Heterobi- and Heterotrimetallic Transition Metal Complexes with Carbon-Rich Bridging Units

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The syntheses of heterobi- and heterotrimetallic complexes based on (2,2′-bipyridine-5-ylethynyl)-ferrocene (**3**) are described. Complex **3** is accessible by the Pd(II)/Cu(I)-catalyzed Sonogashira cross-coupling of FcC≡CH (**1**) (Fc = (η^5-C_5H_4)(η^5-C_5H_5)Fe) with 5-bromo-2,2′-bipyridine (**2**). The complexation behavior of **3** was investigated. Treatment of **3** with (nbd)Mo(CO)$_4$ (**4a**) (nbd = *n*or*b*ornа*d*iene) at 25 °C, or refluxing **3** with Mn(CO)$_5$Br (**4b**), ($Me_2S)_2PtCl_2$ (**4c**), and Ru(bipy)$_2Cl_2$·2H_2O (**4d**) (bipy = 2,2′-bipyridine), respectively, gave the respective heterobimetallic complexes FcC≡C-bipy(ML$_n$) (**5**: ML$_n$ = Mo(CO)$_4$, **6**: ML$_n$ = Mn(CO)$_3$Br, **7**: ML$_n$ = PtCl$_2$, **8**: ML$_n$ = [Ru(bipy)$_2$](PF$_6$)$_2$). Heterotrimetallic FcC≡C-bipy{[Pt(μ-σ,π-C≡CSiMe$_3$)$_2$]CuFBF$_3$} (**12**) can be obtained by the subsequent reaction of **7** with Me$_3$SiC≡CH (**9**) and [Cu(N≡CMe)$_4$]BF$_4$ (**11**), while [FcC≡C-bipy{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M]X (**14a**: M = Cu, X = PF$_6$; **14b**: M = Ag, X = ClO$_4$; [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti) were formed by combining **3** with {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}MX (**13a**: MX = Cu(N≡CMe)PF$_6$, **13b**: MX = AgOClO$_3$). The identity of **3**, **10**, and **14a** was confirmed by single-crystal X-ray structural studies. The main characteristic features of **3** and **10** are the almost eclipsed conformation of the ferrocene cyclopentadienyl rings, the linear C_{Cp}−C≡C−C_{bipy} moieties, and the coplanarity of both the pyridine and the C$_5$H$_4$ rings. The latter structural motif allows an optimal overlap between the π-orbitals of the cyclopentadienyl, ethynyl, and pyridyl rings. However, in **14a** the bipy ligand is tilted by 96.9° toward the η^5-C$_5$H$_4$ unit, which most likely is attributable to cell-packing effects. The platinum atom in **10** is held in a somewhat distorted square-planar surrounding. The chelated copper(I) ion in **14a** possesses a pseudotetrahedral coordination geometry. Mononuclear **3** exhibits redox peaks in its cyclic voltammogram (E_0 = 0.10 V, ΔE_p = 194 mV) for the Fe^{2+}/Fe^{3+} redox couple of the Fc unit and for the bipy ligand ($E_{0.1}$ = −2.36 V, ΔE_p = 200 mV; $E_{0.2}$ = −2.76 V, ΔE_p = 430 mV). Compounds **10**, **12**, **14a**, and **14b** additionally show electrode potentials attributed to the respective ML$_n$ building blocks.

Introduction

The study of homo- and heterometallic transition metal complexes in which the metal atoms are connected by π-conjugated organic and/or inorganic carbon-rich units is an intriguing area of research, since such species may offer the possibility to study electronic communication between the redox-active termini, exhibit nonlinear optical properties, or provide, for example, cooperative effects in homogeneous catalysis.[1] Owing to the redox chemistry, chemical robustness, and synthetic versatility, ferrocenyl building blocks have attracted significant attention as excellent donor groups in transition metal chemistry.[2] Conjugated pyridines and alkynyl-functionalized bipyridines with an end-capped ferrocene moiety offer the possibility to function as valuable precursors for the synthesis of diverse heterometallic complexes.[3]

We report here the synthesis of (2,2′-bipyridine-5-ylethynyl)-ferrocene and its complexation behavior toward different transition metal fragments. The electrochemical and structural properties of the resulting heterodi- and heterotrimetallic complexes are discussed as well.

Results and Discussion

The synthesis of (2,2′-bipyridine-5-ylethynyl)ferrocene (**3**) was accomplished by the palladium(II)/copper(I)-catalyzed Sonogashira cross-coupling of FcC≡CH (**1**) (Fc = Fe(η^5-C$_5$H$_4$)-(η^5-C$_5$H$_5$)) with 5-bromo-2,2′-bipyridine (**2**) in refluxing diisopropylamine (eq 1). After appropriate workup, complex **3** was obtained as an orange, air-stable solid in 68% yield, which

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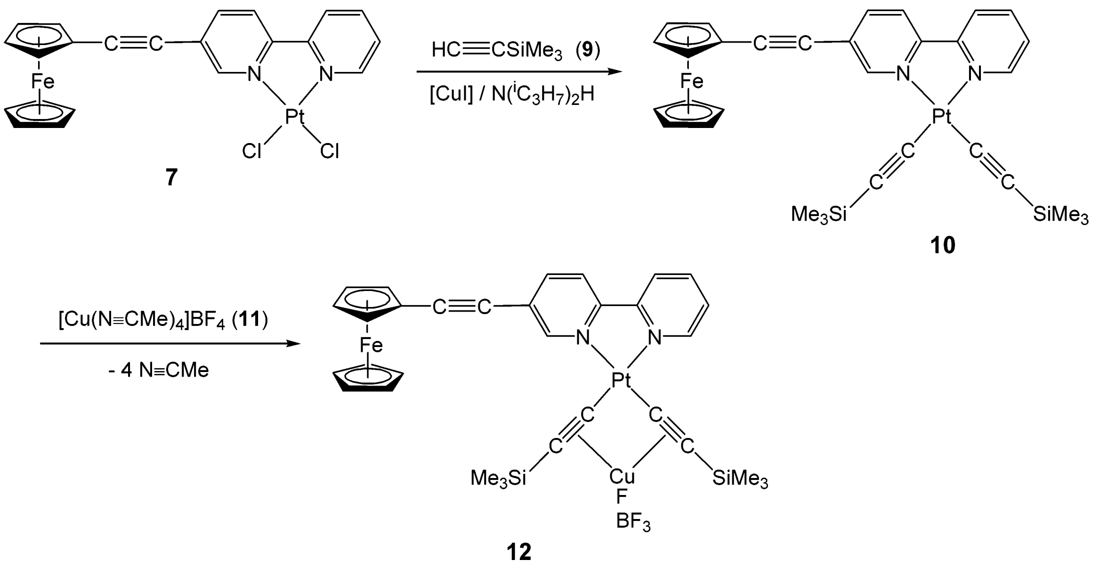
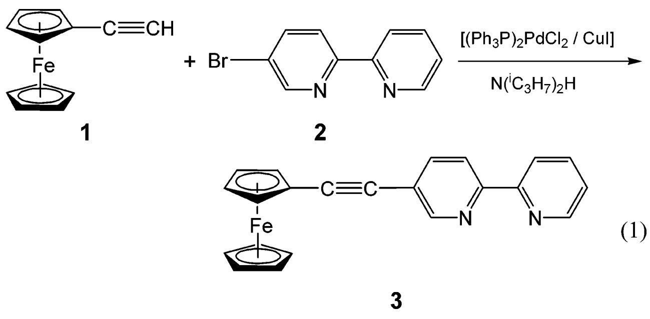
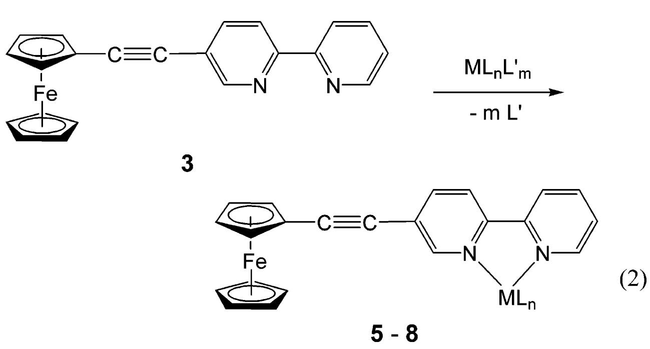
Scheme 1. Synthesis of 10 and 12



dissolves in organic solvents, such as petroleum ether, toluene, diethyl ether, and dichloromethane.



The reaction of **3** with (nbd)Mo(CO)$_4$ (**4a**) (nbd = *n*or*b*or*n*a*d*iene) in a mixture of dichloromethane/tetrahydrofuran (ratio 5:1) at 25 °C afforded FcC≡C-bipy(Mo(CO)$_4$) (**5**) upon replacement of nbd by bipy (eq 2, Table 1). Refluxing **3** in the presence of Mn(CO)$_5$Br (**4b**), (Me$_2$S)$_2$PtCl$_2$ (**4c**), or Ru(bipy)$_2$Cl$_2$·2H$_2$O (**4d**) (bipy = 2,2′-bipyridine) in ethanol or toluene as solvent produced the respective heterobimetallic complexes FcC≡C-bipy(ML$_n$) (**6**: ML$_n$ = Mn(CO)$_3$Br (elimination of two carbonyls), **7**: ML$_n$ = PtCl$_2$ (loss of SMe$_2$), **8**: ML$_n$ = [Ru(bipy)$_2$](PF$_6$)$_2$) (eq 2, Table 1). Complex **8** was formed after subsequent precipitation with aqueous ammonium hexafluorophosphate.



The progress of the complexation of **3** with ML$_n$ can nicely be monitored by the color change upon addition of ML$_n$L′$_m$ (Table 1), whereby the orange solution of **3** turned red (**5**, **6**, **8**) or deep purple (**7**) during the course of the reaction.

Table 1. Synthesis of Heterobimetallic 5−8

compd	ML$_n$L′$_m$	ML$_n$	yield [%]^a
5	(nbd)Mo(CO)$_4$^{b} (**4a**)	Mo(CO)$_4$	77
6	Mn(CO)$_5$Br (**4b**)	Mn(CO)$_3$Br	59
7	(Me$_2$S)$_2$PtCl$_2$ (**4c**)	PtCl$_2$	65
8	Ru(bipy)$_2$Cl$_2$·2H$_2$O^c (**4d**)	[Ru(bipy)$_2$](PF$_6$)$_2$^{d}	92

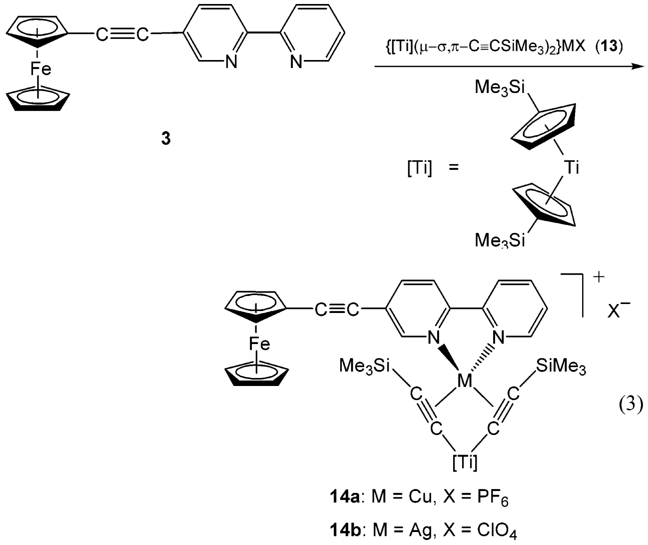
[a] Based on **3**. [b] nbd = *n*or*b*or*n*a*d*iene. [c] bipy = 2,2′-bipyridine. [d] Obtained from the reaction of **3** with **4d** followed by treatment of [**3**·Ru(bipy)$_2$]Cl$_2$ with NH$_4$PF$_6$.

Treatment of **7** with an excess of Me$_3$SiC≡CH (**9**) in the presence of catalytic amounts of [CuI] in a 5:1 mixture of dichloromethane and diisopropylamine produced with concomitant precipitation of [N(^{i}C$_3$H$_7$)$_2$H$_2$]Cl pale red FcC≡C-bipy[Pt(C≡CSiMe$_3$)$_2$] (**10**), which in a further reaction with [Cu(N≡CMe)$_4$]BF$_4$ (**11**) in 1:1 stoichiometry gave deep purple FcC≡C-bipy{[Pt(μ-σ,π-C≡CSiMe$_3$)$_2$]CuFBF$_3$} (**12**) in a 63% overall yield (Scheme 1).

It also was possible to synthesize heterotrimetallic Fe−Ti−M complexes with M = Cu and Ag, respectively (eq 3). Structural type [FcC≡C-bipy{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M]X (**14a**: M = Cu, X = PF$_6$; **14b**: M = Ag, X = ClO$_4$; [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti) molecules are accessible by combining mononuclear **3** with heterobimetallic {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}MX (**13a**: MX = Cu(N≡CMe)PF$_6$, **13b**: MX = AgOClO$_3$) in tetrahydrofuran at 25 °C. In **14a** and **14b** the group 11 metals copper and silver are chelate-bonded by the organometallic π-tweezer [Ti](C≡CSiMe$_3$)$_2$ and the bipy ligand resulting in tetracoordination at M. While red **14a** and **14b** are stable in the solid state, they slowly start to decompose in solution on exposure to air; that is, **14b** gives elemental silver along with **3** and [Ti](C≡CSiMe$_3$)$_2$.

Complexes **3**, **5**−**8**, **10**, **12**, and **14** were characterized by elemental analysis, IR, and NMR spectroscopy. ESI-TOF mass spectrometric experiments were additionally carried out with **7**, **10**, and **12**. The identity of **3**, **10**, and **14a** was further confirmed by single-crystal X-ray diffraction studies.

Characteristic in the IR spectra of **3** is the C≡C stretching vibration at 2205 cm^{-1} for the C≡C-bipy unit. For all other species this absorption is observed at almost the same value (2199−2209 cm^{-1}) (Experimental Section). Further representative vibrations are ν_{CO} (**5**, **6**), $\nu_{C≡C}$ (TiC≡CSiMe$_3$: **14a**, **14b**; PtC≡CSiMe$_3$: **10**, **12**), ν_{PF} (**8**, **14a**), ν_{BF} (**12**), and ν_{ClO} (**14b**), showing the expected patterns; for example, FcC≡C-bipy(Mo-



(CO)$_4$) (**5**) possesses four ν_{CO} absorptions at 1810, 1865, 1912, and 2009 cm^{-1}.[4] Remarkable to note is that due to the unsymmetrical substituted bipyridine ligand in **10** two $C\equiv C$ stretching vibrations are observed at 2039 and 2055 cm^{-1} for the $PtC\equiv CSi$ units. In **12**, these absorptions are shifted to 1961 and 1977 cm^{-1}, confirming the successful complexation of the alkynyl ligands to a low-valent $CuFBF_3$ moiety. For the FBF_3 fragment two vibrations are found at 1053 and 1084 cm^{-1}, which is typical for the σ-binding of this group to a transition metal atom.[5] Upon complexation of the organometallic π-tweezer building block $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}M]^+$ (M = Cu, Ag) by the bipy ligand in **14a** and **14b**, the $C\equiv C$ absorption is somewhat shifted to higher wavenumber when compared with **13a** and **13b**, respectively.[6]

Also the NMR spectroscopic properties of **3**, **5**−**8**, **10**, **12**, and **14** correlate with their formulations as mono-, di-, or trimetallic complexes (vide supra). The cyclopentadienyl protons in **3** show an AA′XX′ pattern with centers lying at 4.27 and 4.51 ppm (C_5H_4) and a singlet at 4.26 ppm (C_5H_5). The bipy ligand gives rise to seven signals found between 7.2 and 8.8 ppm with the characteristic coupling pattern.[7] The assignment of these signals was supported by two-dimensional NMR experiments (Experimental Section). The $^{13}C\{^1H\}$ NMR spectrum of **3** contains the respective carbon signals for Fc (four signals), $C\equiv C$ (two resonances), and bipy (10 signals) (Experimental Section). The protons and carbon atoms of the $FcC\equiv C$ entity do not differ significantly in their chemical shifts upon complexation of the bipy unit in **3** to ML_n as given in **5**−**8**, **10**, **12**, and **14**. However, the hydrogen atoms H6 and H6′ located next to the bipy nitrogen atoms are thereby more influenced and are shifted by ca. 0.5 ppm to lower field, i.e., **5**, **6**, **10**, and **12** (Experimental Section). In addition, representative Pt−H couplings with J_{PtH} = 26 Hz are observed for H6 and H6′ in **10**. Complexes **10** and **12** show in their ^1H NMR spectra two signals for the Me_3Si protons, which is attributed to their unsymmetrical chemical environment (vide supra). Notable in the ^1H NMR spectra of **14a** and **14b**, when compared with **13a** and **13b**, is the highfield shift of the $Me_3SiC\equiv C$ protons from ca. 0.25 ppm (**13**) to −0.41 (**14a**) or −0.29 ppm (**14b**), which can be explained by the ring current of the bipy ligand.

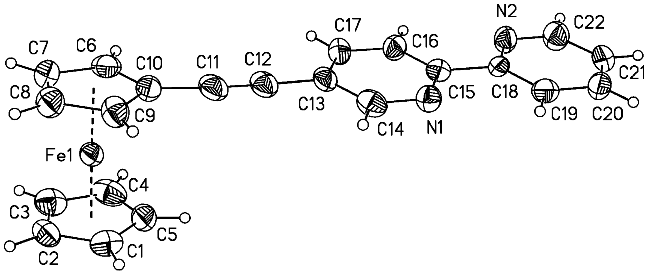


Figure 1. ORTEP plot (50% probability level) of **3** with the atom-numbering scheme. Selected bond distances (Å) and angles (deg): C10−C11, 1.452(5); C11−C12, 1.165(4); C12−C13, 1.447(4); Fe1-D1, 1.649(6); Fe1-D2, 1.642(6); C10−C11−C12, 176.9(6); C11−C12−C13, 178.4(8); D1−Fe1−D2, 178.2(3) (D1 = centroid of C_5H_5, D2 = centroid of C_5H_4).

A striking feature of **6** and **8** is that they exist as two enantiomers and, hence, show a doubling of the resonance signals of the C_5H_4 C_α carbons (**6**: 72.06 and 72.14 ppm; **8**: 72.47, 72.53 ppm).

In the $^{13}C\{^1H\}$ NMR spectrum of **14b** there is coupling to silver on the alkynyl C_α and C_β carbons ($TiC_\alpha\equiv C_\beta SiMe_3$) found at 153.7 ppm ($C_\alpha$) and 138.6 ppm ($C_\beta$), with coupling constants being 15 and 4 Hz, respectively; that is, both alkyne carbon atoms are bonded to silver (Experimental Section). However, the expected splitting of the signals into two doublets, due to the presence of the silver isotopes ^{107}Ag and ^{109}Ag (natural abundance ^{107}Ag ($I = {}^1/_2$) 51.8%, ^{109}Ag ($I = {}^1/_2$) 48.2%), is not observed.[8] This also can nicely be seen from $^{29}Si\{^1H\}$ NMR studies. The doublet found at −18.4 ppm with $^2J_{SiAg}$ = 2.0 Hz can be assigned to the alkynyl-bonded Me_3Si groups.

ESI-TOF mass spectra for **7** and **10** contain the molecular ion [M$^+$] (**7**: *m/z* = 630; **10**: *m/z* = 753) and for **12** [M$^+$ −BF$_4$] (*m/z* = 817). Further characteristic fragments are [M$^+$ − PtCl$_2$] (**7**, *m/z* = 365), [M$_2^+$] (**10**, *m/z* = 1507), and [M$^+$ −BF$_4$ + FcC$_2$bipyPt(C$_2$SiMe$_3$)$_2$] (**12**, *m/z* = 1570).

Single-crystal X-ray structure analysis was performed for **3**, **10**, and **14a**. A view of the molecules is given in Figure 1 (**3**), Figure 2 (**10**), and Figure 3 (**14a**), respectively. Selected bond distances (Å) and angles (deg) are given in the legend of Figures 1−3. The crystal and structure refinement data for **3**, **10**, and **14a** are presented in Table 3 (Experimental Section).

The overall structural features of **3** are similar to those of related structurally characterized phenylethynyl-functionalized ferrocenes.[3,9] The cyclopentadienyl rings are rotated by 6.2° to each other, which verifies an almost eclipsed conformation. The C13−C17, N1 and C18−C22, N2 pyridine rings and the cyclopentadienyl unit C6−C10 are almost coplanar (dihedral angle of 5.92(0.20)° for C13−C17, N1/C6−C10 and 0.95(0.20)° for C13−C17, N1/C18−C22, N2) (Figure 1). This orientation allows an optimal overlap between the π-orbitals of the cyclopentadienyl, ethynyl, and pyridyl fragments.

The asymmetric unit of **10** contains two crystallographically independent molecules together with one molecule of acetonitrile. Geometrical parameters within the $FcC\equiv C$-bipy unit are

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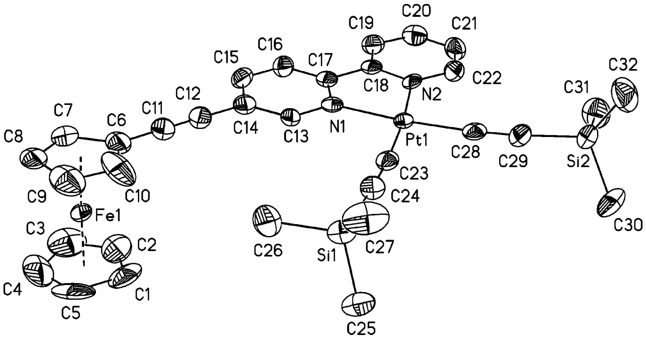

Figure 2. ORTEP plot (50% probability level) of one molecule of **10** with the atom-numbering scheme (the hydrogen atoms and one acetonitrile solvent molecule are omitted for clarity). Selected bond distances (Å) and angles (deg): Pt1−C23, 1.931(8); Pt1−C28, 1.930(9); Pt1−N1, 2.044(7); Pt1−N2, 2.042(7); C23−C24, 1.214(13); C28−C29, 1.213(13); C24−Si1, 1.807(9); C29−Si2, 1.809(9); C11−C12, 1.190(14); Fe1−D1, 1.634(11); Fe1−D2, 1.630(10); N1−Pt1−N2, 78.5(3); N1−Pt1−C23, 95.9(3); N1−Pt1−C28, 173.2(3); N2−Pt1−C28, 94.8(3); N2−Pt1−C23, 174.3(3); C23−Pt1−C28, 90.9(4); Pt1−C23−C24, 174.6(8); C23−C24−Si1, 173.1(8); Pt1−C28−C29, 171.5(8); C28−C29−Si2, 172.9(9); C6−C11−C12, 177.6(11); C11−C12−C14, 177.0(11); D1−Fe1−D2, 177.8(6) (D1 = centroid of C_5H_5, D2 = centroid of C_5H_4).

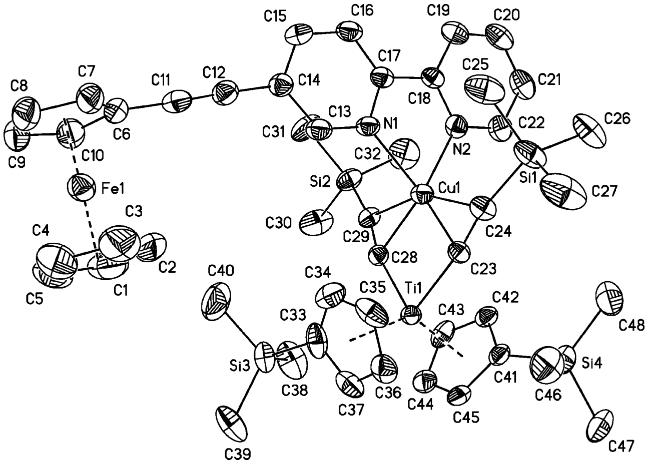

Figure 3. ORTEP plot (30% probability level) of **14a** with the atom-numbering scheme (the hydrogen atoms, the PF_6^- counterion, and the distortion of one Me_3Si group are omitted for clarity). Selected bond distances (Å) and angles (deg): Cu1−N1, 2.225(4); Cu1−N2, 2.044(4); Cu1−C23, 2.085(4); Cu1−C24, 2.198(5); Cu1−C28, 2.089(4); Cu1−C29, 2.202(5); Ti1−C23, 2.105(5); Ti1−C28, 2.118(5); C23−C24, 1.230(6); C28−C29, 1.227(6); C24−Si1, 1.853(5); C29−Si2, 1.853(5); Ti1−D3, 2.051(5); Ti1−D4, 2.040(5); C11−C12, 1.195(7); Fe1−D1, 1.640(8); Fe1−D2, 1.628(6); Ti1−Cu1, 2.9908(9); C23−Ti1−C28, 88.48(17); Ti1−C23−C24, 169.5(4); Ti1−C28−C29, 167.6(4); C23−C24−Si1, 162.6(4); C28−C29−Si2, 161.7(4); N1−Cu1−N2, 76.45(15); C6−C11−C12, 178.2(6); C11−C12−C14, 177.2(6); D1−Fe1−D2, 178.6(5) (D1 = centroid of C_5H_5; D2 = centroid of C_5H_4; D3, D4 = centroids of $C_5H_4SiMe_3$).

comparable to those of **3** (Figures 1 and 2). The (bipy)Pt($C{\equiv}C$-$SiMe_3)_2$ entity has values for metrical parameters similar to those reported previously in comparable complexes.[10] The platinum atom Pt1 is held in a somewhat distorted square-planar environment (mean deviation of Pt1 from the best plane of N1, N2, C23, C28 is 0.0089 Å).

Heterotrimetallic **14a** shows a pseudotetrahedral coordination geometry around Cu1 with two η^2-coordinated $Me_3SiC{\equiv}C$ groups (C23−C24, C28−C29) and the chelate-bonded bipy ligand (N1, N2) (Figure 3). Noteworthy to mention is the difference between Cu1−N1 (2.225(4) Å) and Cu1−N2 (2.044(4) Å), which verifies an asymmetrical chelate binding of the bipyridine ligand to Cu1 (Figure 3). This is, however, not common for Cu(I)-bipy moieties, in which symmetrical copper−nitrogen bonds are typical.[11] The large dissimilarity between Cu1−N1 and Cu1−N2 in **14a** most probably can be ascribed to electronic effects resulting from the electron-rich $FcC{\equiv}C$ unit. All other structural features of the Ti−Cu organometallic π-tweezer part are in accordance with this type of early−late complexes. [6] In comparison to mononuclear **3** (Figure 1) the bipy ligand in **14a** is tilted by 96.9° toward the η^5-coordinated C_5H_4 ring (C6−C10). This orientation is most likely attributed to cell-packing effects.

Preliminary electrochemical investigations of **3**, **10**, **12**, **14a**, and **14b** by cyclic voltammetry demonstrate that the redox couple Fe^{2+}/Fe^{3+} of the ferrocene moieties is not significantly affected by the complexation of bipy by ML_n fragments (Experimental Section, Table 2). Exemplarily, the cyclic voltammograms of **3**, **10**, **12**, and **14a** are depicted in Figures 4−6.

Complex **3** shows two reductions that can be assigned to the bipy ligand at $E_{0,1} = -2.36$ V ($\Delta E_p = 200$ mV) and $E_{0,2} = -2.76$ V ($\Delta E_p = 430$ mV) (Figure 4) (for comparison, free 2,2′-bipyridine: $E_0 = -2.77$ V ($\Delta E_p = 340$ mV);[14] $E_0 = E_{ox} - (E_{ox} - E_{red})/2$; ΔE_p = peak diff). In addition, a ferrocene-based Fe^{2+}/Fe^{3+} redox couple is found at $E_0 = 0.10$ V ($\Delta E_p = 194$ mV), which is somewhat shifted to a more positive value when compared with the FcH/FcH^+ potential (FcH = (η^5-$C_5H_5)_2Fe$, $E_0 = 0.00$ V ($\Delta E_p = 150$ mV)).[12] This displacement can be interpreted by means of a stronger electron-withdrawing group present in **3** than in FcH, taken as standard. The oxidation at $E_{ox} = -0.04$ V (Figure 4, inset) results from the second reduction of the bipy ligand at $E_0 = -2.76$ V, as could be evidenced by measuring only to −2.6 V (Figure 4).

For heterobimetallic **10** two redox waves are observed for the bipy ligand at $E_{0,1} = -1.59$ V ($\Delta E_p = 120$ mV) and $E_{0,2} = -2.24$ V ($\Delta E_p = 130$ mV) in the cyclic voltammogram (Figure 5, top), which is typical for chelate-bonded bipy ligands in platinum transition metal chemistry.[15] The cyclic voltammogram of **10** also exhibits, as **3**, a reversible oxidation wave for the

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Table 2. Electrochemical Data of 3, 10, 12, 14a, and 14b[a]

compd	Fe^{2+}/Fe^{3+} E_0/V (ΔE_p mV)	bipy/bipy$^{\bullet-b}$ E_0 ($E_{p,red}$)/V (ΔE_p/mV)	bipy$^{\bullet-}$/bipy^{2-b} E_0/V (ΔE_p/mV)	M^+/M^c $E_{p,ox}$/V	$E_{p,red}$/V	E_0/V (ΔE_p/mV)
3	0.10 (194)	−2.36 (200)	−2.76 (430)			
10	0.17 (130)	−1.59 (120)	−2.24 (130)			
12	0.16 (120)	−1.60 (130)	−2.23 (120)		−1.82	
14a	0.12 (150)	−2.67		−1.33	−1.45	−1.39 (120)
14b	0.13 (145)	−2.66			−1.26	

[a] In tetrahydrofuran. [b] For electrode potentials of free bipy see ref 14. [c] M = Cu and Ag, respectively.

Table 3. Crystal and Intensity Collection Data for 3, 10 and 14a

	3	**10**	**14a**
fw	364.22	794.79	1089.60
chemical formula	$C_{22}H_{16}FeN_2$	$C_{34}H_{37}FeN_3PtSi_2$	$C_{48}H_{60}CuFeN_2PSi_4Ti$
cryst syst	orthorhombic	triclinic	monoclinic
space group	$Pna2_1$	$P\bar{1}$	$P2_1/c$
a (Å)	23.915(2)	7.0881(6)	18.6503(10)
b (Å)	6.8674(6)	15.1536(13)	16.8592(9)
c (Å)	10.0743(9)	17.1405(15)	19.1245(10)
α (deg)	90	65.152(2)	90
β (deg)	90	88.468(2)	116.716(1)
γ (deg)	90	84.486(2)	90
V (Å^3)	1654.6(3)	1662.7(2)	5371.4(5)
ρ_{calc} (g cm^{-3})	1.462	1.587	1.347
F(000)	752	788	2256
cryst dimens (mm^3)	0.35 × 0.25 × 0.05	0.4 × 0.4 × 0.2	0. 5 × 0.4 × 0.2
Z	4	2	4
max., min. transmn	0.9999, 0.2233	0.9999, 0.5609	0.9999, 0.7818
absorp coeff (μ, mm^{-1})	0.917	4.737	0.977
scan range (deg)	1.70 to 26.41	1.51 to 26.39	1.22 to 26.46
index ranges	$0 \le h \le 29$	$-8 \le h \le 8$	$-23 \le h \le 20$
	$0 \le k \le 8$	$-16 \le k \le 18$	$0 \le k \le 21$
	$-12 \le l \le 12$	$0 \le l \le 21$	$0 \le l \le 23$
total no. of reflns	14 578	25 409	57 721
no. of unique reflns	3392	6767	11 427
R(int)	0.0649	0.0482	0.0931
no. of data/restraints/params	3392/1/226	6767/0/377	11 025/405/693
goodness-of-fit on F^2	1.031	1.118	1.011
R1,[a] wR2[a] [$I \ge 2\sigma(I)$]	0.0396, 0.0820	0.0611, 0.1598	0.0641, 0.1424
R1,[a] wR2[a] (all data)	0.0677, 0.0918	0.0643, 0.1628	0.1308, 0.1715
max., min. peak in final Fourier map (e Å^{-3})	0.262, −0.274	7.803, −3.869	0.784, −0.426

[a] $R1 = [\sum(||F_o| - |F_c|)/\sum|F_o|)$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$. $S = [\sum w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. n = number of reflections, p = parameters used.

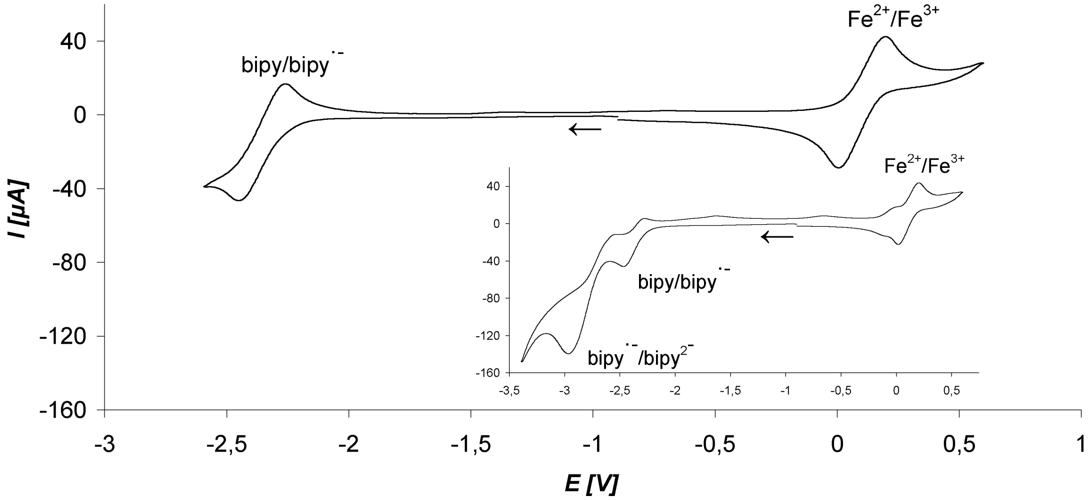

Figure 4. Cyclic voltammogram of **3** in tetrahydrofuran at 25 °C, [^{n}Bu$_4$N]PF$_6$ supporting electrolyte (0.1 M), scan rate = 100 mV s^{-1}. All potentials are referenced to the FcH/FcH$^+$ redox couple (FcH = (η^5-C_5H_5)$_2$Fe) with E_0 = 0.00 V (ΔE_p = 150 mV).[12,13]

ferrocene moiety at E_0 = 0.17 V (ΔE_p = 130 mV), showing that this unit is more difficult to oxidize than **3** and FcH, taken as standard (vide supra).[12] Under the conditions of the measurement, however, platinum reductions could not be observed.[15] Complexation of [CuFBF$_3$] as given in **12** does not influence the oxidation or reduction potentials of the FcC≡C-bipy[Pt(C≡CSiMe$_3$)$_2$] moiety (Fe^{2+}/Fe^{3+}: E_0 = 0.16 V (ΔE_p = 120 mV); bipy: $E_{0,1}$ = −1.60 V (ΔE_p = 130 mV), $E_{0,2}$ = −2.23 V (ΔE_p = 120 mV)). The coordinated copper(I) ion gives rise to an irreversible reduction wave at $E_{p,red}$ = −1.82 V (Figure 5,

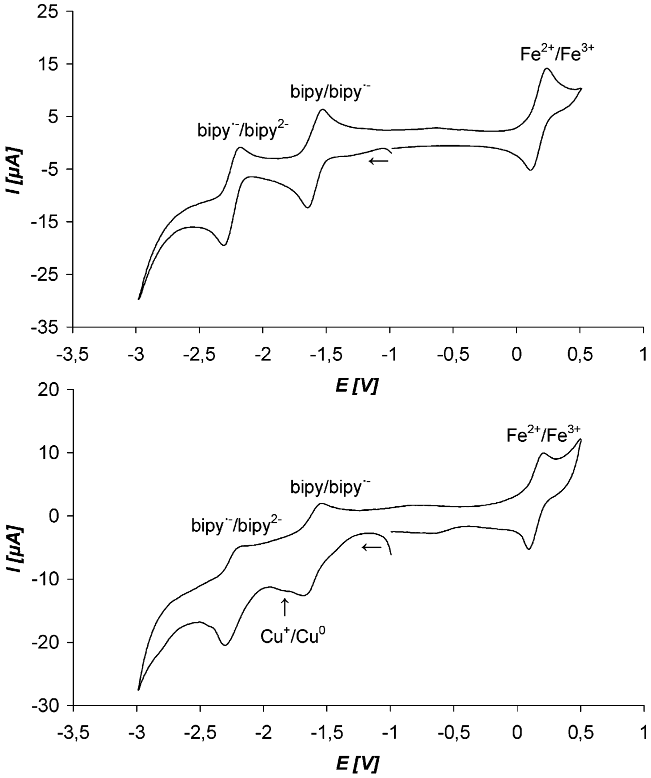

Figure 5. Cyclic voltammograms of **10** (top) and **12** (bottom) in tetrahydrofuran at 25 °C, [^{n}Bu$_4$N]PF$_6$ supporting electrolyte (0.1 M), scan rate = 100 mV s^{-1}. All potentials are referenced to the FcH/FcH$^+$ redox couple (FcH = (η^5-C$_5$H$_5$)$_2$Fe) with E_0 = 0.00 V (ΔE_p = 150 mV).[12,13]

bottom). This observation may imply that the copper(I) reduction occurs initially, resulting in fragmentation of FcC≡C-bipy{[Pt(μ-σ,π-C≡CSiMe$_3$)$_2$]CuFBF$_3$} (**12**). A similar phenomenon was found for other organometallic π-tweezers, i.e., {[Ti](μ-σ,π-C≡CR)$_2$}CuX (X = singly bonded inorganic or organic group).[16] A comparison of **7**, **10**, and **12** is not possible, because **7** is not soluble in tetrahydrofuran and dichloromethane solutions, respectively.

Heterotrimetallic [FcC≡C-bipy{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu]PF$_6$ (**14a**) gives a cyclic voltammogram as shown in Figure 6.

The relevant electrode potentials are for the iron(II) ion, E_0 = 0.12 V (ΔE_p = 150 mV), the reduction of the copper ion at $E_{p,red}$ = −1.45 V, and the reduction process bipy/bipy$^-$ at $E_{p,red}$ = −2.67 V (Figure 6). The reduction of copper(I) to copper(0) is typical in Ti−Cu organometallic π-tweezer chemistry, implying that in such complexes the reduction occurs initially at the Cu(I) ion, resulting in fragmentation of the respective complexes (vide supra).[16] However, when the cyclic voltammogram of **14a** is measured only between −0.4 and −1.6 V (Figure 6, inset), the cathodic reduction of Cu(I) is followed by reoxidation of Cu(0) (E_0 = −1.39 V, ΔE_p = 120 mV) obviously without any change of the chemical identity of the molecule involved. In contrast, this is not the case for isostructural **14b**, where instead of copper(I) a silver(I) center is present. Next to the redox couples Fe^{2+}/Fe^{3+} (E_0 = 0.13 V, ΔE_p = 145 mV) and bipy/bipy$^-$ ($E_{p,red}$ = −2.66 V) an irreversible reduction peak for Ag(I)/Ag(0) is found at $E_{p,red}$ = −1.26 V; that is, no reoxidation peak is observed. In the second run the only observable potentials are those typical for free FcC≡C-bipy and [Ti](C≡C-SiMe$_3$)$_2$,[16] indicating that **14b** fragmented into the starting materials (vide supra).

Conclusion

A straightforward synthesis method for the preparation of heterobi- and heterotrimetallic transition metal complexes of structural type FcC≡C-bipy(ML$_n$) (ML$_n$ = Mo(CO)$_4$, Mn(CO)$_3$Br, PtCl$_2$, Pt(C≡CSiMe$_3$)$_2$, [Ru(bipy)$_2$](PF$_6$)$_2$), FcC≡C-bipy{[Pt(μ-σ,π-C≡CSiMe$_3$)$_2$]CuFBF$_3$}, and [FcC≡C-bipy{[Ti](μ-σ,π−C≡CSiMe$_3$)$_2$}M]X (M = Cu, X = PF$_6$; M = Ag, X = ClO$_4$; [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti) is reported. In the latter species different early−late transition metals are connected via π-conjugated carbon-rich bridging units. Electrochemical studies show that the ferrocenyl moiety in FcC≡C-bipy is not significantly affected by the complexation of the bipy unit by ML$_n$ fragments. Complexation of the organometallic π-tweezers [Pt(μ-σ,π-C≡C-SiMe$_3$)$_2$]CuFBF$_3$ and {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M$^+$ (M = Cu, Ag) by the bipy ligand induces a cationic shift of the respective redox peaks for Fe^{2+}/Fe^{3+}, indicating that in the heterotrimetallic complexes the ferrocene unit is more difficult to oxidize and, hence, the heterobimetallic Pt−Cu and Ti−M building blocks are acting as electron-withdrawing groups. The use of the newly synthesized heterometallic complexes as multicomponent catalysts is subjected to further studies, since it was found that in heterobimetallic titanium−M π-tweezer complexes the appropriate metals show synergetic and cooperative effects.

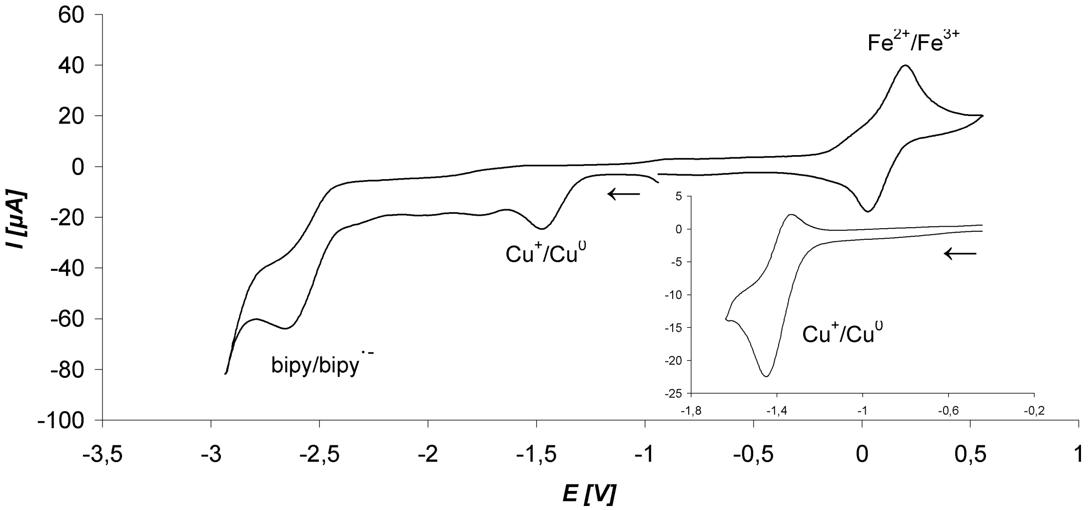

Figure 6. Cyclic voltammogram of **14a** in tetrahydrofuran at 25 °C, [^{n}Bu$_4$N]PF$_6$ supporting electrolyte (0.1 M), scan rate = 100 mV s^{-1}. All potentials are referenced to the FcH/FcH$^+$ redox couple (FcH = (η^5-C$_5$H$_5$)$_2$Fe) with E_0 = 0.00 V (ΔE_p = 150 mV).[12,13]

4. Experimental Section

General Data. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, and *n*-hexane were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations.

Instruments. Infrared spectra were recorded with a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. ^{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. 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%), $\delta = 7.26$; $(CD_3)_2CO$ (99.9%), $\delta = 2.05$; CD_3CN (99.8%), $\delta = 1.94$. ^{13}C{^{1}H} NMR: $CDCl_3$ (99.8%), $\delta = 77.16$; $(CD_3)_2CO$ (99.9%), $\delta = 29.84$, 206.26). The abbreviation *pt* in the ^{1}H NMR spectra corresponds to a pseudotriplet. Cyclic voltammograms were recorded in a dried cell purged with purified argon. A platinum wire served as working electrode, and a platinum wire was used as counter electrode. A saturated calomel electrode in a separate compartment served as reference electrode. For ease of comparison, all electrode potentials are converted using the redox potential of the ferrocene−ferrocenium couple FcH/FcH$^+$ (FcH = $(\eta^5\text{-}C_5H_5)_2Fe$, $E_0 = 0.00$ V)[12,13] as reference. Electrolyte solutions were prepared from tetrahydrofuran and $[^nBu_4N]PF_6$ (Fluka, dried in oil-pump vacuum). The respective organometallic complexes were added at $c = 1.0$ mM. Cyclic voltammograms were recorded in negative-going direction at the starting potentials using a Voltalab 3.1 potentiostat (Radiometer) equipped with a DEA 101 digital electrochemical analyzer and an IMT 102 electrochemical interface. 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 Institute of Organic Chemistry, Chemnitz, University of Technology, and partly by the Institute of Organic Chemistry, University of Heidelberg.

Reagents. Ethynylferrocene,[17] 5-bromo-2,2′-bipyridine,[18] (nbd)-$Mo(CO)_4$,[19] $Mn(CO)_5Br$,[20] $(bipy)_2RuCl_2\cdot 2H_2O$,[21] $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu(N{\equiv}CMe)]PF_6$,[22] $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}AgOClO_3$,[23] $(Et_2S)_2PtCl_2$,[24] and $Me_3SiC{\equiv}CH$[25] were prepared according to published procedures. All other chemicals were purchased by commercial suppliers and were used without further purification.

Synthesis of Fc-C$\equiv$C-bipy (3). 5-Bromo-2,2′-bipyridine (**2**) (200 mg, 0.85 mmol) and ethynylferrocene (**1**) (220 mg, 1.05 mmol) were dissolved in 30 mL of degassed diisopropylamine. To this solution were added $[Pd(PPh_3)_2Cl_2]$ (50 mg) and [CuI] (25 mg). The resulting suspension was heated at reflux for 8 h. After cooling to 25 °C it was filtered through a pad of Celite. The filtrate was evaporated to dryness, and the residue was subjected to column chromatography (silica gel). A 10:1 petroleum ether/diethyl ether mixture was used as eluent. Complex **3** was isolated from the second fraction on removal of all volatiles in an oil pump vacuum. Crystallization from a 5:1 petroleum ether/diethyl ether mixture at 25 °C gave orange, single crystals of **3**. Yield: 210 mg (0.58 mmol, 68% based on **2**). Mp: 163 °C. IR (KBr, cm^{-1}): 2205 (m), ν(C$\equiv$C). ^{1}H NMR ($CDCl_3$): δ 4.26 (s, 5 H, C_5H_5), 4.27 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_β/C_5H_4), 4.51 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_α/C_5H_4), 7.29 (ddd, $^3J_{H5'H4'} = 7.8$ Hz, $^3J_{H5'H6'} = 4.8$ Hz, $^4J_{H5'H3'} = 1$ Hz, 1 H, H5′), 7.80 (ddd, $^3J_{H4'H3'} = {}^3J_{H4'H5'} = 7.8$ Hz, $^4J_{H4'H6'} = 1.8$ Hz, 1 H, H4′), 7.91 (dd, $^3J_{H4H3} = 8.5$ Hz, $^4J_{H4H6} = 2.4$ Hz, 1 H, H4), 8.38 (dd, $^3J_{H3H4} = 8.5$ Hz, $^5J_{H3H6} = 0.6$ Hz, 1 H, H3), 8.41 (ddd, $^3J_{H3'H4'} = 7.8$ Hz, $^4J_{H3'H5'} = 1$ Hz, $^5J_{H3'H6'} = 1$ Hz, 1 H, H3′), 8.67 (ddd, $^3J_{H6'H5'} = 4.8$ Hz, $^4J_{H6'H4'} = 1.8$ Hz, $^5J_{H6'H3'} = 1$ Hz, 1 H, H6′), 8.77 (dd, $^4J_{H6H4} = 2.4$ Hz, $^5J_{H6H3} = 0.6$ Hz, 1 H, H6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 64.5 (C_i/C_5H_4), 69.3 (C_β/C_5H_4), 70.2 (C_5H_5), 71.7 (C_α/C_5H_4), 83.0 (Fc-C$\equiv$*C*-bipy), 93.3 (Fc-*C*$\equiv$C-bipy), 120.4 (*C3*/bipy), 121.1 (*C5*/bipy), 121.3 (*C3′*/bipy), 123.8 (*C5′*/bipy), 137.0 (*C4′*/bipy), 139.1 (*C4*/bipy), 149.3 (*C6′*/bipy), 151.5 (*C6*/bipy), 154.2 (*C2*/bipy), 155.7 (*C2′*/bipy). Anal. Calc for $C_{22}H_{16}FeN_2$ (364.23): C, 72.55; H, 4.43; N, 7.69. Found: C, 72.23; H, 4.46; N, 7.50.

Synthesis of Fc-C$\equiv$C-bipy[Mo(CO)$_4$] (5). (nbd)$Mo(CO)_4$ (**4a**) (80 mg, 0.27 mmol) was dissolved in a mixture of 25 mL of dichloromethane and 5 mL of THF. To this solution was added **3** (90 mg, 0.25 mmol) in one portion. After a few minutes the color of the reaction mixture turned from yellow to deep red. Stirring was continued for 15 h at 25 °C. Afterward the solvent was reduced in volume to 5 mL and the product was precipitated with diethyl ether. The precipitate was washed twice with 10 mL portions of diethyl ether and dried in an oil pump vacuum. Complex **5** was obtained as a red solid. Yield: 110 mg (0.19 mmol, 77% based on **3**). Mp: 183 °C (dec). IR (KBr, cm^{-1}): 2208 (m), ν(C$\equiv$C); 2009 (s), 1912 (s), 1865 (s), 1810 (s) ν(CO). ^{1}H NMR ($CDCl_3$): δ 4.31 (s, 5 H, C_5H_5), 4.36 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_β/C_5H_4), 4.60 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_α/C_5H_4), 7.38 (dd, $^3J_{H5'H4'} = 7.8$ Hz, $^3J_{H5'H6'} = 5.2$ Hz, 1 H, H5′), 7.89−7.96 (m, 2 H, H4, H4′), 8.03 (d, $^3J_{H3H4} = 8.4$ Hz, 1 H, H3), 8.08 (d, $^3J_{H3'H4'} = 8$ Hz, 1 H, H3′), 9.13 (d, $^3J_{H6'H5'} = 5.2$ Hz, 1 H, H6′), 9.19 (d, $^4J_{H6H4} = 2$ Hz, 1 H, H6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 63.2 (C_i/C_5H_4), 69.9 (C_β/C_5H_4), 70.4 (C_5H_5), 72.1 (C_α/C_5H_4), 81.4 (Fc-C$\equiv$*C*-bipy), 97.7 (Fc-*C*$\equiv$C-bipy), 121.4 (bipy), 122.1 (bipy), 123.4 (bipy), 125.1 (bipy), 137.4 (bipy), 138.7 (bipy), 152.1 (bipy), 153.2 (bipy), 154.4 (bipy), 154.5 (bipy), 204.8 (CO), 223.0 (CO). Anal. Calc for $C_{26}H_{16}O_4FeN_2Mo$ (572.2): C, 54.58; H, 2.82; N, 4.90. Found: C, 54.46; H, 3.11; N, 4.66.

Synthesis of Fc-C$\equiv$C-bipy[Mn(CO)$_3$Br] (6). $Mn(CO)_5Br$ (**4b**) (70 mg, 0.255 mmol) and **3** (85 mg, 0.233 mmol) were dissolved in 20 mL of ethanol, and the solution was heated at reflux for 30 min, whereby the color changed from orange to dark red. After cooling the reaction mixture to 25 °C the solvent was reduced in volume to 5 mL, and 15 mL of diethyl ether was added. On cooling the resulting solution to −30 °C, complex **6** precipitated. The obtained solid material was washed twice with 10 mL portions of diethyl ether and dried in an oil pump vacuum. Complex **6** was obtained as a red-brown solid. Yield: 80 mg (0.137 mmol, 59% based on **3**). Mp: 175 °C (dec). IR (KBr, cm^{-1}): 2208 (w), ν(C$\equiv$C); 1914 (s), 1932 (s), 2024 (s), ν(CO). ^{1}H NMR ($CDCl_3$): δ 4.31 (s, 5 H, C_5H_5), 4.37 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_β/C_5H_4), 4.60 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_α/C_5H_4), 7.48 (dd,$^3J_{H5'H4'} = 7.8$ Hz, $^3J_{H5'H6'} = 5.4$ Hz, 1 H, H5′), 7.86−8.06 (m, 4 H, H3, H3′, H4, H4′), 9.23 (d, $^3J_{H6'H5'} = 5.4$ Hz, 1 H, H6′), 9.26 (d, $^4J_{H6H4} = 1.2$ Hz, 1 H, H6). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 63.0 (C_i/C_5H_4), 70.0 (C_β/C_5H_4), 70.4 (C_5H_5), 72.1 (C_α/C_5H_4), 72.1 (C_α/C_5H_4), 81.3 (Fc-C$\equiv$*C*-bipy), 98.2 (Fc-*C*$\equiv$C-bipy), 121.8 (bipy), 122.4 (bipy), 124.2 (bipy), 126.1 (bipy), 138.3 (bipy), 139.7 (bipy), 152.9 (bipy), 153.8 (bipy), 155.3 (bipy), 155.3 (bipy). Anal. Calc for $C_{25}H_{16}BrFeMnN_2O_3$ (583.1): C, 51.50; H, 2.77; N, 4.80. Found: C, 51.37; H, 3.29; N, 4.49.

Synthesis of Fc-C$\equiv$C-bipy(PtCl$_2$) (7). A toluene solution (30 mL) containing **3** (100 mg, 0.275 mmol) and $(Me_2S)_2PtCl_2$ (**4c**) (100 mg, 0.256 mmol) was heated to reflux for 18 h. The reaction solution was decanted, and the precipitated dark purple solid was

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washed twice with 20 mL portions of diethyl ether and dried in an oil pump vacuum. Yield: 70 mg (0.111 mmol, 43% based on **4c**). Mp: 210 °C (dec). IR (KBr, cm^{-1}): 2199 (m), ν(C≡C). ESI-MS [*m*/*z* (rel int)]: [M^+] 630.0 (55), [$M^+ - PtCl_2$] 365 (100). Anal. Calc for $C_{22}H_{16}Cl_2FeN_2Pt$ (630.2): C, 41.93; H, 2.56; N, 4.44. Found: C, 42.29; H, 2.57; N, 4.30. (Due to insolubility in common NMR solvents, no ^{1}H NMR spectrum of **7** could be recorded.)

Synthesis of [Fc-C≡C-bipy{Ru(bipy)$_2$}](PF$_6$)$_2$ (8). An ethanolic solution (20 mL) containing **3** (100 mg, 0.27 mmol) and Ru(bipy)$_2$Cl$_2$·2H$_2$O (**4d**) (142 mg, 0.27 mmol) was heated at reflux for 12 h. The resulting red solution was cooled to 0 °C, and a saturated aqueous solution of ammonium hexafluorophosphate (125 mg, 0.77 mmol) was added. The immediately formed red precipitate was filtered, washed successively with water (10 mL), ethanol (10 mL), and diethyl ether (20 mL), and finally dried in an oil pump vacuum to give 265 mg (0.248 mmol, 92% based on **4d**) of the title complex. Mp: 220 °C (dec). IR (KBr, cm^{-1}): 2201 (w), ν(C≡C); 840 (s), ν(P−F). ^{1}H NMR ((CD_3)$_2$CO): δ 4.19 (s, 5 H, C_5H_5), 4.35 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_β/C_5H_4), 4.46 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_α/C_5H_4), 7.53−7.62 (m, 5 H, bipy), 7.96−7.99 (m, 2 H, bipy), 8.01−8.11 (m, 3 H, bipy), 8.15−8.25 (m, 7 H, bipy), 8.75−8.83 (m, 6 H, bipy). $^{13}C\{^1H\}$ NMR ((CD_3)$_2$CO): δ 63.5 (C_i/C_5H_4), 70.7 (C_β/C_5H_4), 70.9 (C_5H_5), 72.47 (C_α/C_5H_4), 72.53 ($C_{\alpha'}/C_5H_4$), 81.4 (Fc-C≡*C*-bipy), 98.1 (Fc-*C*≡C-bipy), 124.9 (bipy), 125.3 (bipy), 125.4 (bipy), 125.5 (bipy), 125.6 (bipy), 128.7(bipy), 128.8 (bipy), 138.9 (bipy), 139.0 (bipy), 140.3 (bipy), 152.5 (bipy), 152.67 (bipy), 152.7 (bipy), 152.8 (bipy), 153.0 (bipy), 153.7 (bipy), 156.3 (bipy), 157.7 (bipy), 157.9 (bipy), 158.01 (bipy), 158.04 (bipy), 158.1 (bipy). $^{31}P\{^1H\}$ NMR (d_6-acetone): δ −145.2 (septet, $^1J_{PF} = 708$ Hz, PF_6). Anal. Calc for $C_{42}H_{32}F_{12}FeN_6P_2Ru$ (1067.6): C, 47.25; H, 3.02; N, 7.87. Found: C, 46.45; H, 3.21; N, 8.00.

Synthesis of Fc-C≡C-bipy[Pt(C≡CSiMe$_3$)$_2$] (10). To **7** (50 mg, 0.079 mmol) suspended in 50 mL of dichloromethane and 10 mL of diisopropylamine were added trimethylsilylacetylene (50 mg, 0.51 mmol) and [CuI] (1 mg, 0.005 mmol). The reaction mixture was stirred for 15 h at 25 °C. After filtration through alumina the solvent was reduced in volume to 3 mL and **10** was precipitated by addition of *n*-hexane (20 mL), washed twice with *n*-hexane (10 mL), and dried in an oil pump vacuum. Complex **10** was obtained as a pale red solid. Single crystals suitable for X-ray structure determination were grown by distillation of petroleum ether into an acetonitrile solution containing **10** at 25 °C. Yield: 50 mg (0.063 mmol, 84% based on **7**). Mp: 195 °C (dec). IR (KBr, cm^{-1}): 2204 (m), ν(*Fc*C≡C); 2055 (m), 2039 (m), ν(*Pt*C≡C). ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9 H, $SiMe_3$), 0.31 (s, 9 H, $SiMe_3$), 4.25 (s, 5 H, C_5H_5), 4.35 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_β/C_5H_4), 4.53 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_α/C_5H_4), 7.46 (m, 1 H, H5′), 8.07−8.13 (m, 4 H, H3, H3′, H4, H4′), 9.51 (bs, $^3J_{PtH} = 26$ Hz, 2 H, H6, H6′). ESI-MS [*m*/*z* (rel int)]: [M^+] 753 (100), [M_2^+] 1507 (40). Anal. Calc for $C_{32}H_{34}FeN_2PtSi_2$·1/4 CH_2Cl_2 (774.96): C, 49.98; H, 4.49; N, 3.61. Found: C, 50.07; H, 4.60; N, 3.47.

Synthesis of {Fc-C≡C-bipy[Pt(*μ*-*σ*,*π*-C≡CSiMe$_3$)$_2$]Cu}BF$_4$ (12). To **10** (50 mg, 0.063 mmol) dissolved in 30 mL of THF was added [Cu(CH_3C≡N)$_4$]BF$_4$ (**11**) (20 mg, 0.063 mmol) in one portion. Upon 12 h of stirring at 25 °C, the color of the reaction mixture changed from red to purple. The solvent was reduced in volume (5 mL), and **12** was precipitated upon addition of *n*-hexane (20 mL), washed twice with *n*-hexane (10 mL), and dried in an oil-pump vacuum. Trimetallic **12** was obtained as a purple solid. Yield: 55 mg (0.061 mmol, 97% based on **10**). Mp: 188 °C (dec). IR (KBr, cm^{-1}): 2207 (m), ν(*Fc*C≡C); 1977 (m), 1961 (m), ν(*Pt*C≡C); 1084 (s), 1053 (s), ν(BF). ^{1}H NMR (CD_3CN): δ 0.31 (s, 9 H, $SiMe_3$), 0.37 (s, 9 H, $SiMe_3$), 4.31 (s, 5 H, C_5H_5), 4.44 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_β/C_5H_4), 4.61 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_α/C_5H_4), 7.71 (ddd, $^3J_{H5'H4'} = 7.3$ Hz, $^3J_{H5'H6'} = 5.2$ Hz, $^4J_{H5'H3'} = 1.8$ Hz, 1 H, H5′), 8.19−8.25 (m, 3 H, H3, H3′, H4), 8.27 (ddd, $^3J_{H4'H3'} = {}^3J_{H4'H5'} = 8$ Hz, $^4J_{H4'H6'} = 1.4$ Hz, 1 H, H4′), 8.97 (d, $^3J_{H6'H5'} = 5.2$ Hz, 1 H, H6′), 9.01 (dd, $^4J_{H6H4} = 2$ Hz, $^5J_{H6H3} = 1$ Hz, H6). ESI-MS [*m*/*z* (rel int)]: [$M^+ - BF_4$] 817 (85), [$M^+ - BF_4$+Fc-C≡C-bipy[Pt(C≡CSiMe$_3$)$_2$] 1570 (100). Anal. Calc for $C_{32}H_{34}BCuF_4FeN_2PtSi_2$ (904.08): C, 42.51; H, 3.79; N, 3.10. Found: C, 42.31; H, 3.88; N, 4.16.

Synthesis of [Fc-C≡C-bipy{[Ti](*μ*-*σ*,*π*-C≡CSiMe$_3$)$_2$}Cu]PF$_6$ (14a). [{[Ti](*μ*-*σ*,*π*-C≡CSiMe$_3$)$_2$}Cu(N≡CCH$_3$)]PF$_6$ (**13a**) (145 mg, 0.19 mmol) was dissolved in 30 mL of THF, and complex **3** (70 mg, 0.19 mmol) was added in one portion. After 3 h of stirring at 25 °C the color of the reaction mixture was red. The solution was filtered through a pad of Celite, and all volatiles were removed in an oil pump vacuum. The remaining red solid was washed twice with 15 mL portions of *n*-hexane and was dried in an oil pump vacuum. Single crystals of the title compound, suitable for X-ray structure analysis, could be obtained by slow diffusion of *n*-hexane into a dichloromethane solution containing **14a** at 0 °C. Yield: 160 mg (0.147 mmol, 78% based on **13a**). Mp: 215 °C (dec). IR (KBr, cm^{-1}): 2210 (w), ν(*Fc*C≡C); 1925 (w), ν(*Ti*C≡C); 839 (s), ν(PF). ^{1}H NMR ((CD_3)$_2$CO): δ −0.41 (s, 18 H, $SiMe_3$), 0.32 (s, 9 H, $SiMe_3$), 0.34 (s, 9 H, $SiMe_3$), 4.28 (s, 5 H, C_5H_5 [Fc]), 4.41 (pt, $J_{HH} = 1.9$ Hz, H_β/C_5H_4 [Fc]), 4.61 (pt, $J_{HH} = 1.9$ Hz, H_α/C_5H_4 [Fc]), 6.54−6.60 (m, 8 H, C_5H_4), 7.88 (ddd, $^3J_{H5'H4'} = 7.6$ Hz, $^3J_{H5'H6'} = 4.5$ Hz, $^4J_{H5'H3'} = 1$ Hz, 1 H, H5′), 8.33−8.40 (m, 2 H, H4, H4′), 8.80 (d, $^3J_{H3H4} = 8.4$ Hz, 1 H, H3), 8.82 (d, $^3J_{H3'H4'} = 8.2$ Hz, 1 H, H3′), 8.86 (dd, $^4J_{H6H4} = 2$ Hz, $^5J_{H6H3} = 0.8$ Hz, 1 H, H6), 8.94 (ddd, $^3J_{H6'H5'} = 4.5$ Hz, $^4J_{H6'H4'} = 1.7$ Hz, $^5J_{H6'H3'} = 0.8$ Hz, 1 H, H6′). $^{13}C\{^1H\}$ NMR ((CD_3)$_2$CO): δ −0.6 ($SiMe_3$), 0.2 ($SiMe_3$), 0.3 ($SiMe_3$), 64.0 (C_i/C_5H_4 [Fc]), 70.7 (C_β/C_5H_4 [Fc]), 71.0 (C_5H_5 [Fc]), 72.7 (C_α/C_5H_4 [Fc]), 81.8 (Fc-C≡*C*-bipy), 97.5 (Fc-*C*≡C-bipy), 116.6 (*CH*/C_5H_4), 116.7 (*CH*/C_5H_4), 117.8 (*CH*/C_5H_4), 118.1 (*CH*/C_5H_4), 123.4 (bipy), 124.0 (bipy), 124.8 (C_i/C_5H_4), 125.0 (C_i/C_5H_4), 125.1 (bipy), 128.0 (bipy), 133.6 (C≡*C*Si), 141.1 (bipy), 142.3 bipy), 149.9 (bipy), 151.2 (bipy), 151.5 (bipy), 152.0 (bipy), 167.0 (Ti*C*≡C). $^{31}P\{^1H\}$ NMR ((CD_3)$_2$CO): δ −145.2 (septet, $^1J_{P-F} = 708$ Hz, PF_6). Anal. Calc for $C_{48}H_{60}CuF_6FeN_2PSi_4Ti$ (1089.6): C, 52.91; H, 5.55; N, 2.57. Found: C, 52.62; H, 5.67; N, 2.78.

Synthesis of [Fc-C≡C-bipy{[Ti](*μ*-*σ*,*π*-C≡CSiMe$_3$)$_2$}Ag]ClO$_4$ (14b). {[Ti](*μ*-*σ*,*π*-C≡CSiMe$_3$)$_2$}AgOClO$_3$ (**13b**) (140 mg, 0.196 mmol) was dissolved in 30 mL of THF, and **3** (72 mg, 0.196 mmol) was added in one portion. After 2 h of stirring at 25 °C the color of the reaction mixture was red. The solution was filtered through a pad of Celite, and all volatiles were removed in an oil pump vacuum. The remaining red solid was washed twice with 15 mL portions of *n*-hexane and afterward was dried in an oil pump vacuum. Yield: 155 mg (0.143 mmol, 73% based on **13b**). Mp: 135 °C (dec). IR (KBr, cm^{-1}): 2208 (m), ν(*Fc*C≡C); 1953 (w), ν(*Ti*C≡C); 1088 (s), ν(ClO). ^{1}H NMR ($CDCl_3$): δ −0.29 (s, 18 H, $SiMe_3$), 0.29 (s, 18 H, $SiMe_3$), (s, 5 H, C_5H_5 [Fc]), 4.33 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_β/C_5H_4 [Fc]), 4.58 (pt, $J_{HH} = 1.9$ Hz, 2 H, H_α/C_5H_4 [Fc]), 6.46 (pt, $J_{HH} = 2.3$ Hz, 4 H, C_5H_4), 6.51 (pt, $J_{HH} = 2.3$ Hz, 4 H, C_5H_4), 7.62 (ddd, $^3J_{H5'H4'} = 7.8$ Hz, $^3J_{H5'H6'} = 5$ Hz, $^4J_{H5'H3'} = 1$ Hz, 1 H, H5′), 8.18 (dd, $^3J_{H4H3} = 8.4$ Hz, $^4J_{H4H6} = 2.2$ Hz, 1 H, H4), 8.19 (ddd, $^3J_{H4'H3'} = {}^3J_{H4'H5'} = 7.8$ Hz, $^4J_{H4'H6'} = 1.8$ Hz, 1 H, H4′), 8.51−8.56 (m, 3 H, H3, H3′, H6), 8.60 (d, $^3J_{H6'H5'} = 5$ Hz, 1 H, H6′). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −0.06 ($SiMe_3$), 0.15 ($SiMe_3$), 63.4 (C_i/C_5H_4, Fc), 69.8 (C_β/C_5H_4 [Fc]), 70.3 (C_5H_5 [Fc]), 71.9 (C_α/C_5H_4 [Fc]), 81.5 (Fc-C≡*C*-bipy), 96.7 (Fc-*C*≡C-bipy), 117.4 (*CH*/C_5H_4), 119.2 (*CH*/C_5H_4), 123.5 (bipy), 123.6 (C_i/C_5H_4), 124.2 (bipy), 126.0 (bipy), 126.2 (bipy), 138.6 (d, $J_{CAg} = 4.3$ Hz, C≡*C*Si), 140.4 (bipy), 141.7 bipy), 149.7 (bipy), 150.4 (bipy), 151.6 (bipy), 151.6 (bipy), 153.7 (d, $J_{CAg} = 14.9$ Hz, Ti*C*≡C). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −18.4 (d, $^2J_{AgSi} = 2$ Hz, C≡CSiMe$_3$), −5.1 ($C_5H_4SiMe_3$). Anal. Calc for $C_{48}H_{60}AgClFeN_2OSi_4Ti$ (1080.3): C, 52.97; H, 5.56; N, 2.57. Found: C, 52.82; H, 5.70; N, 2.45.

Crystal Structure Determinations. Crystal data for **3**, **10**, and **14a** are presented in Table 3. All data were collected on a Bruker Smart CCD 1k diffractometer at 203(2) K (**3**), 178(2) K (**10**), or

298 K (**14a**) using oil-coated, shock-cooled crystals[26] using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97[27] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[28] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. In **14a** the PF_6 counterion and one Me_3Si group are disordered and have been refined to split occupancies of 0.54/0.46 (PF_6) and 0.61/0.39 ($SiMe_3$), respectively.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, angles, torsion angles, and anisotropic displacement parameters for **3**, **10**, and **14a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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