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

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<th>Journal:</th>
<th>Zeitschrift für Anorganische und Allgemeine Chemie</th>
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<tr>
<td>Manuscript ID:</td>
<td>zaac.201000243</td>
</tr>
<tr>
<td>Wiley - Manuscript type:</td>
<td>Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>16-Jun-2010</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Lang, Heinrich; der TU Chemnitz, Institut fü r Chemie</td>
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<tr>
<td>Keywords:</td>
<td>Heteromultimetallic, Transition Metals, Acetylide, Ferrocene, Solid State Structure</td>
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Transition-Metal Complexes Based on the 1,3,5-Triethynyl Benzene Linking Unit

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Bei der Redaktion eingegangen am ...

Abstract

The synthesis of a unique series of heteromultinuclear transition metal compounds is reported. Complexes 1-I-3-Br-5-(FcC≡C)-C₆H₃ (4), 1-Br-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (6), 1,3-(bpy-C≡C)₂-5-(FcC≡C)-C₆H₃ (7), 1-(XC≡C)-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (8, X = SiMe₃; 9, X = H), 1-(HC≡C)-3-[(CO)₃ClRe(bpy-C≡C)]⁻-5-(FcC≡C)-C₆H₃ (11), 1-[(Ph₃P)Au-C≡C]⁻-3-[(CO)₃ClRe(bpy-C≡C)]⁻-5-(FcC≡C)-C₆H₃ (13), 1-[(Ph₃P)AuC≡C]-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (14), 1-[(Ph₃P)AuC≡C]-3-[(Ti)(C≡CSiMe₃)]₂Cu(bpy-C≡C)]⁻-5-(FcC≡C)-C₆H₃PF₆ (16), and 1,3-[(t-Bu₂bpy)₂Ru(bpy-C≡C)]₂-5-(FcC≡C)-C₆H₃(PF₆)₄ (18) (Fc = (η⁵-
C₅H₆(η⁵-C₅H₅)Fe, bpy = 2,2’-bipyridiyl-5-yl, [Ti] = (η⁵-C₅H₅SiMe₃)₂Ti) were prepared by using consecutive synthesis methodologies including metathesis, desilylation, dehydrohalogenation, and carbon-carbon cross-coupling reactions. In these complexes the corresponding metal atoms are connected via carbon-rich bridging units comprising 1,3-diethynyl-, 1,3,5-triethynylbenzene and bipyridyl units. They have been 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 representative M-C, C-C≡C and C≡C bond distances.

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**Keywords**: Heteromultimetallic; Solid State Structure; Transition Metals; Acetylide; Ferrocene.

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**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 next to the carbon-rich structural units redox-active metal building blocks, 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, \((\eta^5-C_5H_4)(\eta^5-C_5H_5)Fe\), were successfully applied in the synthesis of heteromultimetallic transition metal complexes in which the metal atoms are bridged by carbon-rich connectivities [3]. While homo- and heterobimetallic complexes with carbon-rich organic and/or inorganic connecting units have been designed and synthesized, and their chemical and physical properties intensively studied [4, 5], only less is known about organometallics in which more than three different metals are linked by organic \(\pi\)-conjugated bridging ligands [3]. Such molecules are of great interest, due to their extended organic \(\pi\)-system which can provide remarkable applications and hence, the electrochemical behavior, UV-Vis/NIR characteristics and EPR analysis of \(\textit{in-situ}\) generated associated radical cations have been studied [6 – 8].

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 Ti, Re, Fe, Ru, Cu, and Au, 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. Organometallic 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].

Scheme 1. Consecutive reaction sequence for the synthesis of 9.
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 bond allowed the preferential introduction of one 5-ethynyl-2,2′-bipyridyl moiety (Scheme 1, Experimental Part). After appropriate work-up, mononuclear 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)-C₆H₃ (7) could be isolated in a yield of 7 % (Experimental Part). The exchange of one Br substituent by the more reactive jodide in 3 was necessary to obtain complex 6 as major product. If 3 was reacted under similar reaction conditions with bpyC≡CH (5) a mixture of 6 and 7 was obtained. Complex 6 was further reacted 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-(Me₃SiC≡C)-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (8). Desilylation of 8 with [n-Bu₄N]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, organometallic 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-[(Ph₃P)AuC≡C]-3-[(CO)₃ClRe(bpy-C≡C)]-5-(FcC≡C)-C₆H₃ (13) (Scheme 2) includes following steps: (i) treatment of 9 with equimolar amounts of [Re(CO)₃Cl] (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)-C₆H₃ (11), which in the next step (ii) afforded on addition of [(Ph₃P)AuCl] (12) in presence of catalytic amounts of [CuI] complex 13 in which the three complex fragments Fc, (bpy)Re(CO)₃Cl, and (Ph₃P)Au are connected via a 1,3,5-triethynylbenzene core (Scheme 2).
Even the synthesis of a heterotetrametallic complex featuring Ti, Fe, Cu, and Au metal atoms is possible by starting from 9. In this respect, heterobimetallic 1-[(Ph₃P)AuC≡C]-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (14) was prepared using a mixture of tetrahydrofruan-diethylamine of ratio 1:1 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-[(Ph₃P)AuC≡C]-3-[(Ti)(C≡C)₂Cu(bpy-C≡C)]-5-(FcC≡C)-C₆H₃]PF₆ (16) ([Ti] = (η⁵-C₅H₅)₂Ti) included the addition of the heterobimetallic organometallic π-tweezer molecule [(Ti)(μ-σ,π-C≡CSiMe₃)₂]Cu(N≡CMe)PF₆ (15) to 14. On replacement of the only weakly-bonded acetonitrile by the 2,2'-bipyridyl ligand, heterotetrametallic 16, after appropriate work-up, was obtained as a red solid material in good yield (Scheme 2, Experimental Part).

![Scheme 2. Synthesis of heterometalllic 13 and 16 using 9 as key starting material.](image)

The synthesis of a trimetallic FeRu₂ species, [1,3-[(t-Bu₂bpy)₂Ru(bpy-C≡C)]₂-5-(FcC≡C)- C₆H₃][PF₆]₄ (18) (t-Bu₂bpy = 4,4'-di-tert.-butyl-2,2'-bipyridyl) was possible by reacting 1,3-
(bpy-C≡C)_{2}-5-(FcC≡C)_{6}H_{3} (7) with two equivalents of [(t-Bu_{2}bpy)_{2}RuCl_{2}] (17) in boiling ethanol (Reaction 1). After 20 hours and addition of a aqueous solution of [H_{4}N]PF_{6} ionic 18 could be isolated in 66 % yield as a red 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 have been confirmed by elemental analysis, IR, ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} 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 $\nu_{\text{C≡C}}$ vibrations of the organometallic M-C≡CR (M = Ti, Au, Fc; R = C_{6}H_{3}, SiMe_{3}) and the organic X-C≡C_{6}H_{3} (X
= H, bpy, C₅H₅) units (Experimental Part). These vibrations are found in the range of 2157 – 2214 cm⁻¹ for the organic moieties, while for the metal acetylide fragments typical absorptions are observed at 2115 (Au≡C) [9] and 1924 cm⁻¹ (Ti≡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 ν_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 ν_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 spectroscopic studies (Experimental Part). 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 C₅H₄ protons with a J_HH coupling constant of ca. 1.9 Hz (Experimental Part). The titanium-bonded 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, C₅H₃, and C₅H₅ groups give typical resonances with the anticipated chemical shifts and coupling patterns (Experimental Part). 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 showing up-field shifts upon coordination of the alkynyl units to a transition metal fragment (Experimental Part). 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 Me₃SiC≡C protons in comparison to 15 upon coordination of the bipyridyl entity to the organometallic π-tweezer copper(I) center 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 singlets at 0.28 and 0.30 ppm for the cyclopentadienyl-bonded Me₃Si units (Experimental Part). Similar observations were made in the ¹³C{¹H} 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 indicative of similar phosphine 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 by an acetylide unit [9]. The non-coordinating PF₆⁻ ion in 16 gives rise to a septet at −145.1 ppm with ¹JPF = 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 – PF₆]⁺ (m/z 1525.3, 16) with characteristic isotope distribution patterns. Characteristic for 18 is the molecular ion [M – 4PF₆]⁴⁺ (m/z 479.2) and the formation of fragments such as [M – 4PF₆ – Ru(t-Bu₂bpy)₂]²⁺ (m/z 639.6) (Experimental Part).

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 Figures 1 and 2 (4) and Figures 3 – 5 (11) together with selected bond distances (Å) and bond angles (°). The crystallographic data are summarized in Table 1 (Experimental Part).
Both complexes 4 and 11 crystallize in the monoclinic space group P21/n. From Figures 1 and 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 between 1.640(4) and 1.654(4) Å [15]. The two cyclopentadienyl ligands are thereby rotated by 0.1(6) ° (4) and 2.5(7)° (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 (Figures 1 and 3). The bond distances and bond angles for all the other groups agree well with those reported elsewhere, and therefore it is not necessary to discuss them separately [11, 15].

![Figure 1](image)

**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 distances (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 parenthesis.
Molecule 4 possesses in the solid state \( \pi-\pi \)-interactions between the \( \text{C}_5\text{H}_5 \) ring and the \( \text{C}_6\text{H}_3 \) ring of the next molecule. This gives rise to the formation of 1D chains along the crystallographic \( a \)-axis (Figure 2).

![Figure 2](image_url)

**Figure 2.** Graphical representation of the \( \pi-\pi \)-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 1\textsuperscript{st} - 4\textsuperscript{th} symmetry generated molecules of 4. Hydrogen atoms are omitted for clarity.

Most obvious, the structure of 11 in the solid state shows a somewhat distorted octahedral geometry 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 \( ^\circ \), as required by the bite distance exerted by the steric demand of the chelating bipyridyl building block (Figure 3). Similar observations
were made for other bpy-containing rhenium transition metal complexes, including 1-[(t-
Bu₂bpy)(CO)₃ReC≡C]-3,5-(HC≡C)₂-C₆H₃ [18].

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 distances (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–Cl1 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 parenthesis.

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 Figures 4 and 5. The shortest dis-
tances are thereby 3.339 Å, which represents a quite strong interaction [16].
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 1\textsuperscript{st} and a 2\textsuperscript{nd} symmetry generated molecule of 11. Dotted lines indicate interactions of carbon atoms of 11 and 11A, while 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.
Figure 5. Graphical illustration of the alignment of 1D chains formed by 11 in the solid state with respect to the unit cell.

Conclusion

A novel series of mono-, hetero-, tri- and even tetrametallic transition metal complexes based on the 1,3,5-triethynyl benzene core have successfully been 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≡C)-C₆H₃, 1-(XC≡C)-3-(bpyC≡C)-5-(FcC≡C)-C₆H₃ (X = H, SiMe₃), 1-(HC≡C)-3-[(CO)₃ClRe(bpyC≡C)]-5-(FcC≡C)-C₆H₃. 1-[(Ph₃P)AuC≡C]-3-[(CO)₃ClRe(bpyC≡C)]-5-(FcC≡C)-C₆H₃, 1-[(Ph₃P)AuC≡C]-3-(bpyC≡C)-5-(FcC≡C)-C₆H₃, 1-[(Ph₃P)AuC≡C]-3-(bpyC≡C)-5-(FcC≡C)-C₆H₃, 1-[(Ph₃P)AuC≡C]-3-(bpyC≡C)-5-(FcC≡C)-C₆H₃, 1-[(Ph₃P)AuC≡C]-3-[(CO)₃ClRe(bpyC≡C)]-5-(FcC≡C)-C₆H₃, 1-[(Ph₃P)AuC≡C]-3-[(CO)₃ClRe(bpyC≡C)]-5-(FcC≡C)-C₆H₃, 1-[(Ph₃P)AuC≡C]-3-[(CO)₃ClRe(bpyC≡C)]-5-(FcC≡C)-C₆H₃, 1-[[Ti](C≡CSiMe₃)₂]Cu-(bpyC≡C)]-5-(FcC≡C)-C₆H₃][PF₆]₄, and 1,3-[(t-Bu₂bpy)₂Ru(bpyC≡C)]₂-5-(FcC≡C)-C₆H₃]-{(PF₆)₄ (Fc = (η⁵-C₅H₄)(η⁵-C₅H₅)Fe, bpy = 2,2'-bipyridyl-5-yl, t-Bu₂bpy = 4,4'-di-tert.-butyl-2,2'-bipyridyl, [Ti] = (η⁵-C₅H₅SiMe₃)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 has also been determined showing the characteristic 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 Part

Materials and Methods
Trimethylsilylacetylene [16], 1,3-Br₂-5-(FcC≡C)-C₆H₃ (3) [7, 17], ethynylferrocene (2) [18], 5-ethyl-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 pro-
cedures. 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 so-
dium/benzophenone ketyl; dichloromethane was purified by distillation from phosphorus pen-
toxide. 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, δ 7.26) and ¹³C{¹H} NMR spectra at 62.902 MHz (internal standard, rela-
tive to CDCl₃, δ 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(OMe₃) as external standard (δ 139 ppm, relative to 85 %
H₃PO₄, δ 0.00). Elemental analyses were performed with a Vario EL analyzer from Elementar
Analysensysteme GmbH (Hanau). Melting points were determined using sealed nitrogen
purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus.

Synthesis of 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) was slowly added 1.41 mL (2.25 mmol) of n-BuLi (1.6 M in n-hexane) at -80 °C. Af-
terwards, the reaction solution was stirred for 1.5 hours at this temperature and then a solution
of I₂ (0.65 g, 2.56 mmol) dissolved in 20 mL of tetrahydrofuran was added. After removal of
the cooling bath, the solution was stirred for 1 h at 25 °C and then an aqueous sodium-
thiosulfate solution was added to destroy the excess of I₂. Afterwards, the reaction mixture
was extracted three times with dichloromethane (50 mL) and the combined dichloromethane extracts were dried over MgSO$_4$. Removal of all volatiles in oil-pump vacuum gave a red solid. Yield: 0.99 g (2.02 mmol, 90 % based on 3).

Anal. calc. for C$_{18}$H$_{12}$BrFeI (490.9) C 44.04, H 2.46: found C 44.83, H 2.72 %. IR (KBr, cm$^{-1}$): 2196 (s, $\nu$C≡C$_{\text{Fc}}$). $^1$H NMR ($\delta$, CDCl$_3$): 4.25 (s, 5 H, C$_5$H$_5$), 4.28 (pt, $J_{HH}$ = 1.9 Hz, 2 H, C$_3$H$_4$), 4.50 (pt, $J_{HH}$ = 1.9 Hz, 2 H, C$_3$H$_4$), 7.58 (pt, $J_{HH}$ = 1.6 Hz, 1 H, C$_6$H$_3$), 7.75 (pt, $J_{HH}$ = 1.6 Hz, 1 H, C$_6$H$_3$). $^{13}$C{$^1$H} NMR ($\delta$, CDCl$_3$): 64.1 (C$/C_3$H$_4$), 69.4 (CH$/C_3$H$_4$), 70.2 (C$_6$H$_3$), 71.8 (CH$/C_5$H$_4$), 82.9 (C=O), 91.9 (C=O), 93.9 (C$/C_6$H$_3$), 122.7 (C$/C_6$H$_3$), 127.7 (C$/C_6$H$_3$), 133.4 (CH$/C_6$H$_3$), 138.6 (CH$/C_6$H$_3$), 138.8 (CH$/C_6$H$_3$).

**Synthesis of 1-Br-3-(bpy-C≡C)-5-(FcC≡C)-C$_6$H$_3$ (6) and 1,3-(bpy-C≡C)$_2$-5-(FcC≡C)-C$_6$H$_3$ (7)**

500 mg (1.02 mmol) of 1-I-3-Br-5-(FcC≡C)-C$_6$H$_3$ (4) and 185 mg (1.03 mmol) of 5-ethynyl-2,2′-bipyridine (5) were dissolved in 40 mL of diisopropylamine and 35 mg (5 mol-%) of [(Ph$_3$P)$_2$PdCl$_2$] and 18 mg (10 mol-%) of [CuI] were added in a single portion. The thus obtained reaction mixture was stirred for 3 hours at ambient temperature and then at 40 °C for 12 hours. Afterwards, all volatile materials were evaporated in vacuum and the residue was purified by column chromatography (Silica gel, diethyl ether-petroleum ether of ratio 1:1, v/v). The first fraction contained non-reacted 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: Anal. calc. for C\textsubscript{36}H\textsubscript{19}BrFeN\textsubscript{2} (543.24) C 66.33, H 3.53, N 5.16; found C 66.38, H 3.77, N 4.76 %. IR (KBr, cm\textsuperscript{-1}): 2211 (m, ν\textsubscript{C=O}). \textsuperscript{1}H NMR (δ, CDCl\textsubscript{3}): 4.26 (s, 5 H, C\textsubscript{3}H\textsubscript{3}), 4.28 (pt, J\textsubscript{HH} = 1.9 Hz, 2 H, C\textsubscript{3}H\textsubscript{4}), 4.51 (pt, J\textsubscript{HH} = 1.9 Hz, 2 H, C\textsubscript{3}H\textsubscript{4}), 7.32 (ddd, J\textsubscript{H5'H4'} = 7.8 Hz, J\textsubscript{H5'H6'} = 4.7 Hz, J\textsubscript{H5'H5'} = 1.0 Hz, 1 H, H5'/bpy), 7.60 – 7.64 (m, 3 H, C\textsubscript{3}H\textsubscript{3}), 7.83 (ddd, J\textsubscript{H4'H5'} = J\textsubscript{H4'H5'} = 7.8 Hz, J\textsubscript{H4'H5'} = 1.7 Hz, 2 H, H4'/bpy), 7.93 (dd, J\textsubscript{H6'H5'} = 8.2 Hz, J\textsubscript{H4'H6} = 2.2 Hz, 2 H, H4'/bpy), 8.40 – 8.46 (m, 2 H, H3'H3'/bpy), 8.69 (ddd, J\textsubscript{H6'H5'} = 4.7 Hz, J\textsubscript{H6'H4'} = 1.7 Hz, J\textsubscript{H6'H3'} = 1.0 Hz, 2 H, H6'/bpy), 8.80 (dd, J\textsubscript{H6'H4} = 2.2 Hz, J\textsubscript{H6'H3} = 0.6 Hz, 2 H, H6'/bpy). \textsuperscript{13}C{[\textsuperscript{1}H]} NMR (δ, CDCl\textsubscript{3}): 64.3 (C'/C\textsubscript{2}H\textsubscript{4}), 69.3 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 70.2 (C\textsubscript{3}H\textsubscript{3}), 71.7 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 83.6 (C=C), 88.1 (C=C), 91.3 (C=C), 91.4 (C=C), 119.7 (C5/bpy), 120.5 (C3/bpy), 121.5 (C3'/bpy), 122.1 (C'/C\textsubscript{3}H\textsubscript{3}), 124.2 (C5'/bpy), 124.7 (C'/C\textsubscript{3}H\textsubscript{3}), 126.3 (C'/C\textsubscript{3}H\textsubscript{3}), 133.1 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 133.3 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 134.3 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 137.1 (C4'/bpy), 139.6 (C4/bpy), 149.5 (C6'/bpy), 151.8 (C6/bpy), 155.4 (C'/bpy), 155.5 (C'/bpy).

Compound 7. Anal. calc. for C\textsubscript{42}H\textsubscript{26}FeN\textsubscript{4} (642.54) C 78.51, H 4.08, N 8.72; found C 78.56, H 4.22, N 8.51 %. IR (KBr, cm\textsuperscript{-1}): 2214 (m, ν\textsubscript{C=O}). \textsuperscript{1}H NMR (δ, CDCl\textsubscript{3}): 4.27 (s, 5 H, C\textsubscript{3}H\textsubscript{3}), 4.28 (pt, J\textsubscript{HH} = 1.9 Hz, 2 H, C\textsubscript{3}H\textsubscript{4}), 4.53 (pt, J\textsubscript{HH} = 1.9 Hz, 2 H, C\textsubscript{3}H\textsubscript{4}), 7.33 (ddd, J\textsubscript{H5'H4'} = 7.9 Hz, J\textsubscript{H5'H6'} = 4.7 Hz, J\textsubscript{H5'H5'} = 1.0 Hz, 1 H, H5'/bpy), 7.67 – 7.71 (m, 3 H, C\textsubscript{3}H\textsubscript{3}), 7.83 (ddd, J\textsubscript{H4'H3'} = J\textsubscript{H4'H5'} = 7.9 Hz, J\textsubscript{H4'H6'} = 1.7 Hz, 1 H, H4'/bpy), 7.94 (dd, J\textsubscript{H4'H3} = 8.2 Hz, J\textsubscript{H4'H6} = 2.0 Hz, 2 H, H4'/bpy), 8.43 (ddd, J\textsubscript{H3'H4'} = 7.9 Hz, J\textsubscript{H3'H5'} = J\textsubscript{H3'H6'} = 1.0 Hz, 2 H, H3'/bpy), 8.44 (dd, J\textsubscript{H3'H4} = 8.2 Hz, J\textsubscript{H3'H6} = 0.8 Hz, 2 H, H3'/bpy), 8.70 (ddd, J\textsubscript{H6'H5'} = 4.7 Hz, J\textsubscript{H6'H4'} = 1.7 Hz, J\textsubscript{H6'H3'} = 1.0 Hz, 2 H, H6'/bpy), 8.83 (dd, J\textsubscript{H6'H4} = 2.2 Hz, J\textsubscript{H6'H3} = 0.8 Hz, 2 H, H6'/bpy). \textsuperscript{13}C{[\textsuperscript{1}H]} NMR (δ, CDCl\textsubscript{3}): 64.5 (C'/C\textsubscript{2}H\textsubscript{4}), 69.3 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 70.2 (C\textsubscript{3}H\textsubscript{3}), 71.7 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 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 (C'/C\textsubscript{3}H\textsubscript{3}), 124.2 (C5'/bpy), 125.2 (C'/C\textsubscript{3}H\textsubscript{3}), 133.6 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 134.5 (CH/CH/C\textsubscript{2}H\textsubscript{4}), 137.1 (C4'/bpy), 139.6 (C4/bpy), 149.5 (C6'/bpy), 151.9 (C6/bpy), 155.3 (C'/bpy), 155.5 (C'/bpy).
Synthesis of 1-(Me₃SiC≡C)-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (8)

To 400 mg (0.74 mmol) of 1-Br-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (6) dissolved in 30 mL of diisopropylamine were added 350 mg (3.57 mmol) of trimethylsilylacetylene, 25 mg (5 mol-%) of [(Ph₃P)₂Cl₂Pd] and 13 mg (10 mol-%) of [CuI]. 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. calc. for C₃₅H₂₈FeN₂Si (560.55) C 74.99, H 5.03, N 5.00; found C 74.57, H 5.35, N 4.91 %. IR (KBr, cm⁻¹): 2214 (m, νC≡C), 2157 (m, νC≡CSi).

¹H NMR (δ, CDCl₃): 0.26 (s, 9 H, SiMe₃), 4.25 (s, 5 H, C₅H₅), 4.27 (pt, J_HH = 1.9 Hz, 2 H, C₅H₄), 4.50 (pt, J_HH = 1.9 Hz, 2 H, C₅H₄), 7.32 (ddd, J_H₅'H₄' = 7.6 Hz, J_H₅'H₆' = 4.8 Hz, J_H₅'H₃' = 1.0 Hz, 1 H, H₅'/bpy), 7.58 (pt, J_HH = 1.6 Hz, 1 H, C₆H₃), 7.60 (pt, J_HH = 1.6 Hz, 1 H, C₆H₃), 7.62 (pt, J_HH = 1.6 Hz, 1 H, C₆H₃), 7.83 (ddd, J_H₄'H₃' = J_H₄'H₅' = 7.6 Hz, J_H₄'H₆' = 1.7 Hz, 1 H, H₄'/bpy), 8.40 – 8.45 (m, 2 H, H₃'H₃'/bpy), 8.80 (dd, J_H₆H₄ = 2.0 Hz, J_H₆H₃ = 0.8 Hz, 1 H, H₆'/bpy). ¹³C{¹H} NMR (δ, CDCl₃): 64.6 (C/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 (C'/C₅H₃), 124.10 (C'/C₆H₃), 124.14 (C₅'/bpy), 124.9 (C'/C₆H₃), 133.9 (CH/C₆H₃), 134.2 (CH/C₆H₃), 134.8 (CH/C₅H₃), 137.1 (C₄'/bpy), 139.6 (C₄/bpy), 149.5 (C₆'/bpy), 151.8 (C₆/bpy), 155.3 (C'/bpy), 155.6 (C'/bpy).
Synthesis of 1-(HC≡C)-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (9)

A dichloromethane solution (25 mL) containing 330 mg (0.589 mmol) of 1-(Me₃SiC≡C)-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (8) was cooled to 0 °C and 0.65 mL (0.650 mmol) of [n-Bu₄N]F (1.0 M in tetrahydrofuran) were slowly added. After removal of the cooling bath, the reaction solution was stirred for 1 h and then 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. calc. 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, cm⁻¹): 3290 (m, ν≡C-H), 2212 (m, νC≡C), 2100 (w, νC≡CH).

¹H NMR (δ, CDCl₃): 3.14 (s, 1 H, ≡C-H), 4.26 (s, 5 H, C₅H₅), 4.27 (pt, J_HH = 1.9 Hz, 2 H, C₅H₄), 4.51 (pt, J_HH = 1.9 Hz, 2 H, C₅H₄), 7.33 (ddd, 3_J_H5'H4' = 7.8 Hz, 3_J_H5'H6' = 4.7 Hz, 4_J_H5'H5' = 1.0 Hz, 1 H, H5'/bpy), 7.59 (pt, J_HH = 1.6 Hz, 1 H, C₆H₃), 7.61 (pt, J_HH = 1.6 Hz, 1 H, C₆H₃), 7.66 (pt, J_HH = 1.6 Hz, 1 H, C₆H₃), 7.84 (ddd, 3_J_H4'H5' = 3_J_H4'H5' = 7.8 Hz, 4_J_H4'H6' = 1.7 Hz, 1 H, H4'/bpy), 7.94 (dd, 3_J_H4'H3' = 8.2 Hz, 4_J_H4'H6 = 2.2 Hz, 1 H, H4/bpy), 8.40 – 8.46 (m, 2 H, H3/H3'/bpy), 8.70 (ddd, 3_J_H6'H5' = 4.7 Hz, 4_J_H6'H4' = 1.7 Hz, 5_J_H6'H3' = 1.0 Hz, 1 H, H6'/bpy), 8.81 (dd, 4_J_H6'H4 = 2.2 Hz, 5_J_H6'H3 = 0.8 Hz, 1 H, H6/bpy).

¹³C{¹H} NMR (δ, CDCl₃): 64.5 (C/C₅H₄), 69.3 (CH/C₅H₄), 70.2 (C₅H₃), 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 (C/C₆H₃), 123.5 (C/C₆H₃), 124.2 (C5'/bpy), 125.1 (C/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 (C'/bpy), 155.5 (C'/bpy).

Synthesis of 1-(HC≡C)-3-(C≡C-bpy(Re(CO)₃Cl))-5-(FcC≡C)-C₆H₃ (11)
150 mg (0.415 mmol) of [Re(CO)₅Cl] (10) were dissolved in 70 mL of toluene at 60 °C. To this solution 230 mg (0.471 mmol) of 1-(HC≡C)-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (9) were 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 vacuum and the obtained residue was dissolved in 5 mL of dichloromethane. Addition of 30 mL of n-hexane resulted in the precipitation of the title compound. After washing the precipitate three times with diethyl ether-n-hexane mixtures (ratio 1:1, v/v) and drying the orange solid in *oil-pump vacuum*, 245 mg (0.309 mmol, 74 % based on 9) of 11 could be isolated.

Anal. calc. for C₃₅H₂₀ClFeN₂O₃Re (794.06) C 52.94, H 2.54, N 3.53; found C 53.33, H 2.40, N 3.39 %.

IR (KBr, cm⁻¹): 3294 (m, νC-H), 2211 (m, νC≡C), 2022, 1914, 1894 (s, νCO).

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, J_H5'H4' = 7.6 Hz, J_H5'H6' = 4.6 Hz, 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, H₄H₄'/bpy), 8.14 – 8.20 (m, 2 H, H₃H₃'/bpy), 9.07 (ddd, J_H6'H5' = 4.6 Hz, J_H6'H4' = 1.7 Hz, J_H6'H3' = 1.0 Hz, 1 H, H6'/bpy), 9.15 (dd, J_H6H4 = 2.2 Hz, J_H6H3 = 0.8 Hz, 1 H, H6/bpy).

13C{¹H} NMR (δ, CDCl₃): 64.3 (C/C₅H₅), 69.4 (CH/C₅H₄), 70.2 (C₃H₃), 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 (C/C₆H₃), 123.7 (C3'/bpy), 124.0 (C'/C₆H₃), 125.4 (C'/C₅H₄), 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 (C'/bpy), 155.19 (C'/bpy), 155.24 (C6/bpy), 189.2 (CO), 197.0 (CO).

Synthesis of 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 containing 80 mg (0.101 mmol) of 1-(HC≡C)-3-(C≡C-bpy(Re(CO)₃Cl))-5-(FcC≡C)-C₆H₃ (11) and 50 mg (0.101
mmol) of [(Ph₃P)AuCl] (12) was added 1 mg of [CuI]. 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, v/v). The title complex could be eluted as an orange band. After removal of all volatiles oil-pump vacuum an orange solid remained. Yield: 35 mg (0.033 mmol, 33 % based on 11).

Anal. calc. for C₅₃H₃₄AuClFeN₂O₂PRe×1/4C₇H₈ (1275.33) C 51.56, H 2.85, N 2.20; found C 51.71, H 2.89, N 2.78 %. IR (KBr, cm⁻¹): 2212 (m, νC≡C), 2115 (w, νC≡CAu), 2021, 1915, 1896 (s, νCO).

1H NMR (δ, CDCl₃): 2.36 (s, ¼ × 3 H, CH₃, toluene), 4.25 (s, 5 H, C₅H₅), 4.27 (pt, J_HH = 1.9 Hz, 2 H, C₅H₄), 4.52 (pt, J_HH = 1.9 Hz, 2 H, C₅H₄), 7.17 (m, ¼ × 3 H, toluene), 7.25 (m, ¼ × 2 H, toluene), 7.43 – 7.61 (m, 15 H (C₆H₅) + 1 H (C₆H₃) + 1 H (H₅'/bpy)), 7.63 (pt, J_HH = 1.6 Hz, 1 H, C₆H₃), 7.67 (pt, J_HH = 1.6 Hz, 1 H, C₆H₃), 8.02 – 8.20 (m, H₄/H₃'/bpy), 9.07 (ddd, 3J_H6'/H5' = 4.6 Hz, 4J_H6'/H4' = 1.7 Hz, 5J_H6'H₃' = 1.0 Hz, 1 H, H₆'/bpy), 9.14 (dd, 4J_H6'H₄ = 2.2 Hz, 5J_H6'H₃ = 0.8 Hz, 1 H, H₆/bpy).

31P{¹H} NMR (δ, CDCl₃): 41.1 (s, AuPPh₂).

ESI-MS (m/z): 1253.4 ([M + H]+).

Synthesis of 1-((Ph₃P)AuC≡C)-3-(C≡C-bpy)-5-(FcC≡C)-C₆H₃ (14)

130 mg (0.263 mmol) of [(Ph₃P)AuCl] (12) and 135 mg (0.276 mmol) of 1-(HC≡C)-3-(bpy-C≡C)-5-(FcC≡C)-C₆H₃ (9) were dissolved in tetrahydrofuran (10 mL) and diethylamine (15 mL) and 1 mg of [CuI] was 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, v/v) 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. calc. 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, cm⁻¹): 2211 (m, νC≡C), 2116 (w, νC≡CAu). ¹H NMR (δ, CDCl₃): 4.24 (s, 5 H,
C₃H₅), 4.25 (pt, J₂HH = 1.9 Hz, 2 H, C₃H₅), 4.50 (pt, J₂HH = 1.9 Hz, 2 H, C₃H₅), 7.31 (ddd, J₃H₅H₄ = 7.6 Hz, J₃H₅H₆ = 4.9 Hz, J₄H₅H₆ = 1.0 Hz, 1 H, H₅'/bpy), 7.39 – 7.64 (m, 15 H (C₆H₃) + 3 H (C₆H₅)), 7.82 (ddd, J₃H₄H₅ = J₃H₄H₆ = 7.6 Hz, J₄H₄H₆ = 1.7 Hz, 1 H, H₄'/bpy), 7.92 (dd, J₂H₄H₅ = 8.2 Hz, J₄H₄H₆ = 2.2 Hz, 1 H, H₄'/bpy), 8.41 (dd, J₃H₃H₄ = 8.2 Hz, J₅H₃H₆ = 0.8 Hz, 1 H, H₃/bpy), 8.42 (ddd, J₃H₃H₄ = 7.6 Hz, J₄H₃H₅ = J₅H₃H₆ = 1.0 Hz, 1 H, H₃'/bpy), 8.69 (ddd, J₂H₆H₅ = 4.9 Hz, J₄H₆H₄ = 1.7 Hz, J₅H₆H₃ = 1.0 Hz, 1 H, H₆'/bpy), 8.80 (dd, J₄H₆H₄ = 2.2 Hz, J₅H₆H₃ = 0.8 Hz, 1 H, H₆/bpy). ¹³C{¹H} NMR (δ, CDCl₃): 65.0 (C'/C₅H₅), 69.0 (CH/C₃H₅), 70.2 (C₅H₅), 71.6 (CH/C₃H₅), 84.7 (C=CH), 86.8 (C≡C), 89.4 (C≡C), 92.8 (C≡C), 102.4 (d, J₁CP = 27 Hz, AuC≡C), 120.3 (C₅/bpy), 120.4 (C₃/bpy), 121.5 (C₃'/bpy), 122.9 (C'/C₆H₅), 124.0 (C₅'/bpy), 124.5 (C'/C₅H₅), 125.8 (AuC≡C), 125.9 (C'/C₆H₅), 129.3 (d, J₂CP = 11.4 Hz, C''/C₆H₅), 129.8 (d, J₁CP = 56.1 Hz, C'/C₆H₅), 131.8 (d, J₄CP = 2.4 Hz, C''/C₆H₅), 132.7 (CH/C₆H₅), 134.4 (d, J₁CP = 13.8 Hz, C'/C₆H₅), 134.5 (CH/C₆H₅), 135.6 (CH/C₆H₅), 137.1 (C₄'/bpy), 139.5 (C₄/bpy), 149.4 (C₆'/bpy), 151.9 (C₆/bpy), 155.0 (C'/bpy), 155.6 (C'/bpy). ³¹P{¹H} NMR (δ, CDCl₃): 41.2 (s, AuPPh₂).

Synthesis of [1-((Ph₃P)AuC≡C)-3-(C≡C-bpy)([[Ti]([µ-σ,π-C≡CSiMe₃]₂)₂)Cu)-5-(FcC≡C)-C₆H₅]PF₆ (16)

To a tetrahydrofuran solution (25 mL) containing 50 mg (0.064 mmol) of [([Ti]([µ-σ,π-C≡CSiMe₃]₂)₂)Cu(N≡CMe)]PF₆ (15), 60 mg (0.063 mmol) of 1-((Ph₃P)AuC≡C)-3-(C≡C-bpy)-5-(FcC≡C)-C₆H₅ (14) were 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 3 mL of dichloromethane and the title complex was precipitated by addition of 20 mL of n-hexane. The obtained precipitate was washed twice with 10 mL portions of diethyl ether. Drying the solid material in oil-pump vacuum gave 92 mg (0.055 mmol, 87 % based on 15) of 16.
Anal. calc. for C_{76}H_{76}AuCuF_{6}FeN_{2}P_{2}Si_{4}Ti \times \frac{1}{4}CH_{2}Cl_{2} (1693.18) C 54.09, H 4.67, N 1.65; found C 54.00, H 4.89, N 1.62 %. IR (KBr, cm^{-1}): 2211 (m, \nu_{C=C}), 2115 (w, \nu_{C=Cu}), 1924 (m, \nu_{C=Cu}), 4.23 (s, 5 H, C_{5}H_{5}), 4.25 (pt, J_{HH} = 1.9 Hz, 2 H, C_{5}H_{4}), 4.49 (pt, J_{HH} = 1.9 Hz, 2 H, C_{5}H_{4}), 5.30 (s, \frac{1}{4} \times 2 H, CH_{2}Cl_{2}), 6.27 – 6.32 (m, 8 H, C_{5}H_{4}Si), 7.41 – 7.57 (m, C_{6}H_{5}), 7.59 (pt, J_{HH} = 1.6 Hz, 1 H, C_{6}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). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (δ, CDCl\textsubscript{3}): -145.1 (septett, \textsuperscript{1}J_{PF} = 713 Hz, PF-F).

Synthesis of 1,3-(C≡C-bpy[Ru(t-Bu\textsubscript{2}bpy)]\textsubscript{2})-5-(FcC≡C)-C\textsubscript{6}H\textsubscript{3} (I8)

To 60 mg (0.085 mmol) of [(t-Bu\textsubscript{2}bpy)\textsubscript{2}Cl\textsubscript{2}Ru] (17) dissolved in 25 mL of ethanol were added 25 mg (0.039 mmol) of 1,3-(bpy-C≡C)\textsubscript{2}-5-(FcC≡C)-C\textsubscript{6}H\textsubscript{3} (7) 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\textsubscript{4}N]PF\textsubscript{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. calc. for C\textsubscript{114}H\textsubscript{122}FeF\textsubscript{24}N\textsubscript{12}P\textsubscript{4}Ru\textsubscript{2} (2499.14) C 54.79, H 4.96, N 6.72; found C 55.11, H 4.96, N 6.42 %. IR (KBr, cm^{-1}): 2211 (m, \nu_{C=C}). \textsuperscript{1}H NMR (δ, d\textsubscript{6}-Aceton): 1.39 (s, 18 H, tBu), 1.40 (s, 18 H, tBu), 1.44 (s, 9 H, tBu), 4.26 (s, 5 H, C_{5}H_{5}), 4.38 (pt, J_{HH} = 1.9 Hz, 2 H, C_{5}H_{4}), 4.53 (pt, J_{HH} = 1.9 Hz, 2 H, C_{5}H_{4}), 7.48 – 7.64 (m, bpy/Bu\textsubscript{2}bpy), 7.82 – 8.06 (m, bpy/Bu\textsubscript{2}bpy), 8.21 – 8.35 (m, bpy/Bu\textsubscript{2}bpy), 8.80 – 8.93 (m, bpy/Bu\textsubscript{2}bpy). \textsuperscript{31}P\{\textsuperscript{1}H\} NMR (δ, d\textsubscript{6}-Aceton): -145.1 (septett, \textsuperscript{1}J_{PF} = 713 Hz, PF\textsubscript{6}). ESI MS (m/z): 479.2 ([M – 4 PF\textsubscript{6}]^{4+}), 639.6 ([M – 4 PF\textsubscript{6} – Ru(t-Bu\textsubscript{2}bpy)]^{2+}).
X-ray Structure Determination

The X-ray structure measurements for 4 and 11 were performed with an Oxford Gemini S diffractometer. The structures were solved by direct methods using SHELXS-97 [21] and re fined by full-matrix least-square procedures on F² 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 re fined disordered on two positions, respectively, with occupation factors of 0.49 (C36, Cl1, Cl2) and 0.51 (C36’, Cl1’, Cl2’).

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

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Absorption coefficient ($\mu$, mm$^{-1}$)  
Scan range (deg)  
Index ranges  
Total reflections  
Unique reflections  
$R$(int)  
Data/restraints/parameters  
Goodness-of-fit on $F^2$  
R1,$^a$ wR2$^a$ $[I \geq 2\sigma(I)]$  
R1,$^a$ wR2$^a$ (all data)  
Max., min. peak in final Fourier map  

\[ R1 = \frac{\sum(||F_o| - |F_c||)}{\sum|F_o|}; \ wR2 = \frac{\sum(w(F_o^2 - F_c^2)^2)}{\sum(wF_o^4)}^{1/2}. \]
\[ S = \frac{\sum w(F_o^2 - F_c^2)^2/(n - p)^{1/2}}{n} \]

$^a$ n = number of reflections, p = parameters used.

**Supplementary Material**

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].

**Acknowledgement**

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.
References


[22] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, **1997**.
Pictogram

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

Rico Packheiser, Tobias Rüffer, Petra Ecorchard, and Heinrich Lang
Synopsis

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

Rico Packheiser, Tobias Rüffer, Petra Ecorchard, and Heinrich Lang

The synthesis and spectroscopic properties of multimetallic transition metal complexes with up to four different metal centers in which the metals are connected by carbon-rich bridging units is discussed. The structure of two molecules in the solid state is reported.