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Mixed transition–metal complexes based on multitopic 1,3,5-triethynyl- and 1-diphenylphosphino-3,5-diethynyl-benzene linking units

Rico Packheiser, Heinrich Lang *

Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany

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ABSTRACT

The synthesis and reaction chemistry of heteromultimetallic transition metal complexes in which Fc, $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]$, $[(Ar_3P)Au]$, $[AuC{\equiv}C\text{-bpy}]$ and $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu]^+$ units ($Fc = (\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe$; $[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; bpy = 2,2′-bipyridyl-5-yl) are linked by alkynyl-, benzene- and phosphane- or bipyridyl-based connecting moieties is discussed. In context with this background the preparation of neutral heterotrimetallic 1-$(FcC{\equiv}C)$-3-$[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]$-5-$[(Ph_3P)AuC{\equiv}C]C_6H_3$ (**10**) and ionic heteropentametallic $[1\text{-}(FcC{\equiv}C)\text{-}3\text{-}[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]\text{-}5\text{-}[(PPh_2)AuC{\equiv}C\text{-bpy}(\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu)]C_6H_3](PF_6)$ (**19**) from 1-iodo-3,5-dibromobenzene (**1**) is reported by applying consecutive reaction methodologies including substitution, complexation and carbon–carbon cross-coupling reactions.

The identities of all complexes have been confirmed by elemental analysis and IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy; heteropentametallic **19** was additionally characterized by ESI-TOF mass-spectrometry.

1. Introduction

To connect different early and/or late transition–metal complex fragments in one molecule by forming (hetero)multimetallic organometallic complex systems is from the viewpoint of synthetic chemistry a challenge because multitopic and reactive coordination sites at the central bridging unit are required. So far mainly alkynyls [1,2] or alkynyl-, allenylidene- and/or carbene-based organic molecules including 1,4-diethynyl benzene [3,4], 1,3,5-triethynyl benzene [5,6], 1-ethynyl-4-diphenylphosphino benzene [7], as well as alkynyl-functionalized (poly)pyridyls [8,9] or thiophenes [10,11] were used as connecting units. Recently, we extended this family of bridging entities by introducing the 1,3-diethynyl-5-diphenylphosphino benzene molecule [12]. This compound can serve as a versatile building block allowing the preparation of carbon-rich complexes of higher nuclearity in three directions, *i.e.*, heterotetra- to heterohexametallic complexes [12]. Electronic-based communication between individual transition metal sub-units along the 1,3,(5)-substituted benzene π-backbone was studied as well. It was found that the appropriate conjugated organic spacers mediate significant electronic interactions between the corresponding transition metal centers as evidenced by electrochemical studies [5,6c,13].

We here describe a new series of heteromultimetallic complexes featuring titanium, chromium, iron, copper and gold metal atoms with the 1,3,5-triethynyl benzene and the 1,3-diethynyl-5-diphenylphosphino benzene core as linking unit.

2. Results and discussion

2.1. Synthesis

In order to prepare heterotrimetallic 1-$(FcC{\equiv}C)$-3-$[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]$-5-$[(Ph_3P)AuC{\equiv}C]C_6H_3$ (**10**) we followed the reaction methodologies shown in Scheme 1. A modified synthesis procedure for the preparation of 1-$(FcC{\equiv}C)$-3,5-Br_2-C_6H_3 (**3**) [5a,6e] was used, whereby 1-iodo-3,5-dibromobenzene (**1**) was reacted with ethynylferrocene (**2**) at 40 °C following the Sonogashira carbon–carbon cross-coupling protocol [6e,14]. The more reactive aryl–iodo bond allowed the selective introduction of one organometallic $FcC{\equiv}C$ moiety. Thus formed **3**, further reacted with $[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}CH)]$ (**4**) in HN^iPr_2 as solvent containing catalytic amounts of $[(Ph_3P)_2PdCl_2]$ and [CuI] to produce heterobimetallic 1-$(FcC{\equiv}C)$-3-$[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]$-5-Br-$C_6H_3$ (**5**). For completion of the reaction, heating of the reaction mixture to 80 °C was necessary. The reaction of **3** with **4** always produced as side product (ca. 5%) the disubstituted molecule 1-$(FeC{\equiv}C)$-3,5-$[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]_2C_6H_3$. This organometallic compound could be separated from **5** by column chromatography (Section 4). Compound **5** gave with an excess of trimethylsilylacetylene (**6**) the trialkynyl benzene species 1-$(FcC{\equiv}C)$-3-$[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]$-5-$(Me_3SiC{\equiv}C)$ C_6H_3 (**7**), which by desilylation with $[^nBu_4N]F$ afforded 1-$(FcC{\equiv}C)$-3-$[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]$-5-$(HC{\equiv}C)C_6H_3$ (**8**) as a yellow solid in excellent yield (Scheme 1).

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* Corresponding author. Tel.: +49 371 531 21210; fax: +49 371 531 21219.
E-mail address: heinrich.lang@chemie.tu-chemnitz.de (H. Lang).

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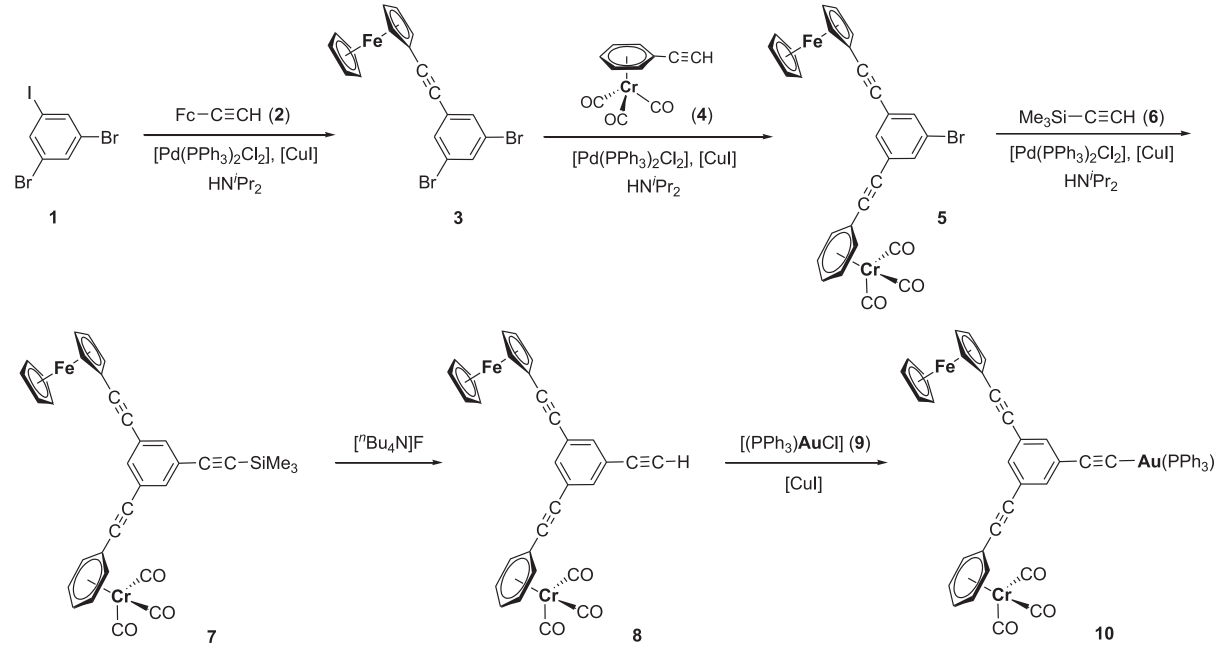


Scheme 1. Consecutive synthesis of heterotrimetallic **10**.

The last step in the synthesis of **10** included the dehydrohalogenation reaction of **8** with $[(Ph_3P)AuCl]$ (**9**) in a 1:1 mixture of tetrahydrofuran–diethylamine at ambient temperature. It was necessary to add a catalytic amount of [CuI] to the tetrahydrofuran–diethylamine reaction medium for completion of the reaction [15]. After appropriate work-up, heterotrimetallic **10** could be isolated as a yellow-orange solid in a yield of 38%.

For the overall synthesis of complex $[1\text{-}(FcC{\equiv}C)\text{-}3\text{-}[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]\text{-}5\text{-}[(PPh_2)AuC{\equiv}C\text{-bpy}(\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu)]C_6H_3](PF_6)$ (**19**) featuring five different transition metal atoms we also chose $1\text{-}(FcC{\equiv}C)\text{-}3,5\text{-}Br_2\text{-}C_6H_3$ (**3**) as key starting material [5a,6b]. Halide exchange and Sonogashira carbon–carbon cross-coupling reactions play an essential role in the synthesis of $1\text{-}(FcC{\equiv}C)\text{-}3\text{-}[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]\text{-}5\text{-}PPh_2\text{-}C_6H_3$ (**13**) (Scheme 2). Selective lithiation of one bromo substituent in **3** gave [**Li-3**] which further reacted with chlorodiphenylphosphine (**11**) to afford orange-red $1\text{-}(FcC{\equiv}C)\text{-}3\text{-}Br\text{-}5\text{-}PPh_2\text{-}C_6H_3$ (**12**) by concomitant formation of lithium chloride. Treatment of the latter molecule with equimolar amounts of $[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}CH)]$ (**4**) in presence of $[(Ph_3P)_2PdCl_2]$/[CuI] produced **13**. However, this molecule could only be isolated in 23% yield (Section 4). To improve the amount of **13** by changing the reaction conditions, either using higher temperature or choosing other amines, was not successful, *i.e.*, at higher temperatures this molecule rapidly decomposed to yield solid materials which are not anymore soluble in common organic solvents (*vide supra*). Just as little, complex **13** represents a very reactive compound which strictly must be handled under inert gas atmosphere.

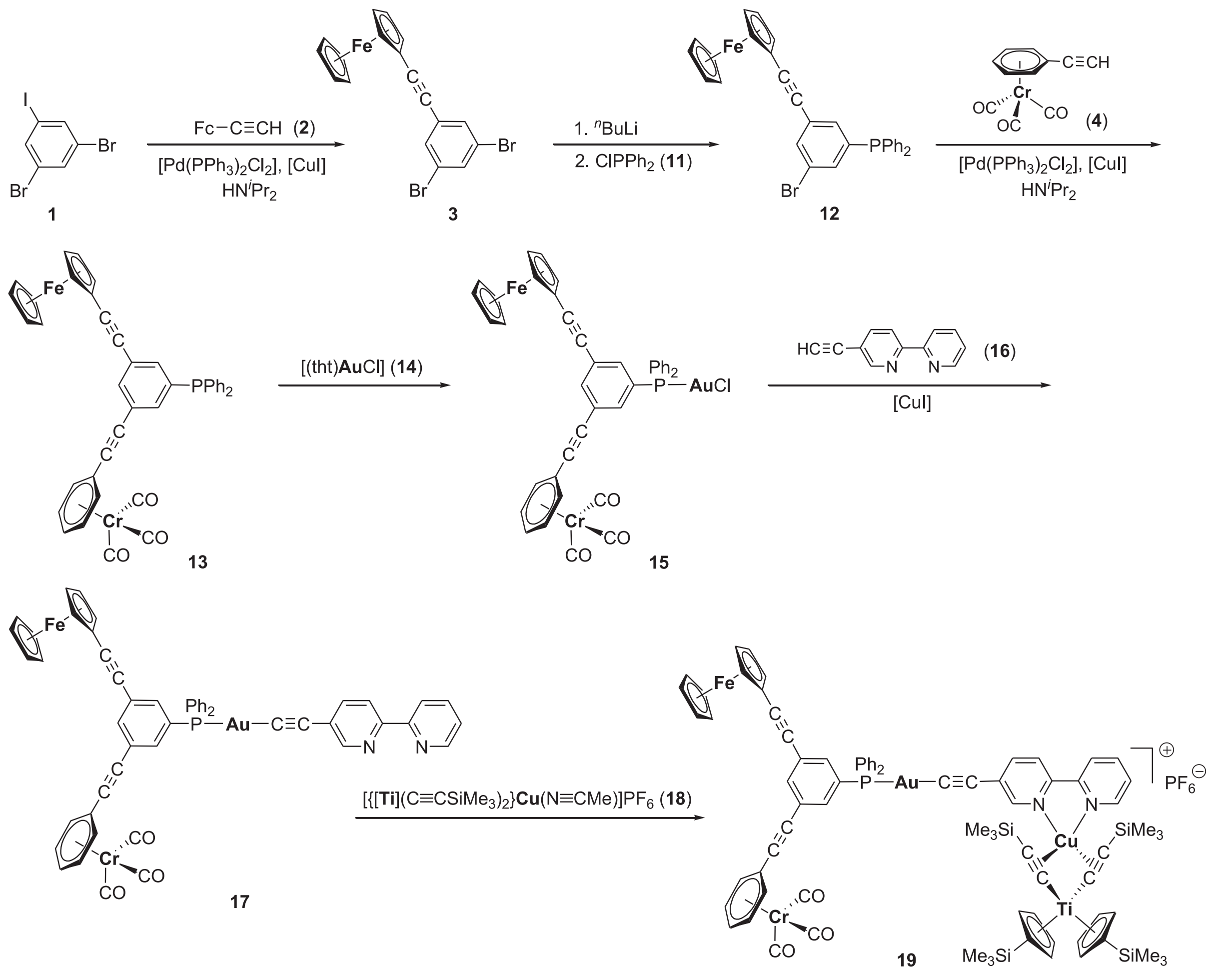
A possibility to introduce a transition metal fragment with a further coordination site allowing to incorporate other metal building blocks is given by the successive reaction of the tertiary phosphine **13** with [(tht)AuCl] (**14**) (tht = tetra*h*ydrothiophene) and 5-ethynyl-2,2′-bipyridine (**16**), respectively. Thus, **13** was reacted with **14** in tetrahydrofuran as solvent at ambient temperature, whereby **15** could be isolated as an orange solid. Reacting heterotrimetallic **15** with 5-ethynyl-2,2′-bipyridine (**16**) in a diethylamine–tetrahydrofuran mixture gave after column chromatography the desired gold(I)–alkynyl complex **17** in reasonable yield (Scheme 2, Section 4). Due to the presence of a pendant 2,2′-bipyridyl fragment, complex **17** was exemplarily reacted with the heterobimetallic organometallic π-tweezer $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu(N{\equiv}CMe)](PF_6)$ (**18**) to obtain a molecule of higher nuclearity (Scheme 2). Exchange of the weakly bonded acetonitrile ligand in **18** by the better donor–acceptor 2,2′-bipyridine gave heteropentametallic $[1\text{-}(FcC{\equiv}C)\text{-}3\text{-}[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]\text{-}5\text{-}[(PPh_2)AuC{\equiv}C\text{-bpy}(\{[Ti]\text{-}(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu)]C_6H_3](PF_6)$ (**19**) which, after appropriate work-up, was obtained in good yield (Section 4). In this molecule five different metal atoms including titanium, chromium, iron, copper and gold are connected *via* carbon-rich organic bridging units such as alkynyls, a 1,3,5-substituted benzene entity and a bipyridyl moiety.

It appeared that all compounds with the $[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]$ fragment are highly reactive both in solution as well as in the solid state. Even under inert gas atmosphere they rapidly decompose to products which could not be further characterized, due to their insolubility in common organic solvents. The process of decomposition is even more facilitated, when these molecules were exposed to air. In addition, these compounds are sensitive to light and therefore should be handled and stored in the dark. Out of these reasons the appropriate molecules are restricted to certain characterization methods (see below). This was disappointing to us because one of our goals was to carry out spectro-electrochemical studies to show if between the appropriate transition metal centers electron transfer is observed as recently demonstrated by similar molecules [6c,13].

2.2. Characterization

The identities of **3**, **5**, **7**, **8**, **10**, **12**, **13**, **15**, **17** and **19** have been confirmed by elemental analysis, IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy as well as ESI-TOF mass-spectrometry (**19**).

The IR spectra of all compounds are characterized by a $\nu_{C{\equiv}CFc}$ vibration at ca. 2210 cm^{-1}. For the AuC≡C unit a characteristic C≡C frequency is observed at 2116 (**17**) and 2118 cm^{-1} (**10**, **19**), respectively [16]. Noteworthy is that the predictable weak $\nu_{C{\equiv}C}$ absorptions for the $[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]$ (**3**, **5**, **7**, **8**, **10**, **13**, **15**, **17** and **19**) and the titanium acetylide units (**19**) are covered by the two very intense carbonyl absorptions at ca. 1970 and 1895 cm^{-1} typical for the $(CO)_3Cr$ building block with C_{3v}



Scheme 2. Reaction sequence for the synthesis of heteropentametallic **19**.

symmetry (Section 4) [17]. The progress of the reaction of **7** with [^{n}Bu$_4$N]F to give **8** could be monitored by IR spectroscopy, since the C≡C vibration for the Me$_3$SiC≡C unit in **7** at 2156 cm^{-1} gradually disappears during the course of the reaction and a new band at 3306 cm^{-1} appears which can be assigned to the $\nu_{C\equiv CH}$ frequency. The $\nu_{C\equiv C}$ absorption is, however, covered by the CO absorptions (vide supra).

The ^{31}P{^{1}H} NMR spectra of **12**, **13**, **15**, **17** and **19** indicate the presence of a single phosphorus environment (Section 4). The chemical shift of the benzene-bonded PPh$_2$ group is almost independent of the appropriate substitution pattern of the benzene core (**12**, −5.6; **13**, −6.2 ppm) which is typical for such type of connectivities [7,12]. Upon coordination of the diphenylphosphino group to the AuCl fragment a representative shift to lower field (**15**, 32.5 ppm) is observed. The exchange of Cl (**15**) by C≡C-bpy (**17**) induced a further shift to 40.8 ppm. In heteropentametallic **19** next to the resonance signal of the Ph$_2$PAu unit at 41.2 ppm, indicating that there is almost no influence on the chemical shift of the Ph$_2$P group by changing from **17** to **19**, a second resonance signal is found for the PF$_6{}^-$ counter-ion at −145.2 ppm with a coupling constant of $^1J_{PF}$ = 713 Hz.

The consecutive formation of higher nuclear heterometallic molecules from **1** is also confirmed by ^{1}H NMR and partly by ^{13}C{^{1}H} NMR spectroscopy since after each individual synthesis step the resonance signals with the corresponding coupling patterns for the new introduced organic or organometallic fragments can be seen (Section 4). For example, the protons of the Fc units always appear as a singlet (C$_5$H$_5$ annulene) and two pseudo-triplets (C$_5$H$_4$ moiety, J_{HH} = 1.9 Hz) in the range of 4.2–4.6 ppm. Upon coordination of the 2,2′-bipyridyl moiety to copper(I) as given in **19**, the separated and well-resolved signals of this entity evince up- and downfield shifts forming broad multiplets. Most expressive for the formation of **19** is the highfield shift of the Me$_3$SiC≡C protons of the bis(alkynyl)titanocene upon coordination of the bipyridyl unit to the organometallic π-tweezer-stabilized copper(I) ion in comparison to **18** [18,25]. This can be explained by the ring current of the chelating bpy entity. Furthermore, the ^{1}H NMR spectrum of **19** reveals two well separated singlets for the cyclopentadienyl-bonded Me$_3$Si groups as a result of the different chemical environment [7a,12b,18].

The identity of **19** was additionally evidenced from mass spectrometric investigations. The electrospray ionization mass spectrum of this compound shows an ion peak at a mass-to-charge ratio (*m*/*z*) of 1662.04, which corresponds to [M−PF$_6$]$^+$, confirming the elemental composition and charge state (Section 4).

3. Conclusion

A series of heteromultimetallic complexes of type 1-(FcC≡C)-3-[(CO)$_3$Cr(η^6-C$_6$H$_5$C≡C)]-5-[(Ph$_3$P)AuC≡C]C$_6$H$_3$ and [1-(FcC≡C)-3-[(CO)$_3$Cr(η^6-C$_6$H$_5$C≡C)]-5-[(PPh$_2$)AuC≡C-bpy({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu)]C$_6$H$_3$](PF$_6$) have been synthesized in straightforward consecutive synthesis methodologies. This significantly enriches the family of heteromultimetallic complexes containing early and late metal centers. In these molecules three or even five different transition metal atoms including titanium, chromium, iron, copper and gold are connected by carbon-rich bridging units based on multi topic 1,3,5-triethynyl- and 1,3-diethynyl-5-diphenylphosphinobenzene linking units, respectively. However, due to the high instability of the $[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}C)]$-containing molecules no satisfying electrochemical investigations could be carried out.

4. Experimental part

4.1. General data

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

4.2. Instruments

Infrared spectra were recorded with a Perkin Elmer FT-IR spectrometer, Spectrum 1000. ^1H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; $^{13}C\{^1H\}$ NMR spectra were recorded at 62.860 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal (^1H NMR: $CDCl_3$, $\delta = 7.26$; $^{13}C\{^1H\}$ NMR: $CDCl_3$, $\delta = 77.16$); $^{31}P\{^1H\}$ NMR spectra were recorded at 101.255 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard ($\delta = 139.0$, rel. to H_3PO_4 (85%) with $\delta = 0.00$ ppm). ESI-TOF mass spectra were recorded using a Mariner biospectrometry workstation 4.0 (Applied Biosystems). Microanalyses were performed by the Institute of Organic Chemistry, Technical University Chemnitz.

4.3. Reagents

Ethynylferrocene (**2**) [19], $[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}CH)]$ (**4**) [20], trimethylsilylacetylene (**6**) [21], $[(Ph_3P)AuCl]$ (**9**) [22], 1-(FcC≡C)-3,5-Br_2-C_6H_3 (**3**) [5a,6e], [(tht)[AuCl] (**14**) [23], 5-ethynyl-2,2′-bipyridine (**16**) [24] and $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu(N{\equiv}CMe)]PF_6$ (**18**) [25] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

*4.3.1. Synthesis of 1-(Fc-C≡C)-3-[(CO)$_3$Cr(η^6-C$_6$H$_5$C≡C)]-5-Br-C$_6$H$_3$ (**5**)*

To 150 mg (0.338 mmol) of 1-(Fc-C≡C)-3,5-Br_2-C_6H_3 (**3**) and 85 mg (0.357 mmol) of $[(CO)_3Cr(\eta^6\text{-}C_6H_5C{\equiv}CH)]$ (**4**) dissolved in 30 mL of Et_3N were added 10 mg (5 mol%) of $[(Ph_3P)_2PdCl_2]$ and 5 mg (10 mol%) of [CuI] at 25 °C. The reaction solution was refluxed for 5 h, cooled to ambient temperature and all volatiles were evaporated in oil-pump vacuum. The thus obtained residue was chromatographed on Alox (*n*-hexane–dichloromethane mixture of ratio 3:1, *v*/*v*). The title compound was obtained as an orange solid material after evaporation of all volatiles. A further band containing the disubstituted complex was discarded. Yield: 120 mg (0.200 mmol, 59% based on **3**).

Anal. Calc. for $C_{29}H_{17}BrCrFeO_3$ (601.20): C, 57.94; H, 2.85. Found: C, 57.69; H, 3.09%. IR (KBr, cm^{-1}): 2213 (w, $\nu_{C\equiv CFc}$), 1973, 1890, 1878 (s, ν_{CO}). ^1H NMR ($CDCl_3$): [δ] 4.25 (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), 5.25–5.40 (m, 3 H, C_6H_5/Cr), 5.52 (dd, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, C_6H_5/Cr), 7.55 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.57 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.61 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3).

*4.3.2. Synthesis of 1-(Fc-C≡C)-3-[(CO)$_3$Cr(η^6-C$_6$H$_5$C≡C)]-5-(Me$_3$SiC≡C)C$_6$H$_3$ (**7**)*

To 100 mg (0.166 mmol) of **5** and 50 mg (0.510 mmol) of trimethylsilylacetylene (**6**) dissolved in 25 mL of Et_3N were added 6 mg (5 mol%) of $[(Ph_3P)_2PdCl_2]$ and 3 mg (10 mol%) of [CuI] at 25 °C. After stirring this reaction solution for 15 h at 50 °C it was cooled to room temperature and all volatiles were evaporated in oil-pump vacuum. The residue was chromatographed on Alox (*n*-hexane–dichloromethane mixture of ratio 3:1, *v*/*v*). Complex **7** was obtained as a yellow–orange solid. Yield: 90 mg (0.146 mmol, 88% based on **5**).

Anal. Calc. for $C_{34}H_{26}CrFeO_3Si$ (618.5): C, 66.03; H, 4.24. Found: C, 66.38; H, 4.39%. IR (KBr, cm^{-1}): 2213 (w, $\nu_{C\equiv CFc}$), 2156 (w, $\nu_{C\equiv CSi}$), 1973, 1890, 1884 (s, ν_{CO}). ^1H NMR ($CDCl_3$): [δ] 0.26 (s, 9 H, SiMe_3), 4.25 (s, 5 H, C_5H_5), 4.26 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 4.49 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 5.25–5.40 (m, 3 H, C_6H_5/Cr), 5.52 (dd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, C_6H_5/Cr), 7.52 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.55 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.56 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3).

*4.3.3. Synthesis of 1-(Fc-C≡C)-3-[(CO)$_3$Cr(η^6-C$_6$H$_5$C≡C)]-5-(HC≡C)C$_6$H$_3$ (**8**)*

Compound **7** (75 mg, 0.121 mmol) was dissolved in 20 mL of tetrahydrofuran and the thus obtained solution was cooled to 0 °C. Afterwards, 0.15 mL (0.150 mmol) of $[^nBu_4N]F$ (1 M in tetrahydrofuran) were added in a single portion and the reaction solution was stirred for 1 h at this temperature. After evaporation of all volatile materials in oil-pump vacuum the obtained residue was chromatographed on Alox (*n*-hexane–dichloromethane mixture of ratio 3:1, *v*/*v*), whereby **8** was obtained in form of an orange solid after evaporation of the solvents. Yield: 60 mg (0.110 mmol, 90% based on **7**).

Anal. Calc. for $C_{31}H_{18}CrFeO_3$ (546.3): C, 68.16; H, 3.32. Found: C, 67.92; H, 3.47%. IR (KBr, cm^{-1}): 3306 (m, $\nu_{\equiv C\text{-}H}$), 2213 (m, $\nu_{C\equiv CFc}$), 1970, 1883 (s, ν_{CO}). ^1H NMR ($CDCl_3$): [δ] 3.11 (s, 1 H, C≡C*H*), 4.25 (s, 5 H, C_5H_5), 4.27 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 4.51 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 5.25–5.40 (m, 3 H, C_6H_5/Cr), 5.53 (dd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, C_6H_5/Cr), 7.54 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.58 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.59 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3).

*4.3.4. Synthesis of 1-(Fc-C≡C)-3-[(CO)$_3$Cr(η^6-C$_6$H$_5$C≡C)]-5-[(Ph$_3$P)AuC≡C]C$_6$H$_3$ (**10**)*

To 50 mg (0.092 mmol) of **8** and 45 mg (0.092 mmol) of $[(Ph_3P)AuCl]$ (**9**) dissolved in 10 mL of tetrahydrofuran were added 10 mL of Et_3N and 1 mg of [CuI] at 25 °C. The reaction mixture was stirred for 5 h at this temperature, whereby it became turbid. After all volatile materials have been removed in oil-pump vacuum, the residue was chromatographed on Alox (diethyl ether–dichloromethane mixture of ratio 3:1, *v*/*v*). Compound **10** was obtained as a yellow–orange solid material after evaporation of the solvents. Yield: 35 mg (0.035 mmol, 38% based on **3**).

Anal. Calc. for $C_{49}H_{32}AuCrFeO_3P$ (1004.60): C, 58.58; H, 3.21. Found: C, 58.76; H, 3.37%. IR (KBr, cm^{-1}): 2210 (m, $\nu_{C\equiv CFc}$), 2118 (w, $\nu_{C\equiv CAu}$), 1969, 1893 (s, ν_{CO}). ^1H NMR ($CDCl_3$): [δ] 4.25 (s, 5 H, C_5H_5), 4.27 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 4.50 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 5.25–5.40 (m, 3 H, C_6H_5/Cr), 5.52 (dd, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, C_6H_5/Cr), 7.40–7.65 (m, 15 H (C_6H_5) + 3 H (C_6H_3)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): [δ] 41.1 (s, Au*P*Ph_2).

*4.3.5. Synthesis of 1-(Fc-C≡C)-3-Br-5-(PPh$_2$)C$_6$H$_3$ (**12**)*

To 2.0 g (4.51 mmol) of 1-(FcC≡C)-3,5-Br_2-C_6H_3 (**3**) in 60 mL of tetrahydrofuran were slowly added (20 min) 2.80 mL (4.50 mmol) of *n*-BuLi (1.6 M in *n*-hexane) at −80 °C. Afterwards, the reaction solution was stirred for 2 h at this temperature. Then 1.10 g (4.99 mmol) of chlorodiphenylphosphine (**11**) were drop-wise added and the cooling bath was removed. After the reaction solution reached room temperature 1 mL of ethanol was added in a single portion and all volatiles were evaporated in oil-pump vacuum. The thus obtained residue was dissolved in diethyl ether (50 mL) and was filtered through a pad of Celite to remove LiBr. After all volatiles were evaporated, the obtained residue was chromatographed on Alox (diethyl ether–tetrahydrofuran mixture of ratio 8:1, *v*/*v*). Compound **12** was obtained as an orange–red solid material after evaporation of the solvents. Yield: 2.08 g (3.79 mmol, 84% based on **3**).

Anal. Calc. for $C_{30}H_{22}BrFeP$ (549.23): C, 65.61; H, 4.04. Found: C, 65.14; H, 4.17%. IR (KBr, cm^{-1}): 2207 (m, $\nu_{C\equiv CFc}$). ^{1}H NMR ($CDCl_3$): [δ] 4.27 (s, 5 H, C_5H_5), 4.29 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 4.53 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 7.36–7.46 (m, 10 H (C_6H_5), 2 H (C_6H_3)), 7.66 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): [δ] 64.4 (C^{i}/C_5H_4), 69.2 (CH/C_5H_4), 70.1 (C_5H_5), 71.6 (CH/C_5H_4), 84.2 ($C\equiv C$), 90.9 ($C\equiv C$), 122.8 (d, $^{3}J_{CP}$ = 6.5 Hz, C^{i}/C_6H_3), 126.2 (d, $^{3}J_{CP}$ = 8.0 Hz, C^{i}/C_6H_3), 128.8 (d, $^{3}J_{CP}$ = 7.1 Hz, C^{m}/C_6H_5), 129.3 (C^{p}/C_6H_5), 133.9 (d, $^{2}J_{CP}$ = 20.0 Hz, C^{o}/C_6H_5), 134.1 (d, $^{2}J_{CP}$ = 4.5 Hz, CH/C_6H_3), 134.7 (d, $^{2}J_{CP}$ = 4.7 Hz, CH/C_6H_3), 135.1 (CH/C_6H_3), 136.0 (d, $^{1}J_{CP}$ = 11.0 Hz, C^{i}/C_6H_5), 140.7 (d, $^{1}J_{CP}$ = 17.2 Hz, C^{i}/C_6H_3). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): [δ] −5.6 (s, PPh_2).

4.3.6. Synthesis of 1-(Fc-C≡C)-3-[(CO)$_3$Cr(η^6-$C_6H_5C\equiv C$)]-5-(PPh_2)C_6H_3 (**13**)

To 150 mg (0.273 mmol) of **12** and 70 mg (0.294 mmol) of **4** in 30 mL of triethylamine were added 10 mg (5 mol%) of [$(PPh_3)_2PdCl_2$] and 5 mg (10 mol%) of [CuI] in a single portion. The thus obtained reaction mixture was heated for 15 h to reflux. After cooling to room temperature all volatiles were removed in vacuum and the residue was purified by column chromatography (Alox, *n*-hexane–tetrahydrofuran mixture of ratio 3:1, *v*/*v*). After un-reacted starting materials were removed, an orange band could be eluted from which complex **13** could be separated as an orange solid material after removal of the solvents. Yield: 45 mg (0.064 mmol, 23% based on **12**).

Anal. Calc. for $C_{41}H_{27}CrFeO_3P$ (706.48): C, 69.71; H, 3.85. Found: C, 69.23; H, 4.14%. IR (KBr, cm^{-1}): 2210 (m, $\nu_{C\equiv CFc}$), 1971, 1897 (s, ν_{CO}). ^{1}H NMR ($CDCl_3$): [δ] 4.22 (s, 5 H, C_5H_5), 4.24 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 4.47 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 5.22–5.38 (m, 3 H, C_6H_5/Cr), 5.49 (dd, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2 H, C_6H_5/Cr), 7.29–7.43 (m, 10 H (C_6H_5), 2 H (C_6H_3)), 7.60 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): [δ] −6.2 (s, PPh_2).

4.3.7. Synthesis of 1-(Fc-C≡C)-3-[(CO)$_3$Cr(η^6-$C_6H_5C\equiv C$)]-5-[(PPh_2)AuCl]C_6H_3 (**15**)

To 30 mg (0.094 mmol) of [(tht)AuCl] (**14**) dissolved in 10 mL of tetrahydrofuran was added at 0 °C during 20 min a solution of 70 mg (0.099 mmol) of **13** in 10 mL of tetrahydrofuran. Afterwards, the cooling bath was removed and the reaction mixture was stirred for 1 h at ambient temperature, and was than filtered through a pad of Celite. The volume of the solution was concentrated to 2–3 mL and than **15** was precipitated by addition of 20 mL of *n*-hexane. The obtained orange solid material was washed twice with 10 mL portions of *n*-hexane and was than dried in oil-pump vacuum. Yield: 68 mg (0.072 mmol, 77% based on **13**).

Anal. Calc. for $C_{41}H_{27}AuClCrFeO_3P$ (938.90): C, 52.45; H, 2.90. Found: C, 52.80; H, 3.05%. IR (KBr, cm^{-1}): 2208 (m, $\nu_{C\equiv CFc}$), 1972, 1899 (s, ν_{CO}). ^{1}H NMR ($CDCl_3$): [δ] 4.25 (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), 5.28–5.38 (m, 3 H, C_6H_5/Cr), 5.52 (dd, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2 H, C_6H_5/Cr), 7.42–7.63 (m, 10 H (C_6H_5), 2 H (C_6H_3)), 7.75 (dpt, J_{HP} = 1.4 Hz, J_{HH} = 1.6 Hz, 1 H, C_6H_3). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): [δ] 32.5 (s, AuPPh_2).

4.3.8. Synthesis of 1-(Fc-C≡C)-3-[(CO)$_3$Cr(η^6-$C_6H_5C\equiv C$)]-5-[(PPh_2)AuC≡C-bpy]C_6H_3 (**17**)

To 60 mg (0.064 mmol) of **15** and 15 mg (0.083 mmol) of 5-ethynyl-2,2′-bipyridine (**16**) dissolved in 10 mL of tetrahydrofuran were added 10 mL of diethylamine and 1 mg of [CuI]. After 2 h of stirring at 25 °C all volatile materials were evaporated in oil-pump vacuum and the residue was chromatographed on Alox (tetrahydrofuran–*n*-hexane 1:1, *v*/*v*). Molecule **17** was eluted as an orange band. After removal of all volatiles, complex **17** was obtained as an orange solid in 72% yield (50 mg, 0.046 mmol, based on **15**).

Anal. Calc. for $C_{53}H_{34}AuCrFeN_2O_3P$ (1082.65): C, 58.80; H, 3.17; N, 2.59. Found: C, 58.99; H, 3.56; N, 2.42%. IR (KBr, cm^{-1}): 2211 (m, $\nu_{C\equiv CFc}$), 2116 (w, $\nu_{C\equiv CAu}$), 1970, 1897 (s, ν_{CO}). ^{1}H NMR ($CDCl_3$): [δ] 4.25 (s, 5 H, C_5H_5), 4.27 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 4.50 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 5.25–5.38 (m, 3 H, C_6H_5/Cr), 5.52 (dd, $^{3}J_{HH}$ = 6.3 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2 H, C_6H_5/Cr), 7.27 (ddd, $^{3}J_{H5'H4'}$ = 7.8 Hz, $^{3}J_{H5'H6'}$ = 4.7 Hz, $^{4}J_{H5'H3'}$ = 1.0 Hz, 1 H, *H5′*/bpy), 7.44–7.65 (m, 10 H (C_6H_5) + 2 H (C_6H_3)), 7.74 (dpt, J_{HP} = 1.4 Hz, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.79 (ddd, $^{3}J_{H4'H3'}$ = $^{3}J_{H4'H5'}$ = 7.8 Hz, $^{4}J_{H4'H6'}$ = 1.7 Hz, 2 H, *H4′*/bpy), 7.91 (dd, $^{3}J_{H4H3}$ = 8.2 Hz, $^{4}J_{H4H6}$ = 2.2 Hz, 2 H, *H4*/bpy), 8.32 (dd, $^{3}J_{H3H4}$ = 8.2 Hz, $^{5}J_{H3H6}$ = 0.6 Hz, 2 H, *H3*/bpy), 8.38 (ddd, $^{3}J_{H3'H4'}$ = 7.8 Hz, $^{4}J_{H3'H5'}$ = $^{5}J_{H3'H6'}$ = 1.0 Hz, 2 H, *H3′*/bpy), 8.66 (ddd, $^{3}J_{H6'H5'}$ = 4.7 Hz, $^{4}J_{H6'H4'}$ = 1.7 Hz, $^{5}J_{H6'H3'}$ = 1.0 Hz, 2 H, *H6′*/bpy), 8.82 (dd, $^{4}J_{H6H4}$ = 2.2 Hz, $^{5}J_{H6H3}$ = 0.6 Hz, 2 H, *H6*/bpy). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): [δ] 41.4 (s, AuPPh_2).

4.3.9. Synthesis of [1-(Fc-C≡C)-3-[(CO)$_3$Cr(η^6-$C_6H_5C\equiv C$)]-5-[(PPh_2)AuC≡C-bpy-Cu-{($Me_3SiC\equiv C$)$_2$[Ti]}]C_6H_3]PF_6 (**19**)

To 40 mg (0.061 mmol) of **17** were dissolved in 15 mL of tetrahydrofuran and 95 mg (0.124 mmol) of [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF_6 (**18**) were added in a single portion. After 2 h of stirring at 25 °C the color of the reaction solution was red. Afterwards, the solvent was reduced in oil-pump vacuum to 3 mL and then 20 mL of *n*-hexane were added whereby **19** precipitated. Washing the residue twice with 10 mL portions of diethyl ether and trying the solid in oil-pump vacuum gave **19** as an orange solid material in 86% yield (145 mg, 0.053 mmol, based on **17**).

Anal. Calc. for $C_{79}H_{78}AuCrCuF_6FeN_2O_3P_2Si_4Ti$ (1808.00): C, 52.48; H, 4.35; N, 1.55. Found: C, 52.14; H, 4.72; N, 1.45%. IR (KBr, cm^{-1}): 2210 (m, $\nu_{C\equiv CFc}$), 2118 (w, $\nu_{C\equiv CAu}$), 1970, 1896, (s, ν_{CO}). ^{1}H NMR ($CDCl_3$): [δ] −0.51 (s, 18 H, SiMe_3), 0.27 (s, 9 H, SiMe_3), 0.28 (s, 9 H, SiMe_3), 4.23 (s, 5 H, C_5H_5), 4.27 (br s, 2 H, C_5H_4), 4.49 (br s, 2 H, C_5H_4), 5.26–5.39 (m, 3 H, C_6H_5/Cr), 5.51 (d, J_{HH} = 6.0 Hz, 2 H, C_6H_5/Cr), 6.27 (br s, 8 H, C_5H_4Si), 7.41–7.77 (m, 10 H (C_6H_5) + 3 H (C_6H_3) + 1 H (*H5*/bpy)), 8.13–8.27 (m, 2 H, *H4*,*H4′*/bpy), 8.40 (d, J_{HH} = 8.2 Hz, 1 H, *H3*/bpy), 8.47–8.57 (m, 3 H, *H3′*,*H6*,*H6′*/bpy). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): [δ] −145.2 (septett, $^{1}J_{PF}$ = 713 Hz, PF_6), 41.2 (s, AuPPh_2). ESI MS (*m/z*): 1662.04 ([M−PF_6]$^{+}$).

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References

[1] Homometallic systems based on all-carbon ligands (a) M.I. Bruce, P.J. Low, Adv. Organomet. Chem. 50 (2004) 179;
(b) S. Szafert, J.A. Gladysz, Chem. Rev. 106 (2006) PR1;
(c) Q. Zheng, J.C. Bohling, T.B. Peters, A.C. Frisch, F. Hampel, J.A. Gladysz, Chem. Eur. J. 12 (2006) 6486;
(d) J. Maurer, R.F. Winter, B. Sarkar, S. Zalis, J. Solid State Electrochem. 9 (2005) 738;
(e) R.L. Roberts, H. Puschmann, J.A.K. Howard, J.H. Yamamoto, A.J. Carty, P.J. Low, Dalton Trans. (2003) 1099;
(f) M.I. Bruce, K. Costuas, T. Davin, J.-F. Halet, K.A. Kramarczuk, P.J. Low, B.K. Nicholson, G.J. Perkins, R.L. Roberts, B.W. Skelton, M.E. Smith, A.H. White, Dalton Trans. (2007) 5387;
(g) F. Coat, F. Paul, C. Lapinte, L. Toupet, K. Costuas, J.-F. Halet, J. Organomet. Chem. 683 (2003) 368.

[2] Heterometallic systems based on all-carbon ligands (a) M.I. Bruce, P.A. Humphrey, M. Jevric, B.W. Skelton, A.H. White, J. Organomet. Chem. 692 (2007) 2564;
(b) M.I. Bruce, K. Costuas, B.G. Ellis, J.-F. Halet, P.J. Low, B. Moubaraki, K.S.

Murray, N. Ouddai, G.J. Perkins, B.W. Skelton, A.H. White, Organometallics 26 (2007) 3735;
(c) M.I. Bruce, M.E. Smith, B.W. Skelton, A.H. White, J. Organomet. Chem. 637–639 (2001) 484;
(d) H. Jiao, K. Costuas, J.A. Gladysz, J.-F. Halet, M. Guillemot, L. Toupet, F. Paul, C. Lapinte, J. Am. Chem. Soc. 125 (2003) 9511;
(e) S. Szafert, F. Paul, W.E. Meyer, J.A. Gladysz, C. Lapinte, C. R. Chimie 11 (2008) 693;
(f) B. Xi, G.-L. Xu, P.E. Fanwick, T. Ren, Organometallics 28 (2009) 2338.

[3] Homometallic systems based on aryldiethynyl ligands (a) A. Klein, O. Lavastre, J. Fiedler, Organometallics 25 (2006) 635;
(b) 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. 689 (2004) 840;
(c) F. de Montigny, G. Argouarch, K. Costuas, J.-F. Halet, T. Roisnel, L. Toupet, C. Lapinte, Organometallics 24 (2005) 4558;
(d) B. Callejas-Gaspar, M. Laubender, H. Werner, J. Organomet. Chem. 684 (2003) 144;
(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. 642 (2002) 259;
(f) S.K. Hurst, T. Ren, J. Organomet. Chem. 660 (2002) 1;
(g) S. Fraysse, S. Coudret, J.P. Launay, J. Am. Chem. Soc. 125 (2003) 5880;
(h) S. Back, M. Lutz, A.L. Spek, H. Lang, G. van Koten, J. Organomet. Chem. 620 (2001) 227;
(i) M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, M. Younus, A.J.P. White, D.J. Williams, N.N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury, R.H. Friend, Organometallics 17 (1998) 3034;
(j) M.I. Bruce, B.C. Hall, B.D. Kelly, P.J. Low, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1999) 3719;
(k) O. Lavastre, M. Even, P.H. Dixneuf, A. Pacreau, J. Vairon, Organometallics 15 (1996) 1530;
(l) S.I. Ghazala, F. Paul, L. Toupet, T. Roisnel, P. Hapiot, C. Lapinte, J. Am. Chem. Soc. 128 (2006) 2463;
(m) C. Ornelas, J. Ruiz, D. Astruc, J. Organomet. Chem. 694 (2009) 1219;
(n) J.M. Keller, K.S. Schanze, Organometallics 28 (2009) 4210.

[4] Heterometallic systems based on aryldiethynyl ligands (a) M. Samoc, N. Gauthier, M.P. Cifuentes, F. Paul, C. Lapinte, M.G. Humphrey, Angew. Chem., Int. Ed. 45 (2006) 7376;
(b) 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. 42 (2003) 7086;
(c) M. Younus, N.J. Long, P.R. Raithby, J. Lewis, J. Organomet. Chem. 570 (1998) 55;
(d) O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, Organometallics 16 (1997) 184;
(e) M.P.Y. Yu, V.W.W. Yam, K.-K. Cheung, A. Mayr, J. Organomet. Chem. 691 (2006) 4514;
(f) W.-Y. Wong, K.-Y. Ho, K.-H. Choi, J. Organomet. Chem. 670 (2003) 17;
(g) M.V. Russo, C. Lo Sterzo, P. Franceschini, G. Biagini, A. Furlani, J. Organomet. Chem. 619 (2001) 49;
(h) N. Szesni, M. Drexler, J. Maurer, R.F. Winter, F. de Montigny, C. Lapinte, S. Steffens, J. Heck, B. Weibert, H. Fischer, Organometallics 25 (2006) 5774;
(i) M.I. Bruce, M. Gaudio, G. Melino, N.N. Zaitseva, B.K. Nicholson, B.W. Skelton, A.H. White, J. Clust. Sci. 19 (2008) 147;
(j) M.L. Lage, I. Fernández, M.J. Mancheño, M. Gómez-Gallego, M.A. Sierra, Chem. Eur. J. 16 (2010) 6616;
(k) B. Bildstein, Coord. Chem. Rev. 206–207 (2000) 369;
(l) T. Haas, S. Oswald, A. Niederwieser, B. Bildstein, F. Kessler, H. Fischer, Inorg. Chim. Acta 362 (2009) 845.

[5] Homometallic systems based on 1,3,5-triethynylbenzene (a) T. Weyland, K. Costuas, A. Mari, J.-F. Halet, C. Lapinte, Organometallics 17 (1998) 5569;
(b) R.R. Tykwinski, P.J. Stang, Organometallics 13 (1994) 3203;
(c) T.J.J. Müller, H.J. Lindner, Chem. Ber. 129 (1996) 607;
(d) M.J. Irwin, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, D.S. Yufit, Chem. Commun. (1997) 219;
(e) 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, A. Persoons, T. Isoshima, J. Am. Chem. Soc. 128 (2006) 10819;
(f) A.M. McDonagh, C.E. Powell, J.P. Morrall, M.P. Cifuentes, M.G. Humphrey, Organometallics 22 (2003) 1402;
(g) N.J. Long, A.J. Martin, F.F. De Biani, P. Zanello, J. Chem. Soc., Dalton Trans. (1998) 2017;
(h) J.P. Morrall, C.E. Powell, R. Stranger, M.P. Cifuentes, M.G. Humphrey, G.A. Heath, J. Organomet. Chem. 670 (2003) 248;
(i) J. Vicente, M.-T. Chicote, M.M. Alvarez-Falcon, P.G. Jones, Organometallics 24 (2005) 5956;
(j) M.S. Khan, D.J. Schwartz, N.A. Pasha, A.K. Kakkar, B. Lin, P.R. Raithby, J. Lewis, Z. Anorg. Allg. Chem. 616 (1992) 121.

[6] Heterometallic systems based on 1,3,5-triethynylbenzene (a) J. Vicente, M.T. Chicote, M.M. Alvarez-Falcon, Organometallics 24 (2005) 2764;
(b) 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 23 (2004) 4924;
(c) N.J. Long, A.J. Martin, A.J.P. White, D.J. Williams, M. Fontani, F. Laschi, P. Zanello, J. Chem. Soc., Dalton Trans. (2000) 3387;
(d) C.E. Powell, M.P. Cifuentes, M.G. Humphrey, A.C. Willis, J.P. Morrall, M. Samoc, Polyhedron 26 (2007) 284;
(e) R. Packheiser, P. Ecorchard, T. Rüffer, M. Lohan, B. Bräuer, F. Justaud, C. Lapinte, H. Lang, Organometallics 27 (2008) 3444.

[7] (a) N.T. Lucas, M.P. Cifuentes, L.T. Nguyen, M.G. Humphrey, J. Clust. Sci. 12 (2001) 201;
(b) R. Packheiser, H. Lang, Inorg. Chem. Commun. 10 (2007) 580;
(c) R. Packheiser, P. Ecorchard, T. Rüffer, B. Walfort, H. Lang, Eur. J. Inorg. Chem. (2008) 4152.

[8] Homometallic systems based on (poly)pyridyl ligands (a) R. Ziessel, V. Grosshenny, M. Hissler, C. Stroh, Inorg. Chem. 43 (2004) 4262;
(b) C.N. Carlson, J.M. Veauthier, K.D. John, D.E. Morris, Chem. Eur. J. 14 (2008) 422;
(c) R. Ziessel, C. Stroh, Tetrahedron Lett. 45 (2004) 4051;
(d) M. Ferrer, L. Rodriguez, O. Rossell, J.C. Lima, P. Gomez-Sal, A. Martin, Organometallics 23 (2004) 5096;
(e) H. Lang, D. Taher, B. Walfort, H. Pritzkow, J. Organomet. Chem. 691 (2006) 3834.

[9] Heterometallic systems based on (poly)pyridyl ligands (a) F. Paul, S. Goeb, F. Justaud, G. Argouarch, L. Toupet, R. Ziessel, C. Lapinte, Inorg. Chem. 46 (2007) 9036;
(b) T.-Y. Dong, M.-C. Lin, S.-W. Chang, C.-C. Ho, S.-F. Lin, L. Lee, J. Organomet. Chem. 692 (2007) 2324;
(c) J.-L. Zuo, F.F. de Biani, A.M. Santos, K. Köhler, F.E. Kühn, Eur. J. Inorg. Chem. (2003) 449;
(d) U. Siemeling, J. Vor der Brüggen, U. Vorfeld, B. Neumann, A. Stammler, H.-G. Stammler, A. Brockhinke, R. Plessow, P. Zanello, F. Laschi, F.F. de Biani, M. Fontani, S. Steenken, M. Stapper, G. Gurzadyan, Chem. Eur. J. 9 (2003) 2819;
(e) T.K. Ronson, T. Lazarides, H. Adams, S.J.A. Pope, D. Sykes, S. Faulkner, S.J. Coles, M.B. Hursthouse, W. Clegg, R.W. Harrington, M.D. Ward, Chem. Eur. J. 12 (2006) 9299;
(f) K.-L. Cheung, S.-K. Yip, V.W.-W. Yam, J. Organomet. Chem. 689 (2004) 4451;
(g) J. Vicente, M.-T. Chicote, M.M. Alvarez-Falcon, D. Bautista, Organometallics 23 (2004) 5707;
(h) A. Harriman, M. Hissler, A. Khatyr, R. Ziessel, Eur. J. Inorg. Chem. (2003) 955;
(i) S. LeStang, D. Lenz, F. Paul, C. Lapinte, J. Organomet. Chem. 572 (1999) 189;
(j) Q.H. Wei, G.Q. Yin, L.Y. Zhang, Z.N. Chen, Inorg. Chem. 45 (2006) 10371;
(k) O. Briel, K.H. Sünkel, I. Krossing, H. Nöth, E. Schmälzlin, K. Meerholz, C. Bräuchle, W. Beck, Eur. J. Inorg. Chem. (1999) 483;
(l) G.A. Koutsantonis, G.I. Jenkins, P.A. Schauer, B. Szczepaniak, B.W. Skelton, C. Tan, A.H. White, Organometallics 28 (2009) 2195.

[10] Homometallic systems based on alkynylthiophenes (a) S. Le Stang, F. Paul, C. Lapinte, Organometallics 19 (2000) 1035;
(b) Y. Zhu, M.O. Wolf, J. Am. Chem. Soc. 122 (2000) 10121;
(c) E. Viola, C. Lo Sterzo, R. Crescenzi, G. Frachey, J. Organomet. Chem. 493 (1995) C9.

[11] Heterometallic systems based on alkynylthiophenes (a) B. Jacques, J.P. Tranchier, F. Rose-Munch, E. Rose, G.R. Stephenson, C. Guyard-Duhayon, Organometallics 23 (2004) 184;
(b) W.Y. Wong, G.L. Lu, K.F. Ng, K.H. Choi, Z. Lin, J. Chem. Soc., Dalton Trans. 22 (2001) 3250;
(c) E. Viola, C. Lo Sterzo, F. Trezzi, Organometallics 15 (1996) 4352;
(d) M.H. Garcia, S. Royer, M.P. Robalo, A.R. Dias, J.-P. Tranchier, R. Chavignon, D. Prim, A. Auffrant, F. Rose-Munch, E. Rose, J. Vaissermann, A. Persoons, I. Asselberghs, Eur. J. Inorg. Chem. (2003) 3895;
(e) Y. Liao, J. Ma, Organometallics 27 (2008) 4636.

[12] (a) R. Packheiser, H. Lang, Eur. J. Inorg. Chem. (2007) 3786;
(b) R. Packheiser, P. Ecorchard, T. Rüffer, H. Lang, Chem. Eur. J. 14 (2008) 4948.

[13] (a) R. Packheiser, M. Lohan, B. Bräuer, F. Justaud, C. Lapinte, H. Lang, J. Organomet. Chem. 693 (2008) 2898;
(b) Y. Fan, I.P.-C. Liu, P.E. Fanwick, T. Ren, Organometallics 28 (2009) 3959.

[14] K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 50 (1975) 4467.

[15] J. Vicente, M.T. Chicote, M.D. Abrisqueta, P.G. Jones, Organometallics 16 (1997) 5628.

[16] (a) I.O. Koshevoy, Y.-C. Lin, A.J. Karttunen, P.-T. Chou, P. Vainiotalo, S.P. Tunik, M. Haukka, T.A. Pakkanen, Inorg. Chem. 48 (2009) 2094;
(b) W.-Y. Wong, Y.-H. Guo, J. Mol. Struct. 890 (2008) 150;
(c) A. Jakob, P. Ecorchard, M. Linseis, R.F. Winter, H. Lang, J. Organomet. Chem. 694 (2009) 655;
(d) J. Vicente, J. Gil-Rubio, N. Barquero, P.G. Jones, D. Bautista, Organometallics 27 (2008) 646.

[17] (a) A.R.E. Brewer, A.F. Drake, S.E. Gibson, J.T. Rendell, Tetrahedron 64 (2008) 6615;
(b) R. Germaneau, R. Chavignon, J.-P. Tranchier, F. Rose-Munch, E. Rose, M. Collot, C. Duhayon, Organometallics 26 (2007) 6139;
(c) F.-E. Hong, J.-W. Liaw, B.-J. Chien, Y.-C. Chang, C.-C. Lin, S.-L. Wang, F.-L. Liao, Polyhedron 18 (1999) 2737;
(d) T.J.J. Müller, A. Netz, M. Ansorge, E. Schmälzlin, C. Bräuchle, K. Meerholz, Organometallics 18 (1999) 5066;
(e) J.-P. Tranchier, R. Chavignon, D. Prim, A. Auffrant, Z.F. Plyta, F. Rose-Munch, E. Rose, Tetrahedron Lett. 41 (2000) 3607.

[18] (a) R. Packheiser, B. Walfort, H. Lang, Organometallics 25 (2006) 4579;
(b) T. Stein, M. Al-Anber, T. Rueffer, H. Lang, Anal. Sci: X-Ray Struct. Anal. 23 (2007) 217.

[19] J. Polin, H. Schottenberger, Org. Synth. 13 (1996) 262.

[20] D.W. Price Jr., S.M. Dirk, F. Maya, J.M. Tour, Tetrahedron 59 (2003) 2497.

[21] L. Brandsma, Preparative Acetylenic Chemistry, Elsevier-Verlag, Amsterdam, 1988. p. 114.
[22] M.I. Bruce, E. Horn, J.G. Matisons, M.R. Snow, Aust. J. Chem. 37 (1984) 1163.
[23] (a) R. Uson, A. Laguna, J. Vicente, J. Organomet. Chem. 131 (1977) 471;
(b) R. Uson, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 85.
[24] (a) V. Grosshenny, F.M. Romero, R. Ziessel, J. Org. Chem. 62 (1997) 1491;
(b) P.F.H. Schwab, F. Fleischer, J. Michl, J. Org. Chem. 67 (2002) 443;
(c) J. Polin, E. Schmohel, V. Balzani, Synthesis 3 (1998) 321.
[25] M.D. Janssen, M. Herres, L. Zsolnai, A.L. Spek, D.M. Grove, H. Lang, G. van Koten, Inorg. Chem. 35 (1996) 2476.