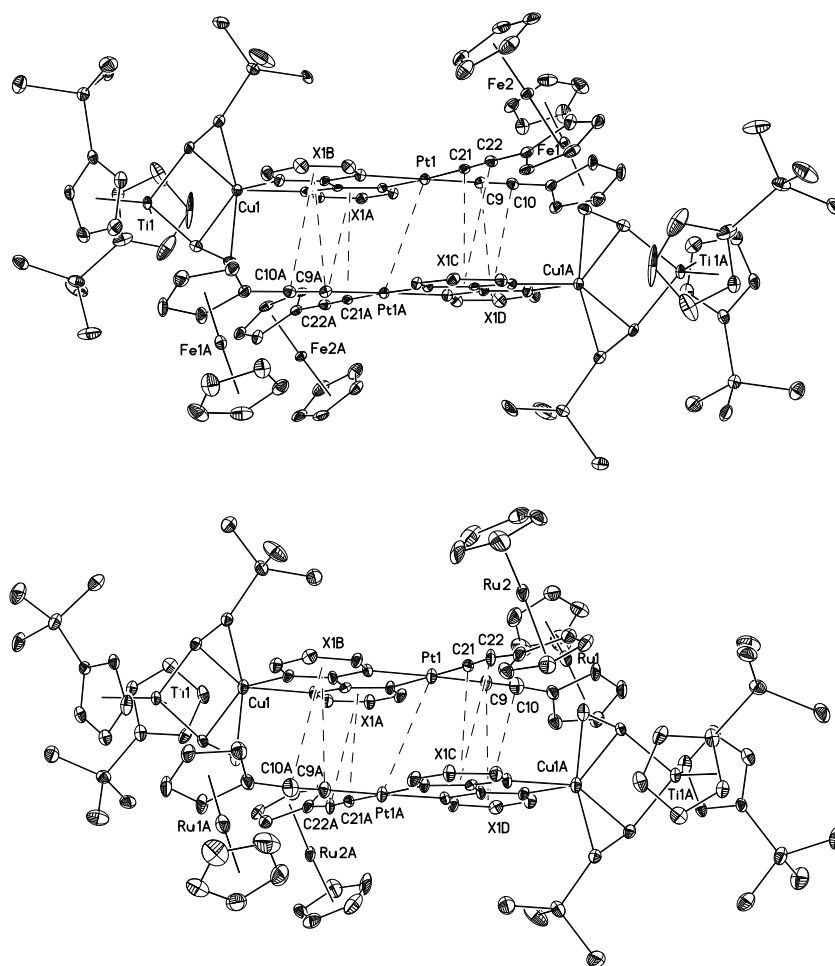[c] From Ref. [1f].
[d] E_{pa}.

Fig. 4. Dimeric structure of **15a′** (top) and **15b′** (bottom) with included Pt–Pt and π–π interactions.

wires served as working and as counter electrode. A saturated calomel electrode in a separated compartment served as reference electrode. For ease of comparison, all electrode potentials are converted using the redox potential of the ferrocene–ferrocinium couple [FcH/FcH$^+$] (FcH = (η^5-C$_5$H$_5$)$_2$Fe, E_0 = 0.00 V, ΔE = 0.15 V) [14] as reference. Electrolyte solutions were prepared from tetrahydrofuran and [^{n}Bu$_4$N]PF$_6$ (Fluka, dried in oil-pump vacuum). The respective organometallic complexes were added at c = 1.0 mM. Cyclic voltammograms were recorded on a Voltalab 3.1 potentiostat (Radiometer) equipped with a digital electrochemical analyzer DEA 101 and an electrochemical interface IMT 102. Microanalyses were performed by the Institute of Organic Chemistry, Chemnitz, University of Technology and by the Institute of Organic Chemistry, University of Heidelberg.

4.3. Reagents

2,2′-Bipyrimidine [18], ethynylferrocene [19], ethynylruthenocene [20], cis-[(bipym)PtCl$_2$] [4], [{[Ti](µ-σ,π-C≡CSiMe$_3$)$_2$}M]X (M = Ag, X = OTf; M = Ag, X = ClO$_4$; M = Cu(N≡CCH$_3$)PF$_6$) [21], [(nbd)(CO)$_4$Mo] [22], [(PhC≡N)$_2$PtCl$_2$] [23] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

4.3.1. Synthesis of [{[Ti](µ-σ,π-C≡CSiMe$_3$)$_2$}Ag(bipym)]OTf (**3**)

To a solution containing 300 mg (0.39 mmol) of {[Ti](µ-σ,π-C≡CSiMe$_3$)$_2$}AgOTf (**2**) in 50 mL of tetrahydrofuran, 60 mg (0.39 mmol) of 2,2′-bipyrimidine (**1**) were added. After 3 h of
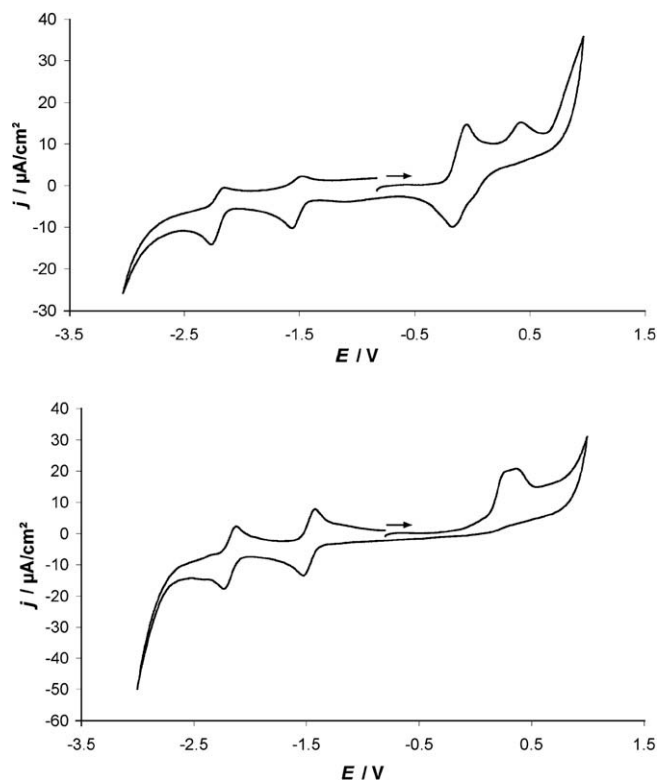
Fig. 5. Cyclic voltammograms of **8b** (top) and **8c** (bottom) in tetrahydrofuran at 25 °C, [$^nBu_4N$]PF_6 supporting electrolyte (0.1 M), scan rate = 0.10 V s^{-1}. All potentials are referenced to the [FcH/FcH$^+$] redox couple (FcH = (η^5-C_5H_5)$_2$Fe) with E_0 = 0.00 V, ΔE_p = 0.15 V) [14].

stirring at 25 °C the color of the reaction solution changed from red to orange and the product precipitated as an orange solid in analytical pure form. The precipitate was isolated by filtration. Yield: 360 mg (0.39 mmol, 98% based on **2**).

Anal. Calc. for $C_{35}H_{50}AgF_3N_4O_3SSi_4Ti$ (931.96): C, 45.10; H, 5.41. Found: C, 44.37; H, 5.41%. **IR** (KBr, cm^{-1}): 1948 (w, $\nu_{C\equiv C}$). **^{1}H NMR** (δ, (CD_3)$_2$CO): −0.21 (s, 18H, SiMe$_3$), 0.32 (s, 18H, SiMe$_3$), 6.70 (pt, J_{HH} = 2.3 Hz, 4H, C_5H_4), 6.84 (pt, J_{HH} = 2.3 Hz, 4H, C_5H_4), 7.82 (d, J_{HH} = 8 Hz, 2H, bipym), 8.09 (pt, J_{HH} = 5 Hz, 2H, bipym), 9.40 (d, J_{HH} = 5 Hz, 2H, bipym). **^{13}C{^{1}H} NMR** (δ, (CD_3)$_2$CO): 0.1 (C/SiMe$_3$), 119.0 (C_5H_4), 120.4 (C_5H_4), 125.0 (bipym), 128.0 (^iC/C_5H_4), 138.8 (d, $^1J_{CAg}$ = 5.5 Hz, C≡CSi), 153.6 (d, $^1J_{CAg}$ = 14.9 Hz, TiC≡C), 159.8 (^iC/bipym), 160.8 (bipym). **M.p.**: 150 °C (decomp.).

4.3.2. Synthesis of [({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Ag)$_2$(μ-1,2,3,4-bipym](OTf)$_2$ (**4**)

To a solution containing 250 mg (0.32 mmol) of **2** in 50 mL of tetrahydrofuran, 25 mg (0.16 mmol) of **1** were added in a single potion. After 3 h of stirring at 25 °C the color changed from red to orange and the title compound precipitated as an orange solid. Complex **4** was filtered and dried in oil-pump vacuum. Yield: 270 mg (0.16 mmol, 98% based on **2**).

Anal. Calc. for $C_{62}H_{96}Ag_2F_6N_4O_6S_2Si_8Ti_2$ (1705.71): C, 43.66; H, 5.56. Found: C, 43.61; H, 5.74%. **IR** (KBr, cm^{-1}): 1954 (w, $\nu_{C\equiv C}$). **^{1}H NMR** (δ, (CD_3)$_2$CO): 0.01 (s, 36H, SiMe$_3$), 0.28 (s, 36H, SiMe$_3$), 6.41 (pt, J_{HH} = 2.3 Hz, 8H, C_5H_4), 6.52 (pt, J_{HH} = 2.3 Hz, 4H, C_5H_4), 8.04 (pt, J_{HH} = 5 Hz, 2H, bipym), 9.24 (d, J_{HH} = 5 Hz, 4H, bipym). **^{13}C{^{1}H} NMR** (δ, (CD_3)$_2$CO): 0.2 (C/SiMe$_3$), 0.7 (C/SiMe$_3$) 119.4 (C_5H_4), 121.2 (C_5H_4), 126.4 (bipym), 128.4 (^iC/C_5H_4), 140.6 (C≡CSi), 152.6 (d, $^1J_{CAg}$ = 9.2 Hz, TiC≡C), 158.2 (^iC/bipym), 162.1 (bipym). **M.p.**: 195 °C (decomp.).

4.3.3. Synthesis of cis-[(bipym)Pt(C≡CSiMe$_3$)$_2$] (**8a**)

Two hundred milligram (0.47 mmol) of *cis*-[(bipym)PtCl$_2$] (**6**) and 115 mg (1.18 mmol) of trimethylsilylacetylene (**7a**) were dissolved in 50 mL of dichloromethane and 10 mL of diisopropyl amine and 1 mg of [CuI] were added. After 4 days of stirring at 25 °C, all volatiles were removed in oil-pump vacuum and dichloromethane (20 mL) was added. The suspension was filtered through a pad of alumina. After evaporation of the solvent, a yellow solid was obtained. Yield: 257 mg (0.45 mmol, 96% based on **6**).

Anal. Calc. for $C_{18}H_{24}N_4PtSi_2$ (547.66): C, 39.48; H, 4.42; N, 10.23. Found: C, 39.74; H, 4.55; N, 9.98%. **IR** (KBr, cm^{-1}): 2057 (s, $\nu_{C\equiv C}$), 2041 (s, $\nu_{C\equiv C}$). **^{1}H NMR** (δ, CDCl$_3$): 0.21 (s, 18H, SiMe$_3$), 7.76 (dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 4.7 Hz, 2H, H^5/bipym), 9.28 (dd, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 2.2 Hz, 2H, H^4/bipym), 9.99 (dd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 2.2 Hz, $^3J_{HPt}$ = 27.0 Hz, 2H, H^6/bipym). **^{13}C{^{1}H} NMR** (δ, CDCl$_3$):1.6 (C/SiMe$_3$), 102.9 (C≡C), 107.8 (C≡C), 124.5 (^iC/bipym), 156.1 (C^5/bipym), 157.8 (C^6/bipym), 158.8 (C^4/bipym). **M.p.**: 178 °C (decomp.).

4.3.4. Synthesis of cis-[(bipym)Pt(C≡CFc)$_2$] (**8b**)

Four hundred milligram (1.90 mmol) of ethynylferrocene (**7b**), 320 mg (0.76 mmol) of **6**, 10 mL of diisopropylamine and 1 mg of [CuI] in 50 mL dichloromethane were stirred for 4 days at 25 °C. Filtration of the reaction mixture through a pad of alumina with a dichloromethane/tetrahydrofuran mixture (1:1, vs/vs) and subsequent addition of 20 mL of petroleum ether gave the title complex in form of a red-brown precipitate. Yield: 409 mg (0.53 mmol, 70%).

Anal. Calc. for $C_{32}H_{24}Fe_2N_4Pt$ (771.31): C, 49.83; H, 3.14; N, 7.26. Found: C, 49.91; H, 3.45; N, 6.59%. **IR** (KBr, cm^{-1}): 2122 (w, $\nu_{C\equiv C}$), 2115 (w, $\nu_{C\equiv C}$). **^{1}H NMR** (δ, CDCl$_3$): 4.11 (pt, J_{HH} = 1.8 Hz, 4H, H$^\beta$/C_5H_4), 4.26 (s, 10H, C_5H_5), 4.48 (pt, J_{HH} = 1.8 Hz, 4H, H$^\alpha$/C_5H_4), 7.77 (dd, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 4.9 Hz, 2H, H^5/bipym), 9.29 (dd, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 2.2 Hz, 2H, H^4/bipym), 9.85 (dd, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 2.2 Hz, $^3J_{HPt}$ = 28.0 Hz, 2H, H^6/bipym). **^{13}C{^{1}H} NMR** (δ, CDCl$_3$): 67.5 (C$^\beta$/C_5H_4), 70.2 (C_5H_5), 71.5 (C$^\alpha$/C_5H_4), 109.7 (C≡C), 117.7 (C≡C), 135.1 (C^5/bipym), 157.8 (C^6/bipym), 158.3 (C^4/bipym).

4.3.5. Synthesis of cis-[(bipym)Pt(C≡CRc)$_2$] (**8c**)

Four hundred and fifty three milligram (1.78 mmol) of ethynylruthenocene (**7c**) was dissolved in 50 mL of dichloromethane and 10 mL of diisopropylamine. 300 mg (0.71 mmol) of **6** and 1 mg of [CuI] were added. After 4 days of stirring at 25 °C, the reaction mixture was filtered through a pad of alumina. The adsorbed title compound was diluted with a mixture of dichloromethane/tetrahydrofuran (1:1, vs/vs). Pure brown **8c** was precipitated by addition of petroleum ether (30 mL). Yield: 213 mg (0.25 mmol, 35%).

Anal. Calc. for $C_{32}H_{24}N_4PtRu_2 \times CH_2Cl_2$ (878.77): C, 44.01; H, 2.80; N, 6.37. Found: C, 44.24; H, 3.12; N, 5.91. **IR** (KBr, cm^{-1}): 2130 (w, $\nu_{C\equiv C}$), 2114 (w, $\nu_{C\equiv C}$). **^{1}H NMR** (δ, CDCl$_3$): 4.49 (pt, J_{HH} = 1.7 Hz, 4H, H$^\beta$/C_5H_4), 4.60 (s, 10H, C_5H_5), 4.87 (pt, J_{HH} = 1.7 Hz, 4H, H$^\alpha$/C_5H_4), 5.30 (s, 2H, CH$_2$Cl$_2$), 7.75 (dd, $^3J_{HH}$ = 5.6 Hz, $^3J_{HH}$ = 4.8 Hz, 2H, H^5/bipym), 9.29 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 2.2 Hz, 2H, H^4/bipym), 9.86 (dd, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 2.2 Hz, $^3J_{HPt}$ = 28.9 Hz, 2H, H^6/bipym). **^{13}C{^{1}H} NMR** (δ, CDCl$_3$): 25.6 (CH$_2$/Thf), 53.3 (CH$_2$Cl$_2$), 68.0 (CH$_2$O/Thf), 69.6 (C$^\beta$/C_5H_4), 71.6 (C_5H_5), 74.1 (C$^\alpha$/C_5H_4), 109.7 (C≡C), 124.4 (C^5/bipym), 158.0 (C^6/bipym), 158.5 (C^4/bipym).

4.3.6. Synthesis of [((CO)$_4$Mo)(μ-1,2,3,4-bipym)Pt(C≡CFc)$_2$] (**10**)

Sixty five milligram (0.22 mmol) of [(CO)$_4$(nbd)Mo] (**9**) and 150 mg (0.2 mmol) of **8b** were dissolved in 30 mL of tetrahydrofu-

ran and stirred for 16 h at 25 °C. A dark green solid precipitated, which could be separated by filtration through a frit (G4). The green solid was washed twice with 20 mL portions of tetrahydrofuran and all volatiles were removed under reduced pressure. Yield: 185 mg (0.19 mmol, 94% based on **8b**).

Anal. Calc. for $C_{36}H_{24}Fe_2MoN_4O_4Pt$ (979.31): C, 44.15; H, 2.47; N, 5.72. Found: C, 44.62; H, 2.87; N 5.11%. **IR** (KBr, cm^{-1}): 2116 (w, $v_{C\equiv C}$), 2022 (s, v_{C-O}), 1919 (vs, v_{C-O}), 1881 (vs, v_{C-O}), 1831 (vs, v_{C-O}). **^{1}H NMR** (δ, (CD$_3$)$_2$SO): 4.13 (pt, J_{HH} = 1.8 Hz, 4H, H$^\beta$/C$_5$H$_4$), 4.20 (s, 10H, C$_5$H$_5$), 4.39 (pt, J_{HH} = 1.8 Hz, 4H, H$^\alpha$/C$_5$H$_4$), 8.11 (pt, J_{HH} = 5.6 Hz, 2H, H/bipym), 9.41 (dd, J_{HH} = 4.7 Hz, J_{HH} = 2.2 Hz, 2H, H/bipym), 9.74 (dd, J_{HH} = 5.6 Hz, J_{HH} = 2.2 Hz, 2H, H/bipym). **^{13}C{^{1}H} NMR** (δ, (CD$_3$)$_2$SO): 67.7 (C$^\beta$/C$_5$H$_4$), 70.1 (C$_5$H$_5$), 71.1 (C$^\alpha$/C$_5$H$_4$), 72.3 (iC/C$_5$H$_4$), 128.8, 129.5.

4.3.7. Synthesis of [(O₃ClOAg)(μ-1,2,3,4-bipym){[Pt(μ-σ,π-C≡CFc)₂]-AgOClO₃}] (12)

Seventy two milligram (0.34 mmol) of silver(I) perchlorate (**11**) was dissolved in 20 mL of tetrahydrofuran and 134 mg (0.17 mmol) of **8b** in 30 mL of tetrahydrofuran were added drop-wise at 25 °C. After 5 min of stirring at this temperature a dark brown solid precipitated. The solid title compound was separated from the solution by filter canula and washed with tetrahydrofuran (2 × 20 mL). All volatiles were removed in oil-pump vacuum, whereby complex **12** could be obtained as a dark brow solid. Yield: 162 mg (0.17 mmol, 98% based on **8b**).

Anal. Calc. for $C_{32}H_{24}Ag_2Cl_2Fe_2N_4O_8Pt$ (1182.74): C, 32.47; H, 2.05; N, 4.74. Found: C, 32.29; H, 2.11; N 4.65%. **IR** (KBr, cm^{-1}): 2103 (w, $v_{C\equiv C}$), 2061 (w, $v_{C\equiv C}$). **^{1}H NMR** (δ, CD$_3$CN): 4.15 (bs, 4H, H$^\beta$/C$_5$H$_4$), 4.23 (s, 10H, C$_5$H$_5$), 4.55 (bs, 4H, H$^\alpha$/C$_5$H$_4$), 7.98 (pt, J_{HH} = 4.7 Hz, 2H, H/bipym), 9.33 (d, J_{HH} = 4.7 Hz, 2H, H/bipym), 9.47 (dd, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 2.3 Hz, $^3J_{HPt}$ = 28.0 Hz, 2H, H/bipym).

4.3.8. Synthesis of [(FcC≡C)₂Pt(μ-1,2,3,4-bipym)({[Ti](μ-σ,π-C≡CSiMe₃)₂}Cu)]PF₆ (15a) and [(FcC≡C)₂Pt(μ-1,2,3,4-bipym)({[Ti](μ-σ,π-C≡CSiMe₃)(μ-σ,π-C≡CH)}Cu)]PF₆ (15a′)

A mixture of 142 mg (0.19 mmol) of [{[Ti](μ-σ,π-C≡CSi Me₃)₂}Cu(N≡CCH₃)]PF₆ (**14a**) and 144 mg (0.19 mmol) of **8b** were dissolved in 30 mL of tetrahydrofuran. This reaction solution was stirred for 2.5 h at 25 °C. Afterward all volatile materials were removed in oil-pump vacuum and the brown residue was dissolved in dichloromethane (10 mL). On addition of petroleum ether (40 mL) dark brown **15a** precipitated. After separation of solid **15a**, compound **15a′** precipitated by reducing the solvent in oil-pump vacuum to 5 mL. Complex **15a′** was obtained as a brown solid. Yield: **15a** 242 mg (0.16 mmol, 85%), **15a′** 8 mg (0.006 mmol, 3%).

Anal. Calc. for $C_{58}H_{68}CuF_6Fe_2N_4PPtSi_4Ti$ (1495.13): C, 46.55; H, 4.58; N, 3.75. Found: C, 46.57; H, 4.75; N 3.47%. **IR** (KBr, cm^{-1}): 2114 (w, $v_{PtC\equiv C}$), 1924 (w, $v_{TiC\equiv C}$), 841 (s, v_{P-F}). **^{1}H NMR** (δ, CDCl$_3$): −0.42 (s, 18H, C≡CSiMe₃), 0.38 (s, 18H, SiMe₃/cp), 4.13 (bs, 4H, H$^\beta$/FeC₅H₄), 4.28 (s, 10H, C₅H₅/Fc), 4.53 (bs, 4H, H$^\alpha$/FeC₅H₄), 6.46 (bs, 8H, TiC₅H₄), 8.56 (bs, 2H, bipym), 9.50 (bs, 2H, bipym), 9.83–10.07 (m, 2H, bipym). **MS** (m/z, ESI-TOF): 579.2 [{[Ti](C₂SiMe₃)₂}-Cu]$^+$, 1350.3 [M−PF₆]$^+$.

4.3.9. Synthesis of [(RcC≡C)₂Pt(μ-1,2,3,4-bipym)({[Ti](μ-σ,π-C≡CSiMe₃)₂}Cu)]PF₆ (15b) and [(RcC≡C)₂Pt(μ-1,2,3,4-bipym)({[Ti](μ-σ,π-C≡CSiMe₃)(μ-σ,π-C≡CH)}Cu)]PF₆ (15b′)

Hundred and thirty three milligram (0.17 mmol) of **14a** and 150 mg (0.17 mmol) of **8c** were dissolved in 30 mL of tetrahydrofuran. After 1.5 h of stirring at 25 °C all volatiles were removed in oil-pump vacuum and the red-brown residue was dissolved in dichloromethane (10 mL) and subsequently red-brown **15b** was precipitated upon addition of petroleum ether (40 mL). Complex **15b′** was

isolated by reducing the solution to 5 mL at reduced pressure, whereby **15b′** precipitated as a brown solid. Yield: **15b** 224 mg (0.16 mmol, 83%), **15b′** 10 mg (0.007 mmol, 4%).

Anal. Calc. for $C_{58}H_{68}CuF_6N_4PPtRu_2Si_4Ti$ × 2/3CH$_2$Cl$_2$ (1643.74): C, 42.87; H, 4.25; N, 3.41. Found: C, 42.79; H, 3.89; N, 3.37%. **IR** (KBr, cm^{-1}): 2115 (w, $v_{PtC\equiv C}$), 1925 (w, $v_{TiC\equiv C}$), 842 (s, v_{P-F}). **^{1}H NMR** (δ, CDCl$_3$): −0.37 (s, 18H, C≡CSiMe₃), 0.32 (s, 18H, SiMe₃/C₅H₄), 4.57 (bs, 4H, H$^\beta$/RuC₅H₄), 4.63 (s, 10H, C₅H₅/Rc), 4.92 (bs, 4H, H$^\alpha$/RuC₅H₄), 5.29 (CH₂Cl₂), 6.51 (bs, 8H, TiC₅H₄), 8.02 (bs, 2H, bipym), 8.58 (bs, 2H, bipym), 9.48–9.78 (m, 2H, bipym). **MS** (m/z, ESI-TOF): 580.6 [{[Ti](C₂SiMe₃)₂}Cu]$^+$, 619.6 [bipymPt(C₃Rc)]$^+$ 1442.0 [M−PF₆]$^+$.

4.3.10. Synthesis of [(FcC≡C)₂Pt(μ-1,2,3,4-bipym)({[Ti](μ-σ,π-C≡CSiMe₃)₂}Ag)]ClO₄ (15c)

Fifty milligram (0.07 mmol) of **14b** and 53 mg (0.07 mmol) of **8b** were dissolved in 30 mL tetrahydrofuran at 25 °C. After 1.5 h stirring at this temperature all volatile materials were removed in oil-pump vacuum and the brown residue was redissolved in dichloromethane (10 mL). The title complex precipitated upon addition of petroleum ether (40 mL). Yield: 90 mg (0.06 mmol, 87%).

Anal. Calc. for $C_{58}H_{68}AgClFe_2N_4O_4PtSi_4Ti$ (1495.48): C, 46.58; H, 4.58; N, 3.75. Found: C, 46.48; H, 4.86; N 3.84%. **IR** (KBr, cm^{-1}): 2100 (w, $v_{PtC\equiv C}$), 1959 (w, $v_{TiC\equiv C}$), 1104 (s, v_{Cl-O}). **^{1}H NMR** (δ, CDCl$_3$): 0.16 (s, 18H, C≡CSiMe₃), 0.42 (s, 18H, SiMe₃/cp), 4.23 (bs, 4H, H$^\beta$/FeC₅H₄), 4.28 (s, 10H, C₅H₅), 4.56 (bs, 4H, H$^\alpha$/FeC₅H₄), 6.05 (bs, 8H, TiC₅H₄), 8.15 (bs, 2H, H/bipym), 9.53 (bs, 2H, H/bipym), 9.93 (bs, 2H, H/bipym).

4.3.11. Synthesis of [(FcC≡C)₂Pt(μ-1,2,3,4-bipym)PtCl₂] (17)

Fifty five milligram (0.07 mmol) of **8b** and 44 mg (0.09 mmol) of [(PhC≡N)₂PtCl₂] (**16**) in 40 mL of tetrahydrofuran were stirred for 8 h at 60 °C. A black insoluble solid precipitated which was washed twice with 20 mL of dichloromethane and separated by centrifuge. All volatiles were removed under reduced pressure. Complex **17** was isolated as dark brown solid, which is insoluble in most common organic solvents. Yield: 65 mg (0.06 mmol, 88%).

Anal. Calc. for $C_{32}H_{24}Cl_2Fe_2N_4Pt_2$ (1037.31): C, 37.05; H, 2.33; N, 5.40. Found: C, 37.05; H, 2.41; N 5.43%. **IR** (KBr, cm^{-1}): 2098 (w, $v_{PtC\equiv C}$).

4.3.12. Crystal structure determinations

Crystal data for **8b**, **8c**, **15a′**, and **15b′** are summarized in Table 4. All data were collected on a Oxford Gemini S diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at 100 K using oil-coated shock-cooled crystals [24]. The structures were solved by direct methods using SHELXS-97 [25] and refined by full-matrix least-square procedures on F^2 using SHELXL-97 [26]. All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions. In **8c** the solvent molecule CH₂Cl₂ is disordered and have been refined to split occupancies of 0.76/0.24 (C35 and Cl5). In case of **15a′** the SiMe₃ group, PF₆⁻ and the solvent molecule CHCl₃ are disordered and have been refined to split occupancies of 0.76/0.24 (Si1, C43−C45), 0.49/0.51 (P1, F1−F6) and 0.54/0.46 (C59, Cl10−Cl12).

Supplementary material

CCDC 688495, 688494, 688497 and 688496 contains the supplementary crystallographic data for **8b**, **8c**, **15a′** and **15b′**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4
Crystal and Intensity collection data for **8a**, **8b**, **15a′**, and **15b′**

	8b	8c	15a′	15b′
Formula weight	941.19	1116.56	1902.01	1659.19
Chemical formula	$C_{32}H_{24}Fe_2N_4Pt$ 2 CH_2Cl_2	$C_{32}H_{24}N_4PtRu_2$ 3 CH_2Cl_2	$C_{55}H_{60}CuF_6Fe_2N_4PPtSi_3$ Ti 4 $CHCl_3$	$C_{55}H_{60}CuF_6N_4PPtRu_2Si_3Ti$ 2 Thf
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2(1)/c$	$P2(1)/a$	$P\bar{1}$
a (Å)	11.0181(8)	11.2316(8)	16.01800(10)	14.0036(9)
b (Å)	11.5702(13)	26.9174(18)	27.7827(2)	16.2805(13)
c (Å)	13.0445(14)	11.9144(8)	17.4768(2)	16.7570(9)
α (°)	100.791(9)			105.860(6)
β (°)	93.009(7)	101.475(6)	98.8750(10)	98.895(5)
γ (°)	93.662(7)			109.703(7)
V (Å^3)	1626.7(3)	3530.0(4)	7684.46(11)	3328.9(4)
$\rho_{calc.}$ (g cm^{-3})	1.922	2.101	1.644	1.655
$F(000)$	916	2144	3768	1652
Crystal dimensions (mm)	$0.3 \times 0.2 \times 0.1$	$0.4 \times 0.3 \times 0.2$	$0.6 \times 0.3 \times 0.2$	$0.1 \times 0.1 \times 0.05$
Z	2	4	4	2
Maximum and minimum transition	1.00000, 0. 68786	1.00000, 0. 47624	1.00000, 0.68315	1.00000, 0.87415
Absorption coefficient (λ, mm^{-1})	5.530	5.286	3.092	3.105
Scan range (°)	2.83–26.10	2.86–26.08	2.89–26.08	2.90–26.08
Index ranges	$-13 \leqslant h \leqslant 13, -14 \leqslant k \leqslant 14,$ $-16 \leqslant l \leqslant 16$	$-13 \leqslant h \leqslant 13, -33 \leqslant k \leqslant 33,$ $-14 \leqslant l \leqslant 14$	$-19 \leqslant h \leqslant 19, -34 \leqslant k \leqslant 34,$ $-21 \leqslant l \leqslant 21$	$-17 \leqslant h \leqslant 17, -20 \leqslant k \leqslant 20,$ $-20 \leqslant l \leqslant 20$
Total reflections	16419	28719	72961	30803
Unique reflections	6384	6939	15017	12946
$R_{(int)}$	0.0399	0.0388	0.0310	0.0768
Data/restraints/parameters	6384/0/406	6939/34/452	15017/351/949	12946/9/766
Goodness-of-fit on F^2	1.016	1.080	1.256	0.817
$R_1{}^a$, $wR_2{}^a$ [I $2\sigma(I)$]	0.0385, 0.0861	0.0294, 0.0589	0.0540, 0.1112	0.0494, 0.0923
$R_1{}^a$, $wR_2{}^a$ (all data)	0.0561, 0.0937	0.0550, 0.0716	0.0675, 0.1181	0.1059, 0.1029
Maximum and minimum peak in final Fourier map (e Å^{-3})	3.829, −1.687	1.973, −1.065	1.970, −1.292	2.294, −0.659

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

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