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

Heinrich Lang

► To cite this version:

Heinrich Lang. Transition-Metal Complexes Based on the 1,3,5-Triethynyl Benzene Linking Unit. Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie, 2010, 636 (15), pp.2607. 10.1002/zaac.201000243 . hal-00574817

HAL Id: hal-00574817

<https://hal.science/hal-00574817>

Submitted on 9 Mar 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Zeitschrift für Anorganische und
Allgemeine Chemie

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

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.201000243
Wiley - Manuscript type:	Article
Date Submitted by the Author:	16-Jun-2010
Complete List of Authors:	Lang, Heinrich; der TU Chemnitz, Institut für Chemie
Keywords:	Heteromultimetallic, Transition Metals, Acetylide, Ferrocene, Solid State Structure

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

Linking Unit

Rico Packheiser, Tobias Rüffer, Petra Ecorchard, and Heinrich Lang^{*)}

Chemnitz, Technische Universität, Fakultät für Naturwissenschaften, Institut für Chemie,
Lehrstuhl für Anorganische Chemie

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-[(Ph₃PAuC≡C)-3-[[Ti](C≡CSiMe₃)₂]Cu(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-

$\text{C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$, bpy = 2,2'-bipyridyl-5-yl, $[\text{Ti}] = (\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$) 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 $\equiv$ C and C $\equiv$ C bond distances.

* Prof. Dr. H. Lang

Techn. Universität

Inst. f. Chemie, Anorganische Chemie

Straße der Nationen 62

D-09111 Chemnitz

E-mail: heinrich.lang@chemie.tu-chemnitz.de. Phone: (+49)371-531-21210. Fax: (+49)371-531-21219.

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

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, $(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$, 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 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, the electrochemical behavior, UV-Vis/NIR characteristics and EPR analysis of *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'-bipyridyl-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 iodide 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)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)-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 tetrahydrofuran-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≡CSiMe₃)₂]Cu(bpy-C≡C)]-5-(FcC≡C)-C₆H₃PF₆ (**16**) ([Ti] = (η⁵-C₅H₄SiMe₃)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 heterometallic **13** and **16** using **9** as key starting material.

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)-C₆H₃ (**7**) with two equivalents of [(*t*-Bu₂bpy)₂RuCl₂] (**17**) in boiling ethanol (Reaction 1). After 20 hours and addition of a aqueous solution of [H₄N]PF₆ 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, 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 ν_{C≡C} vibrations of the organometallic M-C≡CR (M = Ti, Au, Fc; R = C₆H₃, SiMe₃) and the organic X-C≡C-C₆H₃ (X

= H, bpy, C₅H₄) 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 (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 $\nu_{\text{H-C}\equiv\text{C}}$ 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, C₆H₃, and C₆H₅ 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 Me_3Si units (Experimental Part). Similar observations were made in the $^{13}C\{^1H\}$ NMR spectra of the complexes described above.

The $^{31}P\{^1H\}$ NMR spectra of the $(Ph_3P)Au$ -containing molecules **13**, **14**, and **16** show a singlet at ca. 41.5 ppm indicative of similar phosphine environments. Compared to the starting material $[(Ph_3P)AuCl]$ (**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 PF_6^- ion in **16** gives rise to a septet at -145.1 ppm with $^1J_{PF} = 713$ 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 $[M - 4PF_6 - Ru(t-Bu_2bpy)_2]^{2+}$ (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 $P2_1/n$. 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. 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 π - π -interactions between the C_5H_5 ring and the C_6H_3 ring of the next molecule. This gives rise to the formation of 1D chains along the crystallographic a -axis (Figure 2).

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 $\triangle$ giving the interplanar angle. Labels ‘A’ to ‘D’ refer to the 1st - 4th 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) ° 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 observations

were made for other bpy-containing rhenium transition metal complexes, including 1-[(*t*-Bu₂bpy)(CO)₃ReC≡C]-3,5-(HC≡C)₂-C₆H₃ [1s].

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–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 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 distances 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 1st and a 2nd 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-, heterobi-, -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-[(Ph₃PAuC≡C)-3-[[Ti](C≡CSiMe₃)₂]}Cu-(bpy-C≡C)]-5-(FcC≡C)-C₆H₃]PF₆, and [1,3-[(*t*-Bu₂bpy)₂Ru(bpy-C≡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-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 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-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, δ 7.26) and ¹³C{¹H} NMR spectra at 62.902 MHz (internal standard, relative 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. Afterwards, 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 $\text{C}_{18}\text{H}_{12}\text{BrFeI}$ (490.9) C 44.04, H 2.46; found C 44.83, H 2.72 %. IR (KBr, cm^{-1}): 2196 (s, $\nu_{\text{C}\equiv\text{CFc}}$). ^1H NMR (δ , CDCl_3): 4.25 (s, 5 H, C_5H_5), 4.28 (pt, $J_{\text{HH}} = 1.9$ Hz, 2 H, C_5H_4), 4.50 (pt, $J_{\text{HH}} = 1.9$ Hz, 2 H, C_5H_4), 7.58 (pt, $J_{\text{HH}} = 1.6$ Hz, 1 H, C_6H_3), 7.75 (pt, $J_{\text{HH}} = 1.6$ Hz, 1 H, C_6H_3), 7.79 (pt, $J_{\text{HH}} = 1.6$ Hz, 1 H, C_6H_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , CDCl_3): 64.1 ($\text{C}^i/\text{C}_5\text{H}_4$), 69.4 ($\text{CH}/\text{C}_5\text{H}_4$), 70.2 (C_5H_5), 71.8 ($\text{CH}/\text{C}_5\text{H}_4$), 82.9 ($\text{C}\equiv\text{C}$), 91.9 ($\text{C}\equiv\text{C}$), 93.9 ($\text{C}^i/\text{C}_6\text{H}_3$), 122.7 ($\text{C}^i/\text{C}_6\text{H}_3$), 127.7 ($\text{C}^i/\text{C}_6\text{H}_3$), 133.4 ($\text{CH}/\text{C}_6\text{H}_3$), 138.6 ($\text{CH}/\text{C}_6\text{H}_3$), 138.8 ($\text{CH}/\text{C}_6\text{H}_3$).

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

500 mg (1.02 mmol) of 1-I-3-Br-5-(FcC $\equiv$ 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 $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ and 18 mg (10 mol-%) of $[\text{CuI}]$ 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 $C_{30}H_{19}BrFeN_2$ (543.24) C 66.33, H 3.53, N 5.16; found C 66.38, H 3.77, N 4.76 %. IR (KBr, cm^{-1}): 2211 (m, $\nu_{C\equiv C}$). 1H NMR (δ , $CDCl_3$): 4.26 (s, 5 H, C_5H_5), 4.28 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.51 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 7.32 (ddd, $^3J_{H_5'H_4'} = 7.8$ Hz, $^3J_{H_5'H_6'} = 4.7$ Hz, $^4J_{H_5'H_3'} = 1.0$ Hz, 1 H, H_5'/bpy), 7.60 – 7.64 (m, 3 H, C_6H_3), 7.83 (ddd, $^3J_{H_4'H_3'} = ^3J_{H_4'H_5'} = 7.8$ Hz, $^4J_{H_4'H_6'} = 1.7$ Hz, 2 H, H_4'/bpy), 7.93 (dd, $^3J_{H_4H_3} = 8.2$ Hz, $^4J_{H_4H_6} = 2.2$ Hz, 2 H, H_4/bpy), 8.40 – 8.46 (m, 2 H, $H_3, H_3'/bpy$), 8.69 (ddd, $^3J_{H_6'H_5'} = 4.7$ Hz, $^4J_{H_6'H_4'} = 1.7$ Hz, $^5J_{H_6'H_3'} = 1.0$ Hz, 2 H, H_6'/bpy), 8.80 (dd, $^4J_{H_6H_4} = 2.2$ Hz, $^5J_{H_6H_3} = 0.6$ Hz, 2 H, H_6/bpy). $^{13}C\{^1H\}$ NMR (δ , $CDCl_3$): 64.3 (C^i/C_5H_4), 69.3 (CH/C_5H_4), 70.2 (C_5H_5), 71.7 (CH/C_5H_4), 83.6 ($C\equiv C$), 88.1 ($C\equiv C$), 91.3 ($C\equiv C$), 91.4 ($C\equiv C$), 119.7 (C_5/bpy), 120.5 (C_3/bpy), 121.5 (C_3'/bpy), 122.1 (C^i/C_6H_3), 124.2 (C_5'/bpy), 124.7 (C^i/C_6H_3), 126.3 (C^i/C_6H_3), 133.1 (CH/C_6H_3), 133.3 (CH/C_6H_3), 134.3 (CH/C_6H_3), 137.1 (C_4'/bpy), 139.6 (C_4/bpy), 149.5 (C_6'/bpy), 151.8 (C_6/bpy), 155.4 (C^i/bpy), 155.5 (C^i/bpy).

Compound 7. Anal. calc. for $C_{42}H_{26}FeN_4$ (642.54) C 78.51, H 4.08, N 8.72; found C 78.56, H 4.22, N 8.51 %. IR (KBr, cm^{-1}): 2214 (m, $\nu_{C\equiv C}$). 1H NMR (δ , $CDCl_3$): 4.27 (s, 5 H, C_5H_5), 4.28 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.53 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 7.33 (ddd, $^3J_{H_5'H_4'} = 7.9$ Hz, $^3J_{H_5'H_6'} = 4.7$ Hz, $^4J_{H_5'H_3'} = 1.0$ Hz, 1 H, H_5'/bpy), 7.67 – 7.71 (m, 3 H, C_6H_3), 7.83 (ddd, $^3J_{H_4'H_3'} = ^3J_{H_4'H_5'} = 7.9$ Hz, $^4J_{H_4'H_6'} = 1.7$ Hz, 1 H, H_4'/bpy), 7.94 (dd, $^3J_{H_4H_3} = 8.2$ Hz, $^4J_{H_4H_6} = 2.0$ Hz, 2 H, H_4/bpy), 8.43 (ddd, $^3J_{H_3'H_4'} = 7.9$ Hz, $^4J_{H_3'H_5'} = ^5J_{H_3'H_6'} = 1.0$ Hz, 2 H, H_3'/bpy), 8.44 (dd, $^3J_{H_3H_4} = 8.2$ Hz, $^5J_{H_3H_6} = 0.8$ Hz, 2 H, H_3/bpy), 8.70 (ddd, $^3J_{H_6'H_5'} = 4.7$ Hz, $^4J_{H_6'H_4'} = 1.7$ Hz, $^5J_{H_6'H_3'} = 1.0$ Hz, 2 H, H_6'/bpy), 8.83 (dd, $^4J_{H_6H_4} = 2.2$ Hz, $^5J_{H_6H_3} = 0.8$ Hz, 2 H, H_6/bpy). $^{13}C\{^1H\}$ NMR (δ , $CDCl_3$): 64.5 (C^i/C_5H_4), 69.3 (CH/C_5H_4), 70.2 (C_5H_5), 71.7 (CH/C_5H_4), 84.1 ($C\equiv C$), 87.7 ($C\equiv C$), 90.6 ($C\equiv C$), 92.0 ($C\equiv C$), 119.9 (C_5/bpy), 120.5 (C_3/bpy), 121.5 (C_3'/bpy), 123.6 (C^i/C_6H_3), 124.2 (C_5'/bpy), 125.2 (C^i/C_6H_3), 133.6 (CH/C_6H_3), 134.5 (CH/C_6H_3), 137.1 (C_4'/bpy), 139.6 (C_4/bpy), 149.5 (C_6'/bpy), 151.9 (C_6/bpy), 155.3 (C^i/bpy), 155.5 (C^i/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, ν_{C≡C}), 2157 (m, ν_{C≡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, ³*J*_{H5'H4'} = 7.6 Hz, ³*J*_{H5'H6'} = 4.8 Hz, ⁴*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, ³*J*_{H4'H3'} = ³*J*_{H4'H5'} = 7.6 Hz, ⁴*J*_{H4'H6'} = 1.7 Hz, 1 H, H4'/bpy), 7.92 (dd, ³*J*_{H4H3} = 8.2 Hz, ⁴*J*_{H4H6} = 2.0 Hz, 1 H, H4/bpy), 8.40 – 8.45 (m, 2 H, H3,H3'/bpy), 8.70 (ddd, ³*J*_{H6'H5'} = 4.8 Hz, ⁴*J*_{H6'H4'} = 1.7 Hz, ⁵*J*_{H6'H3'} = 1.0 Hz, 1 H, H6'/bpy), 8.80 (dd, ⁴*J*_{H6H4} = 2.0 Hz, ⁵*J*_{H6H3} = 0.8 Hz, 1 H, H6/bpy). ¹³C{¹H} 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).

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, $\nu_{C\equiv C}$), 2100 (w, $\nu_{C\equiv CH}$). ¹H NMR (δ , CDCl₃): 3.14 (s, 1 H, $\equiv CH$), 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, $^3J_{H5'H4'} = 7.8$ Hz, $^3J_{H5'H6'} = 4.7$ Hz, $^4J_{H5'H3'} = 1.0$ 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, $^3J_{H4'H3'} = ^3J_{H4'H5'} = 7.8$ Hz, $^4J_{H4'H6'} = 1.7$ Hz, 1 H, H4'/bpy), 7.94 (dd, $^3J_{H4'H3} = 8.2$ Hz, $^4J_{H4'H6} = 2.2$ Hz, 1 H, H4/bpy), 8.40 – 8.46 (m, 2 H, H3, H3'/bpy), 8.70 (ddd, $^3J_{H6'H5'} = 4.7$ Hz, $^4J_{H6'H4'} = 1.7$ Hz, $^5J_{H6'H3'} = 1.0$ Hz, 1 H, H6'/bpy), 8.81 (dd, $^4J_{H6'H4} = 2.2$ Hz, $^5J_{H6'H3} = 0.8$ Hz, 1 H, H6/bpy). ¹³C{¹H} 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 (C5'/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).

Synthesis of 1-(HC≡C)-3-(C≡C-bpy(Re(CO)₃Cl))-5-(FcC≡C)-C₆H₃ (11)

150 mg (0.415 mmol) of $[\text{Re}(\text{CO})_5\text{Cl}]$ (**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, $\nu_{\text{C-H}}$), 2211 (m, $\nu_{\text{C}\equiv\text{C}}$), 2022, 1914, 1894 (s, ν_{CO}). ¹H NMR (δ, CDCl₃): 4.26 (s, 5 H, C₅H₅), 4.28 (pt, $J_{\text{HH}} = 1.9$ Hz, 2 H, C₅H₄), 4.53 (pt, $J_{\text{HH}} = 1.9$ Hz, 2 H, C₅H₄), 7.55 (ddd, $^3J_{\text{H5}'\text{H4}'} = 7.6$ Hz, $^3J_{\text{H5}'\text{H6}'} = 4.6$ Hz, $^4J_{\text{H5}'\text{H3}'} = 1.0$ Hz, 1 H, H5'/bpy), 7.62 (pt, $J_{\text{HH}} = 1.6$ Hz, 1 H, C₆H₃), 7.65 (pt, $J_{\text{HH}} = 1.6$ Hz, 1 H, C₆H₃), 7.68 (pt, $J_{\text{HH}} = 1.6$ 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, $^3J_{\text{H6}'\text{H5}'} = 4.6$ Hz, $^4J_{\text{H6}'\text{H4}'} = 1.7$ Hz, $^5J_{\text{H6}'\text{H3}'} = 1.0$ Hz, 1 H, H6'/bpy), 9.15 (dd, $^4J_{\text{H6H4}} = 2.2$ Hz, $^5J_{\text{H6H3}} = 0.8$ 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).

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 $[(\text{Ph}_3\text{P})\text{AuCl}]$ (**12**) was added 1 mg of $[\text{CuI}]$. 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 $\text{C}_{53}\text{H}_{34}\text{AuClFeN}_2\text{O}_3\text{PRe}\times 1/4\text{C}_7\text{H}_8$ (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, $\nu_{\text{C}\equiv\text{C}}$), 2115 (w, $\nu_{\text{C}\equiv\text{CAu}}$), 2021, 1915, 1896 (s, ν_{CO}). ^1H NMR (δ , CDCl_3): 2.36 (s, $\frac{1}{4} \times 3$ H, CH_3 , toluene), 4.25 (s, 5 H, C_5H_5), 4.27 (pt, $J_{\text{HH}} = 1.9$ Hz, 2 H, C_5H_4), 4.52 (pt, $J_{\text{HH}} = 1.9$ Hz, 2 H, C_5H_4), 7.17 (m, $\frac{1}{4} \times 3$ H, toluene), 7.25 (m, $\frac{1}{4} \times 2$ H, toluene), 7.43 – 7.61 (m, 15 H (C_6H_5) + 1 H (C_6H_3) + 1 H ($\text{H}5'/\text{bpy}$)), 7.63 (pt, $J_{\text{HH}} = 1.6$ Hz, 1 H, C_6H_3), 7.67 (pt, $J_{\text{HH}} = 1.6$ Hz, 1 H, C_6H_3), 8.02 – 8.20 (m, 4 H, $\text{H}3, \text{H}3', \text{H}4, \text{H}4'/\text{bpy}$), 9.07 (ddd, $^3J_{\text{H}6'\text{H}5'} = 4.6$ Hz, $^4J_{\text{H}6'\text{H}4'} = 1.7$ Hz, $^5J_{\text{H}6'\text{H}3'} = 1.0$ Hz, 1 H, $\text{H}6'/\text{bpy}$), 9.14 (dd, $^4J_{\text{H}6\text{H}4} = 2.2$ Hz, $^5J_{\text{H}6\text{H}3} = 0.8$ Hz, 1 H, $\text{H}6/\text{bpy}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , CDCl_3): 41.1 (s, AuPPh_2). ESI-MS (*m/z*): 1253.4 ($[\text{M} + \text{H}]^+$).

Synthesis of 1-((Ph_3P) $\text{AuC}\equiv\text{C}$)-3-($\text{C}\equiv\text{C}$ -bpy)-5-($\text{FcC}\equiv\text{C}$)- C_6H_3 (**14**)

130 mg (0.263 mmol) of $[(\text{Ph}_3\text{P})\text{AuCl}]$ (**12**) and 135 mg (0.276 mmol) of 1-($\text{HC}\equiv\text{C}$)-3-(bpy- $\text{C}\equiv\text{C}$)-5-($\text{FcC}\equiv\text{C}$)- C_6H_3 (**9**) were dissolved in tetrahydrofuran (10 mL) and diethylamine (15 mL) and 1 mg of $[\text{CuI}]$ 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 $\text{C}_{50}\text{H}_{34}\text{AuFeN}_2\text{P}$ (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, $\nu_{\text{C}\equiv\text{C}}$), 2116 (w, $\nu_{\text{C}\equiv\text{CAu}}$). ^1H NMR (δ , CDCl_3): 4.24 (s, 5 H,

C_5H_5), 4.25 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.50 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 7.31 (ddd, $^3J_{H_5'H_4'} = 7.6$ Hz, $^3J_{H_5'H_6'} = 4.9$ Hz, $^4J_{H_5'H_3'} = 1.0$ Hz, 1 H, H_5'/bpy), 7.39 – 7.64 (m, 15 H (C_6H_5) + 3 H (C_6H_3)), 7.82 (ddd, $^3J_{H_4'H_3'} = ^3J_{H_4'H_5'} = 7.6$ Hz, $^4J_{H_4'H_6'} = 1.7$ Hz, 1 H, H_4'/bpy), 7.92 (dd, $^3J_{H_4H_3} = 8.2$ Hz, $^4J_{H_4H_6} = 2.2$ Hz, 1 H, H_4/bpy), 8.41 (dd, $^3J_{H_3H_4} = 8.2$ Hz, $^5J_{H_3H_6} = 0.8$ Hz, 1 H, H_3/bpy), 8.42 (ddd, $^3J_{H_3'H_4'} = 7.6$ Hz, $^4J_{H_3'H_5'} = ^5J_{H_3'H_6'} = 1.0$ Hz, 1 H, H_3'/bpy), 8.69 (ddd, $^3J_{H_6'H_5'} = 4.9$ Hz, $^4J_{H_6'H_4'} = 1.7$ Hz, $^5J_{H_6'H_3'} = 1.0$ Hz, 1 H, H_6'/bpy), 8.80 (dd, $^4J_{H_6H_4} = 2.2$ Hz, $^5J_{H_6H_3} = 0.8$ Hz, 1 H, H_6/bpy). $^{13}C\{^1H\}$ NMR (δ , $CDCl_3$): 65.0 (C^i/C_5H_4), 69.0 (CH/C_5H_4), 70.2 (C_5H_5), 71.6 (CH/C_5H_4), 84.7 ($C\equiv C$), 86.8 ($C\equiv C$), 89.4 ($C\equiv C$), 92.8 ($C\equiv C$), 102.4 (d, $J_{CP} = 27$ Hz, $AuC\equiv C$), 120.3 (C_5/bpy), 120.4 (C_3/bpy), 121.5 (C_3'/bpy), 122.9 (C^i/C_6H_3), 124.0 (C_5'/bpy), 124.5 (C^i/C_6H_3), 125.8 ($AuC\equiv C$), 125.9 (C^i/C_6H_3), 129.3 (d, $^3J_{CP} = 11.4$ Hz, C^m/C_6H_5), 129.8 (d, $^1J_{CP} = 56.1$ Hz, C^i/C_6H_5), 131.8 (d, $^4J_{CP} = 2.4$ Hz, C^p/C_6H_5), 132.7 (CH/C_6H_3), 134.4 (d, $^1J_{CP} = 13.8$ Hz, C^o/C_6H_5), 134.5 (CH/C_6H_3), 135.6 (CH/C_6H_3), 137.1 (C_4'/bpy), 139.5 (C_4/bpy), 149.4 (C_6'/bpy), 151.9 (C_6/bpy), 155.0 (C^i/bpy), 155.6 (C^i/bpy). $^{31}P\{^1H\}$ NMR (δ , $CDCl_3$): 41.2 (s, $AuPPh_2$).

*Synthesis of [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 50 mg (0.064 mmol) of $[[Ti](\mu-\sigma,\pi-C\equiv CSiMe_3)_2]Cu(N\equiv CMe)]PF_6$ (**15**), 60 mg (0.063 mmol) of 1-((Ph₃P)AuC≡C)-3-(C≡C-bpy)-5-(FcC≡C)-C₆H₃ (**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 $C_{76}H_{78}AuCuF_6FeN_2P_2Si_4Ti \times \frac{1}{4}CH_2Cl_2$ (1693.18) C 54.09, H 4.67, N 1.65; found C 54.00, H 4.89, N 1.62 %. IR (KBr, cm^{-1}): 2211 (m, $\nu_{C\equiv C}$), 2115 (w, $\nu_{C\equiv CAu}$), 1924 (m, $\nu_{C\equiv CTi}$). 1H NMR (δ , $CDCl_3$): -0.48 (s, 18 H, $SiMe_3$), 0.28 (s, 9 H, $SiMe_3$), 0.30 (s, 9 H, $SiMe_3$), 4.23 (s, 5 H, C_5H_5), 4.25 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.49 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 5.30 (s, $\frac{1}{4} \times 2$ H, CH_2Cl_2), 6.27 – 6.32 (m, 8 H, C_5H_4Si), 7.41 – 7.57 (m, 15 H, C_6H_5), 7.59 (pt, $J_{HH} = 1.6$ Hz, 1 H, C_6H_3), 7.63 (pt, $J_{HH} = 1.6$ Hz, 1 H, C_6H_3), 7.65 (pt, $J_{HH} = 1.6$ Hz, 1 H, C_6H_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, $H3,H3',H6,H6'/bpy$). $^{31}P\{^1H\}$ NMR (δ , $CDCl_3$): -145.1 (septublet, $^1J_{PF} = 713$ Hz, PF_6), 41.1 (s, $AuPPh_2$). ESI MS (m/z): 1525.3 ($[M-PF_6]^+$).

Synthesis of 1,3-($C\equiv C$ -bpy($Ru(t-Bu_2bpy)_2$)₂)-5-($FcC\equiv C$)- C_6H_3 (**18**)

To 60 mg (0.085 mmol) of $[(t-Bu_2bpy)_2Cl_2Ru]$ (**17**) dissolved in 25 mL of ethanol were added 25 mg (0.039 mmol) of 1,3-(bpy- $C\equiv C$)₂-5-($FcC\equiv C$)- C_6H_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 $[H_4N]PF_6$ (50 mg, 0.307 mmol) was added and the solid precipitated was separated and washed with water, ethanol, and diethyl ether, and was then 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 $C_{114}H_{122}FeF_{24}N_{12}P_4Ru_2$ (2499.14) C 54.79, H 4.96, N 6.72; found C 55.11, H 4.96, N 6.42 %. IR (KBr, cm^{-1}): 2211 (m, $\nu_{C\equiv C}$). 1H NMR (δ , d_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_5H_5), 4.38 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 4.53 (pt, $J_{HH} = 1.9$ Hz, 2 H, C_5H_4), 7.48 – 7.64 (m, bpy/tBu_2bpy), 7.82 – 8.06 (m, bpy/tBu_2bpy), 8.21 – 8.35 (m, bpy/tBu_2bpy), 8.80 – 8.93 (m, bpy/tBu_2bpy). $^{31}P\{^1H\}$ NMR (δ , d_6 -Aceton): -145.1 (septett, $^1J_{PF} = 713$ Hz, PF_6). ESI MS (m/z): 479.2 ($[M - 4 PF_6]^{4+}$), 639.6 ($[M - 4 PF_6 - Ru(tBu_2bpy)_2]^{2+}$).

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 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 CH_2Cl_2 molecule as noncoordinating packing solvent has been refined 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**.

	4	11
Empirical formula	$\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{BrFeI}$	$\text{C}_{36}\text{H}_{22}\text{Cl}_3\text{FeN}_2\text{O}_3\text{Re}$
Formula weight	490.94	878.96
Temperature (K)	100(2)	110(2)
Wavelength ($\text{\AA}$)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$\text{P2}_1/\text{n}$	$\text{P2}/\text{n}$
a ($\text{\AA}$)	9.6235(6)	14.0324(9)
b ($\text{\AA}$)	13.7445(9)	7.5197(6)
c ($\text{\AA}$)	11.9791(8)	32.398(2)
α (deg)	90	90
β (deg)	94.295(5)	100.613(5)
γ (deg)	90	90
V ($\text{\AA}^3$)	1580.03(18)	3360.2(4)
ρ_{calc} (g cm^{-3})	2.064	1.737
$F(000)$	936	1712
Crystal dimensions (mm^3)	$0.6 \times 0.4 \times 0.1$	$0.1 \times 0.05 \times 0.03$
Z	4	4
Max., min. transmission	1.29694, 0.61021	1.00000, 0.84325

1			
2			
3			
4	Absorption coefficient (μ , mm ⁻¹)	5.426	4.308
5	Scan range (deg)	3.01 to 26.08	2.95 to 26.00
6			
7	Index ranges	-10 $\leq h \leq$ 11	-17 $\leq h \leq$ 15
8			
9		-16 $\leq k \leq$ 16	-9 $\leq k \leq$ 9
10			
11		-13 $\leq l \leq$ 14	-39 $\leq l \leq$ 39
12	Total reflections	7503	25110
13	Unique reflections	3072	6582
14			
15	$R(\text{int})$	0.0216	0.0720
16			
17	Data/restraints/parameters	3072 / 0 / 190	6582 / 58 / 445
18			
19	Goodness-of-fit on F^2	1.075	1.030
20			
21	$R1,^a wR2^a [I \geq 2\sigma(I)]$	0.0514, 0.1628	0.0490, 0.0732
22	$R1,^a wR2^a$ (all data)	0.0558, 0.1658	0.1077, 0.0883
23			
24	Max., min. peak in final Fourier map	3.066, -2.747	1.403, -0.847
25	<hr/>		
26	^a $R1 = [\sum(F_o - F_c)/\sum F_o]$; $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$. $S = [\sum w(F_o^2 - F_c^2)^2]/(n -$		
27	$p)^{1/2}$. n = number of reflections, p = parameters used.		
28			
29			
30			
31			
32			
33			

34 **Supplementary Material**

35
36 The crystallographic data for **4** and **11** have been deposited with the Cambridge Crystallo-
37
38 graphic Data Centre as supplementary publication no. CCDC-753340 (**4**) and CCDC-753341
39
40 (**11**). Copies of this information can be obtained free of charge on application to CCDC, 12
41
42 Union Road, Cambridge CB2 1ET, UK. [fax: +44-1223-336033, E-mail: deposit@
43
44 ccdc.cam.ac.uk].
45
46
47
48
49
50
51
52

53 **Acknowledgement**

54
55 Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der
56
57 Chemischen Industrie is gratefully acknowledged.
58
59
60

References

- [1] a) N. J. Long, C. K. Williams, *Angew. Chem., Int. Ed.* **2003**, 42, 2586. b) F. Paul, C. Lapinte, *Coord. Chem. Rev.* **1998**, 178, 180. c) C.E. Powell, M.G. Humphrey, *Coord. Chem. Rev.* **2004**, 248, 725. d) V. W. W. Yam, K. K. W. Lo, K. M. C. Wong, *J. Organomet. Chem.* **1999**, 578, 3. e) P. J. Low, *Dalton Trans.* **2005**, 17, 2821; f) M. P. Cifuentes, M. G. Humphrey, J. P. Morall, M. Samoc, F. Paul, T. Roisnel, C. Lapinte, *Organometallics* **2005**, 24, 4280. g) B. S. Brunshwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, 31, 168. h) A. Ceccon, S. Santi, L. Orian, A. Bisello, *Coord. Chem. Rev.* **2004**, 248, 683. i) D. Astruc, *Acc. Chem. Res.* **1997**, 30, 383. j) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, 31, 26. k) Q. S. Hu, V. Pugh, M. Sabat, L. Pu, *J. Org. Chem.* **1999**, 64, 7528. l) K. Onitsuka, M. Fujimoto, H. Kitajima, N. Ohshiro, F. Takei, S. Takahashi, *Chem. Eur. J.* **2004**, 10, 6433. m) N. J. Long, A. J. Martin, F. Fabrizi de Biani, P. Zanello, J. Chem. Soc., *Dalton Trans.* **1998**, 2017. n) M. P. Cifuentes, C. E. Powell, J. P. Morrall, A. M. McDonagh, N. T. Lucas, M. G. Humphrey, M. Samoc, S. Houbrechts, I. Asselberghs, K. Clays, *J. Am. Chem. Soc.* **2006**, 128, 10819. o) M. P. Cifuentes, M. G. Humphrey, *J. Organomet. Chem.* **2004**, 689, 3968. p) S. Szafert, J. A. Gladysz, *Chem. Rev.* **2006**, 106, (2006) 1. q) C. E. Powell, M. P. Cifuentes, M. G. Humphrey, A. C. Willis, J. P. Morrall, M. Samoc, *Polyhedron* **2007**, 26, 284. r) J. Vicente, M. T. Chicote, M. M. Alvarez-Falcon, *Organometallics* **2005**, 24, 2764. s) S. H. F. Chong, S. C. F. Lam, V. W. W. Yam, N. Zhu, K. K. Cheung, S. Fathallah, K. Costuas, J. F. Halet, *Organometallics* **2004**, 23, 4924. t) A. Klein, O. Lavastre, J. Fiedler, *Organometallics* **2006**, 25, 635.
- [2] a) Special issue, "50th Anniversary of the Discovery of Ferrocene", *J. Organomet. Chem.* **2001**, 637-639, R. D. Adams. ed., and references cited therein. b) Ferrocenes,

- ed. A. Togni and T. Hayashi, VCH Publishers, New York, **1995**. c) Ferrocenes, ed. P. Stepnicka, John Wiley & Sons, **2008**.
- [3] a) H. Lang, R. Packheiser, *Collect. Czech. Chem. Commun.* **2007**, 72, 435. b) H. Lang, R. Packheiser, B. Walfort, *Organometallics*, **2006**, 25, 1836. c) R. Packheiser, A. Jakob, P. Ecorchard, B. Walfort, H. Lang, *Organometallics* **2008**, 27, 1214. d) R. Packheiser, P. Ecorchard, T. Rüffer, H. Lang, *Organometallics* **2008**, 27, 3534. e) R. Packheiser, P. Ecorchard, B. Walfort, H. Lang, *J. Organomet. Chem.* **2008**, 693, 933. (f) R. Packheiser, P. Ecorchard, T. Rüffer, B. Walfort, H. Lang, *Eur. J. Inorg. Chem.* **2008**, 4152. g) R. Packheiser, P. Ecorchard, T. Rüffer, H. Lang, *Chem. Eur. J.* **2008**, 14, 4948. h) A. Jakob, P. Ecorchard, K. Köhler, H. Lang, *J. Organomet. Chem.* **2008**, 693, 3479. i) H. Lang, A. Jakob, In *Organometallic Chemistry Research Perspectives*; R. P. Irwin, ed.; Nova Publishers, **2007**, 99.
- [4] a) X. H. Wu, S. Jin, J. H. Liang, Z. Y. Li, G. Yu, S. H. Liu, *Organometallics* **2009**, 28, 2450. b) C. Lapinte, *J. Organomet. Chem.* **2008**, 693, 793. c) N. Chawdhury, N. J. Long, M. F. Mahon, L. Ooi, P. R. Raithby, S. Rooke, A. J. P. White, D. J. Williams, M. Younus, *J. Organomet. Chem.* **2004**, 689, 840. d) F. de Montigny, G. Argouarch, K. Costuas, J. F. Halet, T. Roisnel, L. Toupet, C. Lapinte, *Organometallics* **2005**, 24, 4558. e) S. K. Hurst, M. P. Cifuentes, A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs, A. Persoons, *J. Organomet. Chem.* **2002**, 642, 259. f) S. Frayssé, S. Coudret, J. P. Launay, *J. Am. Chem. Soc.* **2003**, 125, 5880. g) T. Weyland, I. Ledoux, S. Brasselet, J. Zyss, C. Lapinte, *Organometallics* **2000**, 19, 5235. (k) M. I. Bruce, B. C. Hall, B. D. Kelly, P. J. Low, B. W. Skelton A. H. J., White, *J. Chem. Soc., Dalton Trans.* **1999**, 3719. l) S. I. Ghazala, F. Paul, L. Toupet, T. Roisnel, P. Hapiot, C. Lapinte, *J. Am. Chem. Soc.* **2006**, 128, 2463.
- [5] a) J. Moussa, M. N. Rager, L. M. Chamoreau, L. Ricard, H. Amouri, *Organometallics* **2009**, 28, 397. b) G. A. Koutsantonis, G. I. Jenkins, P. A. Schauer, B. Szczepaniak, B.

- W. Skelton, C. Tan, A. H. White, *Organometallics* **2009**, 28, 2195. c) S. Santi, L. Ori-an, A. Donoli, C. Durante, A. Bisello, M. D. Valentin, P. Ganis, F. Benetollo, A. Cec-con, *J. Organomet. Chem.* **2008**, 693, 3797. d) O. Pélerin, C. Olivier, T. Roisnel, D. Touchard, S. Rigaut, *J. Organomet. Chem.* **2008**, 693, 2153. e) S. C. F. Lam, V. W.-W. Yam, K. M. C. Wong, E. C. C. Cheng, N. Zhu, *Organometallics* **2005**, 24, 4298. f) M. Samoc, N. Gauthier, M. P. Cifuentes, F. Paul, C. Lapinte, M. G. Humphrey, *Angew. Chem. Int. Ed.* **2006**, 45, 7376. g) K. M. C. Wong, S. C. F. Lam, C. C. Ko, N. Zhu, V. W.-W. Yam, S. Roué, C. Lapinte, S. Fathallah, K. Costuas, S. Kahlal, J. F. Halet, *Inorg. Chem.* **2003**, 42, 7086. h) M. Younus, N. J. Long, P. R. Raithby, J. Lewis, *J. Organomet. Chem.* **1998**, 570, 55. i) M. V. Russo, C. Lo Sterzo, P. Franceschini, G. Biagini, A. Furlani, *J. Organomet. Chem.* **2001**, 619, 49. j) N. Szesni, M. Drexler, J. Maurer, R. F. Winter, F. de Montigny, C. Lapinte, S. Steffens, J. Heck, B. Weibert, H. Fischer, *Organometallics* **2006**, 25, 5774. k) V. W.-W. Yam, W.-Y. Lo, C.-H. Lam, W. K.-M. Fung, K. M.-C. Wong, V. C.-Y. Lau, N. Zhu, *Coord. Chem. Rev.* **2003**, 245, 39.
- [6] a) R. Packheiser, M. Lohan, B. Bräuer, F. Justaud, C. Lapinte, H. Lang, *J. Organomet. Chem.* **2008**, 693, 2898. b) M. Lohan, P. Ecorchard, T. Rüffer, F. Justaud, C. Lapinte, H. Lang, *Organometallics* **2009**, 28, 1878. c) Y. Fan, I. P.-C. Liu, P. E. Fanwick, T. Ren, *Organometallics* **2009**, 28, 3959. d) K. Kowalski, M. Linseis, R. F. Winter, M. Zabel, S. Záliš, H. Kelm, H.-J. Krüger, B. Sarkar, W. Kaim, *Organometallics* **2009**, 28, 4196. e) T.-Y. Dong, S.-F. Lin, C.-P. Chen, S.-W. Yeh, H.-Y. Chen, Y.-S. Wen, *J. Organomet. Chem.* **2009**, 694, 1529. f) S. Szafert, F. Paul, W. E. Meyer, J. A. Gladysz, C. Lapinte, *C. R. Chim.* **2008**, 11, 693. g) H. Jiao, K. Costuas, J. A. Gladysz, J.-F. Halet, M. Guillemot, L. Toupet, F. Paul, C. Lapinte, *J. Am. Chem. Soc.* **2003**, 125, 9511. h) F. Paul, W. E. Meyer, L. Toupet, H. Jiao, J. A. Gladysz, C. Lapinte, *J. Am. Chem. Soc.* **2000**, 122, 9405. i) H. Jiao, K. Costuas, J. A. Gladysz, J.-F. Halet, M. Guillemot

- 1
2
3 L. Toupet F. Paul, C. Lapinte, *J. Am. Chem. Soc.* **2003**, *125*, 9511. j) F. de Montigny,
4
5 G. Argouarch, T. Roisnel, L. Toupet, C. Lapinte, S. C.-F. Lam, C.-H. Tao, V.W.-W.
6
7 Yam, *Organometallics* **2008**, *27*, 1912. k) K. M.-C. Wong, S. C.-F. Lam, C.-C. Ko, N.
8
9 Zhu, V. W.-W. Yam, S. Roué, C. Lapinte, S. Fathallah, K. Costuas, S. Kahlal, J.-F.
10
11 Halet, *Inorg. Chem.* **2003**, *42*, 7086. l) F. Paul, B. G. Ellis, M. I. Bruce, L. Toupet, T.
12
13 Roisnel, K. Costuas, J.-F. Halet, C. Lapinte, *Organometallics* **2006**, *25*, 649. m) M. I.
14
15 Bruce, P. J. Low, F. Hartl, P. A. Humphrey, F. Montigny, M. Jevric, C. Lapinte, G. J.
16
17 Perkins, R. L. Roberts, B. W. Skelton, A. H. White, *Organometallics* **2005**, *24*, 5241.
18
19 n) M. I. Bruce, K. Costuas, T. Davin, B. G. Ellis, J.-F. Halet, C. Lapinte, P. J. Low, M.
20
21 E. Smith, B. W. Skelton, L. Toupet, A. H. White, *Organometallics* **2005**, *24*, 3864. o)
22
23 M. I. Bruce, F. de Montigny, M. Jevric, C. Lapinte, B. W. Skelton, M. E. Smith, A. H.
24
25 White, *J. Organomet. Chem.* **2004**, *689*, 2860. p) M. I. Bruce, B. G. Ellis, M. Gaudio,
26
27 C. Lapinte, G. Melino, F. Paul, B. W. Skelton, M. E. Smith, L. Toupet, A. H. White,
28
29 *Dalton Trans.* 2004, *10*, 1601.
30
31
32
33
34
35
36 [7] R. Packheiser, H. Lang, *Inorg. Chim. Acta* **2010**, submitted.
37
38
39 [8] a) J. Vicente, M. T. Chicote, M. D. Abrisqueta, P. G. Jones, *Organometallics* **1997**, *16*,
40
41 5628. b) M. I. Bruce, E. Horn, J. G. Matison, M. R. Snow, *Aust. J. Chem.* **1984**, *37*,
42
43 1163.
44
45
46 [9] a) I. O. Koshevoy, Y.-C. Lin, A. J. Karttunen, P.-T. Chou, P. Vainiotalo, S. P. Tunik,
47
48 M. Haukka, T. A. Pakkanen, *Inorganic Chemistry* **2009**, *48*, 2094. b) W.-Y. Wong, S.-
49
50 Y. Poon, *J. Inorg. Organomet. Polym.* **2008**, *18*, 155. c) D. J. Armitt, M. I. Bruce, B.
51
52 W. Skelton, A. H. White, *J. Organomet. Chem.* **2008**, *693*, 3571. d) W.-Y. Wong, Y.-
53
54 H. Guo, *J. Molecular Structure* **2008**, *150*. e) A. Jakob, P. Ecorchard, M. Linseis, R. F.
55
56 Winter, H. Lang, *J. Organomet. Chem.* **2009**, *694*, 655. f) J. Vicente, J. Gil-Rubio, N.
57
58 Barquero, P. G. Jones, D. Bautista, *Organometallics* **2008**, *27*, 646. g) X. He, N. Zhu,
59
60 V. W.-W. Yam, *Organometallics* **2009**, *28*, 3621.

- [10] a) H. Lang, D. S. A. George, G. Rheinwald, *Coord. Chem. Rev.* **2000**, 206-207, 101. b) H. Lang, G. Rheinwald, *J. Prakt. Chem.* **1991**, 341, 1. c) H. Lang, K. Köhler S., Blau, *Coord. Chem. Rev.* **1995**, 143, 113.
- [11] a) P. Kurz, B. Probst, B. Spingler, R. Alberto, *Eur. J. Inorg. Chem.* **2006**, 2966. (b) E. R. Civitello, P. S. Dragovich, T. B. Karpishin, S. G. Novick, G. Bierach, J. F. O'Connell, T. D. Westmoreland, *Inorg. Chem.* **1993**, 32, 237. c) Y.-B. Dong, L. Yang, K.-K. Cheung, A. Mayr, *J. Organomet. Chem.* **2000**, 598, 55. d) H.-B. Xu, L.-Y. Zhang, Z.-N. Chen, *Inorg. Chim. Acta* **2007**, 360, 163. e) M. Wrighton, D. L. Morse, *J. Am. Chem. Soc.* **1974**, 96, 998. (f) T. R. O'Toole, J. N. Younathan, B. P. Sullivan, T. J. Meyer, *Inorg. Chem.* **1989**, 28, 3923. g) P. A. Anderson, F. R. Keene, E. Horn, E. R. T. Tiekink, *Appl. Organomet. Chem.* **1990**, 4, 523.
- [12] M. D. Janssen, M. Herres, L. Zsolnai, A. L. Spek, D. M. Grove, H. Lang, G. van Koten, *Inorg. Chem.* **1996**, 35, 2476.
- [13] R. Packheiser, B. Walfort, H. Lang, *Organometallics* **2006**, 25, 4579.
- [14] M. I. Bruce, E. Horn, J. G. Matison, M. R. Snow, *Aust. J. Chem.* **1984**, 37, 1163.
- [15] a) M. O. Sinnokrot, E. F. Valeev, C. D. Sherrill, *J. Am. Chem. Soc.* **2002**, 124, 10887. b) Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, 109, 4209. c) T. Dahl, *Acta Chem. Scand.* **1994**, 48, 95.
- [16] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier-Verlag, Amsterdam **1998**, 114.
- [17] H. Fink, N. J. Long, A. J. Martin, G. Opromolla, A. J. P. White, D. J. Williams, P. Zanello, *Organometallics* **1997**, 16, 2646.
- [18] J. Polin, H. Schottenberger, *Org. Synth.* **1996**, 13, 262.
- [19] a) V. Grosshenny, F. M. Romero, R. Ziessel, *J. Org. Chem.* **1997**, 62, 1491. b) P. F. H. Schwab, F. Fleischer, J. Michl, *J. Org. Chem.* **2002**, 67, 443. c) J. Polin, E. Schmohel, V. Balzani, *Synthesis* **1998**, 3, 321.

- 1
2
3 [20] S. P. Schmidt, W. C. Trogler, F. Basolo, *Inorg. Synth.* **1990**, 28, 160.
4
5
6 [21] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, 46, 467.
7
8 [22] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University
9
10 of Göttingen, **1997**.
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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.