Transition-Metal Complexes Based on the 1,3,5-Triethynyl Benzene Linking Unit

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Abstract. The synthesis of a unique series of heteromultinuclear transition metal compounds is reported. Complexes 1-I-3-Br-5-(FcC=C)- C_6H_3 (4), 1-Br-3-(bpy-C=C)-5-(FcC=C)- C_6H_3 (6), 1,3-(bpy-C=C)₂-5-(FcC=C)- C_6H_3 (7), 1-(XC=C)-3-(bpy-C=C)-5-(FcC=C)- C_6H_3 (8, X =SiMe₃; 9, X = H), 1-(HC=C)-3-[(CO)₃ClRe(bpy-C=C)]-5-(FcC=C)- C_6H_3 (11), 1-[(Ph₃P)AuC=C]-3-[(CO)₃ClRe(bpy-C=C)]-5-(FcC=C)- C_6H_3 (13), 1-[(Ph₃P)AuC=C]-3-(bpy-C=C)-5-(FcC=C)- C_6H_3 (14), [1-[(Ph₃PAuC=C]-3-[{[Ti](C=CSiMe₃)₂}Cu(bpy-C=C)]-5-(FcC=C)- C_6H_3]PF₆ (16), and [1,3-[($tBu_2bpy)_2Ru(bpy-C=C)$]₂-5-(FcC=C)- C_6H_3](PF₆)₄ (18) (Fc = (η^5 - C_5H_4)(η^5 - C_5H_5)Fe, bpy = 2,2'-bipyridiyl-5-yl, [Ti] = (η^5 - C_5H_4 SiMe₃)₂Ti) were prepared by using consecutive

Introduction

The synthesis of carbon-rich acetylide-containing molecules opens new avenues of fundamental and technological research at the interface between chemistry and materials science. Unusual structures, high stability and useful electronic properties are some of the desirable fundamental characteristics of such systems, which have captured much attention during the last years [1]. In this context, interest centers on those compounds that contain redox-active metal building blocks next to the carbon-rich structural units, among which the ferrocenyl moiety has been most studied. The ferrocenyl group is, for example, robust, represents a one-electron reservoir and can undergo reversible redox processes [2]. Very recently, ferrocenyl entities, $(\eta^5-C_5H_4)(\eta^5-C_5H_5)Fe$, have been successfully applied in the synthesis of heteromultimetallic transition metal complexes, in which the metal atoms are bridged by carbon-rich connectivities [3]. Whereas homo- and heterobimetallic complexes with carbon-rich organic and/or inorganic connecting units were designed and synthesized, and their chemical and physical properties were intensively studied [4, 5], only less is known about organometallics in which more than three different metals are linked by organic π -conjugated bridging ligands [3]. Such molecules are of great interest, due to their extended organic π system which can provide remarkable applications and hence, synthesis methodologies including metathesis, desilylation, dehydrohalogenation, and carbon–carbon cross-coupling reactions. In these complexes the corresponding metal atoms are connected by carbon-rich bridging units comprising 1,3-diethynyl-, 1,3,5-triethynylbenzene and bipyridyl units. They were characterized by elemental analysis, IR and NMR spectroscopy, and partly by ESI-TOF mass spectrometry. The structures of **4** and **11** in the solid state are reported. Both molecules are characterized by the central benzene core bridging the individual transition metal complex fragments. The corresponding acetylide entities are, as typical, found in a linear arrangement with representa-

the electrochemical behavior, UV/Vis/NIR characteristics and EPR analysis of in-situ generated associated radical cations were studied [6–8].

tive *M*–C, C–C_{C=C} and C=C bond lengths.

As an extension of our previous work in the field of heteromultimetallic chemistry, in which we connected different early and late transition metal atoms with carbon-rich organic and inorganic bridging units, we here focus on some further straightforward synthesis methods for the preparation and characterization of diverse unsymmetrical compounds featuring the transition metals titanium, rhenium, iron, ruthenium, copper, and gold, and comprising 1,3,5-triethynylbenzene and 2,2'-bipyridiyl-5-yl (= bpy) organic connecting units. The structure of two molecules in the solid state is discussed as well.

Results and Discussion

In terms of synthesizing heteromultimetallic transition metal complexes based on the 1,3,5-triethynylbenzene core, we chose ferrocenyl-functionalized 1-I-3-Br-5-(FcC=C)-C₆H₃ (4) as suitable key starting material. The organometallic compound 4 was synthesized by subsequent treatment of 1-I-3,5-Br₂-C₆H₃ (1) with FcC=CH (2) under Sonogashira cross-coupling conditions to produce 1,3-Br₂-5-FcC=C-C₆H₃ (3), which on Br–I exchange eventually resulted in the formation of 4 (Scheme 1) [7].

The diethynyl-substituted compound 1-Br-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (6) was accessible by the reaction of 4 with one equivalent of 5-ethynyl-2,2'-bipyridine (5) under typical Sonogashira carbon–carbon cross-coupling conditions (diisopropylamine, 40 °C), whereby the more reactive aryl–iodo

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Scheme 1. Consecutive reaction sequence for the synthesis of 9.

bond allowed the preferential introduction of one 5-ethynyl-2,2'-bipyridyl moiety (Scheme 1, Experimental Section). After appropriate work-up, mononuclear compound 6 was isolated as an orange solid in 78 % yield. As side product the corresponding disubstituted molecule 1,3-(bpy-C≡C)₂-5-(FcC≡C)- C_6H_3 (7) could be isolated in a yield of 7 % (Experimental Section). The exchange of one bromide substituent by the more reactive iodide in 3 was necessary to obtain complex 6 as major product. If 3 reacted under similar reaction conditions with bpyC=CH (5), a mixture of 6 and 7 was obtained. Complex 6 reacted further with an excess of trimethylsilylacetylene under similar reaction conditions whereby the reaction mixture had to be heated to 80 °C for completion and hence, forming 1- $(Me_3SiC\equiv C)-3-(bpy-C\equiv C)-5-(FcC\equiv C)-C_6H_3$ (8). Desilylation of 8 with $[nBu_4N]F$ in tetrahydrofuran at ambient temperature finally gave 1-(HC=C)-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (9) as a yellow solid (Scheme 1).

With its different functionalities, the organometallic compound 9 was used as starting material for the synthesis of higher nuclear transition metal complexes featuring up to four different metal atoms as outlined in Scheme 2.

The synthesis of $1-[(Ph_3P)AuC=C]-3-[(CO)_3ClRe(bpy-C=C)]-5-(FcC=C)-C_6H_3$ (13) (Scheme 2) includes following steps: (i) treatment of 9 with equimolar amounts of [Re(CO)_5Cl] (10) in toluene and heating the reaction medium for 8 hours to 60 °C gave $1-(HC=C)-3-[(CO)_3ClRe(bpy-C=C)]-5-(FcC=C)-C_6H_3$ (11), which in the next step (ii) afforded on addition of [(Ph_3P)AuCl] (12) in presence of cata-

lytic amounts of [CuI] complex **13**, in which the three complex fragments Fc, (bpy)Re(CO)₃Cl, and (Ph₃P)Au are connected by a 1,3,5-triethynylbenzene core (Scheme 2).

Even the synthesis of a heterotetrametallic complex featuring titanium, iron, copper, and gold metal atoms was possible by starting from **9**. In this respect, the heterobimetallic complex $1-[(Ph_3P)AuC\equiv C]-3-(bpy-C\equiv C)-5-(FcC\equiv C)-C_6H_3$ (**14**) was prepared using a mixture of tetrahydrofuran-diethylamine in 1:1 ratio at 25 °C (Scheme 2). It was necessary to add a catalytic amount of [CuI] to the reaction medium for completion of the reaction [8]. The last step in the synthesis of [1-[(Ph_3P)AuC\equiv C]-3-[{[Ti](C\equiv CSiMe_3)_2}Cu(bpy-C\equiv C)]-5-(FcC\equiv C)-C_6H_3]PF_6 (**16**) ([Ti] = (η^5 -C_5H_4SiMe_3)_2Ti) included the addition of the heterobimetallic organometallic π -tweezed molecule [{[Ti](μ - σ , π -C \equiv CSiMe_3)_2}Cu(N \equiv CMe)]PF_6 (**15**) to

14. On replacement of the only weakly-bonded acetonitrile by the 2,2'-bipyridyl ligand, the heterotetrametallic complex **16** was obtained as a red solid material in good yield after appropriate work-up (Scheme 2, Experimental Section).

The synthesis of a trimetallic FeRu₂ species, $[1,3-[(tBu_2bpy)_2Ru(bpy-C=C)]_2$ -5-(FcC=C)-C₆H₃](PF₆)₄ (18) (tBu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) was possible by the reaction of 1,3-(bpy-C=C)_2-5-(FcC=C)-C₆H₃ (7) with two equivalents of $[(tBu_2bpy)_2RuCl_2]$ (17) in boiling ethanol (Reaction 1). After 20 hours and addition of a aqueous solution of [H₄N]PF₆, the ionic compound 18 could be isolated in 66 % yield as a red material.



Scheme 2. Synthesis of heterometallic 13 and 16 using 9 as key starting material.



All new synthesized multimetallic transition metal complexes are stable both in solid state and solution, with exception of **16**. This molecule slowly decomposes in solution over prolonged time on precipitation of *non*-soluble materials in common organic solvents.

The identities of 4, 6–9, 11, 13, 14, 16, and 18 were confirmed by elemental analysis, IR, ¹H, ¹³C{¹H}, ³¹P{¹H} NMR spectroscopy, and partly by ESI-TOF mass spectrometry. The structure of complexes 4 and 11, respectively, in the solid state was additionally determined by single-crystal X-ray structure analysis, thus confirming the structural assignment made from spectroscopic characterization. The IR spectra of all compounds are characterized by very dominant $v_{C\equiv C}$ vibrations of the organometallic M-C=CR (M = Ti, Au, Fc; $R = C_6H_3$, SiMe₃) and the organic X-C=C- C_6H_3 (X = H, bpy, C_5H_4) units (Experimental Section). These vibrations are found in the range of 2157–2214 cm⁻¹ for the organic moieties, whereas for the metal acetylide fragments typical absorptions are observed at 2115 (AuC=C) [9] and 1924 cm⁻¹ (TiC=C) [10], respectively. For the HC=C group present in **9** an additional strong absorption band is found at 3290 cm⁻¹. Furthermore, in the IR spectra of the corresponding metal–carbonyl molecules **11** and **13**, the CO stretching vibrations are very diagnostic and represent a useful monitoring tool along

with the appearance and disappearance of the $v_{H-C=C}$ vibration (complex 11 vs. 13). For 11 and 13 three (11: 1894, 1914, and 2022 cm⁻¹; 13: 1896, 1915, and 2021 cm⁻¹) very strong v_{CO} bands are observed, which is typical for this type of species [11].

The consecutive formation of the multimetallic assemblies from 3 and 4 is also confirmed by ¹H NMR spectroscopy (Experimental Section). Characteristic for all compounds is the appearance of typical ferrocenyl signals at ca. 4.25 ppm (singlet) for the C₅H₅ ring protons and between 4.2–4.6 ppm (pseudo-triplets) for the C_5H_4 protons with a J_{HH} coupling constant of ca. 1.9 Hz (Experimental Section). The titaniumbonded cyclopentadienyl ligands in 16 are observed between 6.2–6.3 ppm as multiplet differing from the starting material 15, where *pseudo*-triplets are characteristic. [12] The ¹H NMR spectrum of 9 consists of a singlet at 3.14 ppm, which can be assigned to the acetylenic proton. The bpy, C₆H₃, and C₆H₅ groups give typical resonances with the anticipated chemical shifts and coupling patterns (Experimental Section). For example, the aryl protons of the central phenylene ring were found as three separated *pseudo*-triplets in the range of 7.4–7.8 ppm, which show up-field shifts upon coordination of the alkynyl units to a transition metal fragment (Experimental Section). Most significant for 8 is the appearance of a resonance signal at 0.26 ppm for the trimethylsilyl group. In this context, most diagnostic for the formation of 16 is the high-field shift (-0.48 ppm) of the $Me_3SiC=C$ protons in comparison to 15 upon coordination of the bipyridyl entity to the organometallic π -tweezed copper(I) atom, which can be explained by the ring current of the chelating bipyridyl ligand [12, 13]. In addition, as a result of the different chemical environment, the spectrum of 16 reveals two well separated singlet signals at 0.28 and 0.30 ppm for the cyclopentadienyl-bonded Me₃Si units (Experimental Section). Similar observations were made in the $^{13}C{^{1}H}$ NMR spectra of the complexes described above.

The ³¹P{¹H} NMR spectra of the (Ph₃P)Au-containing molecules **13**, **14**, and **16** show a singlet at ca. 41.5 ppm, which is indicative of similar phosphane environments. Compared to the starting material [(Ph₃P)AuCl] (**12**) (33.8 ppm [14]), a shift to lower field is observed, which is typical for exchanging the gold(I)-bonded chloride ion by an acetylide unit [9]. The *non*coordinating PF₆⁻ ion in **16** gives rise to a septet at –145.1 ppm with ${}^{1}J_{\text{PF}} = 713$ Hz.

For multimetallic complexes **13** and **16** electrospray ionization mass spectrometric investigations indicated the presence of the appropriate molecular ions $[M + H]^+$ (*m*/*z* 1253.4, **13**), $[M - PF_6]^+$ (*m*/*z* 1525.3, **16**) with characteristic isotope distribution patterns. Characteristic for **18** is the molecular ion $[M - 4PF_6]^{4+}$ (*m*/*z* 479.2) and the formation of fragments such as $[M - 4PF_6 - Ru(tBu_2bpy)_2]^{2+}$ (*m*/*z* 639.6) (Experimental Section).

Additionally, the molecular structures of 4 and 11 in the solid state were determined by single-crystal X-ray diffraction. Single crystals could be obtained by slow diffusion of *n*-hexane into a chloroform solution containing either 4 or 11 at ambient temperature. The perspective drawings with the atomic numbering scheme of these molecules are shown in Figure 1 and

Figure 2 (4) and Figure 3, Figure 4, and Figure 5 (11) together with selected bond lengths (in Å) and bond angles (in °). The crystallographic data are summarized in Table 1 (Experimental Section).



Figure 1. The molecular solid-state structure (ORTEP diagram, 50 % probability level) of 4 with the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /°: Fe1–D1 1.644(4), Fe1–D2 1.654(4), C11–C12 1.206(12), C17–Br1 1.947(9), C15–I1 2.031(8); C1–C11–C12 178.6(8), C11–C15–C13 178.4(8). D1 = centroid of C1–C5, D2 = centroid of C6–C10. Standard uncertainties of the last significant digit(s) are shown in parentheses.



Figure 2. Graphical representation of the π - π -interactions of molecules of **4** in the solid state giving rise to the formation of 1D chains along the crystallographic *a*-axis. Dotted lines refer to the shortest (3.480 Å) and dashed lines to the longest C–C contacts (3.561 Å) of interacting cyclopentadienyl and phenyl rings with \angle giving the interplanar angle. Labels 'A' to 'D' refer to the 1st-4th symmetry generated molecules of **4**. Hydrogen atoms are omitted for clarity.

Both complexes 4 and 11 crystallize in the monoclinic space group $P2_1/n$. From Figure 1 and Figure 3 it can be seen that the structures of 4 and 11 are essentially similar as far as the molecule backbone is concerned.

As typical for other ferrocenyl complexes, the Fe1–D1 and Fe1–D2 separations in **4** and **11** are found to be in the range 1.640(4) and 1.654(4) Å [15]. The two cyclopentadienyl ligands are thereby rotated by $0.1(6)^{\circ}$ (**4**) and $2.5(7)^{\circ}$ (**11**) with respect to each other, which verifies an almost eclipsed conformation. The Fc-C=C-, ((CO)₃ClRe)bpy-C=C-, and HC=C-acetylide units are, as expected, linear with typical C=C separations (Figure 1 and Figure 3). The bond lengths and bond angles for all the other groups agree well with those reported



Figure 3. The molecular solid-state structure (ORTEP diagram, 50 % probability level) of **11** with the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths /Å and bond angles /°: Fe1–D1 1.646(4), Fe1–D2 1.640(4), C11–C12 1.176(9), C19–C20 1.188(11), C21–C22 1.212(10), Re1–N1 2.166(5), Re1–N2 2.184(6), Re1–C11 2.471(2), Re1–C33 1.904(9), Re1–C34 1.935(8), Re1–C35 1.917(9), C33–O1 1.171(9), C34–O2 1.120(8), C35–O3 1.156(9); C1–C11–C12 174.3(8), C11–C12–C13 178.0(9), C17–C19–C20 173.9(10), C15–C21–C22 177.5(8), C21–C22–C24 177.8(9), N1–Re1–N2 74.8(2), C33–Re1–C35 89.1(3), C34–Re1–C11 176.5(2). D1 = centroid of C1–C5, D2 = centroid of C6–C10. Standard uncertainties of the last significant digit(s) are shown in parentheses.



Figure 4. Graphical illustration of the repeating unit of the 1D chains formed by **11** in the solid state. Labels 'A' and 'B' refer to a 1st and a 2^{nd} symmetry generated molecule of **11**. Dotted lines indicate interactions of carbon atoms of **11** and **11A**, whereas the dashed lines representing the longest (3.427 Å) and open lines representing the shortest (3.367 Å) distances. **11A/11B**: Dashed lines the longest (3.558 Å) and open lines the shortest (3.339 Å) distances.

elsewhere, and therefore it is not necessary to discuss them separately [11, 15].

Molecule 4 has in the solid state π - π interactions between the C₅H₅ ring and the C₆H₃ ring of the next molecule. This gives rise to the formation of 1D chains along the crystallographic *a* axis (Figure 2).

Most obvious, the structure of **11** in the solid state shows a somewhat distorted octahedral arrangement around Re1 with three carbonyl ligands, arranged in a facial fashion. The N1– Re1–N2 angle at $74.8(2)^{\circ}$ is significantly less than 90°, as required by the bite distance exerted by the steric demand of the chelating bipyridyl building block (Figure 3). Similar observa-



Figure 5. Graphical illustration of the alignment of 1D chains formed by 11 in the solid state with respect to the unit cell.

tions were made for other bpy-containing rhenium transition metal complexes, including $1-[(tBu_2bpy)(CO)_3ReC \equiv C]-3,5-(HC \equiv C)_2-C_6H_3$ [1s].

Furthermore, molecule **11** forms in the solid state a 1D chain set up by π - π interactions among the pyridyl and phenyl rings as it can be seen from Figure 4 and Figure 5. The shortest distances are thereby 3.339 Å, which represents a quite strong interaction [16].

Conclusions

A novel series of mono-, heterobi-, -tri- and even -tetrametallic transition metal complexes based on the 1,3,5-triethynyl benzene core was successfully synthesized using different consecutive synthesis methodologies including metathesis, desilylation, dehydrohalogenation, and carbon-carbon cross-coupling reactions. In the thus formed organometallic molecules 1-I-3-Br-5-(FcC=C)-C₆H₃, 1-Br-3-(bpyC=C)-5-(FcC=C)-C₆H₃, 1,3-(bpyC=C)₂-5- $(FcC \equiv C) - C_6H_3$, 1- $(XC \equiv C) - 3$ - $(bpyC \equiv C) - 5$ - $(FcC \equiv C) - C_6H_3$ (X = H, SiMe₃), 1-(HC=C)-3-[(CO)₃ClRe(bpy-C=C)]-5-(FcC=C)-C₆H₃, $1-[(Ph_3P)AuC \equiv C]-3-[(CO)_3ClRe(bpyC \equiv C)]-5-(FcC \equiv C)-C_6H_3$ $1-[(Ph_3P)AuC \equiv C]-3-(bpyC \equiv C)-5-(FcC \equiv C)-C_6H_3, [1-[(Ph_3 = C)-C_6H_3)]$ $PAuC \equiv C]-3-[{[Ti](C \equiv CSiMe_3)_2}Cu(bpy-C \equiv C)]-5-(FcC \equiv C) C_{6}H_{3}$]PF₆, and $[1,3-[(tBu_{2}bpy)_{2}Ru(bpy-C=C)]_{2}-5-(FcC=C) C_6H_3$](PF₆)₄ (Fc = (η^5 -C₅H₄)(η^5 -C₅H₅)Fe, bpy = 2,2'-bipyridiyl-5-yl, $tBu_2bpy = 4,4'-di-tert-butyl-2,2'-bipyridyl, [Ti] = (\eta^5-$ C₅H₄SiMe₃)₂Ti), the corresponding transition metal atoms are connected by a π -conjugated triethynyl benzene backbone and bipyridyl-5-yl ligands. The X-ray crystal structure analysis of two compounds was also determined showing the characteristic

Table 1. Crystal and Intensity Collection Data for 4 and 11.

	4	11
Empirical formula	C ₁₈ H ₁₂ Cl ₂ BrFeI	C ₃₆ H ₂₂ Cl ₃ FeN ₂ O ₃ Re
Formula weight	490.94	878.96
Temperature /K	100(2)	110(2)
Wavelength /Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	9.6235(6)	14.0324(9)
b /Å	13.7445(9)	7.5197(6)
c /Å	11.9791(8)	32.398(2)
β /°	94.295(5)	100.613(5)
$V/Å^3$	1580.03(18)	3360.2(4)
$\rho_{\rm calc}/{\rm g}\cdot{\rm cm}^{-3}$	2.064	1.737
F(000)	936	1712
Crystal dimensions /mm	0.6 imes 0.4 imes 0.1	0.1 imes 0.05 imes 0.03
Z	4	4
Max., min. transmission	1.29694, 0.61021	1.00000, 0.84325
Absorption coefficient (μ /mm ⁻¹)	5.426	4.308
Scan range (°)	3.01 to 26.08	2.95 to 26.00
Index ranges	$-10 \le h \le 11$	$-17 \le h \le 15$
	$-16 \le k \le 16$	$-9 \le k \le 9$
	$-13 \le l \le 14$	$-39 \le l \le 39$
Total reflections	7503	25110
Unique reflections	3072	6582
R(int)	0.0216	0.0720
Data/restraints/parameters	3072 / 0 / 190	6582 / 58 / 445
Goodness-of-fit on F^2	1.075	1.030
$R1^{(a)}, wR2^{(a)}, [I \ge 2\sigma, (I)]$	0.0514, 0.1628	0.0490, 0.0732
$R1^{(a)}$ w $R2^{(a)}$ (all data)	0.0558, 0.1658	0.1077, 0.0883
Max., min. peak in final Fourier map (e·Å ⁻³)	3.066, -2.747	1.403, -0.847

a) $R1 = [\Sigma(||F_0| - |\overline{F_c}|)/\Sigma|F_0|); wR2 = [\Sigma(w(F_0^2 - F_c^2)^2)/\Sigma(wF_0^4)]^{1/2}. S = [\Sigma w(F_0^2 - F_c^2)^2]/(n-p)^{1/2}. n = number of reflections, p = parameters used.$

features expected for this type of molecules. Noteworthy is the formation of 1D chains in the solid state of 1-I-3-Br-5-(FcC=C)-C₆H₃ and 1-(HC=C)-3-(C=C-bpy(Re(CO)₃Cl))-5-(FcC=C)-C₆H₃, respectively, set up by strong π - π interactions between aromatic rings of adjacent molecules.

Experimental Section

Materials and Methods

Trimethylsilylacetylene [16], 1,3-Br₂-5-(FcC=C)-C₆H₃ (**3**) [7, 17], ethynylferrocene (**2**) [18], 5-ethynyl-2,2'-bipyridine (**5**) [19], [(Ph₃P)AuCl] (**12**) [14], [Re(CO)₅Cl] (**10**) [20] and [{[Ti](μ - σ , π -C=CSiMe₃)₂}-Cu(N=CMe)]PF₆ (**15**) [12] were prepared following published procedures. All other chemicals are commercially available and were used as received.

All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. *n*-Hexane and tetrahydrofuran were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from phosphorus pentoxide. Triethylamine was dried by distillation from KOH. Infrared spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 250 spectrometer. ¹H NMR spectra were recorded at 250.130 MHz (internal standard, relative to CDCl₃, $\delta = 7.26$) and ¹³C (¹H) NMR spectra at 62.902 MHz (internal standard, relative to CDCl₃, $\delta = 77.16$). Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal. ³¹P (¹H) NMR spectra were recorded at 101.254 MHz with

 $P(OMe)_3$ as external standard ($\delta = 139$, relative to 85 % H₃PO₄, $\delta = 0.00$). Elemental analyses were performed with a Vario EL analyzer from Elementar Analysensysteme GmbH (Hanau, Germany). Melting points were determined using sealed nitrogen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus.

Syntheses

1-I-3-Br-5-(FcC=C)-C₆H₃ (4): To a tetrahydrofuran solution (50 mL) containing 1,3-Br₂-5-(FcC=C)-C₆H₃ (3) (1.0 g, 2.25 mmol) *n*BuLi (1.41 mL, 2.25 mmol, 1.6 M in *n*-hexane) was slowly added at -80 °C. The reaction solution was stirred for 1.5 hours at this temperature and afterwards a solution of I₂ (0.65 g, 2.56 mmol) dissolved in tetrahydrofuran (20 mL) was added. After removal of the cooling bath, the solution was stirred for 1 h at 25 °C and afterwards an aqueous sodium-thiosulfate solution was added to destroy the excess of I₂. The reaction mixture was then extracted three times with dichloromethane (50 mL) and the combined dichloromethane extracts were dried with MgSO₄. Removal of all volatiles in *oil-pump vacuum* gave a red solid. Yield: 0.99 g (2.02 mmol, 90 % based on **3**).

Anal. calcd. for $C_{18}H_{12}BrFeI$ (490.9) C 44.04, H 2.46: found C 44.83, H 2.72 %. **IR** (KBr): 2196 (s, $v_{C=CFc}$) cm⁻¹. ¹H **NMR** (δ , CDCl₃): 4.25 (s, 5 H, C₅H₅), 4.28 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 4.50 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 7.58 (pt, $J_{HH} = 1.6$ Hz, 1 H, C₆H₃), 7.75 (pt, $J_{HH} = 1.6$ Hz, 1 H, C₆H₃), 7.79 (pt, $J_{HH} = 1.6$ Hz, 1 H, C₆H₃). ¹³C{¹H} **NMR** (δ , CDCl₃): 64.1 (*Ci*/C₅H₄), 69.4 (*CH*/C₅H₄), 70.2 (C₅H₅), 71.8 (*CH*/C₅H₄), 82.9 (C=C), 91.9 (C=C), 93.9 (*Ci*/C₆H₃), 122.7 (*Ci*/C₆H₃), 127.7 (*Ci*/C₆H₃), 133.4 (*CH*/C₆H₃), 138.6 (*CH*/C₆H₃), 138.8 (*CH*/C₆H₃).



1-Br-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (6) and **1,3-(bpy-C=C)₂-5-(FcC=C)-C₆H₃ (7): 1-I-3-Br-5-(FcC=C)-C₆H₃ (4) (500 mg, 1.02 mmol) and 5-ethynyl-2,2'-bipyridine (5) (185 mg, 1.03 mmol) were dissolved in diisopropylamine (40 mL). [(Ph₃P)₂PdCl₂] (35 mg, 5 mol-%) and [CuI] (18 mg, 10 mol-%) were added in a single portion. The thus obtained reaction mixture was stirred for 3 hours at ambient temperature and afterwards at 40 °C for 12 hours. All volatile materials were evaporated in vacuo and the residue was purified by column chromatography (Silica gel, diethyl ether-petroleum ether of ratio 1:1, \nu/\nu). The first fraction contained** *unreacted* **4**. The second orange fraction contained compound **6** and the third one organometallic **7**. Yield: Complex **6**: 430 mg (0.79 mmol, 78 % based on **4**); complex **7**: 45 mg (0.07 mmol, 7 % based on **4**).

Compound **6**: C₃₀H₁₉BrFeN₂ (543.24) C 66.33, H 3.53, N 5.16; found C 66.38, H 3.77, N 4.76 %. **IR** (KBr): 2211 (m, $v_{C=C}$) cm⁻¹. ¹**H NMR** (δ , CDCl₃): 4.26 (s, 5 H, C₅H₅), 4.28 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 4.51 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 7.32 (ddd, ³ $J_{HS'H4'} = 7.8$, ³ $J_{HS'H6'} = 4.7$, ⁴ $J_{HS'H3'} = 1.0$ Hz, 1 H, H5′bpy), 7.60–7.64 (m, 3 H, C₆H₃), 7.83 (ddd, ³ $J_{H4'H3'} = ^{3}J_{H4'H5'} = 7.8$, ⁴ $J_{H4'H6'} = 1.7$ Hz, 2 H, H4′bpy), 7.93 (dd, ³ $J_{H4'H3'} = ^{3}J_{H4'H6} = 2.2$ Hz, 2 H, H4′bpy), 8.40–8.46 (m, 2 H, H3,H3′ bpy), 8.69 (ddd, ³ $J_{H6'H5'} = 4.7$, ⁴ $J_{H6'H4'} = 1.7$, ⁵ $J_{H6'H3'} = 1.0$ Hz, 2 H, H6′ by), 8.80 (dd, ⁴ $J_{H6'H4} = 2.2$, ⁵ $J_{H6'H3} = 0.6$ Hz, 2 H, H6′bpy). ¹³C{¹H} **NMR** (δ , CDCl₃): 64.3 (Ci/C₅H₄), 69.3 (CH/C₅H₄), 70.2 (C₅H₅), 71.7 (CH/C₅H₄), 83.6 (C=C), 88.1 (C=C), 91.3 (C=C), 91.4 (C=C), 119.7 (C5′ by), 120.5 (C3′bpy), 121.5 (C3′bpy), 122.1 (Ci/C₆H₃), 124.2 (C5′/bpy), 124.7 (Ci/C₆H₃), 126.3 (Ci/C₆H₃), 133.1 (CH/C₆H₃), 133.3 (CH/C₆H₃), 137.1 (C4′/bpy), 139.6 (C4′bpy), 149.5 (C6′/bpy), 151.8 (C6′bpy), 155.4 (Ci/bpy), 155.5 (Ci/bpy).

Compound 7: C42H26FeN4 (642.54) C 78.51, H 4.08, N 8.72; found C 78.56, H 4.22, N 8.51 %. IR (KBr): 2214 (m, $v_{C=C}$) cm⁻¹. ¹H NMR (δ , CDCl₃): 4.27 (s, 5 H, C₅ H_5), 4.28 (pt, J_{HH} = 1.9 Hz, 2 H, C₅ H_4), 4.53 (pt, $J_{\rm HH} = 1.9$ Hz, 2 H, C₅ H_4), 7.33 (ddd, ${}^{3}J_{\rm H5'H4'} = 7.9$, ${}^{3}J_{\rm H5'H6'} = 4.7$, ${}^{4}J_{\text{H5'H3'}} = 1.0 \text{ Hz}, 1 \text{ H}, H5'/\text{bpy}), 7.67-7.71 (m, 3 \text{ H}, C_{6}H_{3}), 7.83 (ddd, 100)$ ${}^{3}J_{\text{H4'H3'}} = {}^{3}J_{\text{H4'H5'}} = 7.9, \; {}^{4}J_{\text{H4'H6'}} = 1.7 \text{ Hz}, \; 1 \text{ H}, \; H4'/\text{bpy}), \; 7.94 \; (\text{dd},$ ${}^{3}J_{\text{H4H3}} = 8.2, {}^{4}J_{\text{H4H6}} = 2.0 \text{ Hz}, 2 \text{ H}, H4/\text{bpy}), 8.43 \text{ (ddd, } {}^{3}J_{\text{H3'H4'}} = 7.9,$ ${}^{4}J_{\text{H3'H5'}} = {}^{5}J_{\text{H3'H6'}} = 1.0 \text{ Hz}, 2 \text{ H}, H3'/\text{bpy}), 8.44 \text{ (dd, } {}^{3}J_{\text{H3H4}} = 8.2, {}^{5}J_{\text{H3H6}} =$ 0.8 Hz, 2 H, H3/bpy), 8.70 (ddd, ${}^{3}J_{H6'H5'} = 4.7$, ${}^{4}J_{H6'H4'} = 1.7$, ${}^{5}J_{H6'H3'} =$ 1.0 Hz, 2 H, *H6*/bpy), 8.83 (dd, ${}^{4}J_{H6H4} = 2.2$, ${}^{5}J_{H6H3} = 0.8$ Hz, 2 H, *H6*/ bpy). ¹³C{¹H} NMR (δ, CDCl₃): 64.5 (*Ci*/C₅H₄), 69.3 (*CH*/C₅H₄), 70.2 (C₅H₅), 71.7 (CH/C₅H₄), 84.1 (C≡C), 87.7 (C≡C), 90.6 (C≡C), 92.0 (C=C), 119.9 (C5/bpy), 120.5 (C3/bpy), 121.5 (C3/bpy), 123.6 (Ci/ C₆H₃), 124.2 (C5[']/bpy), 125.2 (Ci/C₆H₃), 133.6 (CH/C₆H₃), 134.5 (CH/ C₆H₃), 137.1 (C4'/bpy), 139.6 (C4/bpy), 149.5 (C6'/bpy), 151.9 (C6/bpy), 155.3 (Ci/bpy), 155.5 (Ci/bpy).

1-(Me₃SiC=C)-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (8): To 1-Br-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (6) (400 mg, 0.74 mmol) dissolved in diisopropylamine (30 mL) were added trimethylsilylacetylene (350 mg, 3.57 mmol), [(Ph₃P)₂Cl₂Pd] (25 mg, 5 mol-%) and [CuI] (13 mg, 10 mol-%). After stirring this reaction mixture for 20 hours at 50 °C all volatiles were evaporated in *oil-pump vacuum* and the residue was chromatographed on Silica gel using a mixture of diethyl ether-petroleum ether (1:1, v/v) as eluent. After removal of the solvents, complex **8** was obtained as an orange solid material. Yield: 355 mg (0.63 mmol, 86 % based on **6**).

Anal. calcd. for $C_{35}H_{28}FeN_2Si$ (560.55) C 74.99, H 5.03, N 5.00; found C 74.57, H 5.35, N 4.91 %. **IR** (KBr): 2214 (m, $v_{C=C}$), 2157 (m, $v_{C=CSi}$) cm⁻¹. ¹**H NMR** (δ , CDCl₃): 0.26 (s, 9 H, Si*Me*₃), 4.25 (s, 5 H, C₅*H*₅), 4.27 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅*H*₄), 4.50 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅*H*₄), 7.32 (ddd, ³ $J_{H5'H4'} = 7.6$, ³ $J_{H5'H6'} = 4.8$, ⁴ $J_{H5'H3'} = 1.0$ Hz, 1 H, *H*5'/bpy), 7.58 (pt, $J_{HH} = 1.6$ Hz, 1 H, C₆*H*₃), 7.60 (pt, $J_{HH} = 1.6$ Hz, 1 H, C₆*H*₃),

7.62 (pt, $J_{\text{HH}} = 1.6$ Hz, 1 H, C_6H_3), 7.83 (ddd, ${}^{3}J_{\text{H4'H3'}} = {}^{3}J_{\text{H4'H5'}} = 7.6$, ${}^{4}J_{\text{H4'H6'}} = 1.7$ Hz, 1 H, H4'/bpy), 7.92 (dd, ${}^{3}J_{\text{H4'H3'}} = 8.2$, ${}^{4}J_{\text{H4H6}} = 2.0$ Hz, 1 H, H4/bpy), 8.40–8.45 (m, 2 H, H3,H3'/bpy), 8.70 (ddd, ${}^{3}J_{\text{H6'H5'}} = 4.8$, ${}^{4}J_{\text{H6'H4'}} = 1.7$, ${}^{5}J_{\text{H6'H3'}} = 1.0$ Hz, 1 H, H6'/bpy), 8.80 (dd, ${}^{4}J_{\text{H6'H4}} = 2.0$, ${}^{5}J_{\text{H6'H3}} = 0.8$ Hz, 1 H, H6/bpy). ${}^{13}\text{C}\{^{1}\text{H}\}$ NMR (δ , CDCl₃): 64.6 (*Ci*/ C₅H₄), 69.2 (*CH*/C₅H₄), 70.2 (C₅H₅), 71.7 (*CH*/C₅H₄), 84.2 (C=C), 87.4 (C=C), 90.3 (C=C), 92.1 (C=C), 96.0 (C=C), 103.4 (C=C), 120.0 (C5/ bpy), 120.5 (*C3/*bpy), 121.5 (*C3'/*bpy), 123.3 (*Ci*/C₆H₃), 124.10 (*Ci*/ C₆H₃), 124.14 (*C5'/*bpy), 124.9 (*Ci*/C₆H₃), 133.9 (*CH*/C₆H₃), 134.2 (*CH*/ C₆H₃), 134.8 (*CH*/C₆H₃), 137.1 (*C4'/*bpy), 139.6 (*C4/*bpy), 149.5 (*C6'/* bpy), 151.8 (*C6/*bpy), 155.3 (*Ci/bpy*), 155.6 (*Ci/bpy*).

1-(HC=C)-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (9): A dichloromethane solution (25 mL) containing 1-(Me₃SiC=C)-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (8) (330 mg, 0.589 mmol) was cooled to 0 °C and [*n*Bu₄N]F (0.65 mL, 0.650 mmol, 1.0 M in tetrahydrofuran) was slowly added. After removal of the cooling bath, the reaction solution was stirred for 1 h and afterwards all volatile materials were removed in *oil-pump vacuum*. The obtained residue was purified on a Silica gel column (diethyl ether-petroleum ether mixture of ratio 3:2, v/v). After removal of the solvents, an orange-red solid was obtained. Yield: 248 mg (0.508 mmol, 86 % based on 8).

Anal. calcd. for C32H20FeN2 (488.37) C 78.70, H 4.13, N 5.74; found C 78.49, H 4.41, N 5.62 %. **IR** (KBr): 3290 (m, $v_{=C-H}$), 2212 (m, $v_{C=C}$), 2100 (w, $v_{C=CH}$) cm⁻¹. ¹H NMR (δ , CDCl₃): 3.14 (s, 1 H, =CH), 4.26 (s, 5 H, C₅ H_5), 4.27 (pt, $J_{\rm HH}$ = 1.9 Hz, 2 H, C₅ H_4), 4.51 (pt, $J_{\rm HH}$ = 1.9 Hz, 2 H, C₅ H_4), 7.33 (ddd, ${}^{3}J_{\text{H5'H4'}} = 7.8$, ${}^{3}J_{\text{H5'H6'}} = 4.7$, ${}^{4}J_{\text{H5'H3'}} =$ 1.0 Hz, 1 H, H5'/bpy), 7.59 (pt, $J_{\rm HH} = 1.6$ Hz, 1 H, C₆H₃), 7.61 (pt, $J_{\rm HH} = 1.6$ Hz, 1 H, C₆ H_3), 7.66 (pt, $J_{\rm HH} = 1.6$ Hz, 1 H, C₆ H_3), 7.84 (ddd, ${}^{3}J_{\text{H4'H3'}} = {}^{3}J_{\text{H4'H5'}} = 7.8, {}^{4}J_{\text{H4'H6'}} = 1.7 \text{ Hz}, 1 \text{ H}, H4'/\text{bpy}), 7.94 \text{ (dd,}$ ${}^{3}J_{H4H3} = 8.2, {}^{4}J_{H4H6} = 2.2$ Hz, 1 H, H4/bpy), 8.40–8.46 (m, 2 H, H3,H3'/ bpy), 8.70 (ddd, ${}^{3}J_{\text{H6'H5'}} = 4.7$, ${}^{4}J_{\text{H6'H4'}} = 1.7$, ${}^{5}J_{\text{H6'H3'}} = 1.0$ Hz, 1 H, H6¹/ bpy), 8.81 (dd, ${}^{4}J_{H6H4} = 2.2$, ${}^{5}J_{H6H3} = 0.8$ Hz, 1 H, *H6*/bpy). ${}^{13}C{}^{1}H{}$ NMR (δ, CDCl₃): 64.5 (Ci/C₅H₄), 69.3 (CH/C₅H₄), 70.2 (C₅H₅), 71.7 (CH/C5H4), 78.7 (C=C), 82.2 (C=C), 84.1 (C=C), 87.7 (C=C), 90.6 (C=C), 92.0 (C=C), 119.9 (C5/bpy), 120.5 (C3/bpy), 121.6 (C3/bpy), 123.1 (Ci/C₆H₃), 123.5 (Ci/C₆H₃), 124.2 (C51/bpy), 125.1 (Ci/C₆H₃), 134.0 (CH/C₆H₃), 134.6 (CH/C₆H₃), 134.9 (CH/C₆H₃), 137.1 (C4'/bpy), 139.6 (C4/bpy), 149.5 (C6'/bpy), 151.9 (C6/bpy), 155.3 (Ci/bpy), 155.5 (Ci/bpy).

1-(HC=C)-3-(C=C-bpy(Re(CO)₃CI))-5-(FcC=C)-C₆H₃ (11): [Re(CO)₅CI] (10) (150 mg, 0.415 mmol) was dissolved in toluene (70 mL) at 60 °C. To this solution 1-(HC=C)-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (9) (230 mg, 0.471 mmol) was added in a single portion and stirring was continued for 8 hours at 60 °C whereby the formed product partly precipitated. After cooling to ambient temperature, the toluene was removed in vacuo and the obtained residue was dissolved in dichloromethane (5 mL). Addition of *n*-hexane (30 mL) resulted in the precipitation of the title compound. After washing the precipitate three times with diethyl ether-*n*-hexane mixtures (ratio 1:1, ν/ν) and drying the orange solid in *oil-pump vacuum*, 245 mg (0.309 mmol, 74 % based on 9) of 11 could be isolated.

Anal. calcd. for $C_{35}H_{20}$ ClFeN₂O₃Re (794.06) C 52.94, H 2.54, N 3.53; found C 53.33, H 2.40, N 3.39 %. **IR** (KBr): 3294 (m, $v_{\equiv C-H}$), 2211 (m, $v_{C=C}$), 2022, 1914, 1894 (s, v_{CO}) cm⁻¹. ¹H NMR (δ , CDCl₃): 4.26 (s, 5 H, C₅H₅), 4.28 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 4.53 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 7.55 (ddd, ³ $J_{H5'H4'} = 7.6$, ³ $J_{H5'H6'} = 4.6$, ⁴ $J_{H5'H3'} = 1.0$ Hz, 1 H, H5'/bpy), 7.62 (pt, $J_{HH} = 1.6$ Hz, 1 H, C₆H₃), 7.65 (pt, $J_{HH} = 1.6$ Hz, 1 H, C₆H₃), 7.68 (pt, $J_{HH} = 1.6$ Hz, 1 H, C₆H₃), 8.01–8.10 (m, 2 H, H4,H4'/ bpy), 8.14–8.20 (m, 2 H, H3,H3'/bpy), 9.07 (ddd, ³ $J_{H6'H5'} = 4.6$, ⁴ $J_{H6'H4'} =$ 1.7, ⁵ $J_{H6'H3'} = 1.0$ Hz, 1 H, H6'/bpy), 9.15 (dd, ⁴ $J_{H6'H4} = 2.2$, ⁵ $J_{H6'H3} =$

0.8 Hz, 1 H, *H6*/bpy). ¹³C{¹H} **NMR** (δ , CDCl₃): 64.3 (*Ci*/C₅H₄), 69.4 (*CH*/C₅H₄), 70.2 (C₅H₅), 71.8 (*CH*/C₅H₄), 79.1 (C=C), 81.8 (C=C), 83.8 (C=C), 84.5 (C=C), 91.2 (C=C), 96.2 (C=C), 122.0 (*C5*/bpy), 122.9 (*C3*/bpy), 123.4 (*Ci*/C₆H₃), 123.7 (*C3*/bpy), 124.0 (*Ci*/C₆H₃), 125.4 (*Ci*/C₆H₃), 127.3 (*C5*/bpy), 134.1 (*CH*/C₆H₃), 134.7 (*CH*/C₆H₃), 135.9 (*CH*/C₆H₃), 139.1 (*C4*/bpy), 141.0 (*C4*/bpy), 153.4 (*C6*/bpy), 154.2 (*Ci*/bpy), 155.19 (*Ci*/bpy), 155.24 (*C6*/bpy), 189.2 (CO), 197.0 (CO).

1-((Ph₃P)AuC=C)-3-(C=C-bpy(Re(CO)₃Cl))-5-(FcC=C)-C₆H₃ (13): To a tetrahydrofuran (5 mL) and diethylamine (15 mL) solution of 1-(HC=C)-3-(C=C-bpy(Re(CO)₃Cl))-5-(FcC=C)-C₆H₃ (11) (80 mg, 0.101 mmol) and [(Ph₃P)AuCl] (12) (50 mg, 0.101 mmol) [CuI] (1 mg) was added. After stirring this reaction solution for 15 hours at 25 °C all volatile materials were evaporated in *oil-pump vacuum* and the residue was purified by column chromatography (Silica gel, toluene-tetrahydrofuran mixture of ratio 3:1, ν/ν). The title complex could be eluted as an orange band. After removal of all volatiles in *oil-pump vacuum* an orange solid remained. Yield: 35 mg (0.033 mmol, 33 % based on 11).

Anal. calcd. for $C_{53}H_{34}AuClFeN_2O_3PRe^{-1/4}C_7H_8$ (1275.33) C 51.56, H 2.85, N 2.20; found C 51.71, H 2.89, N 2.78 %. IR (KBr): 2212 (m, $v_{C=C}$), 2115 (w, $v_{C=CAu}$), 2021, 1915, 1896 (s, v_{CO}) cm⁻¹. ¹**H NMR** (δ , CDCl_3): 2.36 (s, ${}^{1}\!\!/_4 \times 3$ H, CH₃, toluene), 4.25 (s, 5 H, C_5H_5), 4.27 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.52 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 7.17 (m, ${}^{1}\!\!/_4 \times 3$ H, toluene), 7.25 (m, ${}^{1}\!\!/_4 \times 2$ H, toluene), 7.43–7.61 (m, 15 H (C_6H_5) + 1 H (C_6H_3) + 1 H (H5'/bpy)), 7.63 (pt, $J_{HH} = 1.6$ Hz, 1 H, C_6H_3), 7.67 (pt, $J_{HH} = 1.6$ Hz, 1 H, C_6H_3), 8.02–8.20 (m, 4 H, H3,H3',H4,H4'/bpy), 9.07 (ddd, ${}^{3}J_{H6H5'} = 4.6$, ${}^{4}J_{H6'H4'} = 1.7$, ${}^{5}J_{H6'H3'} = 1.0$ Hz, 1 H, H6'/bpy), 9.14 (dd, ${}^{4}J_{H6H4} = 2.2$, ${}^{5}J_{H6H3} = 0.8$ Hz, 1 H, H6/ bpy). ${}^{31}P{}^{1}H{}$ NMR (δ , CDCl₃): 41.1 (s, AuPPh₂). ESI-MS (m/z): 1253.4 ($[M + H]^+$).

1-((Ph₃P)AuC=C)-3-(C=C-bpy)-5-(FcC=C)-C₆H₃ (14): [(Ph₃P)AuCl] (12) (130 mg, 0.263 mmol) and 1-(HC=C)-3-(bpy-C=C)-5-(FcC=C)-C₆H₃ (9) (135 mg, 0.276 mmol) were dissolved in tetrahydrofuran (10 mL). Diethylamine (15 mL) and [CuI] (1 mg) were added at ambient temperature. After 8 hours of stirring at this temperature, all volatiles were evaporated in *oil-pump vacuum***. Column chromatography of the residue (Silica gel, diethyl ether-dichloromethane mixture of ratio 10:1, \nu/\nu) gave an orange band from which 14 could be isolated as an orange solid. Yield: 165 mg (0.174 mmol, 66 % based on 9).**

Anal. calcd. for C50H34AuFeN2P (946.62) C 63.44, H 3.62, N 2.96; found C 63.33, H 3.77, N 2.87 %. **IR** (KBr): 2211 (m, $v_{C=C}$), 2116 (w, $v_{C=CAu}$) cm⁻¹. ¹**H NMR** (δ , CDCl₃): 4.24 (s, 5 H, C₅H₅), 4.25 (pt, J_{HH} = 1.9 Hz, 2 H, C₅H₄), 4.50 (pt, J_{HH} = 1.9 Hz, 2 H, C₅H₄), 7.31 (ddd, ${}^{3}J_{\text{H5'H4'}}$ = 7.6, ${}^{3}J_{\text{H5'H6'}} = 4.9, {}^{4}J_{\text{H5'H3'}} = 1.0 \text{ Hz}, 1 \text{ H}, H5'/\text{bpy}), 7.39-7.64 \text{ (m, 15 H (C_{6}H_{5}))}$ + 3 H (C₆H₃)), 7.82 (ddd, ${}^{3}J_{H4'H3'} = {}^{3}J_{H4'H5'} = 7.6$, ${}^{4}J_{H4'H6'} = 1.7$ Hz, 1 H, *H4'*/bpy), 7.92 (dd, ${}^{3}J_{H4H3} = 8.2$, ${}^{4}J_{H4H6} = 2.2$ Hz, 1 H, *H4*/bpy), 8.41 (dd, ${}^{3}J_{H3H4} = 8.2$, ${}^{5}J_{H3H6} = 0.8$ Hz, 1 H, H3/bpy), 8.42 (ddd, ${}^{3}J_{H3'H4'} =$ 7.6, ${}^{4}J_{\text{H3'H5'}} = {}^{5}J_{\text{H3'H6'}} = 1.0$ Hz, 1 H, H3'/bpy), 8.69 (ddd, ${}^{3}J_{\text{H6'H5'}} = 4.9$, ${}^{4}J_{\text{H6'H4'}} = 1.7, {}^{5}J_{\text{H6'H3'}} = 1.0 \text{ Hz}, 1 \text{ H}, H6'/\text{bpy}), 8.80 \text{ (dd, } {}^{4}J_{\text{H6H4}} = 2.2,$ ${}^{5}J_{\text{H6H3}} = 0.8 \text{ Hz}, 1 \text{ H}, H6/\text{bpy}).$ ${}^{13}\text{C}\{{}^{1}\text{H}\} \text{ NMR } (\delta, \text{ CDCl}_{3}): 65.0 (Ci/$ C₅H₄), 69.0 (*CH*/C₅H₄), 70.2 (C₅H₅), 71.6 (*CH*/C₅H₄), 84.7 (C≡C), 86.8 (C≡C), 89.4 (C≡C), 92.8 (C≡C), 102.4 (d, J_{CP} = 27 Hz, AuC≡C), 120.3 (C5/bpy), 120.4 (C3/bpy), 121.5 (C3'/bpy), 122.9 (Ci/C₆H₃), 124.0 (C5'/ bpy), 124.5 (*Ci*/C₆H₃), 125.8 (AuC=C), 125.9 (*Ci*/C₆H₃), 129.3 (d, ³J_{CP} = 11.4 Hz, C^m/C_6H_5), 129.8 (d, ${}^{1}J_{CP} = 56.1$ Hz, Ci/C_6H_5), 131.8 (d, ${}^{4}J_{CP} =$ 2.4 Hz, $C^{p}/C_{6}H_{5}$), 132.7 (*CH*/C₆H₃), 134.4 (d, ${}^{1}J_{CP} = 13.8$ Hz, $C^{o}/C_{6}H_{5}$), 134.5 (CH/C₆H₃), 135.6 (CH/C₆H₃), 137.1 (C4'/bpy), 139.5 (C4/bpy), 149.4 (*C6*/bpy), 151.9 (*C6*/bpy), 155.0 (*Ci*/bpy), 155.6 (*Ci*/bpy). ³¹P{¹H} NMR (δ, CDCl₃): 41.2 (s, AuPPh₂).

[1-((Ph₃P)AuC=C)-3-(C=C-bpy({[Ti](μ-σ,π-C=CSiMe₃)₂}Cu))-5-(FcC=C)-C₆H₃]PF₆ (16): To a tetrahydrofuran solution (25 mL) containing $[{[Ti](\mu-\sigma,\pi-C=CSiMe_3)_2}Cu(N=CMe)]PF_6$ (15) (50 mg, 0.064 mmol), 1-((Ph₃P)AuC=C)-3-(C=C-bpy)-5-(FcC=C)-C₆H₃ (14) (60 mg, 0.063 mmol) was added in a single portion. During the course of the reaction (3 hours, 25 °C) the color of the reaction solution changed from orange to red. After removal of all volatile materials in *oil-pump vacuum* the residue was dissolved in dichloromethane (3 mL) and the title complex was precipitated by addition of *n*-hexane (20 mL). The obtained precipitate was washed twice with diethyl ether (2 × 10 mL). Drying the solid material in *oil-pump vacuum* gave 92 mg (0.055 mmol, 87 % based on 15) of 16.

Anal. calcd. for $C_{76}H_{78}AuCuF_6FeN_2P_2Si_4Ti-¹/4CH_2Cl_2$ (1693.18) C 54.09, H 4.67, N 1.65; found C 54.00, H 4.89, N 1.62 %. **IR** (KBr): 2211 (m, $v_{C=C}$), 2115 (w, $v_{C=CAu}$), 1924 (m, $v_{C=CTi}$) cm⁻¹. ¹**H NMR** (δ , CDCl_3): – 0.48 (s, 18 H, Si*Me*₃), 0.28 (s, 9 H, Si*Me*₃), 0.30 (s, 9 H, Si*Me*₃), 4.23 (s, 5 H, C₅*H*₅), 4.25 (pt, *J*_{HH} = 1.9 Hz, 2 H, C₅*H*₄), 4.49 (pt, *J*_{HH} = 1.9 Hz, 2 H, C₅*H*₄), 5.30 (s, ¹/₄ × 2 H, CH₂Cl₂), 6.27–6.32 (m, 8 H, C₅*H*₄Si), 7.41–7.57 (m, 15 H, C₆*H*₅), 7.59 (pt, *J*_{HH} = 1.6 Hz, 1 H, C₆*H*₃), 7.63 (pt, *J*_{HH} = 1.6 Hz, 1 H, C₆*H*₃), 7.65 (pt, *J*_{HH} = 1.6 Hz, 1 H, C₆*H*₃), 7.69–7.75 (m, 1 H, *H5*/bpy), 8.21–8.30 (m, 2 H, *H4*,*H4*/bpy), 8.51– 8.69 (m, 4 H, *H3*,*H3*',*H6*,*H6*'/bpy). ³¹P{¹H} NMR (δ , CDCl₃): –145.1 (septublet, ¹*J*_{PF} = 713 Hz, *P*F₆), 41.1 (s, Au*P*Ph₂). ESI MS (*m*/*z*): 1525.3 ([M – PF₆]⁺).

1,3-(C=C-bpy(Ru(/Bu₂bpy)₂)₂-5-(FcC=C)-C₆H₃ (18): To $[(tBu_2bpy)_2Cl_2Ru]$ (17) (60 mg, 0.085 mmol) dissolved in ethanol (25 mL) 1,3-(bpy-C=C)₂-5-(FcC=C)-C₆H₃ (7) (25 mg, 0.039 mmol) was added in a single portion and the reaction solution was heated for 20 hours to reflux whereby a color change from purple to red occurred. After cooling to ambient temperature, an aqueous solution (5 mL) of $[H_4N]PF_6$ (50 mg, 0.307 mmol) was added and the solid precipitated was separated and washed with water, ethanol, and diethyl ether, and was than dried in *oil-pump vacuum*. The title complex was obtained as a red solid. Yield: 64 mg (0.026 mmol, 66 % based on 7).

Anal. calcd. for $C_{114}H_{122}FeF_{24}N_{12}P_4Ru_2$ (2499.14) C 54.79, H 4.96, N 6.72; found C 55.11, H 4.96, N 6.42 %. **IR** (KBr): 2211 (m, $v_{C=C}$) cm⁻¹. ¹**H NMR** (δ , d₆-Aceton): 1.39 (s, 18 H, *t*Bu), 1.40 (s, 18 H, *t*Bu), 1.44 (s, 9 H, *t*Bu), 4.26 (s, 5 H, C₅H₅), 4.38 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 4.53 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 7.48–7.64 (m, bpy/*t*Bu₂bpy), 7.82– 8.06 (m, bpy/*t*Bu₂bpy), 8.21–8.35 (m, bpy/*t*Bu₂bpy), 8.80–8.93 (m, bpy/ *t*Bu₂bpy). ³¹P{¹H</sup> **NMR** (δ ,d₆-Aceton): -145.1 (septet, ¹ $J_{PF} = 713$ Hz, *P*F₆). **ESI MS** (*m*/*z*): 479.2 ([M - 4 PF₆]⁴⁺), 639.6 ([M - 4 PF₆ - Ru(*t*Bu₂bpy)₂]²⁺).

X-ray Structure Determination

The X-ray structure measurements for **4** and **11** were performed with an Oxford Gemini S diffractomter. The structures were solved by direct methods using SHELXS-97 [21] and refined by full-matrix least-square procedures on F^2 using SHELXL-97 [22]. All *non*-hydrogen atoms were refined anisotropically. All hydrogen atom positions were refined using a riding model. In case of **11** the CH₂Cl₂ molecule as noncoordinating packing solvent has been refined disordered on two positions, with occupation factors of 0.49 (C36, C11, Cl2) and 0.51 (C36', C11', Cl2').

The crystallographic data for **4** and **11** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-753340 (**4**) and CCDC-753341 (**11**). Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1ET, UK. [Fax: +44-1223-336033, E-Mail: deposit@ ccdc.cam.ac.uk].



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