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Diphenylphosphinoferrocene Gold(I) Acetylides: Synthesis of Heterotri- and Heterotetrametallic Transition Metal Complexes

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The synthesis and reaction chemistry of heterobimetallic $FcPPh_2AuCl$ (**1**) and $FcPPh_2Au\text{-}C\equiv CR$ compounds (**3a**, R = bipy; **3b**, R = $C_6H_4\text{-}4\text{-}C\equiv N$; **3c**, R = $C_5H_4N\text{-}4$; **3d**, R = NCN-H; **3e**, R = NCN-I; Fc = $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Fe$; bipy = 2,2′-bipyridyl-5-yl; NCN = $[C_6H_2(CH_2NMe_2)_2\text{-}2,6]^-$) toward diverse organometallic molecules is described. In context with this background, **1** was prepared by reacting $FcPPh_2$ with (tht)AuCl (tht = *t*etra*h*ydro*t*hiophene). The reaction of **1** either with $HC\equiv CR$ (**2a**, R = bipy; **2b**, R = $C_6H_4\text{-}4\text{-}C\equiv N$; **2c**, R = $C_5H_4N\text{-}4$) or with the lithium acetylides $LiC\equiv CR$ (**2d**, R = NCN-H; **2e**, R = NCN-I) gave complexes **3a**−**3e** in good yield. In **1** the gold(I) chloride entity was further reacted with the organometallic alkyne $HC\equiv CML_n$ (**4a**, ML_n = $(\eta^6\text{-}C_6H_5)Cr(CO)_3$; **4b**, ML_n = Fc; **4c**, ML_n = Rc; Rc = $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Ru$) to afford the heterotrimetallic complexes $FcPPh_2Au\text{-}C\equiv CML_n$ (**5a**, ML_n = $(\eta^6\text{-}C_6H_5)Cr(CO)_3$; **5b**, ML_n = Fc; **5c**, ML_n = Rc) in which three different transition metal atoms are connected via rigid-rod structured carbon-rich units. Complexes **3a**−**3e** feature with their terminal nitrogen donor groups a further binding site, which allows the introduction of a third metal-containing fragment. In this context, the reaction of **3b** with $[Ru]N\equiv N[Ru]$ (**6**) ([Ru] = $[\eta^3\text{-}mer\text{-}\{2,6\text{-}(Me_2NCH_2)_2C_5H_3N\}RuCl_2]$) resulted in the formation of neutral heterotrimetallic $FcPPh_2Au\text{-}C\equiv C\text{-}C_6H_4\text{-}4\text{-}C\equiv N\text{-}[Ru]$ (**7**). The synthesis of an even heterotetrametallic complex $[FcPPh_2Au\text{-}C\equiv C\text{-}C_5H_4N\text{-}Cu\{(Me_3SiC\equiv C)_2[Ti]\}]OTf$ (**9**) could be achieved by treatment of **3c** with the organometallic *π*-tweezer $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}CuOTf$ (**8a**). Heterobimetallic **3a** afforded in a straightforward reaction with equimolar amounts of $(nbd)Mo(CO)_4$ (**14**) (nbd = 1,5-*nor*bor*na*diene) and $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}MX$ (**8b**, M = $Cu(N\equiv CMe)$, X = PF_6; **8c**, M = Ag, X = $OClO_3$), respectively, compounds $FcPPh_2Au\text{-}C\equiv C\text{-}bipy[Mo(CO)_4]$ (**15**) and $(FcPPh_2Au\text{-}C\equiv C\text{-}bipy[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}M])X$ (**16a**, M = Cu, X = PF_6; **16b**, M = Ag, X = ClO_4). The synthesis of the Fe-Au-Pt NCN pincer molecule $FcPPh_2Au\text{-}C\equiv C\text{-}NCN\text{-}Pt\text{-}C\equiv CR$ (**13a**, R = bipy; **13b**, R = $C_6H_4\text{-}4\text{-}C\equiv N$) was possible by the consecutive reaction of $Me_3SiC\equiv C\text{-}NCN\text{-}PtCl$ (**10**) with **Li-2a** or **Li-2b** to give $Me_3SiC\equiv C\text{-}NCN\text{-}Pt\text{-}C\equiv CR$ (**11a**, R = bipy; **11b**, R = $C_6H_4\text{-}4\text{-}C\equiv N$), which with $[n\text{-}Bu_4N]F$ produced $HC\equiv C\text{-}NCN\text{-}Pt\text{-}C\equiv CR$ (**12a**, R = bipy; **12b**, R = $C_6H_4\text{-}4\text{-}C\equiv N$). On reacting **12a** and **12b** with **1**, complexes **13a** and **13b** were formed, which are highly insoluble, and hence, no further reactions were carried out. The solid state structures of **3a**, **3b**, **3e**, **5b**, **5c**, and **16a** are reported. Most characteristic for these complexes is that the appropriate transition metals are linked by carbon-rich organic bridging units. The electrochemical properties of selected samples (**3a**−**3c**, **5a**−**5c**, **7**, **9**, **16a**, and **16b**) are reported. The cyclovoltammetric data show that there is no significant influence of the organic and organometallic acetylide units on the redox potential of the diphenylphosphino ferrocene in **3a**− **3c** and **5a**−**5c**. Remarkable is that the chelate coordination of the bipyridyl unit to Cu(I) in **16a** results in a reduction of Cu(I) followed by reoxidation of Cu(0) without any structural change of the molecule involved, which is unique in titanium(IV)−copper(I) chemistry.

Introduction

In recent years, the chemistry of organometallic complexes in which transition metals are spanned by organic and/or inorganic bridging units was intensively studied in regard to their novel structural, spectroscopic, and photophysical properties.[1,2] For example, employing alkynyls as linking groups between transition metal atoms allowed the synthesis of diverse rigid-rod structured assemblies with redox-active metal-organic or organometallic complex termini, e.g. functionalized ferrocenes.[1] Due to its robustness, electron richness, redox properties, and the well-established synthesis methodologies for its incorporation into more complex structures, ferrocene has become an excellent building block for the preparation of diverse organometallic molecules with tailor-made properties.[3] In this respect, ferrocenyl moieties could successfully be introduced in heteromultimetallic coordination complex chemistry by using the molecular, modular "Tinkertoy" approach.[4] This concept allows the specific building design of new types of complexes with novel and, hence, unique chemical and physical properties.[4]

Another extensively investigated building block in the synthesis of higher nuclear rigid-rod structured compounds is gold(I) phosphine acetylide $(R_3P)Au\text{-}C\equiv CR$ (R = singly bonded organic or organometallic group), since such species have attracted growing attention due to their rich luminescence properties and their ability to build supramolecular structures based on the aurophilic nature of gold.[5]

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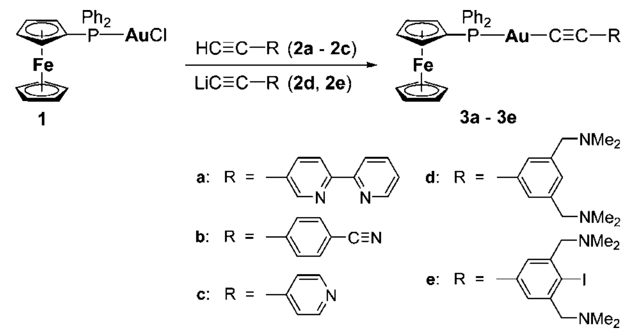
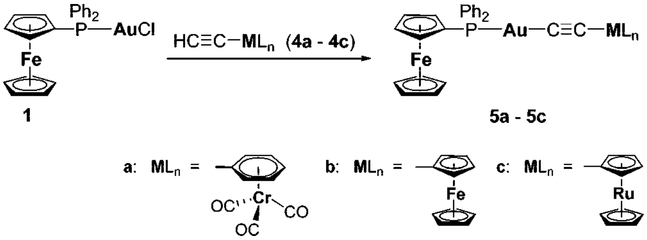
In the context of this background, herein we report the synthesis, reaction chemistry, structure, and electrochemical behavior of diphenylphosphinoferrocene-coordinated gold(I) acetylides.

Results and Discussion

Scheme 1



Scheme 2



The diphenylphosphinoferrocene gold(I) acetylides Fc-PPh$_2$-Au-C≡CR (**3a**, R = bipy; **3b**, R = C_6H_4-4-C≡N; **3c**, R = C_5H_4N-4; **3d**, R = NCN-H; **3e**, R = NCN-I; Fc = (η^5-C_5H_5)(η^5-C_5H_4)Fe; bipy = 2,2′-bipyridyl-5-yl; NCN = [$C_6H_2(CH_2NMe_2)_2$-2,6]$^-$) were prepared from the reaction of their chloro precursor Fc-PPh$_2$-AuCl (**1**) with terminal alkynes HC≡CR (**2a**, R = bipy; **2b**, R = C_6H_4-4-C≡N; **2c**, R = C_5H_4N-4) in the presence of [CuI] in diethyl amine at 25 °C (Scheme 1).[5a] However, this method is limited to the preparation of **3a**−**3c**. Treatment of **1** with HC≡CR (**2d**, R = NCN-H; **2e**, R = NCN-I) admittedly gave the desired complexes **3d** and **3e** in very low yield, but these compounds could not be separated from the unreacted starting materials, and hence, another synthesis route had to be developed. Reacting **1** with a 50% excess of the lithium acetylides **Li-2d** and **Li-2e** in diethyl ether at low temperature resulted in the formation of yellow **3d** and **3e**, which, after appropriate workup, could be isolated in good yield (Experimental Section).

The synthesis strategy used in the preparation of **3a**−**3c** (Scheme 1) could successfully be transferred to organometallic alkynes of type HC≡C-ML$_n$ (**4a**, ML$_n$ = (η^6-C_6H_5)Cr(CO)$_3$; **4b**, ML$_n$ = Fc; **4c**, ML$_n$ = Rc; Rc = (η^5-C_5H_5)(η^5-C_5H_4)Ru), as shown in Scheme 2. Reacting the gold(I) chloride **1** with **4a**−**4c** gave the heterotrimetallic Fe-Au-M system FcPPh$_2$Au-C≡CML$_n$ (**5a**, ML$_n$ = (η^6-C_6H_5)Cr(CO)$_3$; **5b**, ML$_n$ = Fc; **5c**, ML$_n$ = Rc), in which three different transition metal atoms are connected by carbon-rich bridging units. After column chromatography these compounds were isolated as orange solid materials (Experimental Section).

Compounds **3a**−**3e** and **5a**−**5c** are soluble in organic solvents such as diethyl ether, tetrahydrofuran, dichloromethane, and toluene. While solutions containing **5a** rapidly turn green after exposure to air, due to oxidation processes, all other heterobi- and heterotrimetallic compounds are stable.

All newly synthesized complexes gave satisfactory elemental analyses and have been fully characterized by IR and NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}). The solid state structures of **3a**, **3b**, **3e**, **5b**, and **5c** were determined by single-crystal X-ray structure analysis.

The IR spectra of **3** and **5** display a characteristic absorption band for the C≡C unit at ca. 2120 cm^{-1}, which is almost not influenced by the organic or organometallic groups R or ML$_n$. Further typical vibrations are found at 2225 cm^{-1} for the cyano unit in **3b** and at 1883 and 1963 cm^{-1} for the carbonyl ligands in **5a**.[6,7]

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Table 1. Selected Bond Distances and Angles for 3a, 3b, 3e, 5b, and 5c

	3a	**3b**	**3e**	**5b**	**5c**
			Bond Distances (Å)		
P1−Au1	2.2792(9)	2.2715(8)	2.2716(13)	2.2653(8)	2.2719(11)
Au1−C23	2.051(4)	1.995(3)	1.993(5)	2.010(3)	1.999(5)
C23−C24	1.128(6)	1.192(5)	1.181(7)	1.177(5)	1.189(5)
C24−C25	1.462(5)	1.429(5)	1.454(7)	1.416(5)	1.429(6)
Fe1−D_1[a]	1.6551(2)	1.6453(1)	1.6489(3)	1.6311(2)	1.6337(2)
Fe1−D_2[b]	1.6377(2)	1.6572(1)	1.6321(3)	1.6561(2)	1.6482(2)
Fe2(Ru1)−D_3[c]				1.6367(1)	1.8024(1)
Fe2(Ru1)−D_4[d]				1.6431(1)	1.8053(2)
C28−I1			2.111(5)		
C31−N1		1.131(5)			
			Angles (deg)		
P1−Au1−C23	176.79(10)	177.88(12)	177.23(15)	178.07(10)	178.59(13)
Au1−C23−C24	175.4(4)	175.1(3)	178.6(5)	170.6(3)	173.3(4)
C23−C24−C25	175.5(5)	175.8(4)	176.8(6)	176.4(4)	175.9(5)

[a] D_1 = centroid of C_5H_4 at Fe1. [b] D_2 = centroid of C_5H_5 at Fe1. [c] D_3 = centroid of C_5H_4 at Fe2 (Ru1). [d] D_4 = centroid of C_5H_5 at Fe2 (Ru1).

Table 2. Electrochemical Data of 3a−3c, 5a−5c, 7, 9, 16a, and 16b[a]

	Reduction			*Oxidation*	
compd	bipy/bipy$^-$ E_0 (ΔE_p)	M(I)/M(0) $E_{p,red}/E_0$ (ΔE_p)	Ti(IV)/Ti(III) E_0 (ΔE_p)	Fe(II)/Fe(III) E_0 (ΔE_p)	M^n/M^{n+1} $E_{p,ox}/E_0$ (ΔE_p)
3a	−2.69 (0.23)[b]			0.305 (0.10) 0.28 (0.135)[b]	
3b				0.31 (0.105)	
3c				0.31 (0.10)	
5a				0.325 (0.18)	0.56[c]
5b				0.32 (0.10)	−0.005 (0.10)[d]
5c				0.35 (0.12)	0.30[e]
7				0.31 (0.10)	−0.245 (0.085)[e]
9[b]		−1.30[f]	−1.80 (0.18)[h]	0.28 (0.115)	
16a[b]	−2.72 (0.16)	−1.41 (0.115)[f]	−1.635 (0.18) −1.76 (0.18)[h]	0.27 (0.115)	
16b[b]	−2.71 (0.18)	−1.30[g]	−1.75 (0.16)[h]	0.27 (0.12)	

[a] Cyclic voltammograms from 10^{-3} M solutions in dichloromethane at 25 °C with $[n\text{-}Bu_4N]PF_6$ (0.1 M) as supporting electrolyte, scan rate = 0.10 $V \cdot s^{-1}$. All potentials are given in V and are referenced to the FcH/FcH$^+$ redox couple (FcH = $(\eta^5\text{-}C_5H_5)_2Fe$) with E_0 = 0.00 V (ΔE_p = 0.10 V)).[20,21] [b] In tetrahydrofuran. [c] M^n = Cr(0). [d] M^n = Fe(II). [e] M^n = Ru(II). [f] M = Cu. [g] M = Ag. [h] From $[Ti](C{\equiv}CSiMe_3)_2$.

The $^{31}P\{^1H\}$ NMR spectra of **3** and **5** show one singlet at ca. 36 ppm, which is, compared to **1** (27.6 ppm),[5d] shifted by 8 ppm to lower field. This can be used to monitor the progress of the reaction of **1** with **2** or **4**. The chemical shift of this group is thereby not dependent on the nature of R.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of all complexes show resonance signals and coupling patterns that are consistent with their proposed structures (Experimental Section). In all cases, no residual signals attributable to acetylenic hydrogens were observed in the ^1H NMR spectra of **3** and **5**, proving that in the synthesis of these complexes the substitution of acetylenic protons by the corresponding gold(I) fragment has been quantitative. In the $^{13}C\{^1H\}$ NMR spectra of **3a**−**3e** a resonance signal at 102–105 ppm is observed which can be assigned to one of the sp-hybridized acetylide carbon atoms at gold(I). Nevertheless for **5a**−**5c** such a signal could not be detected. However, due to the fact that only for **3e** a splitting of this signal into a doublet is observed, we cannot unequivocally assign this resonance. Most representative for **1**, **3**, and **5**, compared to the starting material diphenylphosphinoferrocene, is the increase of their C_6H_5 and C_5H_4 J_{CP} coupling constants as a result of the phosphorus coordination to gold(I) (Experimental Section).[5]

Single crystals of **3a**, **3b**, **3e**, **5b**, and **5c** suitable for X-ray diffraction studies could be grown by slow vapor diffusion of petroleum ether into a dichloromethane solution of the respective transition metal complexes at room temperature. The solid state structures of **3a**, **3b**, **3e**, **5b**, and **5c** are shown in Figures 1–5. Their bond distances (Å) and angles (deg) are given in Table 1. The crystal and structure refinement data are summarized in Table 3 (**3a**, **3b**, and **3e**) and Table 4 (**5b**, **5c**) (Experimental Section).

The overall structural features of **3a**, **3b**, **3e**, **5b**, and **5c** are similar to those of related structurally characterized diphenylphosphinoferrocene- and phosphine−gold(I) acetylide-containing compounds with gold in an essentially linear arrangement (P1-Au1-C23-C24) (Figures 1–5, Table 1).[5] The cyclopentadienyl rings of the ferrocene and ruthenocene (**5c**) entities, respectively, are rotated by 3.13(3)° (**3a**), 7.66(1)° (**3b**), 9.90(6)° (**3e**), 9.86(4)° and 7.16(6)° (**5b**), as well as 9.29(6)° and 9.74(1)° (**5c**) to each other, which verifies an almost eclipsed conformation. The distance of the C≡C bond that is attached to gold(I) is for the bipyridyl-substituted species **3a** 1.128(6) Å, while in all other molecules this separation is found between 1.177(5) and 1.192(5) Å (Table 1). All other bond distances and angles require no further discussion, because they agree well with those parameters described for related transition metal complexes.[5] The torsion angle between the two pyridine rings of the bipyridyl unit in **3a** is 18.8(6)°, indicating the nonplanarity of this building block (Figure 1).

The pendant nitrogen-containing mono- and bidentate ligands in **3a**−**3e** should be able to coordinate to different transition

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Table 3. Crystal and Intensity Collection Data for 3a, 3b, and 3e

	3a	**3b**	**3e**
fw	831.28	693.29	908.36
chemical formula	$C_{35}H_{28}AuCl_2FeN_2P$	$C_{31}H_{23}AuFeNP$	$C_{36}H_{37}AuFeIN_2P$
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$P2(1)/c$
a (Å)	9.0155(10)	25.095(2)	8.993(2)
b (Å)	13.2674(15)	9.5949(8)	12.464(3)
c (Å)	14.0530(16)	21.9949(14)	31.133(8)
α (deg)	89.565(2)	90.014(6)	90
β (deg)	85.665(2)	102.725(6)	90.645(5)
γ (deg)	72.289(2)	89.967(7)	90
V (Å^3)	1596.5(3)	5166.0(7)	3489.5(16)
ρ_{calc} (g cm^{-3})	1.729	1.783	1.729
F(000)	812	2688	1760
cryst dimens (mm^3)	0.3 × 0.3 × 0.2	0.3 × 0.2 × 0.1	0.4 × 0.3 × 0.2
Z	2	8	4
max., min. transmn	0.9999, 0.48753	25.9997, 2.8406	0.99999, 0.65829
absorp coeff (μ, mm^{-1})	5.289	6.317	5.572
scan range (deg)	1.45 to 28.31	2.85 to 26.07	1.76 to 26.44
index ranges	$-11 \leq h \leq 12$ $-17 \leq k \leq 17$ $0 \leq l \leq 18$	$-31 \leq$ h ′ 31 $-11 \leq k \leq 11$ $-27 \leq l \leq 27$	$-11 \leq h \leq 11$ $0 \leq k \leq 15$ $0 \leq l \leq 38$
total no. of reflns	19 287	24 146	40 100
no. of unique reflns	7765	5108	7521
R(int)	0.0352	0.0261	0.0354
no. of data/restraints/params	7765/0/379	5108/0/316	7168/87/413
goodness-of-fit on F^2	1.011	0.989	1.049
R1,[a] wR2[a] [$I \geq 2\sigma(I)$]	0.0352, 0.0839	0.0235, 0.0486	0.0344, 0.0861
R1,[a] wR2[a] (all data)	0.0436, 0.0883	0.0454, 0.0519	0.0453, 0.0930
max., min. peak in final Fourier map (e Å^{-3})	1.068, −1.172	0.731, −0.277	1.407, −1.468

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

Table 4. Crystal and Intensity Collection Data for 5b, 5c, and 16a

	5b	**5c**	**16a**
fw	776.20	821.42	1501.33
chemical formula	$C_{34}H_{28}AuFe_2P$	$C_{34}H_{28}AuFePRu$	$C_{60}H_{70}AuCuF_6FeN_2P_2Si_4Ti$
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.9659(6)	8.2561(8)	16.9879(8)
b (Å)	12.0238(10)	11.9946(14)	21.3635(11)
c (Å)	15.1400(13)	14.9913(19)	22.9555(11)
α (deg)	100.165(7)	99.395(10)	98.8570(10)
β (deg)	94.558(7)	93.651(9)	95.7660(10)
γ (deg)	96.371(7)	96.474(9)	105.0720(10)
V (Å^3)	1411.2(2)	1450.2(3)	7861.9(7)
ρ_{calc} (g cm^{-3})	1.827	1.881	1.268
F(000)	756	792	3017
cryst dimens (mm^3)	0.5 × 0.4 × 0.1	0.3 × 0.2 × 0.1	0.3 × 0.06 × 0.05
Z	2	2	4
max., min. transmn	1.56047, 0.27804	1.10872, 0.74670	0.99999, 0.62478
absorp coeff (μ, mm^{-1})	6.278	6.130	2.579
scan range (deg)	2.93 to 26.11	2.85 to 26.00	0.91 to 26.41
index ranges	$-9 \leq h \leq 9$ $-14 \leq k \leq 14$ $-18 \leq l \leq 18$	$-10 \leq h \leq 10$ $-14 \leq k \leq 14$ $-18 \leq l \leq 18$	$-21 \leq h \leq 21$ $-26 \leq k \leq 26$ $0 \leq l \leq 28$
total no. of reflns	13 338	14 629	69 529
no. of unique reflns	5535	5703	32 186
R(int)	0.0227	0.0328	0.0819
no. of data/restraints/params	5535/0/343	5703/0/343	32186/109/1465
goodness-of-fit on F^2	0.999	0.823	1.028
R1,[a] wR2[a] [I ³ $2\sigma(I)$]	0.0231, 0.0535	0.0258, 0.0449	0.0742, 0.2056
R1,[a] wR2[a] (all data)	0.0316, 0.0558	0.0560, 0.0476	0.1488, 0.2472
max., min. peak in final Fourier map (e Å^{-3})	0.628, −0.715	0.667, −0.854	1.888, −1.128

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

metal fragments and consequently should be suitable for the construction of transition metal assemblies of higher nuclearity. Thus, these complexes were reacted with different transition metal sources, of which not all were successful. For example, when **3b** was treated with the metal–carbonyl $W(CO)_5(thf)$, the phosphorus−gold bond was cleaved to form $FcPPh_2W(CO)_5$.[8] A similar behavior was observed for **3c**. A further product could not be characterized and probably results from decomposition.

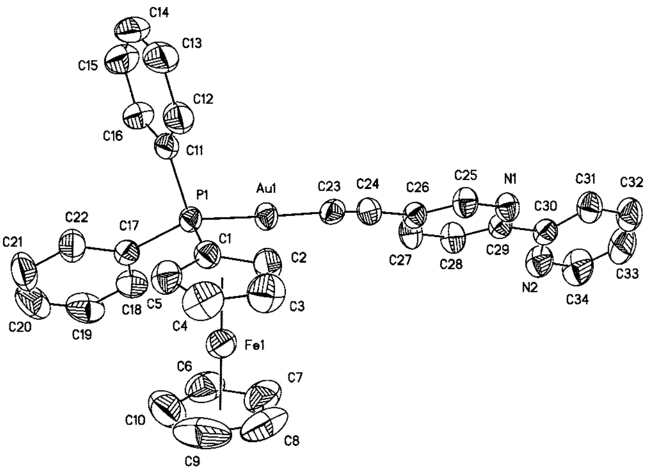


Figure 1. ORTEP (50% ellipsoid probability level) of **3a** with the atom-numbering scheme (the hydrogen atoms and one molecule of dichloromethane are omitted for clarity).

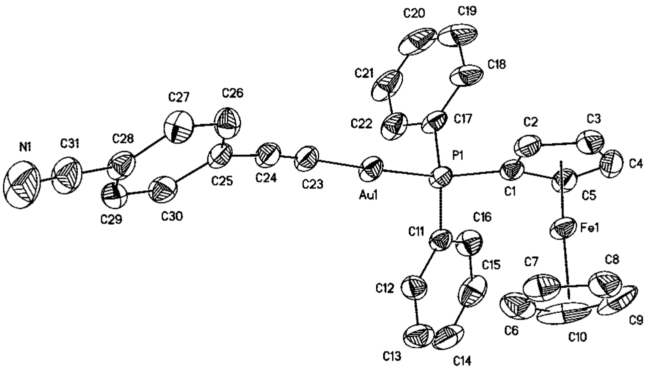


Figure 2. ORTEP (50% ellipsoid probability level) of **3b** with the atom-numbering scheme (the hydrogen atoms are omitted for clarity).

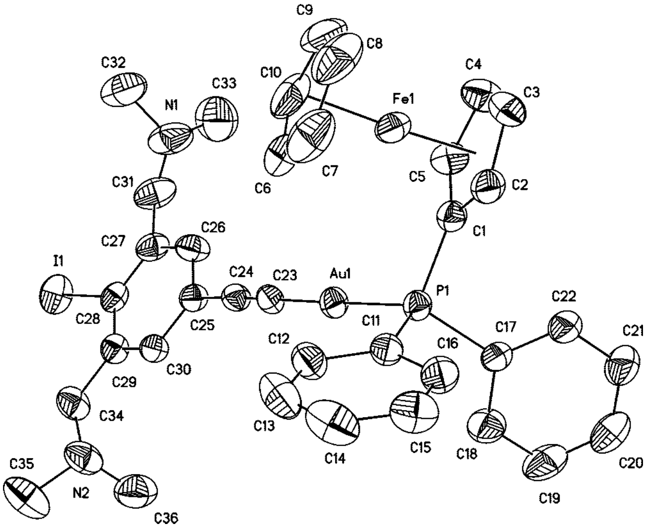


Figure 3. ORTEP (50% ellipsoid probability level) of **3e** with the atom-numbering scheme (the hydrogen atoms are omitted for clarity).

When **3b** is treated with the dinitrogen-bridged diruthenium complex [Ru]N≡N[Ru] (**6**) ([Ru] = [η^3-*mer*-{2,6-$(Me_2NCH_2)_2C_5H_3N$}$RuCl_2$]),[9] the formation of neutral heterotrimetallic **7** occurs by liberation of N_2. The reaction could be followed visually by the change of the color of the reaction solution from yellow to intense red. Monitoring the progress of the reaction was also possible by following the shift of the $\nu_{C\equiv N}$ vibration from 2225 in **3b** to 2199 in **7**, which is a rather unusual shift for η^1-bonded nitriles and points to a C≡N bond weakening, due to the back-bonding properties of the coordinated [Ru] fragment.[6,10]

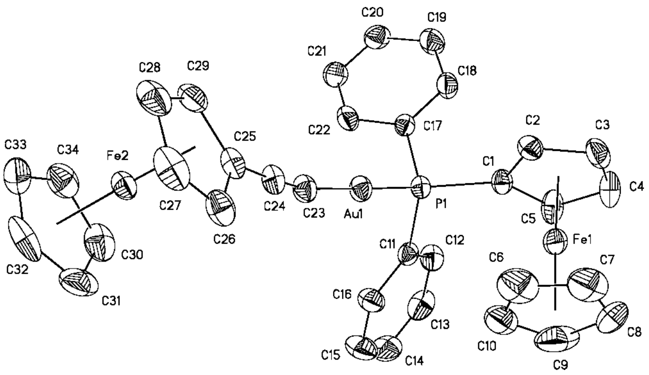


Figure 4. ORTEP (50% ellipsoid probability level) of **5b** with the atom-numbering scheme (the hydrogen atoms are omitted for clarity).

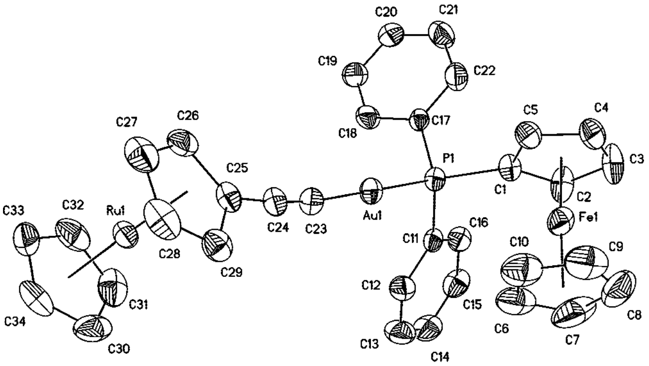
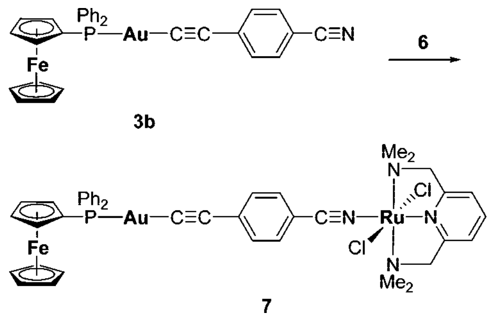


Figure 5. ORTEP (50% ellipsoid probability level) of **5c** with the atom-numbering scheme (the hydrogen atoms are omitted for clarity).



Also complex **3c** should permit the synthesis of heteromultimetallic systems. The capability of the pyridine entity to coordinate to further transition metal building blocks was proven by its reaction with the bis(alkynyl) titanocene−copper(I) complex $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}CuOTf$ (**8a**). Performing this reaction in diethyl ether as the solvent, the desired product precipitated and could be isolated as a shiny golden solid in

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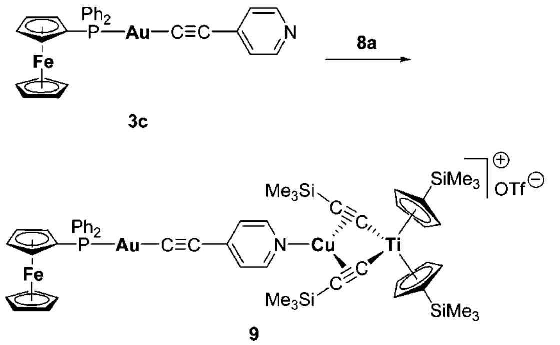
[8] (a) Kotz, J. C.; Nivert, C. L.; Lieber, J. M.; Reed, R. C. *J. Organomet. Chem.* **1975**, *91*, 87. (b) Kotz, J. C.; Nivert, C. L. *J. Organomet. Chem.* **1973**, *52*, 387.

[9] Abbenhuis, R. A. T. M.; del Río, I.; Bergshoef, M. M.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 1749.

[10] Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1.

good yield. In [FcPPh$_2$Au-C$\equiv$C-C$_5$H$_4$N-Cu{(Me$_3$SiC$\equiv$C)$_2$-[Ti]}]OTf (**9**) the metals gold, copper, and titanium are brought in close proximity to each other in a linear fashion. The formation of tetrametallic **9** was evidenced by IR spectroscopy. Upon coordination of the pyridine donor group to copper(I) both C$\equiv$C vibrations, as well at titanium as at gold, are influenced. Compared to **8a** (1924 cm^{-1})[11] the $\nu_{C\equiv CTi}$ frequency is shifted to lower wavenumbers and is found at 1915 cm^{-1} (**9**), while the $\nu_{C\equiv CAu}$ vibration at gold is shifted somewhat to higher wavenumbers due to coordination to copper (Experimental Section).

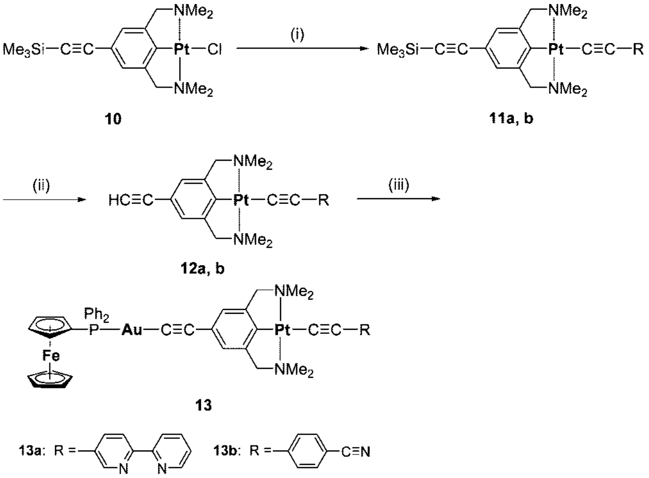


The identity of heterotrimetallic **7** and heterotetrametallic **9** was additionally evidenced from mass spectrometric investigations. The electrospray ionization mass spectra (ESI-MS) show the molecular ion peaks at m/z = 1058.2 [M]$^+$ (**7**) and 1248.2 [M − CF$_3$SO$_3$]$^+$ (**9**), whose mass and isotope distribution pattern are in agreement with the formulated structures.

The standard procedure involving lithiation-*trans*-metalation for the synthesis of platinum-NCN pincers[12] from **3d** and **3e** could not be applied for the preparation of FcPPh$_2$Au-C$\equiv$C-4-NCN-PtCl, a compound that would enable one to anchor further N-ligating sites to the platinum atom via an acetylide bridging unit. Our results showed that the introduction of a PtCl entity to a NCN pincer unit was unsuccessful since competitive reactions occur. Oxidative addition of the C−I bond to palladium(0) by reacting **3e** with [Pd$_2$(dba)$_3$(CHCl$_3$)] (dba = *dib*enzylidene *a*cetone) in benzene also did not give the respective Fe-Au-Pd complex.[13] Instead, reaction mixtures were obtained from which no unequivocally characterizable compounds could be separated. Refluxing **3e** with half an equivalent of [Pt(tol)$_2$(SEt$_2$)]$_2$ (tol = 4-tolyl) in toluene as solvent also did not give the desired Fe-Au-Pt product.[13] Thus, we had to choose another synthetic way to prepare FcPPh$_2$Au-C$\equiv$C-NCN-Pt-C$\equiv$C-R (**13a**, R = bipy; **13b**, R = C$_6$H$_4$-4-C$\equiv$N). A straightforward synthesis procedure for the latter molecules is outlined in Scheme 3.

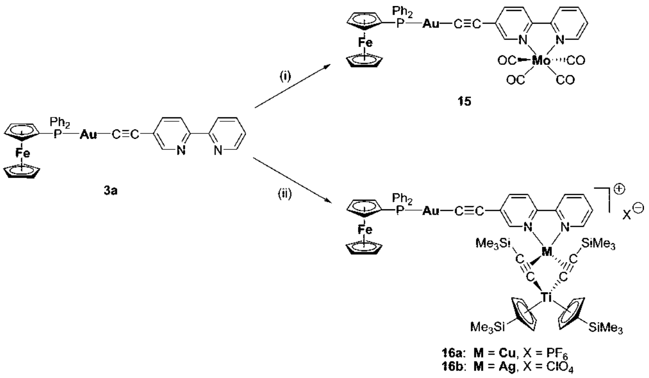
The reaction of Me$_3$SiC$\equiv$C-NCN-PtCl (**10**) with **Li-2a** or **Li-2b** in diethyl ether at ambient temperature gave Me$_3$SiC$\equiv$C-NCN-Pt-C$\equiv$CR (**11a**, R = bipy; **11b**, R = C$_6$H$_4$-C$\equiv$N).[14] Desilylation of **11a** and **11b** was achieved by addition of tetrabutyl ammonium fluoride in dichloromethane at room temperature. However, HC$\equiv$C-NCN-Pt-C$\equiv$CR (**12a**, R = bipy; **12b**, R = C$_6$H$_4$-4-C$\equiv$N) was obtained only in low yield, which is attributed to the workup method applied (Experimental Section). Addition of FcPPh$_2$AuCl (**1**) to **12a** and **12b**, respectively, under similar reaction conditions as already described for the preparation of **3a**−**3c**, afforded the appropriate FcPPh$_2$Au-C$\equiv$C-NCN-Pt-C$\equiv$CR complexes **13a** and **13b** (Scheme 3). Notable is that due to the low solubility of **13a** and **13b**, even in polar organic solvents, full characterization of these species was not possible (Experimental Section). Consequently, we did not carry out any further reaction with these species.

Scheme 3. Synthesis of 13a and 13b^a



^{a} (i) LiC$\equiv$CR, Et$_2$O, −80 – 25 °C; (ii) [^{n}Bu$_4$N]F, CH$_2$Cl$_2$, 25 °C; (iii) FcPPh$_2$AuCl (**1**), [CuI], Thf, HNEt$_2$, 25 °C.

Scheme 4. Synthesis of 15, 16a and 16b.^{a}



^{a} (i) (nbd)Mo(CO)$_4$ (**14**) CH$_2$Cl$_2$/Thf, 25 °C; (ii) {[Ti](μ-σ,π-C$\equiv$CSiMe$_3$)$_2$}MX (**8b**, M = Cu(N$\equiv$CMe), X = PF$_6$; **8c**, M = Ag, X = OClO$_3$), Thf, 25 °C.

Another molecule with a multifunctional ligand allowing to introduce further metal-containing building blocks is FcPPh$_2$Au-C$\equiv$C-bipy (**3a**) as outlined earlier. Thus, complex **3a** was reacted with 1 equiv of (nbd)Mo(CO)$_4$ (**14**) in a 1:5 mixture of tetrahydrofuran/dichloromethane at room temperature. Replacement of nbd by the better donor–acceptor component 2,2′-bipyridyl gave trimetallic FcPPh$_2$Au-C$\equiv$C-bipy[Mo(CO)$_4$] (**15**) in 78% yield (Scheme 4). When instead of **14** the organometallic π-tweezer molecule {[Ti](μ-σ,π-C$\equiv$CSiMe$_3$)$_2$}MX (**8b**, M = Cu(N$\equiv$CMe), X = PF$_6$; **8c**, M = Ag, X = OClO$_3$) was reacted with **3a**, then heterotetrametallic [FcPPh$_2$Au-C$\equiv$Cbipy({[Ti](μ-σ,π-C$\equiv$CSiMe$_3$)$_2$}M)]X (**16a**, M = Cu, X = PF$_6$; **16b**, M = Ag, X = ClO$_4$) could be isolated as a red crystalline solid in excellent yield (Scheme 4).[15] In **15**, **16a**, and **16b** different

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(11) Janssen, M. D.; Herres, M.; Zsolnai, L.; Spek, A. L.; Grove, D. M.; Lang, H.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 2476.

(12) (a) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (b) Lagunas, M. C.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 731.

(13) Köcher, S.; Walfort, B.; van Klink, G. P. M.; van Koten, G.; Lang, H. *J. Organomet. Chem.* **2006**, *691*, 3955.

(14) Back, S.; Gossage, R. A.; Lang, H.; van Koten, G. *Eur. J. Inorg. Chem.* **2000**, 1457.

transition metals such as Fe, Au, Mo, Cu, Ag, and Ti are bridged by carbon-rich connecting units. These complexes are astonishingly stable in the solid state; that is, no intramolecular redox processes are observed. In solution, however, they slowly decompose to yield materials that are insoluble in organic solvents. An exception is complex **16b**. This molecule decomposes in solution to produce elemental silver and the free organometallic π-tweezer molecule $[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2$ together with **3a**.[16]

Complexes **15**, **16a**, and **16b** gave satisfactory elemental analysis and have been characterized by IR and ^{1}H, ^{13}C{^{1}H} (with the exception of **16b**), and ^{31}P{^{1}H} NMR spectroscopy. The identity of tetrametallic **16a** was further confirmed by a single-crystal X-ray diffraction study (see below).

The IR spectra of **15**, **16a**, and **16b** show, as do complexes **3** and **5**, characteristic $\nu_{\mathrm{C{\equiv}C}}$ absorptions for the Au-C≡C and Ti-C≡C fragments at ca. 2118 and 1924 (**16a**) or 1952 cm^{-1} (**16b**).[5,16,17] Consistent with the structure of **15**, the IR spectra of this molecule present in the carbonyl region, as expected for this type of metal–carbonyl entity, four strong CO vibrations between 1829 and 2011 cm^{-1} (Experimental Section).[18]

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **15**, **16a**, and **16b** show representative chemical shifts for the organic building blocks (Experimental Section). Noteworthy to mention in the ^{1}H NMR spectra of **16a** and **16b**, when compared with **8b** and **8c**, is the highfield shift of the $\mathrm{Me_3SiC{\equiv}C}$ protons from ca. 0.20 ppm (**8b**, **8c**)[17] to −0.49 (**16a**) or −0.30 ppm (**16b**), which can be explained by the ring current of the chelating bipyridyl ligand. Furthermore, heterotetrametallic **16a** shows two separated singlets for the $\mathrm{Me_3Si}$ protons of the titanium-coordinated cyclopentadienyl ligands, which is attributed to their unsymmetrical chemical environment. These observations prove the successful formation of multimetallic **15**, **16a**, and **16b**.[16]

The ^{31}P{^{1}H} NMR spectra of **15**, **16a**, and **16b** show one typical signal at ca. 36 ppm for the $\mathrm{Ph_2PAu}$ moiety.[5] Additionally, complex **16a**, which features a hexafluorophosphate counterion, possesses a second signal at −145 ppm splitting into a septet due to J_{PF} coupling ($^1J_{\mathrm{PF}} = 713$ Hz).

The solid state structure of **16a** was determined by single-crystal X-ray structure analysis (Figure 6). Complex **16a** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit cell contains two crystallographically independent molecules, which are shown in Figure 6. Selected bond distances (Å) and angles (deg) are presented in the legend of Figure 6. The crystal and structure refinement data are summarized in Table 4 (Experimental Section).

Heterotetranuclear **16a** contains the transition metals gold, copper, iron, and titanium, whereby Au1 is two-coordinated, Fe1 is part of a sandwich structure, and Cu1 and Ti1 possess pseudotetrahedral environments (Figure 6). A linear one-dimensional P1-Au1-C23-C24-C26 arrangement is set up, which is typical for phosphine gold(I) acetylides.[5] The cyclopentadienyl rings of the ferrocene entity are rotated by 14.00(6)° (molecule **A**) and 17.36(9)° (molecule **B**), respectively, to each other, which verifies a staggered conformation. The distance of the alkynyl unit that is attached to gold(I) is 1.191(12) (molecule **A**) and 1.219(13) Å (molecule **B**), respectively (Figure 6). All other bond separations and angles require no further discussion because they agree well with those parameters described for related transition metal complexes.[5] The bipyridyl building block chelates via the nitrogen atoms N1 and N2 to Cu1 (molecule **A**) or N3 and N4 to Cu2 (molecule **B**), thus resulting in a pseudotetrahedral coordination at copper(I). The structural features of the heterobimetallic organometallic π-tweezer unit $[\{[\mathrm{Ti}](\mu\text{-}\sigma,\pi\text{-}\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{Cu}]^+$ are in accordance with this type of molecule.[16,17] The torsion angles between the two pyridine rings of the bipyridyl unit are 3.87(6)° (molecule **A**) (rms deviation 0.0341°) and 1.70(6)° (molecule **B**) (rms deviation 0.0179°), indicating the planarity of this building block (Figure 6). The dihedral angle formed by the calculated mean planes I (N1, N2, C28, C29, C30 and C31) and II (Ti1, C35, C36, C40 and C41) is 85.45(2)° (rms deviation of fitted atoms = 0.0284 (plane I) and 0.0246 Å (plane II)) for molecule **A** and mean planes III (N3, N4, C88, C89, C90 and C91) and IV (Ti2, C95, C96, C100 and C101) is 89.89(2)° (rms deviation of fitted atoms = 0.0137 (plane III) and 0.0411 Å (plane IV)) for molecule **B**. Both the bipyridyl moiety and the π-tweezer unit ($[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2$) coordinate copper in plane.

Electrochemistry. Complexes **3a**−**3c**, **5a**−**5c**, **7**, **9**, **16a**, and **16b** were subjected to cyclovoltammetric studies. The electrochemical data are summarized in Table 2. The Fe(II)/Fe(III) redox potentials of the $\mathrm{FcPPh_2}$ units are almost not influenced by the nature of R of the acetylenic ligands C≡CR. The values show that, compared to $\mathrm{FcPPh_2}$ ($E_0 = 0.09$ V, $\Delta E_{\mathrm{p}} = 0.15$ V),[8a] a decreased electron density at Fe(II) in **3a**−**3c** and **5a**−**5c** is characteristic; that is, these species are more difficult to oxidize, which can be explained by the electron-withdrawing effect of the respective Au(I) moieties. Nevertheless, a gold(I) reduction could not be observed, either in dichloromethane or in tetrahydrofuran solutions for all newly synthesized compounds.[5d] The reduction of the bipyridyl entity in **3a** is only observed in tetrahydrofuran, enabling the measurement to be carried out into a more negative region and is found at $E_0 = -2.69$ V ($\Delta E_{\mathrm{p}} = 0.23$ V).[19]

The cyclic voltammograms of complexes **5a**−**5c** show additional oxidation processes in the anodic region which can be assigned to the appropriate $\mathrm{ML_n}$ building blocks. Compound **5b** depicts a further reversible Fe(II)/Fe(III) oxidation issuing from the ethynyl ferrocene unit (Figure 7), while the oxidation processes of ruthenium(II) (**5c**) and chromium(0) (**5a**) are found to be irreversible (Table 2).

The coordination of the nitrile ligand to the [Ru] entity in **7** does not influence the oxidation of the Fc unit ($E_0 = 0.31$ V, $\Delta E_{\mathrm{p}} = 0.10$ V) (Figure 8). The Ru(II)/Ru(III) oxidation is observed at $E_0 = -0.245$ V ($\Delta E_{\mathrm{p}} = 0.085$ V). Compared to $[\mathrm{Ru}]\text{-}\mathrm{N{\equiv}C\text{-}C_6H_5}$ this process is somewhat shifted to a more positive potential.[22]

The electrochemical measurements of all complexes containing the bis(alkynyl)titanocene building block were carried out in tetrahydrofuran solutions. The cyclic voltammogram of

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(17) (a) Lang, H.; George, D. S. A.; Rheinwald, G. *Coord. Chem. Rev.* **2000**, *206–207*, 101. (b) Lang, H.; Rheinwald, G. *J. Prakt. Chem.* **1999**, *341*, 1. (c) Lang, H.; Köhler, K.; Blau, S. *Coord. Chem. Rev.* **1995**, *143*, 113.

(18) Herrmann, W. A.; Thiel, W. R.; Kuchler, J. K. *Chem. Ber.* **1990**, 1953.

(19) (a) For free 2,2′-bipyridine see Al-Anber, M.; Vatsadze, S.; Holze, R.; Thiel, W. R.; Lang, H. *J. Chem. Soc., Dalton Trans.* **2005**, 3632. (b) Vatsadze, S.; Al-Anber, M.; Thiel, W. R.; Lang, H.; Holze, R. *J. Solid State Electrochem.* **2005**, *9*, 764.

(20) Ferrocene/ferrocenium redox couple: Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.

(21) A conversion of given electrode potentials to the standard normal hydrogen electrode is possible: Strehlow, H.; Knoche, W.; Schneider, H. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 760.

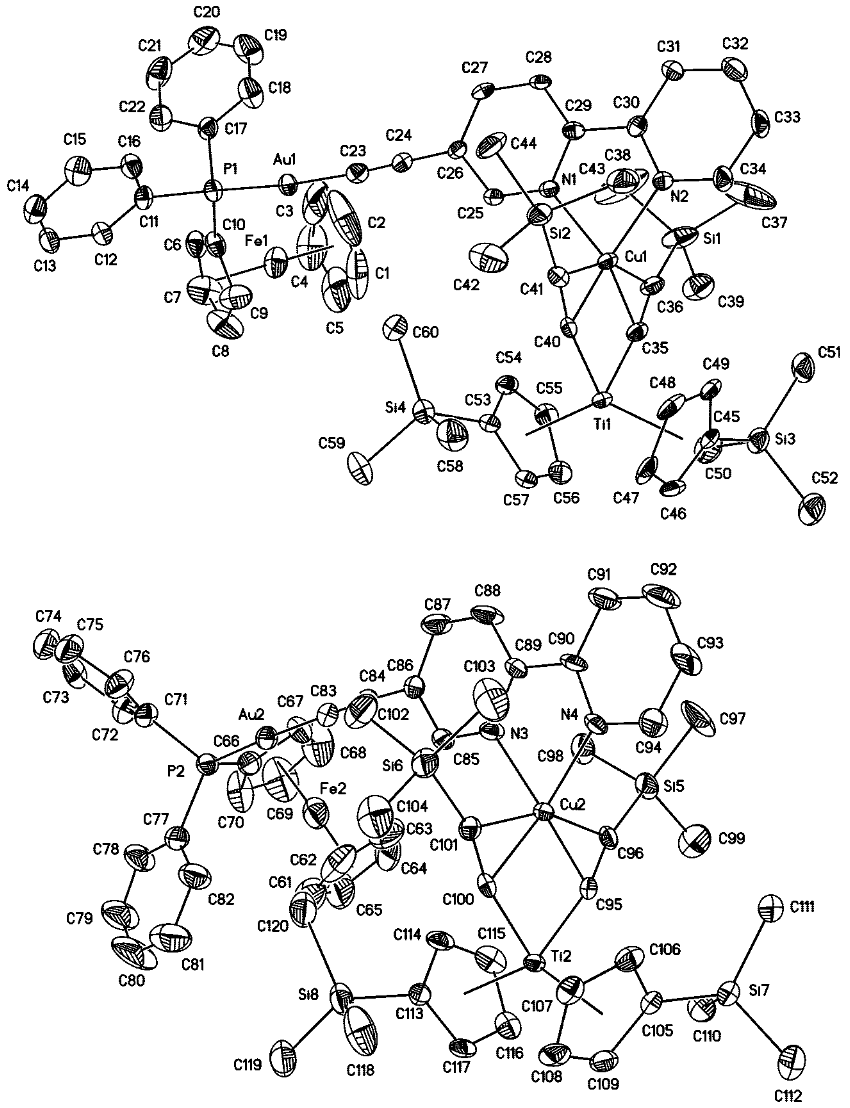

Figure 6. ORTEP (30% ellipsoid probability level) of the two crystallographically independent molecules in **16a** (molecule **A**, top; molecule **B**, bottom) with the atom-numbering scheme (the hydrogen atoms and the PF_6^- counterion are omitted for clarity). Selected bond distances (Å) and angles (deg): Molecule **A**: P1−Au1, 2.268(2); Au1−C23, 2.007(10); C23−C24, 1.191(12); Cu1−N1, 2.109(7); Cu1−N2, 2.082(7); Cu1−C35, 2.104(9); Cu1−C36, 2.214(10); Cu1−C40, 2.090(8); Cu1−C41, 2.197(9); Ti1−C35, 2.106(9); Ti1−C40, 2.120(9); C35−C36, 1.234(12); C40−C41, 1.223(12); P1−Au1−C23, 175.7(3); Au1−C23−C24, 174.0(8); C23−C24−C26, 177.7(11); Ti1−C35−C36, 167.5(8); Ti1−C40−C41, 166.7(7); C35−C36−Si1, 161.8(9); C40−C41−Si2, 162.6(8); Fe1−D_1, 1.6349(6); Fe1−D_2, 1.6290(5); Ti1−D_3, 2.0541(4); Ti1−D_4, 2.0495(4). Molecule **B**: P2−Au2, 2.275(3); Au2−C83, 1.984(10); C83−C84, 1.219(13); Cu2−N3, 2.131(7); Cu2−N4, 2.079(7); Cu2−C95, 2.066(9); Cu2−C96, 2.174(9); Cu2−C100, 2.093(8); Cu2−C101, 2.175(9); Ti2−C95, 2.087(9); Ti2−C100, 2.092(9); C95−C96, 1.233(12); C100−C101, 1.244(12); P2−Au2−C83, 175.4(3); Au2−C83−C84, 178.4(10); C83−C84−C86, 176.3(10); Ti2−C95−C96, 166.8(7); Ti2−C100−C101, 165.5(7); C95−C96−Si5, 160.0(9); C100−C101−Si6, 159.9(8); Fe2−D_5, 1.6126(8); Fe2−D_6, 1.6135(7); Ti2−D_7, 2.0422(4); Ti2−D_8, 2.0442(4). (D_1, D_5 = centroids of the cyclopentadienyl rings C_5H_5; D_{2-4}, D_{6-8} = centroids of the cyclopentadienyl rings C_5H_4).

heterotetrametallic **9** presents next to the Fe(II)/Fe(III) oxidation at $E_0 = 0.28$ V ($\Delta E_p = 0.115$ V) an irreversible reduction at $E_{p,red} = -1.30$ V, which results from the Cu(I)/Cu(0) reduction. 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.[23] Owing to this, a further reduction wave is observed at $E_0 = -1.80$ V ($\Delta E_p = 0.18$ V), which results from the free π-tweezer [Ti](C≡CSiMe$_3$)$_2$ (Ti(IV)/Ti(III)) increasing during multicyclic experiments, while the Cu(I)/Cu(0) reduction wave disappears.[23]

Electrochemical studies on **16a** show a reversible wave at 0.27 V ($\Delta E_p = 0.115$ V) for the Fc group, similar to **3a** ($E_0 = 0.28$ V, $\Delta E_p = 0.135$ V). A characteristic reversible one-electron reduction at −2.72 V with $\Delta E_p = 0.16$ V is additionally found, which can be assigned to the bipy/bipy$^-$ redox couple.[19] The organometallic π-tweezer part in **16a** gives rise to two further one-electron processes. In contrast to **9**, in which the copper(I) ion is monodentate-bonded by a pyridine ligand, the chelate coordination of the bipyridyl unit to Cu(I) in **16a** results in a reduction of Cu(I) followed by a partial reoxidation of Cu(0) ($E_0 = -1.41$ V, $\Delta E_p = 0.115$ V), presumably without any structural change of the molecule involved (Figure 9).[16] This is unique in titanium(IV)−copper(I) chemistry. At more negative potentials two reductions are found resulting from the Ti(IV)/

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[22] Back, S.; Gossage, R. A.; Rheinwald, G.; del Río, I.; Lang, H.; van Koten, G. *J. Organomet. Chem.* **1999**, *582*, 126.

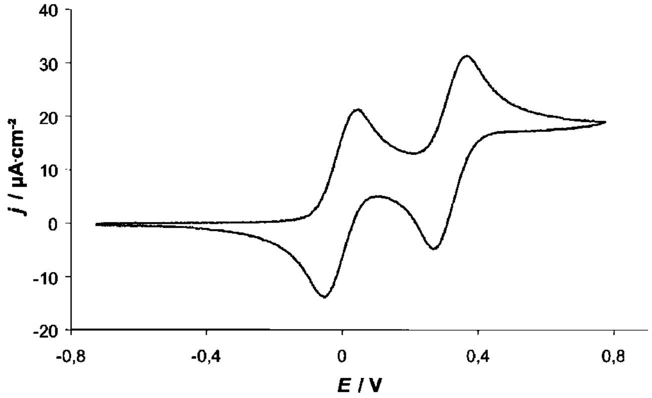

Figure 7. Cyclic voltammogram (anodic region) of **5b** (10^{-3} M solution in dichloromethane at 25 °C with [n-Bu_4N]PF_6 (0.1 M) as supporting electrolyte, scan rate = 0.10 $V \cdot s^{-1}$). All potentials are referenced to the FcH/FcH^+ redox couple (FcH = (η^5-C_5H_5)$_2$Fe) with E_0 = 0.00 V (ΔE_p = 0.10 V)).[20,21]

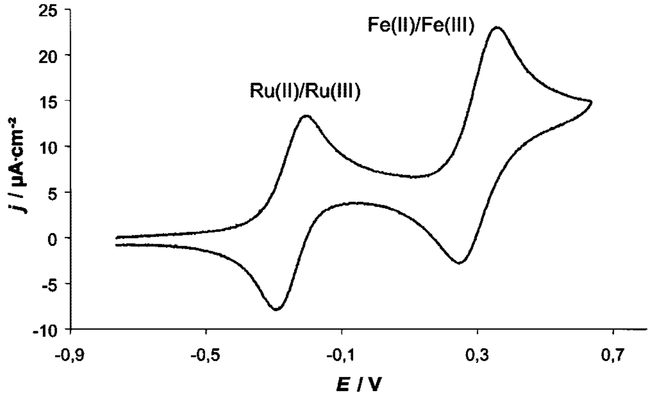

Figure 8. Cyclic voltammogram (anodic region) of **7** (10^{-3} M solution in dichloromethane at 25 °C with [n-Bu_4N]PF_6 (0.1 M) as supporting electrolyte, scan rate = 0.10 $V \cdot s^{-1}$). All potentials are referenced to the FcH/FcH^+ redox couple (FcH = (η^5-C_5H_5)$_2$Fe) with E_0 = 0.00 V (ΔE_p = 0.10 V).[20,21]

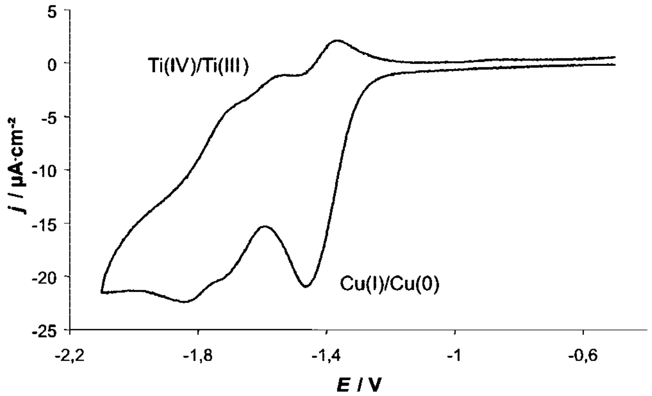

Figure 9. Cyclic voltammogram (cathodic region) of **16a** (10^{-3} M solution in tetrahydrofuran at 25 °C with [n-Bu_4N]PF_6 (0.1 M) as supporting electrolyte, scan rate = 0.10 $V \cdot s^{-1}$). All potentials are referenced to the FcH/FcH^+ redox couple (FcH = (η^5-C_5H_5)$_2$Fe) with E_0 = 0.00 V (ΔE_p = 0.10 V).[20,21]

Ti(III) redox couple of intact **16a** (E_0 = −1.635 V, ΔE_p = 0.18 V) and the free tweezer molecule [Ti]($C\equiv CSiMe_3$)$_2$ (E_0 = −1.76 V, ΔE_p = 0.18 V) (Figure 9).[23]

In contrast to **16a**, tetrametallic **16b** shows a somewhat different electrochemical behavior. While the Fc and bipy moieties behave in the same manner as discussed earlier for **16a**, for the Ti-Ag tweezer part an irreversible wave at $E_{p,red}$ = −1.30 V for Ag(I) is characteristic; that is, no reoxidation peak is observed. Presumably reduction of the coinage metal to its elemental form results in disaggregation of **16b**, thus affording the free organometallic π-tweezer [Ti]($C\equiv CSiMe_3$)$_2$.[23] For the latter species a reduction current peak at $E_{p,red}$ = −1.83 V assigned to the reaction Ti(IV) + e^- → Ti(III) is displayed, together with the corresponding oxidation peak, and a value of ΔE_p = 0.16 V is calculated. This redox potential is typical for [Ti]($C\equiv CSiMe_3$)$_2$.[23]

Conclusion

A series of heterometallic complexes featuring two, three, or even four different transition metal atoms such as titanium, molybdenum, iron, platinum, copper, and silver of structural type $FcPPh_2Au$-$C\equiv CR$ (R = bipy, C_6H_4-4-$C\equiv N$, C_5H_4N-4, NCN-H, NCN-I; Fc = (η^5-C_5H_5)(η^5-C_5H_4)Fe; bipy = 2,2′-bipyridyl-5-yl; NCN = [$C_6H_2(CH_2NMe_2)_2$-2,6]$^-$), $FcPPh_2Au$-$C\equiv CML_n$ (ML_n = (η^6-C_6H_5)Cr$(CO)_3$, Fc, Rc; Rc = (η^5-C_5H_5)(η^5-C_5H_4)Ru), $FcPPh_2Au$-$C\equiv C$-C_6H_4-4-$C\equiv N$-[Ru], [$FcPPh_2Au$-$C\equiv C$-C_5H_4N-Cu{($Me_3SiC\equiv C$)$_2$[Ti]}]OTf, $FcPPh_2Au$-$C\equiv C$-NCN-Pt-$C\equiv CR$ (R = bipy, C_6H_4-$C\equiv N$), $FcPPh_2Au$-$C\equiv C$bipy[Mo$(CO)_4$], and [$FcPPh_2Au$-$C\equiv C$bipy({[Ti](μ-σ,π-$C\equiv CSiMe_3$)$_2$}M)])X (M = Cu, X = PF_6; M = Ag, X = ClO_4) have been synthesized in straightforward consecutive synthesis procedures. In these molecules the appropriate transition metals are spanned by carbon-rich connectivities based on alkynyls, and hence, they enrich the so far only scarcely described class of multimetallic organometallic compounds featuring different early and late transition metal atoms. These complexes have been subjected to cyclovoltammetric studies, showing redox processes attributed to the relevant metal centers. The influence of the metal atoms on each other has thereby turned out to be relatively tenuous. Noteworthy is that in [$FcPPh_2Au$-$C\equiv C$bipy({[Ti](μ-σ,π-$C\equiv CSiMe_3$)$_2$}Cu)]PF_6 the chelate coordination of the bipyridyl unit to Cu(I) results in a reduction of Cu(I) followed by reoxidation of Cu(0) presumably without any structural change of the molecule involved, which is unique in titanium(IV)−copper(I) chemistry.

Experimental Section

General Data. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, petroleum ether, n-hexane, and n-pentane 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 FT-IR spectrometer Spectrum 1000. ^1H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; $^{13}C\{^1H\}$ NMR spectra were recorded at 62.860 MHz. Chemical shifts are reported in δ (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^1H NMR: $CDCl_3$, δ = 7.26; $^{13}C\{^1H\}$ NMR: $CDCl_3$, δ = 77.16).[24] $^{31}P\{^1H\}$ NMR spectra were recorded at 101.255 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard (δ = 139.0, relative to H_3PO_4 (85%) with δ = 0.00 ppm). ESI-TOF mass spectra were recorded using a Mariner biospectrometry workstation

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4.0 (Applied Biosystems). Cyclic voltammograms were recorded in a dried cell purged with purified argon. Platinum wires served as the working electrode and the 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 = (η^5-C_5H_5)$_2$Fe, E_0 = 0.00 V) as reference.[20,21] Electrolyte solutions were prepared from tetrahydrofuran or dichloromethane and [^{n}Bu$_4$N]PF$_6$ (Fluka, dried in oil-pump vacuum). The appropriate organometallic complexes were added at c = 1.0 mM. Cyclic voltammograms were recorded on a Voltalab 3.1 potentiostiat (Radiometer) equipped with a digital electrochemical analyzer DEA 101 and an electrochemical interface IMT 102. Microanalyses were performed by the Institute of Inorganic Chemistry and partly the Institute of Organic Chemistry, Chemnitz, Technical University.

Reagents. FcPPh$_2$AuCl (**1**),[5d] 5-ethynyl-2,2′-bipyridyl (**2a**),[25] 4-ethynylbenzonitrile (**2b**),[26] 4-ethynylpyridine (**2c**),[27] HC≡C-1-C_6H_3(CH_2NMe_2)$_2$-3,5 (**2d**),[28] I-1-HC≡C-4-C_6H_3(CH_2NMe_2)$_2$-2,6 (**2e**),[29] (η^6-C_6H_5C≡CH)Cr(CO)$_3$ (**4a**),[30] ethynylferrocene (**4b**),[31] ethynylruthenocene (**4c**),[32] [Ru]N≡N[Ru] (**6**),[9] Me$_3$Si-C≡C-NC-NPtCl (**10**),[14,33] HC≡C-NCNPt-C≡C-C_6H_4C≡N (**12b**),[14] (nbd)-Mo(CO)$_4$, (**14**),[34] {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}CuOTf (**8a**),[11] [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF$_6$ (**8b**),[11] and {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}AgOClO$_3$ (**8c**)[35] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

Synthesis of FcPPh$_2$AuC≡C-bipy (3a). To 150 mg (0.25 mmol) of FcPPh$_2$AuCl (**1**) and 50 mg (0.27 mmol) of 5-ethynyl-2,2′-bipyridyl (**2a**) dissolved in 50 mL of diethyl amine was added 1 mg of [CuI]. After stirring the reaction solution for 16 h at 25 °C it was filtered through a pad of Celite and all volatiles were removed in an oil-pump vacuum. The remaining solid was purified by column chromatography on silica gel eluting with a diethyl ether/*n*-hexane mixture (4:1, v/v). After evaporation of the solvents under reduced pressure compound **3a** was obtained as a yellow solid. Yield: 130 mg (0.17 mmol, 68% based on **1**).

Anal. Calc for $C_{34}H_{26}AuFeP$ (746.13): C, 54.71; H, 3.51; N, 3.75. Found: C, 55.20; H, 3.69; N, 3.67. Mp: 105 °C. IR (KBr, cm^{-1}): 2115 (m, $\nu_{\mathrm{Au}C\equiv C}$). ^{1}H NMR (CDCl$_3$, δ): 4.21 (s, 5H, C_5H_5), 4.39 (dpt, J_{HP} = 2.8 Hz, J_{HH} = 1.9 Hz, 2 H, H^α/C_5H_4), 4.55 (dpt, J_{HP} = 1.0 Hz, J_{HH} = 1.9 Hz, 2 H, H^β/C_5H_4), 7.26 (ddd, $^3J_{\mathrm{H5'H4'}}$ = 7.8 Hz, $^3J_{\mathrm{H5'H6'}}$ = 4.8 Hz, $^4J_{\mathrm{H5'H3'}}$ = 1 Hz, 1 H, *H5′*/bipy), 7.40–7.65 (m, 10 H, C_6H_5), 7.79 (ddd, $^3J_{\mathrm{H4'H3'}}$ = 7.8 Hz, $^3J_{\mathrm{H4'H5'}}$ = 7.8 Hz, $^4J_{\mathrm{H4'H6'}}$ = 1.8 Hz, 1 H, *H4′*/bipy), 7.92 (dd, $^3J_{\mathrm{H4H3}}$ = 8.5 Hz, $^4J_{\mathrm{H4H6}}$ = 2.4 Hz, 1 H, *H4*/bipy), 8.31 (dd, $^3J_{\mathrm{H3H4}}$ = 8.5 Hz, $^5J_{\mathrm{H3H6}}$ = 0.6 Hz, 1 H, *H3*/bipy), 8.37 (ddd, $^3J_{\mathrm{H3'H4'}}$ = 7.8 Hz, $^4J_{\mathrm{H3'H5'}}$ = 1 Hz, $^5J_{\mathrm{H3'H6'}}$ = 1 Hz, 1 H, *H3′*/bipy), 8.66 (ddd, $^3J_{\mathrm{H6'H5'}}$ = 4.8 Hz, $^4J_{\mathrm{H6'H4'}}$ = 1.8 Hz, $^5J_{\mathrm{H6'H3'}}$ = 1 Hz, 1 H, *H6′*/bipy), 8.83 (dd, $^4J_{\mathrm{H6H4}}$ = 2.4 Hz, $^5J_{\mathrm{H6H3}}$ = 0.6 Hz, 1 H, *H6*/bipy). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 68.6 (d, $^1J_{\mathrm{CP}}$ = 64.9 Hz, C^i/C_5H_4), 70.1 (C_5H_5), 72.5 (d, $^3J_{\mathrm{CP}}$ = 8.5 Hz, C^β/C_5H_4), 73.7 (d, $^2J_{\mathrm{CP}}$ = 13.8 Hz, C^α/C_5H_4), 101.0 (C≡C) 120.3 (*C3*/bipy), 121.3 (*C3′*/bipy), 122.3 (*C5*/bipy), 123.6 (*C5′*/bipy), 128.9 (d, $^3J_{\mathrm{CP}}$ = 11.2 Hz, C^m/C_6H_5), 131.3 (d, $^4J_{\mathrm{CP}}$ = 2.3 Hz, C^p/C_6H_5), 132.1 (d, $^1J_{\mathrm{CP}}$ = 56.7 Hz, C^i/C_6H_5), 133.8 (d, $^2J_{\mathrm{CP}}$ = 13.8 Hz, C^o/C_6H_5), 136.9 (*C4′*/bipy), 140.2 (*C4*/bipy), 149.3 (*C6′*/bipy), 152.7 (*C6*/bipy), 153.4 (*C2*/bipy), 156.1 (*C2′*/bipy). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.249 MHz, δ): 35.95 (s, *P*Ph$_2$). (The second signal for the C≡C entity could not be detected.)

Synthesis of FcPPh$_2$AuC≡C-C_6H_4-4-C≡N (3b). To 300 mg (0.50 mmol) of FcPPh$_2$AuCl (**1**) dissolved in 50 mL of diethyl amine were added 80 mg (0.63 mmol) of 4-ethynyl-benzonitrile (**2b**) and 1 mg of [CuI]. The resulting turbid reaction mixture was stirred for 16 h at 25 °C. Afterward all volatiles were removed under reduced pressure and the remaining solid was subjected to column chromatography on alumina using toluene as eluent. The title compound was obtained as an orange solid after evaporation of the solvent under reduced pressure. Yield: 270 mg (0.39 mmol, 78% based on **1**).

Anal. Calc for $C_{31}H_{23}NPAuFe$ (693.3): C, 53.70; H, 3.34; N, 2.02. Found: C, 53.72; H, 3.32; N, 2.04. Mp: 92 °C. IR (KBr, cm^{-1}): 2225 (s, $\nu_{\mathrm{C\equiv N}}$), 2116 (m, $\nu_{\mathrm{Au}C\equiv C}$). ^{1}H NMR (CDCl$_3$, δ): 4.21 (s, 5 H, C_5H_5), 4.38 (dpt, J_{HP} = 3.0 Hz, J_{HH} = 1.8 Hz, 2 H, H^α/C_5H_4), 4.56 (dpt, J_{HP} = 1.0 Hz, J_{HH} = 1.8 Hz, 2 H, H^β/C_5H_4), 7.42–7.61 (m, 14 H, C_6H_5 + C_6H_4). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 69.8 (d, $^1J_{\mathrm{CP}}$ = 64.3 Hz, C^i/C_5H_4), 72.5 (d, $^3J_{\mathrm{CP}}$ = 8.3 Hz, C^β/C_5H_4), 73.6 (d, $^2J_{\mathrm{CP}}$ = 13.8 Hz, C^α/C_5H_4), 102.7 (C≡C), 109.8 (C^i/C_6H_4), 119.2 (C≡N), 128.9 (d, $^3J_{\mathrm{CP}}$ = 11.1 Hz, C^m/C_6H_5), 130.4 (C^i/C_6H_4), 131.3 (d, $^4J_{\mathrm{CP}}$ = 2.1 Hz, C^p/C_6H_5), 131.9 (*CH*/C_6H_4), 132.2 (d, $^1J_{\mathrm{CP}}$ = 54.7 Hz, C^i/C_6H_5), 132.9 (*CH*/C_6H_4), 133.8 (d, $^2J_{\mathrm{CP}}$ = 14.0 Hz, C^o/C_6H_5). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.249 MHz, δ): 36.3 (s, *P*Ph$_2$). (The second signal for the C≡C entity could not be detected.)

Synthesis of FcPPh$_2$AuC≡C-C_5H_4N (3c). To 150 mg (0.25 mmol) of FcPPh$_2$AuCl (**1**) dissolved in 50 mL of diethyl amine were added 30 mg (0.29 mmol) of 4-ethynylpyridine (**2c**) and 1 mg of [CuI]. The resulting turbid reaction mixture was stirred for 16 h at 25 °C. All volatiles were removed under reduced pressure and the remaining solid was purified by column chromatography on alumina using a mixture of toluene/tetrahydrofuran (8:1, v/v) as eluent. After removal of all volatiles in an oil-pump vacuum compound **3c** was obtained as an orange solid. Yield: 100 mg (0.15 mmol, 60% based on **1**).

Anal. Calc for $C_{29}H_{23}NPAuFe$ (669.3): C, 52.04; H, 3.46; N, 2.09. Found: C, 52.35; H, 3.78; N, 2.28. Mp: 196 °C (dec). IR (KBr, cm^{-1}): 2119 (m, $\nu_{\mathrm{Au}C\equiv C}$). ^{1}H NMR (CDCl$_3$, δ): 4.21 (s, 5 H, C_5H_5), 4.38 (dpt, J_{HP} = 2.8 Hz, J_{HH} = 1.8 Hz, 2 H, H^α/C_5H_4), 4.56 (dpt, J_{HP} = 1.0 Hz, J_{HH} = 1.8 Hz, 2 H, H^β/C_5H_4), 7.34–7.38 (m, 2 H, C_5H_4N), 7.40–7.65 (m, 10 H, C_6H_5), 8.47–8.51 (m, 2 H, C_5H_4N). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 69.6 (d, $^1J_{\mathrm{CP}}$ = 67.2 Hz, C^i/C_5H_4), 70.2 (C_5H_5), 72.5 (d, $^3J_{\mathrm{CP}}$ = 8.6 Hz, C^β/C_5H_4), 73.7 (d, $^2J_{\mathrm{CP}}$ = 13.9 Hz, C^α/C_5H_4), 101.5 (C≡C), 126.7 (*CH*/C_5H_4N), 129.0 (d, $^3J_{\mathrm{CP}}$ = 11.5 Hz, C^m/C_6H_5), 131.4 (d, $^4J_{\mathrm{CP}}$ = 2.4 Hz, C^p/C_6H_5), 132.0 (d, $^1J_{\mathrm{CP}}$ = 57.1 Hz, C^i/C_6H_5), 133.4 (C^i/C_5H_4N), 133.8 (d, $^2J_{\mathrm{CP}}$ = 13.4 Hz, C^o/C_6H_5), 149.8 (*CH*/C_5H_4N). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.249 MHz, δ): 36.0 (s, *P*Ph$_2$). (The second signal for the C≡C entity could not be detected.)

Synthesis of FcPPh$_2$AuC≡C-NCNH (3d). To a cooled solution (−50 °C) of 100 mg (0.46 mmol) HC≡C-NCNH (**2d**) in 50 mL of diethyl ether was dropwise added 0.27 mL (0.43 mmol) of methyl lithium (1.6 M in diethyl ether). Stirring was continued for 30 min at this temperature followed by addition of 150 mg (0.25 mmol) of FcPPh$_2$AuCl (**1**). The reaction mixture was allowed to warm to 25 °C. After 15 h of stirring it was filtered through a pad of Celite and concentrated to 2 mL. The title compound was precipitated by

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[35] Lang, H.; Herres, M.; Zsolnai, L. *Organometallics* **1993**, *12*, 5008.

addition of 30 mL of *n*-pentane. The obtained solid was washed twice with 10 mL portions of *n*-pentane and dried in an oil-pump vacuum to give **3d** as a yellow solid. Yield: 110 mg (0.14 mmol, 56% based on **1**).

Anal. Calc for $C_{36}H_{38}N_2PAuFe$ (782.5): C, 55.26; H, 4.89; N, 3.58. Found: C, 55.27; H, 4.95; N, 3.14. Mp: 75 °C. IR (KBr, cm^{-1}): 2103 (m, $\nu_{AuC\equiv C}$). ^{1}H NMR ($CDCl_3$, δ): 2.21 (s, 12 H, NCH_3), 3.36 (s, 4 H, NCH_2), 4.20 (s, 5 H, C_5H_5), 4.38 (dpt, J_{HP} = 2.8 Hz, J_{HH} = 1.9 Hz, 2 H, H^{α}/C_5H_4), 4.54 (dpt, J_{HP} = 1.0 Hz, J_{HH} = 1.9 Hz, 2 H, H^{β}/C_5H_4), 7.17 (s, 1 H, C_6H_3), 7.34–7.50 (m, 8 H, $C_6H_5 + C_6H_3$), 7.55–7.65 (m, 4 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 45.4 (NCH_3), 64.1 (NCH_2), 69.8 (d, $^1J_{CP}$ = 65.7 Hz, C^i/C_5H_4) 70.1 (C_5H_5), 72.4 (d, $^3J_{CP}$ = 8.6 Hz, C^{β}/C_5H_4), 73.6 (d, $^2J_{CP}$ = 13.4 Hz, C^{α}/C_5H_4), 104.2 (C≡C), 124.5 (C^i/C_6H_3), 128.6 (CH/C_6H_3), 128.8 (d, $^3J_{CP}$ = 11 Hz, C^m/C_6H_5), 131.2 (d, $^4J_{CP}$ = 1.9 Hz, C^p/C_6H_5), 132.1 (CH/C_6H_3), 132.2 (d, $^1J_{CP}$ = 56.2 Hz, C^i/C_6H_5), 133.8 (d, $^2J_{CP}$ = 13.8 Hz, C^o/C_6H_5), 138.7 (C^i/C_6H_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.4 (s, PPh_2). (The second signal for the C≡C entity could not be detected.)

Synthesis of FcPPh$_2$AuC≡C-NCNI (3e). To a solution of 150 mg (0.44 mmol) of HC≡C-NCNI (**2e**) in 25 mL of diethyl ether was added $LiN(SiMe_3)_2$ (70 mg, 0.42 mmol) in a single portion, and the reaction mixture was stirred for 3 h at ambient temperature. After addition of 150 mg (0.25 mmol) of $FcPPh_2AuCl$ (**1**) stirring was continued for 15 h. The reaction mixture was then filtered through a pad of Celite and concentrated to 2 mL. Addition of 30 mL of *n*-pentane led to the precipitation of **3e**. The yellow precipitate was washed twice with 10 mL portions of *n*-pentane and dried in an oil-pump vacuum. Yield: 140 mg (0.15 mmol, 62% based on **1**).

Anal. Calc for $C_{36}H_{37}N_2PIAuFe$ (908.4): C, 47.60; H, 4.11; N, 3.08. Found: C, 48.53; H, 4.31; N, 3.04. Mp: >150 °C (dec). IR (KBr, cm^{-1}): 2117 (m, $\nu_{AuC\equiv C}$). ^{1}H NMR ($CDCl_3$, δ): 2.29 (s, 12 H, NCH_3), 3.44 (s, 4 H, NCH_2), 4.20 (s, 5 H, C_5H_5), 4.38 (dpt, J_{HP} = 2.8 Hz, J_{HH} = 1.9 Hz, 2 H, H^{α}/C_5H_4), 4.55 (dpt, J_{HP} = 1.0 Hz, J_{HH} = 1.9 Hz, 2 H, H^{β}/C_5H_4), 7.36–7.50 (m, 8 H, $C_6H_5 + C_6H_2$), 7.55–7.66 (m, 4 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 45.6 (NCH_3), 68.2 (d, $^1J_{CP}$ = 66.8 Hz, C^i/C_5H_4), 69.0 (NCH_2), 70.1 (C_5H_5), 72.4 (d, $^3J_{CP}$ = 8.5 Hz, C^{β}/C_5H_4), 73.6 (d, $^2J_{CP}$ = 13.8 Hz, C^{α}/C_5H_4), 103.4 (d, J_{CP} = 27 Hz, C≡C), 106.0 (C-I/C_6H_2), 124.3 (C^i/C_6H_2), 128.8 (d, $^3J_{CP}$ = 11.3 Hz, C^m/C_6H_5), 131.3 (d, $^4J_{CP}$ = 2.2 Hz, C^p/C_6H_5), 132.1 (d, $^1J_{CP}$ = 57.2 Hz, C^i/C_6H_5), 133.0 (CH/C_6H_2), 133.8 (d, $^2J_{CP}$ = 13.8 Hz, C^o/C_6H_5), 141.7 (C^i/C_6H_2), 171.1 (C≡C). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.5 (s, PPh_2).

Synthesis of FcPPh$_2$Au[(C≡CC$_6$H$_5$)Cr(CO)$_3$] (5a). To 150 mg (0.25 mmol) of $FcPPh_2AuCl$ (**1**) dissolved in 50 mL of degassed diethyl amine was added 80 mg (0.33 mmol) of (η^6-C_6H_5C≡CH)$Cr(CO)_3$ (**4a**) and 1 mg of [CuI]. The resulting mixture was stirred for 5 h at 25 °C. Afterward all volatiles were removed under reduced pressure and the remaining residue was purified by column chromatography on silica gel using a mixture of dichloromethane/*n*-hexane (1:1, v/v) as eluent. After removal of the solvents in an oil-pump vacuum complex **5a** could be isolated as an orange solid. Yield: 145 mg (0.18 mmol, 72% based on **1**).

Anal. Calc for $C_{33}H_{24}O_3PAuCrFe$ (804.3): C, 49.28; H, 3.01. Found: C, 49.13; H, 3.15. Mp: >87 °C (dec). IR (KBr, cm^{-1}): 2122 (m, $\nu_{AuC\equiv C}$), 1963, 1883 (s, ν_{CO}). ^{1}H NMR ($CDCl_3$, δ): 4.21 (s, 5 H, C_5H_5), 4.37 (br s, H^{α}/C_5H_4), 4.55 (br s, H^{β}/C_5H_4), 5.16 (pt, J_{HH} = 6.3 Hz, 1 H, C_6H_5/Cr), 5.32 (pt, J_{HH} = 6.3 Hz, 2 H, C_6H_5/Cr), 5.53 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1 Hz, 2 H, C_6H_5/Cr), 7.38–7.64 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 69.6 (d, $^1J_{CP}$ = 65.2 Hz, C^i/C_5H_4), 70.2 (C_5H_5), 72.5 (d, $^3J_{CP}$ = 8.5 Hz, C^{β}/C_5H_4), 73.7 (d, $^2J_{CP}$ = 13.7 Hz, C^{α}/C_5H_4), 90.0 (CH/C_6H_5), 92.4 (CH/C_6H_5), 95.0 (C^i/C_6H_5), 95.9 (CH/C_6H_5), 129.0 (d, $^3J_{CP}$ = 11.3 Hz, C^m/C_6H_5), 131.4 (C^p/C_6H_5), 132.0 (d, $^1J_{CP}$ = 52.5 Hz, C^i/C_6H_5), 133.8 (d, $^2J_{CP}$ = 13.7 Hz, C^o/C_6H_5), 223.1 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.1 (s, PPh_2). (The signals for the C≡C entity could not be detected.)

Synthesis of FcPPh$_2$AuC≡CFc (5b). To 50 mL of diethyl amine containing 185 mg (0.38 mmol) of $FcPPh_2AuCl$ (**1**) and 90 mg (0.43 mmol) of ethynylferrocene (**4b**) was added 1 mg of [CuI]. After a reaction period of 2 h at 25 °C the mixture was filtered through a pad of Celite and all volatile materials were removed in an oil-pump vacuum. The remaining solid was chromatographed on silica gel using diethyl ether/*n*-hexane (4:1, v/v) as eluent. After removal of the solvents under reduced pressure the product was obtained as an orange solid. Yield: 225 mg (0.29 mmol, 76% based on **1**).

Anal. Calc for $C_{34}H_{28}AuFe_2P$ (776.03): C, 52.58; H, 3.64. Found: C, 52.33; H, 3.88. Mp: >82 °C (dec). IR (KBr, cm^{-1}): 2112 (m, $\nu_{AuC\equiv C}$). ^{1}H NMR ($CDCl_3$, δ): 4.13 (pt, J_{HH} = 1.8 Hz, 2 H, H^{β}/C_5H_4/FcC≡C), 4.19 (s, 5 H, C_5H_5/FcPPh$_2$), 4.24 (s, 5 H, C_5H_5/FcC≡C), 4.38 (dpt, J_{HP} = 3.0 Hz, J_{HH} = 1.8 Hz, 2 H, H^{α}/C_5H_4/FcPPh$_2$), 4.47 (pt, J_{HH} = 1.8 Hz, 2 H, H^{α}/C_5H_4/FcC≡C), 4.54 (dpt, J_{HP} = 1.0 Hz, J_{HH} = 1.8 Hz, 2 H, H^{β}/C_5H_4/FcPPh$_2$), 7.37–7.66 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 67.8 (C^i/C_5H_4/FcC≡C), 67.9 (CH/C_5H_4/FcC≡C), 70.0 (d, $^1J_{CP}$ = 66.3 Hz, C^i/C_5H_4/FcPPh$_2$), 70.1 (C_5H_5/FcPPh$_2$), 70.1 (C_5H_5/FcC≡C), 72.0 (CH/C_5H_4/FcC≡C), 72.4 (d, $^3J_{CP}$ = 8.5 Hz, C^{β}/C_5H_4/FcPPh$_2$), 73.7 (d, $^2J_{CP}$ = 13.8 Hz, C^{α}/C_5H_4/FcPPh$_2$), 128.9 (d, $^3J_{CP}$ = 11.1 Hz, C^m/C_6H_5), 131.2 (d, $^4J_{CP}$ = 2.3 Hz, C^p/C_6H_5), 132.4 (d, $^1J_{CP}$ = 57.1 Hz, C^i/C_6H_5), 133.9 (d, $^2J_{CP}$ = 13.8 Hz, C^o/C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.4 (s, PPh_2). (The signals for the C≡C entity could not be detected.)

Synthesis of FcPPh$_2$AuC≡CRc (5c). Compound **5c** was prepared in the same manner as **5b**. To 185 mg (0.38 mmol) of $FcPPh_2AuCl$ (**1**) and 110 mg (0.43 mmol) of ethynylruthenocene (**4c**) dissolved in 50 mL of diethyl amine was added 1 mg of [CuI]. After appropriate workup, **5c** was obtained as an orange solid. Yield: 192 mg (0.23 mmol, 61% based on **1**).

Anal. Calc for $C_{34}H_{28}AuFePRu$ (822.00): C, 49.64; H, 3.43. Found: C, 49.78; H, 3.69. Mp: >90 °C (dec). IR (KBr, cm^{-1}): 2107 (m, $\nu_{AuC\equiv C}$). ^{1}H NMR ($CDCl_3$, δ): 4.17 (s, 5 H, C_5H_5/Fc), 4.38 (dpt, J_{HP} = 3.0 Hz, J_{HH} = 1.8 Hz, 2 H, H^{α}/C_5H_4/Fc), 4.49 (pt, J_{HH} = 1.7 Hz, 2 H, H^{β}/C_5H_4/Rc), 4.53 (dpt, J_{HP} = 1.0 Hz, J_{HH} = 1.8 Hz, 2 H, H^{β}/C_5H_4/Fc) 4.47 (pt, J_{HH} = 1.8 Hz, 2 H, H^{α}/C_5H_4/Rc), 4.61 (s, 5 H, C_5H_5/Rc), 7.35–7.63 (m, 10 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 69.9 (CH/C_5H_4/Rc), 70.1 (C_5H_5/Fc), 70.6 (d, $^1J_{CP}$ = 41.6 Hz, C^i/C_5H_4/Fc), 71.9 (C_5H_5/Rc), 72.4 (d, $^3J_{CP}$ = 8.4 Hz, C^{β}/C_5H_4/Fc), 73.7 (d, $^2J_{CP}$ = 13.8 Hz, C^{α}/C_5H_4/Fc), 74.5 (CH/C_5H_4/Rc), 128.8 (d, $^3J_{CP}$ = 11.1 Hz, C^m/C_6H_5), 131.2 (d, $^4J_{CP}$ = 2.3 Hz, C^p/C_6H_5), 132.4 (d, $^1J_{CP}$ = 57.1 Hz, C^i/C_6H_5), 133.9 (d, $^2J_{CP}$ = 13.8 Hz, C^o/C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.3 (s, PPh_2). (The signals for the C≡C entity and the C^i/Rc could not be detected.)

Synthesis of FcPPh$_2$AuC≡C-C$_6$H$_4$-4-C≡N-[Ru] (7). To 30 mg (0.04 mmol) of [Ru]N≡N[Ru] (**6**) in 15 mL of dichloromethane was added 60 mg (0.09 mmol) of $FcPPh_2AuC$≡C-C_6H_4-4-C≡N (**3b**) in a single portion. The reaction solution was stirred for 3 h at 25 °C, whereby the color of the solution changed from orange to deep red. The solvent was concentrated to 3 mL, and the product was precipitated by addition of 20 mL of *n*-hexane, washed twice with 10 mL portions of diethyl ether, and dried in an oil-pump vacuum. Complex **7** was obtained as a red solid. Yield: 75 mg (0.07 mmol, 88% based on **6**).

$C_{42}H_{42}N_4Cl_2PAuFeRu$ (1058.59): C, 47.65; H, 4.00; N, 5.29; Found: C, 47.32; H, 3.73; N, 5.47. Mp: >105 °C (dec). IR (KBr, cm^{-1}): 2199 (m, $\nu_{C\equiv N}$), 2112 (w, $\nu_{AuC\equiv C}$). ^{1}H NMR ($CDCl_3$, δ): 2.65 (s, 12 H, NCH_3), 4.10 (s, 4 H, NCH_2), 4.22 (s, 5 H, C_5H_5), 4.38 (br s, 2 H, H^{α}/C_5H_4), 4.56 (br s, 2 H, H^{β}/C_5H_4), 7.20 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, C_5H_3N), 7.39–7.74 (m, 15 H, $C_6H_5 + C_6H_4 + C_5H_3N$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.5 (s, PPh_2). MS (ESI-TOF, *m/z*): 1058.2 (40) $[M]^+$, 365.0 (30) $[M - \mathbf{3b}]^+$.

Synthesis of $[FcPPh_2AuC\equiv C\text{-}C_5H_4N\text{-}Cu\{(Me_3SiC\equiv C)_2[Ti]\}]$-OTf (9). To 50 mg (0.075 mmol) of $FcPPh_2AuC\equiv C\text{-}C_5H_4N$ (**3c**) dissolved in diethyl ether (40 mL) was added 60 mg (0.08 mmol) of $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2]\}CuOTf$ (**8a**), and the resulting reaction mixture was stirred for 2 h. Afterward the resulting precipitate was filtered, washed with diethyl ether (10 mL), and dried in an oil-pump vacuum. Complex **9** was obtained as a golden-yellow solid. Yield: 75 mg (0.054 mmol, 71% based on **3c**).

Anal. Calc for $C_{56}H_{67}O_3NF_3PSSi_4AuCuFeTi$ (1398.8): C, 48.09; H, 4.83; N, 1.00. Found: C, 48.11; H, 4.76; N, 1.01. Mp: >124 °C (dec). IR (KBr, cm^{-1}): 2126 (m, $\nu_{AuC\equiv C}$), 1915 (m, $\nu_{TiC\equiv C}$). ^1H NMR ($CDCl_3$, δ): −0.06 (s, 18 H, $SiMe_3$), 0.26 (s, 18 H, $SiMe_3$), 4.22 (s, 5 H, C_5H_5), 4.38 (dpt, $J_{HP} = 2.7$ Hz, $J_{HH} = 1.9$ Hz, 2 H, H^{α}/C_5H_4), 4.58 (dpt, $J_{HP} = 1.0$ Hz, $J_{HH} = 1.9$ Hz, 2 H, H^{β}/C_5H_4), 6.26–6.32 (m, 8 H, $C_5H_4SiMe_3$), 7.41–7.65 (m, 12 H, C_6H_5 + C_5H_4N), 8.53–8.57 (m, 2 H, C_5H_4N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.1 (s, PPh_2). MS (ESI-TOF, *m/z*): 1248.2 (100) $[M - CF_3SO_3]^+$, 579.2 (10) $[M - \mathbf{3c}]^+$.

Synthesis of $Me_3SiC\equiv C$-NCN-Pt-$C\equiv C$-bipy (11a). A 140 mg (0.78 mmol) amount of 5-ethynyl-2,2′-bipyridyl (**2a**) was dissolved in 100 mL of diethyl ether, and at −80 °C 0.45 mL (0.72 mmol) of ^{n}BuLi (1.6 M in *n*-hexane) was slowly added. The resulting violet solution was stirred for 30 min at this temperature, and then **10** (250 mg, 0.48 mmol) was added in a single portion. The mixture was allowed to warm to 25 °C, and stirring was continued for 16 h. All volatiles were evaporated in vacuum, and the residue was dissolved in dichloromethane (20 mL) and filtered through a pad of Celite. The solution was concentrated to 3 mL, and addition of *n*-hexane (50 mL) led to the precipitation of **11a**. The separation of the solid material was effected by centrifugation. After washing it twice with diethyl ether (10 mL), complex **11a** was obtained as an off-white solid. Yield: 240 mg (0.36 mmol, 75% based on **10**).

$C_{29}H_{34}N_4SiPt$ (661.78). IR (KBr, cm^{-1}): 2146 (m, $\nu_{SiC\equiv C}$), 2089 (m, $\nu_{PtC\equiv C}$). ^1H NMR ($CDCl_3$, δ): 0.22 (s, 9 H, $SiMe_3$), 3.22 (s, $^3J_{HPt} = 42.8$ Hz, 12 H, NCH_3), 4.09 (s, $^3J_{HPt} = 43.6$ Hz, 4 H, NCH_2), 7.04 (s, 2 H, C_6H_2), 7.24 (ddd, $^3J_{H5'H4'} = 8$ Hz, $^3J_{H5'H6'} = 4.8$ Hz, $^4J_{H5'H3'} = 1$ Hz, 1 H, *H5′*/bipy), 7.73–7.81 (m, 2 H, *H4,H4′*/bipy), 8.23 (dd, $^3J_{H3H4} = 8.3$ Hz, $^5J_{H3H6} = 0.6$ Hz, 1 H, *H3*/bipy), 8.35 (ddd, $^3J_{H3H4'} = 8$ Hz, $^4J_{H3'H5'} = 1$ Hz, $^5J_{H3'H6'} = 1$ Hz, 1 H, *H3′*/bipy), 8.65 (ddd, $^3J_{H6'H5'} = 4.8$ Hz, $^4J_{H6'H4'} = 1.8$ Hz, $^5J_{H6'H3'} = 1$ Hz, 1 H, *H6′*/bipy), 8.69 (dd, $^4J_{H6H4} = 2.4$ Hz, $^5J_{H6H3} = 0.6$ Hz, 1 H, *H6*/bipy).

Synthesis of $HC\equiv C$-NCN-Pt-$C\equiv C$-bipy (12a). To **11a** (200 mg, 0.30 mmol) dissolved in dichloromethane (50 mL) was added 0.35 mL (0.35 mmol) of $[^nBu_4N]F$ (1 M in tetrahydrofuran). After stirring for 2 h at 25 °C all volatiles were evaporated under reduced pressure and the residue was extracted with ethanol (3 × 10 mL). Separation by centrifugation and drying in an oil-pump vacuum yielded **12a** as a pale brown solid. Yield: 90 mg (0.15 mmol, 51% based on **11a**).

$C_{26}H_{26}N_4Pt$ (589.6). IR (KBr, cm^{-1}): 3287 (m, $\nu_{\equiv C\text{-}H}$), 2080 (s, $\nu_{PtC\equiv C}$). ^1H NMR ($CDCl_3$, δ): 3.01 (s, 1 H, $\equiv CH$), 3.23 (s, $^3J_{HPt} = 42.8$ Hz, 12 H, NCH_3), 4.11 (s, $^3J_{HPt} = 43.6$ Hz, 4 H, NCH_2), 7.05 (s, 2 H, C_6H_2), 7.24 (ddd, $^3J_{H5'H4'} = 8$ Hz, $^3J_{H5'H6'} = 4.8$ Hz, $^4J_{H5'H3'} = 1$ Hz, 1 H, *H5′*/bipy), 7.73–7.81 (m, 2 H, *H4,H4′*/bipy), 8.23 (dd, $^3J_{H3H4} = 8.3$ Hz, $^5J_{H3H6} = 0.6$ Hz, 1 H, *H3*/bipy), 8.35 (ddd, $^3J_{H3H4'} = 8$ Hz, $^4J_{H3'H5'} = 1$ Hz, $^5J_{H3'H6'} = 1$ Hz, 1 H, *H3′*/bipy), 8.65 (ddd, $^3J_{H6'H5'} = 4.8$ Hz, $^4J_{H6'H4'} = 1.8$ Hz, $^5J_{H6'H3'} = 1$ Hz, 1 H, *H6′*/bipy), 8.69 (dd, $^4J_{H6H4} = 2.4$ Hz, $^5J_{H6H3} = 0.6$ Hz, 1 H, *H6*/bipy).

Synthesis of $FcPPh_2AuC\equiv C$-NCN-Pt-$C\equiv C$-bipy (13a). Compound **12a** (80 mg, 0.136 mmol) and $FcPPh_2AuCl$ (**1**) (100 mg, 0.166 mmol) were dissolved in 15 mL of tetrahydrofuran and 10 mL of diethyl amine. After addition of 1 mg of [CuI] the resulting reaction mixture was stirred overnight at 25 °C. The solvents were evaporated under reduced pressure, and the residue was extracted with acetone (3 × 10 mL). Separation by centrifugation and drying in vacuum yielded **13a** as an orange solid. Yield: 75 mg (0.065 mmol, 48% based on **11a**).

$C_{48}H_{44}N_4PAuFePt$ (1155.77). IR (KBr, cm^{-1}): 2103 (m, $\nu_{AuC\equiv C}$), 2080 (m, $\nu_{PtC\equiv C}$). Further characterization was not possible, due to the high insolubility of **13a** in organic solvents (vide supra).

Synthesis of $FcPPh_2AuC\equiv C$-NCN-Pt-$C\equiv C$-C_6H_4-4-$C\equiv N$ (13b). Experimental conditions and workup were identical to those for compound **13a**. Experimental details: **12b** (70 mg, 0.13 mmol), $FcPPh_2AuCl$ (**1**) (100 mg, 0.166 mmol). Yield: 60 mg (0.054 mmol, 42% based on **12b**).

$C_{45}H_{41}N_3PAuFePt$ (1102.7). IR (KBr, cm^{-1}): 2223 (m, $\nu_{C\equiv N}$), 2096 (m, $\nu_{AuC\equiv C}$), 2079 (m, $\nu_{PtC\equiv C}$). MS (ESI-TOF, *m/z*): 1103.2 $[M + H]^+$. Further characterization was not possible, due to the high insolubility of **13b** in organic solvents (vide supra).

Synthesis of $FcPPh_2AuC\equiv C$-bipy$[Mo(CO)_4]$ (15). To 70 mg (0.094 mmol) of $FcPPh_2AuC\equiv C$-bipy (**3a**) dissolved in 30 mL of dichloromethane/tetrahydofuran (ratio 5:1) was added 30 mg (0.1 mmol) of $(nbd)Mo(CO)_4$ (**14**). After a few minutes the color of the solution turned from yellow to dark red. Stirring was continued for 15 h at 25 °C. Afterward all volatiles were removed in an oil-pump vacuum and the residue was washed twice with 15 mL portions of diethyl ether and dried in an oil-pump vacuum. Compound **15** was obtained as a dark red solid (Yield: 70 mg, 0.073 mmol, 78% based on **3a**).

Anal. Calc for $C_{38}H_{26}O_4AuFeMoN_2P$ (954.37): C, 47.82; H, 2.75; N, 2.94. Found: C, 47.67; H, 2.76, N, 3.02. Mp: >175 °C (dec). IR (KBr, cm^{-1}): 2119 (m, $\nu_{AuC\equiv C}$), 2011, 1890, 1867, 1829 (s, ν_{CO}). ^1H NMR ($CDCl_3$, δ): 4.23 (s, 5 H, C_5H_5), 4.41 (bs, 2 H, H^{α}/C_5H_4), 4.58 (bs, 2 H, H^{β}/C_5H_4), 7.33 (ddd, $^3J_{H5'H4'} = 7.6$ Hz, $^3J_{H5'H6'} = 5$ Hz, $^4J_{H5'H3'} = 1$ Hz, 1 H, *H5′*/bipy), 7.42–7.66 (m, 10 H, C_6H_5), 7.89 (ddd, $^3J_{H4'H3'} = {}^3J_{H4'H5'} = 8$ Hz, $^4J_{H4'H6'} = 1.4$ Hz, 1 H, *H4′*/bipy), 7.91–8.05 (m, 3 H, *H3,H3′,H4*/bipy), 9.12 (d, $^3J_{H6'H5'} = 5$ Hz, 1 H, *H6′*/bipy), 9.27 (d, $^4J_{H6H4} = 1.2$ Hz, 1 H, *H6*/bipy). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.19 (s, PPh_2).

Synthesis of $[FcPPh_2AuC\equiv C\text{-bipy-}Cu\{(Me_3SiC\equiv C)_2[Ti]\}]PF_6$ (16a). To 65 mg (0.087 mmol) of $FcPPh_2AuC\equiv C$-bipy (**3a**) dissolved in 30 mL of tetrahydrofuran were added 65 mg (0.085 mmol) of $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}Cu(N\equiv CCH_3)]PF_6$ (**8b**). The reaction solution was stirred for 3 h at 25 °C. Afterward it was filtered through a pad of Celite and all volatiles were removed under reduced pressure. The residue was washed twice with 15 mL portions of petroleum ether and dried in an oil-pump vacuum. Complex **16a** was obtained as an orange-red solid. Yield: 120 mg (0.082 mmol, 96% based on **8b**).

Anal. Calc for $C_{60}H_{70}AuCuF_6FeN_2P_2Si_4Ti$ (1471.76): C, 48.97; H, 4.79; N, 1.90. Found: C, 48.70; H, 4.68; N, 2.18. Mp: >172 °C (dec). IR (KBr, cm^{-1}): 2118 (m, $\nu_{AuC\equiv C}$), 1924 (w, $\nu_{TiC\equiv C}$), 841 (s, ν_{PF}). ^1H NMR ($CDCl_3$, δ): −0.49 (s, 18 H, $SiMe_3$), 0.27 (s, 9 H, $SiMe_3$), 0.28 (s, 9 H, $SiMe_3$), 4.21 (s, 5 H, C_5H_5), 4.39 (dpt, $J_{HP} = 2.5$ Hz, $J_{HH} = 1.9$ Hz, 2 H, H^{α}/C_5H_4/Fc), 4.58 (br s, 2 H, H^{β}/C_5H_4/Fc), 6.26–6.30 (m, 8 H, $C_5H_4SiMe_3$), 7.41–7.64 (m, 10 H, C_6H_5) 7.69 (dd, $^3J_{H5'H4'} = 7.8$ Hz, $^3J_{H5'H6'} = 5$ Hz, 1 H, *H5′*/bipy), 8.18 (dd, $^3J_{H4H3} = 8.5$ Hz, $^4J_{H4H6} = 2$ Hz, 1 H, *H4*/bipy), 8.22 (ddd, $^3J_{H4'H3'} = {}^3J_{H4'H5'} = 7.8$ Hz, $^4J_{H4'H6'} = 1.8$ Hz, 1 H, *H4′*/bipy), 8.39 (d, $^3J_{H3'H4'} = 7.8$ Hz, 1 H, *H3′*/bipy), 8.50 (d, $^3J_{H3H4} = 8.5$ Hz, 1 H, *H3*/bipy), 8.53 (d, $^3J_{H6'H5'} = 4.4$ Hz, 1 H, *H6′*/bipy), 8.56 (d, $^4J_{H6H4} = 2$ Hz, 1 H, *H6*/bipy). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): −0.6 ($SiMe_3$), 0.17 ($SiMe_3$), 0.23 ($SiMe_3$), 69.2 (d, $^1J_{CP} = 68.2$ Hz, C^i/C_5H_4/Fc), 70.1 (C_5H_5/Fc), 72.7 (d, $^3J_{CP} = 8.6$ Hz, C^{β}/C_5H_4/Fc), 73.7 (d, $^2J_{CP} = 13.8$ Hz, C^{α}/C_5H_4/Fc), 98.7 ($AuC\equiv C$), 115.2 (CH/C_5H_4), 115.3 (CH/C_5H_4), 117.2 (CH/C_5H_4), 117.3 (CH/C_5H_4), 122.0 (bipy), 122.9 (bipy), 122.9 (C^i/C_5H_4), 123.3 (C^i/C_5H_4), 125.8 (bipy), 126.8 (bipy), 129.1 (d, $^3J_{CP} = 11.3$ Hz, C^m/C_6H_5), 131.6 (d, $^4J_{CP} = 2.4$ Hz, C^p/C_6H_5), 131.7 (d, $^1J_{CP} = 58.3$ Hz, C^i/C_6H_5), 133.7 ($TiC\equiv C$), 133.8 (d, $^2J_{CP} = 13.7$ Hz, C^o/C_6H_5), 140.5 (bipy), 142.7 (bipy), 147.8 (bipy), 149.2 (bipy), 150.7 (bipy), 151.8 (bipy), 165.9 ($TiC\equiv C$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.249 MHz, δ): 36.2

(s, *P*Ph$_2$), −145.1 (septuplett, $^1J_{\mathrm{PF}}$ = 713 Hz, *P*F$_6$). (The second signal for the AuC≡C entity could not be detected.)

Synthesis of [FcPPh$_2$AuC≡C-bipy-Ag{(Me$_3$SiC≡C)$_2$[Ti]}]ClO$_4$ (16b). Experimental conditions and workup were the same as for the preparation of **16a**. Specific experimental details: {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$]}AgOClO$_3$ (**8c**) (75 mg, 0.105 mmol), FcPPh$_2$AuC≡C-bipy (**3a**) (80 mg, 0.107 mmol), 2 h stirring, orange solid. Yield: 115 mg (0.078 mmol), 74% based on **8c**.

Anal. Calc for $C_{60}H_{70}O_4AgAuClFeN_2PSi_4Ti$ (1470.56): C, 49.01; H, 4.80; N, 1.91. Found: C, 49.00; H, 4.80; N, 1.88. Mp: >145 °C (dec). IR (KBr, cm^{-1}): 2116 (m, $\nu_{\mathrm{Au}C\equiv C}$), 1952 (w, $\nu_{\mathrm{Ti}C\equiv C}$), 1097 (s, ν_{ClO}). ^{1}H NMR (CDCl$_3$, δ): −0.30 (br s, 18 H, Si*Me*$_3$), 0.27 (s, 18 H, Si*Me*$_3$), 4.20 (s, 5 H, C$_5$*H*$_5$/Fc), 4.38 (br s, 2 H, H^{α}/C$_5$*H*$_4$/Fc), 4.58 (br s, 2 H, H^{β}/C$_5$*H*$_4$/Fc), 6.42 (pt, J_{HH} = 2.2 Hz, 4 H, C$_5$*H*$_4$SiMe$_3$), 6.49 (pt, J_{HH} = 2.2 Hz, 4 H, C$_5$*H*$_4$SiMe$_3$) 7.39–7.65 (m, 11 H, C$_6$H$_5$ + *H5′*/bipy), 8.13 (dd, $^3J_{\mathrm{H4H3}}$ = 8.4 Hz, $^4J_{\mathrm{H4H6}}$ = 2 Hz, 1 H, *H4*/bipy), 8.18 (ddd, $^3J_{\mathrm{H4'H3'}}$ = $^3J_{\mathrm{H4'H5'}}$ = 8 Hz, $^4J_{\mathrm{H4'H6'}}$ = 1.5 Hz, 1 H, *H4′*/bipy), 8.31 (d, $^3J_{\mathrm{H3H4}}$ = 8.4 Hz, 1 H, *H3*/bipy), 8.41 (d, $^3J_{\mathrm{H3'H4'}}$ = 8 Hz, 1 H, *H3′*/bipy), 8.58 (d, $^3J_{\mathrm{H6'H5'}}$ = 5 Hz, 1 H, *H6′*/bipy), 8.64 (dd, $^4J_{\mathrm{H6H4}}$ = 2 Hz, $^5J_{\mathrm{H6H3}}$ = 0.6 Hz, 1 H, *H6*/bipy). ^{31}P{^{1}H} NMR (CDCl$_3$, 101.249 MHz, δ): 36.1 (s, *P*Ph$_2$).

Crystal Structure Determinations. Crystal data for **3a**, **3b**, **3e**, **5b**, **5c**, and **16a** are presented in Tables 3 (**3a**, **3b**, **3e**) and 4 (**5b**, **5c**, **16a**). The data for **3a**, **3e**, and **16a** were collected on a Bruker Smart CCD 1k diffractometer and for **3b**, **5b**, and **5c** on a Oxford Gemini S diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 293(2) K (**3b**, **3e**, **5b**, **5c**), 203(2) K (**3a**), and 183(2) (**16a**) using oil-coated shock-cooled crystals.[36] The structures were solved by direct methods using SHELXS-97[37] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[38] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. In **3e** the NMe$_2$ group is disordered and has been refined to split occupancies of 0.35/0.65 (N1, C32, and C33).

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Supporting Information Available: Tables of atomic coordinates, bond lengths, angles, torsion angles, and anisotropic displacement parameters for **3a**, **3b**, **3e**, **5b**, **5c**, and **16a** and a cyclic voltammogram of **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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