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Mixed Heterotri- to Heteropentametallic Transition-Metal Complexes: Synthesis, Characterization and Electrochemical Behavior

Rico Packheiser,[a] Petra Ecorchard,[a] Tobias Rüffer,[a] Bernhard Walfort,[a] and Heinrich Lang*[a]

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The synthesis and reaction chemistry of heteromultimetallic transition-metal complexes are discussed. Complex [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2] (**3**) [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene], accessible by treating [(η^2-dppf)(η^5-C_5H_5)RuCl] (**1**) with equimolar amounts of HC≡C-C_6H_4-4-PPh_2 (**2**), gives on treatment with [(cod)RhCl]$_2$ (**4**), [(η^5-C_5Me_5)RhCl$_2$]$_2$ (**6**), and [(tht)AuCl] (**8**) heterotrimetallic [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-{Rh}] [**5**, {Rh} = (cod)RhCl; **7**, {Rh} = (η^5-C_5Me_5)RhCl$_2$] and [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-AuCl] (**9**), respectively. Tetra- and even pentametallic heteronuclear complexes can be prepared by following consecutive reaction sequences: Treatment of **9** with HC≡CR {**10a**, R = C_5H_4N-4; **10b**, R = C_6H_4-4-C≡N; **10c**, R = bpy (= 2,2′-*bipy*ridyl-5-yl); **12a**, R = bpy[-Re(CO)$_3$Cl]} in the presence of HNEt$_2$ and [CuI] gave [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡CR] {**11a**, R = C_5H_4N-4; **11b**, R = C_6H_4-4-C≡N; **11c**, R = bpy; **13**, R = bpy-[Re(CO)$_3$Cl]}. Compound **11c** is the key starting material for complexes of higher nuclearity. Treatment of **11c** with [(nbd)-Mo(CO)$_4$] (**14**) afforded heterotetrametallic {(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡C-bpy[Mo(CO)$_4$]} (**15**), whereas with [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M]X [**16a**, MX = Cu(N≡CMe)PF$_6$; **16b**, MX = AgOClO$_3$] novel heteropentametallic [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡C-bpy({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M)]X (**17a**, M = Cu, X = PF$_6$; **17b**, M = Ag, X = ClO$_4$) is formed. The reaction of **11a** with [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu]OTf (**16c**) produced [(η^2-dppf)-(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡C-4-C_5H_4N({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu)]OTf (**18**). The structures of **9**, **11b**, **11c**, and **12** in the solid state and the electrochemical behavior of selected complexes are also reported.

Introduction

In recent years, the chemistry of organometallic complexes, in which transition metals are spanned by organic and/or inorganic bridging units, was intensively studied in regard to their novel structural, spectroscopic, and photophysical properties.[1,2] For example, employing alkynyl units as linking groups allowed the synthesis of diverse rigid-rod-structured molecules, including one that involved 20 carbon atoms in the chain bridging two redox-active [(η^5-C_5Me_5)(NO)(PPh$_3$)Re] entities.[1i]

Whereas homo- and heterodimetallic transition-metal acetylides based on, for example, the 1,4-diethynylbenzene moiety are well studied,[3,4] examples of heteronuclear metal-containing molecules with 1-(diphenylphosphanyl)-4-ethynylbenzene as the bridging unit are less documented.[5] This prompted us to use this molecule as a multitopic starting material for the synthesis of complexes of higher nuclearity, because it is of particular interest due to its geometry and its active coordination sites. On one hand, simple dehydrohalogenation reactions should allow us to prepare diverse transition-metal acetylides, whereas on the other hand the diphenylphosphanyl entity should tolerate the introduction of 16-valence electron-building blocks ML$_n$ in a consecutive way. Depending on the nature of ML$_n$ even heteromultimetallic transition-metal complexes should be accessible.

As a first target, we chose to develop a straightforward synthesis procedure for the preparation of [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2] [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene]. On the basis of this heterodinuclear Fe–Ru compound, the synthesis of heterotri- (Fe–Ru–Rh, Fe–Ru–Au), heterotetra- (Fe–Ru–Au–Re), and even heteropentametallic (Fe–Ru–Au–Cu–Ti) mixed-metal-containing carbon-rich complexes will be presented.

Results and Discussion

In contrast to the literature procedure for the preparation of HC≡C-C_6H_4-4-PPh_2 (**2**),[5] the introduction of the phosphane unit was followed by lithiation of Me$_3$SiC≡C-C_6H_4-4-Br and subsequent treatment with chlorodiphenylphosphane. This method was preferred over the nucleophilic substitution with LiPPh$_2$, because the yield of Me$_3$SiC≡C-C_6H_4-4-PPh_2 could be doubled. The desilylation by

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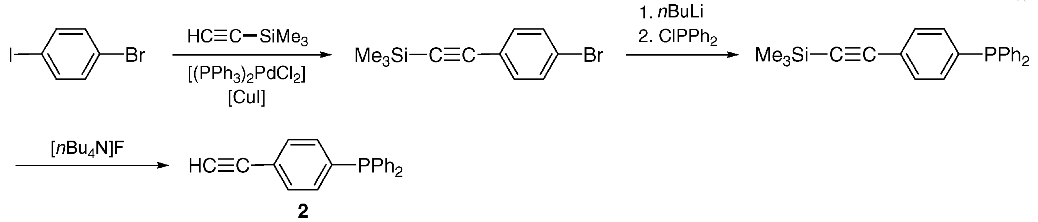
[a] Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany
E-mail: heinrich.lang@chemie.tu-chemnitz.de



Scheme 1. Synthesis of HC≡C-C_6H_4-4-PPh_2 (**2**).

fluoride afforded HC≡C-C_6H_4-4-PPh_2 (**2**) in excellent yield (Scheme 1).

The heterodimetallic iron–ruthenium complex [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2] (**3**) [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene] is accessible by the reaction of [(η^2-dppf)(η^5-C_5H_5)RuCl] (**1**) with HC≡C-C_6H_4-4-PPh_2 (**2**) in refluxing methanol followed by the addition of sodium metal (Scheme 2).[6] After appropriate workup, the yellow complex **3** could be obtained in 80% yield (Experimental Section). To obtain heterotrimetallic [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-{Rh}] [**5**, {Rh} = (cod)RhCl; **7**, {Rh} = (η^5-C_5Me_5)$RhCl_2$; cod = 1,5-*c*yclo*o*cta*d*iene] complex **3** was treated with 0.5 equiv. of the chlorido-bridged dimers $[(cod)RhCl]_2$ (**4**) and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (**6**), respectively (Scheme 2). For the synthesis of **5** it was necessary to heat the respective reaction mixture to 50 °C, whereas **7** was already formed at room temperature. Trimetallic **5** and **7** could be isolated from these solutions as yellow (**5**) or red (**7**) solids after precipitation from concentrated solutions with *n*-hexane. On treating **3** with stoichiometric amounts of [(tht)AuCl] (**8**) (tht = *t*etra*h*ydro*t*hiophene) in tetrahydrofuran, [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-AuCl] (**9**) could be isolated after column chromatography in good yield as a yellow solid (Scheme 2, Experimental Section).

Complexes **3**, **5**, **7**, and **9** were characterized by elemental analysis, ^1H, $^{31}P\{^1H\}$ NMR, and IR spectroscopy (Experimental Section).

Very characteristic for all new compounds is their C≡C stretching vibration found at ca. 2065 cm^{-1} which is not influenced when the Ph_2P group in **3** is coordinated to a rhodium or gold fragment in **5**, **7**, and **9**.

The $^{31}P\{^1H\}$ NMR spectrum of **3** displays two resonance signals at δ = 53.9 and –6.7 ppm due to the presence of the dppf and Ph_2P units. The *P*-coordination of the diphenylphosphanyl entity to a (cod)RhCl, (η^5-C_5Me_5)$RhCl_2$, or AuCl fragment is best reflected by a downfield shift to δ = 29.0 (**5**), 28.7 (**7**), and 31.4 ppm (**9**).[7,9] The signals of **5** and **7** thereby show a characteristic coupling with ^{103}Rh (I = 1/2, 100% abundance) giving doublets with typical $^1J_{PRh}$ coupling constants of 149 Hz (**5**) and 143 Hz (**7**), respectively.[7]

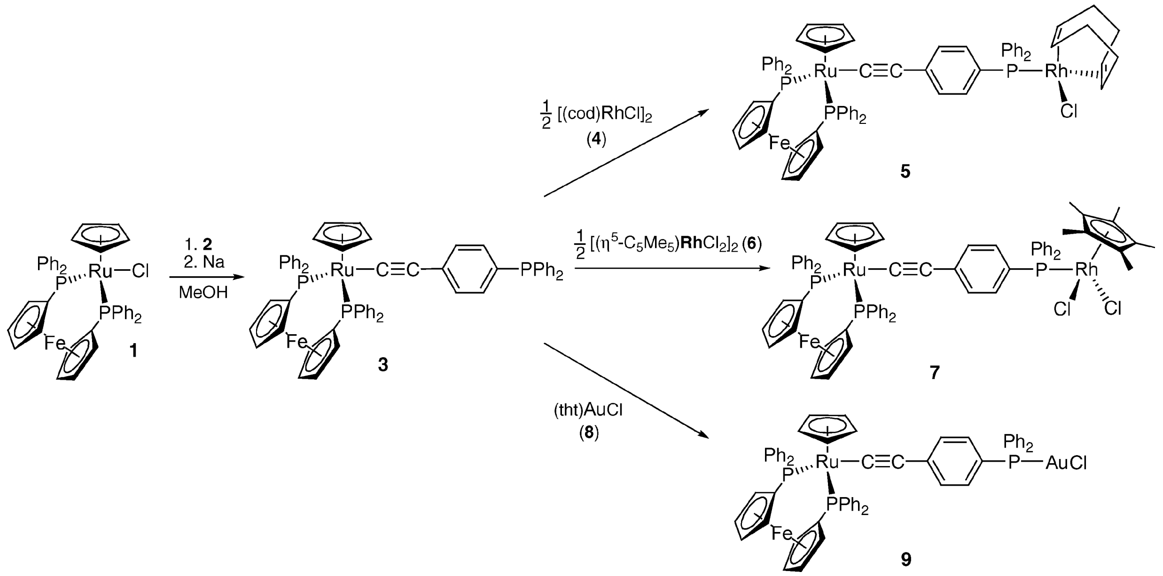
The key spectroscopic ^1H NMR feature of all compounds is that the protons of the dppf cyclopentadienyl groups appear as separated doublet-of-pseudo-triplets or as broad signals, whereby one of the four resonance signals is found at $\delta \approx 5.3$ ppm and the others between δ = 3.98 and 4.30 ppm. This is attributed to the chemical environment around ruthenium(II) (Scheme 2). The presence of the (cod)-RhCl and (η^5-C_5Me_5)$RhCl_2$ entities in **5** and **7** is additionally supported by the observation of a doublet ($^3J_{HRh}$ = 3.5 Hz) for the C_5Me_5 protons in **5**, whereas in **7** multiplets are characteristic for the olefinic CH protons (Experimental Section).

Single-crystal X-ray structure analysis was performed for **9**. A view of the molecular structure of **9** is given in Figure 1. Selected bond lengths [Å] and angles [°] are listed in the caption of Figure 1. The crystal and structure refinement data are presented in Table 2 (Experimental Section).

The overall structural features of **9** are similar to those of related structurally characterized bis(diphenylphosphanyl)ferrocene, cyclopentadienylruthenium, and (phosphane)gold(I) halide containing compounds with ruthenium in a pseudo-tetrahedral and gold in a linear arrangement.[8,9] The cyclopentadienyl rings of the dppf entity are rotated by 2.79(0.32)° to each other which verifies an almost eclipsed conformation.

Complex **9** can be functionalized by alkynyl units featuring mono- and bidentate nitrogen-containing donor ligands (Scheme 3). In this respect, trimetallic **9** was treated with 4-ethynylpyridine (**10a**), 4-ethynylbenzonitrile (**10b**), and 5-ethynyl-2,2′-bipyridyl (**10c**), respectively, in tetrahydrofuran as the solvent. The gold acetylides **11a**–**11c** (Scheme 3) were prepared basically in accordance with the method reported by Vicente et al., i.e. treatment of **9** with **10a**–**10c** in the presence of diethylamine.[10] These reactions, however, require the addition of catalytic amounts of [CuI] to obtain yellow **11a**–**11c** in good yield.

Compounds **11a**–**11c** with their mono- and bidentate donor coordination sites allow one to add further transition-metal-containing building blocks. Thus, complex **11b** was treated with 1 equiv. of the NCN pincer molecule [NCN-Pt(OH_2)(BF_4)] {NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$} to give [($\eta^2$-dppf)($\eta^5$-$C_5H_5$)Ru-C≡C-$C_6H_4$-4-$PPh_2$-Au-C≡C-$C_6H_4$-4-C≡N-Pt-NCN]$BF_4$. However, it appeared that no complete conversion of the starting materials to the desired heterotetrametallic Fe–Ru–Au–Pt system took place, even when the reaction time was extended and/or the temperature increased. The coordination of the cyano group in **11b** to a platinum(II) ion was evidenced by IR spectroscopy, whereby a new absorption band was observed at 2250 cm^{-1} (for comparison, **11b**: 2224 cm^{-1}). Also, the reaction of **11a** with [(bpy′)Re$(CO)_3$]BPh_4 (bpy′ = 4,4′-dimethyl-2,2′-bipyridyl) afforded reaction mixtures from which the separation of the appropriate Fe–Ru–Au–Re complex could not be accomplished.



Scheme 2. Synthesis of **3** and heterotrimetallic **5**, **7**, and **9**.

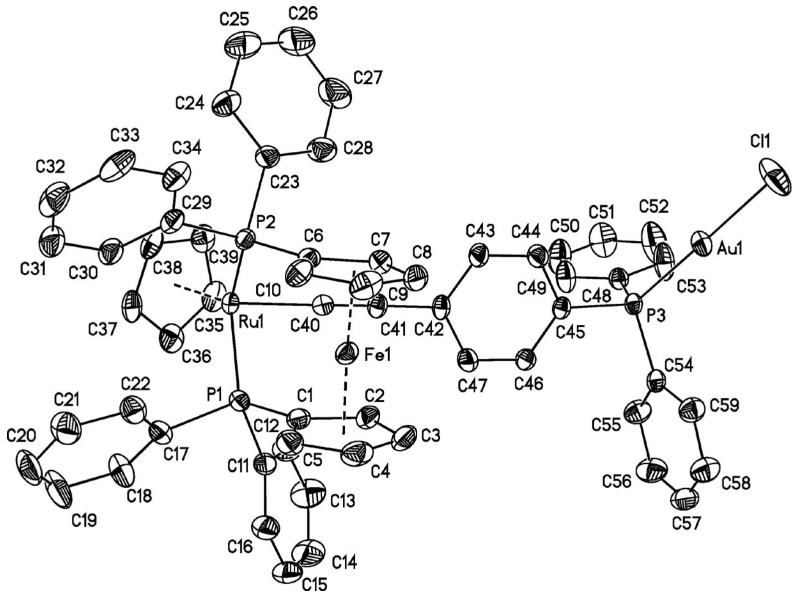
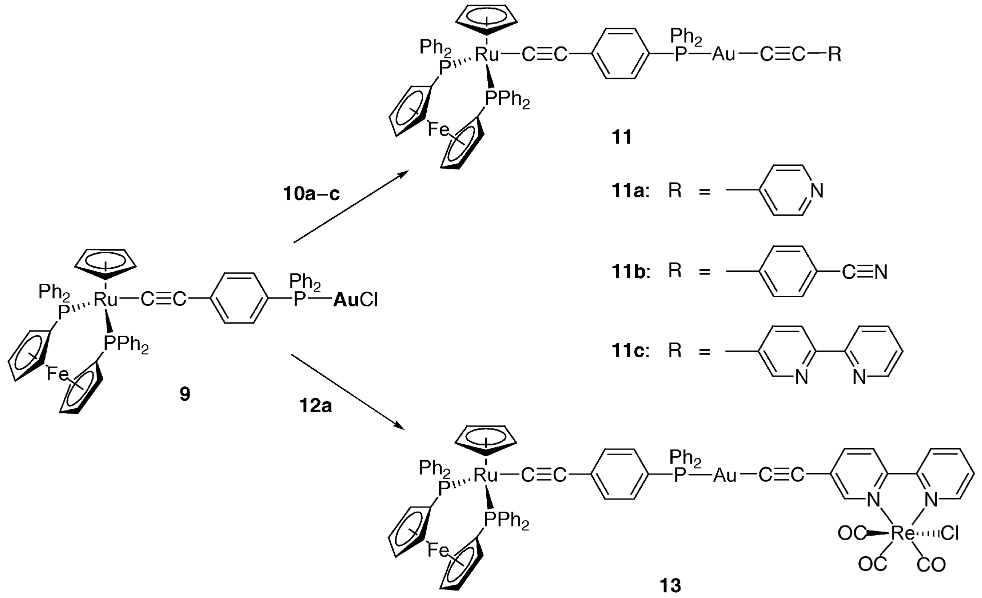


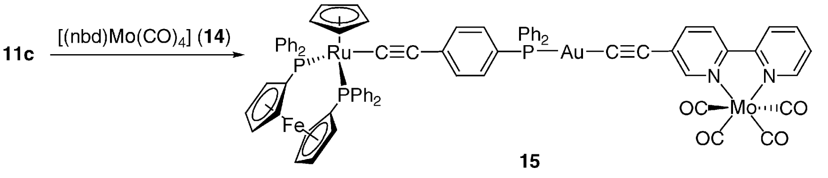
Figure 1. ORTEP diagram of **9** (30% probability level) with atom numbering scheme; hydrogen atoms and packing solvent molecules (CH_2Cl_2, $CHCl_3$) are omitted for clarity; selected bond lengths [Å] and angles [°]: Ru1–C40 1.997(4), C40–C41 1.209(6), Ru1–P1 2.2699(12), Ru1–P2 2.2881(12), Ru1–D3 1.894(2), Fe1–D1 1.648(2), Fe1–D2 1.642(2), P3–Au1 2.2288(12), Au1–Cl1 2.2776(16); P1–Ru1–P2 97.25(4), Ru1–C40–C41 176.3(4), C40–C41–C42 178.8(5), P3–Au1–Cl1 178.04(7) (D1 = centroid of C1–C5, D2 = centroid of C6–C10, D3 = centroid of C35–C39).

Another possibility to introduce a rhenium(I) fragment in organometallic chemistry is given by the reaction of 2,2′-bipyridyl derivatives with $Re(CO)_5Cl$.[11] Unfortunately, treatment of **11c** with [$Re(CO)_5Cl$] in benzene at 60 °C led to decomposition. For this reason, we synthesized [(HC≡C-bpy)$Re(CO)_3Cl$] (**12a**) by combining 5-ethynyl-2,2′-bipyridyl and [$Re(CO)_5Cl$] in benzene as the solvent. Upon loss of carbon monoxide, **12a** was formed as a yellow solid in high yield. On treating **9** with **12a** under similar reaction conditions as described earlier, heterotetrametallic [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡C-bpy{$Re(CO)_3$-Cl}] (**13**) was produced (Scheme 3), which, after appropriate workup, could be isolated in 30% yield as a yellow solid.

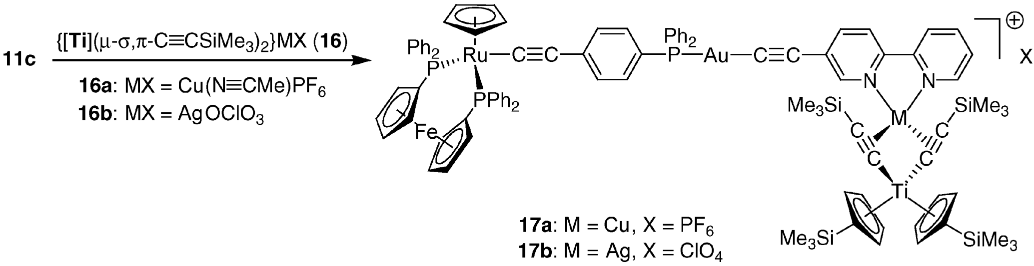
A further example of a tetrametallic transition-metal compound is [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡C-bpy{$Mo(CO)_4$}] (**15**), which is accessible by the reaction of **11c** with [(nbd)$Mo(CO)_4$] (**14**) (nbd = 2,5-*nor*-*borna**di*ene) [Equation (1)]. For comparison, the mononuclear complex [(HC≡C-bpy)$Mo(CO)_4$] (**12b**) was synthesized under identical reaction conditions.



Scheme 3. Synthesis of trimetallic **11a**–**11c** from **9** and HC≡CR (**10a**–**10c**) and tetranuclear **13** from **9** and [(HC≡C-bpy)Re(CO)$_3$Cl] (**12a**).



(1)



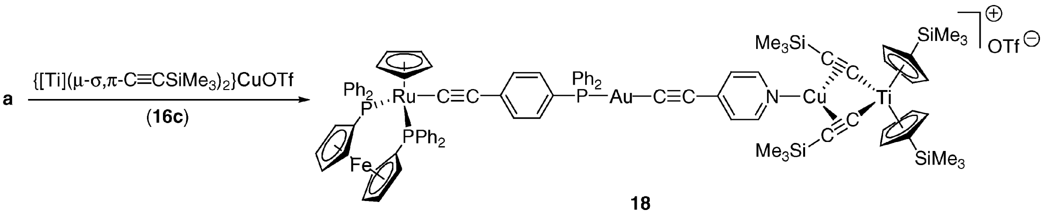
(2)

Even the synthesis of heteropentametallic complexes with Fe, Ru, Au, Ti, Cu, or Ag metals is possible. This could be done in a straightforward manner by combining heterotrimetallic **11c** with the organometallic π-tweezer {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}MX (**16a**, MX = Cu(N≡CMe)-PF$_6$; **16b**, MX = AgOClO$_3$) in tetrahydrofuran at room temperature [Equation (2)]. Replacement of the copper-bonded acetonitrile or the silver-bonded perchlorate by 2,2′-bipyridyl produced orange **17a** and **17b** in ca. 90% yield.

The π-tweezer-stabilized Cu^{I} center can also coordinate to a monodentate Lewis base. In this respect, treatment of {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}CuOTf (**16c**) with pyridine-functionalized **11a** led to the formation of the heteropentanuclear complex **18** [Equation (3)]. When this reaction was carried out in a mixture of toluene and diethyl ether, the title complex precipitated and could be isolated in pure form; in contrast to tetrahydrofuran or dichloromethane solutions, only mixtures could be obtained.

Yellow to orange-red **11**–**13**, **15**, **17**, and **18** dissolve in polar organic solvents such as tetrahydrofuran and dichloromethane. They are stable in the solid state, while solutions containing these compounds slowly decompose after exposure to air and moisture to give materials that are no longer soluble in common organic solvents.

Complexes **11**–**13**, **15**, **17**, and **18** gave satisfactory elemental analyses and have been characterized by IR, ^{1}H and



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(3)

$^{31}P\{^1H\}$ NMR spectroscopy and partly by ESI-TOF mass spectrometry. The identity of mononuclear **12a** and trimetallic **11b** and **11c** was further confirmed by single-crystal X-ray diffraction studies.

The IR spectra of **11a**–**11c**, **13**, **15**, **17**, and **18** show characteristic $\nu_{C\equiv C}$ absorptions for the Ru-C≡C and Au-C≡C fragments at ca. 2060 and 2115 cm^{-1}, respectively. In **12a** and **12b** the C≡C and C–H stretching frequencies are observed at 2105 and 3184 (**12a**) and 2116 and 3285 cm^{-1} (**12b**), respectively.[12] Consistent with the structure of **13** and **15**, the IR spectra of these compounds present in the carbonyl region three (**13**) or four (**15**) strong vibrations between 2020 and 1830 cm^{-1}, characteristic for this type of carbonylmetal entity.[11,13] The stretching frequency for the cyano unit in **11b** appears at 2224 cm^{-1}. In complexes **17** and **18**, in which the organometallic π-tweezer part $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}M]^+$ is coordinated by the bipyridyl or pyridyl ligand, a third $\nu_{C\equiv C}$ vibration is found at ca. 1920 cm^{-1} (M = Cu) or 1955 cm^{-1} (M = Ag), which is typical for this type of structural motif.[14]

The ^1H NMR spectra of **11a**–**11c** show representative chemical shifts for the new introduced building blocks 4-ethynylpyridine (**11a**), 4-ethynylbenzonitrile (**11b**), and 5-ethynyl-2,2′-bipyridyl (**11c**) (Experimental Section). The coordination to further transition-metal building blocks as given in **13**, **15**, **17**, and **18** is reflected by a change of the resonance signals, e.g. of the bipyridyl protons. Notable in the ^1H NMR spectra of **17a** and **17b**, when compared with **16a** and **16b**, is the high-field shift of the $Me_3SiC\equiv C$ proton signal from $\delta \approx 0.25$ (**16**) to –0.50 (**17a**) and –0.30 ppm (**17b**), respectively, which can be explained by the ring current of the chelating bipyridyl group.[14d] Furthermore, **17a** shows a splitting for the $SiMe_3$ proton signals of the titanium-bonded cyclopentadienyl ligands into two separated singlets, which is attributed to their unsymmetrical chemical environment. The formation of pentametallic **18** is also evidenced by a small shift (δ = 0.20 ppm) of the $Me_3SiC\equiv C$ proton signal to higher field.

The $^{31}P\{^1H\}$ NMR spectra of **11**, **13**, **15**, **17**, and **18** possess two resonance signals at δ = 53.9 (dppf) and 40 ppm (Ph_2PAu). Compared to **9** (δ = 31 ppm), the phosphorus signal for the (diphenylphosphanyl)gold(I) acetylide entity is shifted by 9 ppm to lower field. This can be used to monitor the progress of the reaction of **9** with **10a**–**10c**.[15]

The identities of the tetra- and pentametallic assemblies **13**, **15**, **17**, and **18** were additionally confirmed by electrospray ionization mass spectrometric investigations (Experimental Section). The presence of the molecular ions [M + H]$^+$ (**13**, **15**) or [M – X]$^+$ (**17**, **18**) confirms the structural composition of the appropriate complexes. The ESI mass spectrum of pentametallic **17a** is presented in Figure 2. It exhibits a prominent ion peak at *m*/*z* = 1963.4 for which the mass and isotope distribution pattern comply with [**17a** – PF_6]$^+$ and confirm the elemental composition and charge state. Further assigned peaks are at *m*/*z* = 1890.3 [**17a** – PF_6 – $SiMe_3$]$^+$, 749.1 $[(C_5H_5)(PPh_3)_2Ru(CO)]^{+[16]}$, and 581.1 $[\{Ti\}(C\equiv CSiMe_3)_2Cu]^+$ (Figure 2).

Single crystals of **11b** and **11c** suitable for X-ray diffraction studies could be grown by slow vapor diffusion of *n*-pentane into an acetone solution containing **11b** at 25 °C, or from a dichloromethane/*n*-pentane solvent mixture containing **11c** at room temperature. Figures 3 and 4 show the perspective drawings of **11b** and **11c** together with the atomic numbering schemes. Selected bond lengths and angles are presented in the captions. The crystallographic data are summarized in Table 2 (Experimental Section). From Figures 3 and 4 it can be seen that the structures of both heterotrimetallic transition-metal complexes are essentially similar as far as the molecule backbone is concerned.

Trimetallic **11b** crystallizes with two crystallographically independent molecules in the asymmetric unit. The difference between these two molecules is a slightly variable orientation of one of the Ph rings of the $C_6H_4PPh_2$ fragment. Complex **11c** exhibits a disorder of its packing solvent molecule *n*-pentane with occupation factors of 0.49 and 0.51.

The molecular structures of **11b** and **11c** consist of an $(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)Ru\text{-}C\equiv C\text{-}C_6H_4\text{-}4\text{-}PPh_2$ building block of which the 1,1′-bis(diphenylphosphanyl)ferrocene unit is in an eclipsed geometry [**11b**, 1.63(0.13); **11c**, 0.92(0.14)°], and the cyclopentadienyl rings are inclined at an angle of 2.69(0.18) (**11b**) and 2.22(0.28)° (**11c**). The phosphorus atom P3 in **11b** is coordinated to a (4-ethynylbenzonitrile)-gold(I) moiety, whereas in **11c** a (5-ethynyl-2,2′-bipyridyl)-gold(I) unit is present. The gold(I) ion possesses, as typical for this type of compounds, a linear arrangement.[15] The distance of the C≡C bond that is attached to the ruthenium atom is 1.215(5) Å (**11b**) and 1.208(4) Å (**11c**), whereas the one bonded to the gold atom is 1.066(5) Å (**11b**) and 1.158(5) Å (**11c**) (Figures 2 and 3), which is comparable to those of other (σ-alkynyl)gold(I) and -ruthenium(II) systems.[8,15] The respective Ru-C≡C and Au-C≡C units are essentially linear (Figures 3 and 4).[8,15] All other bond lengths and angles require no further discussion, because they agree well with those parameters described for related transition-metal complexes.[8,15]

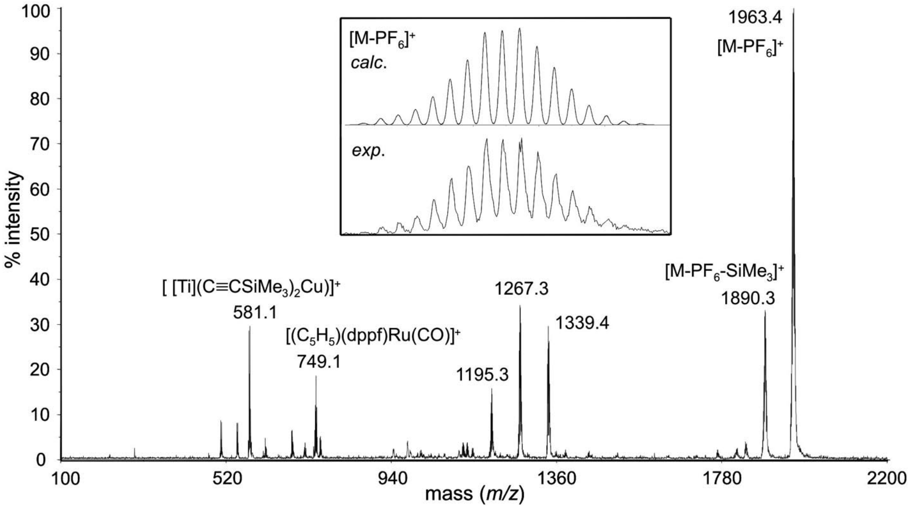

Figure 2. ESI TOF mass spectrum of **17a** (inset: comparison of the calculated and experimental found isotope distribution pattern of the molecular peak $[M - PF_6]^+$).

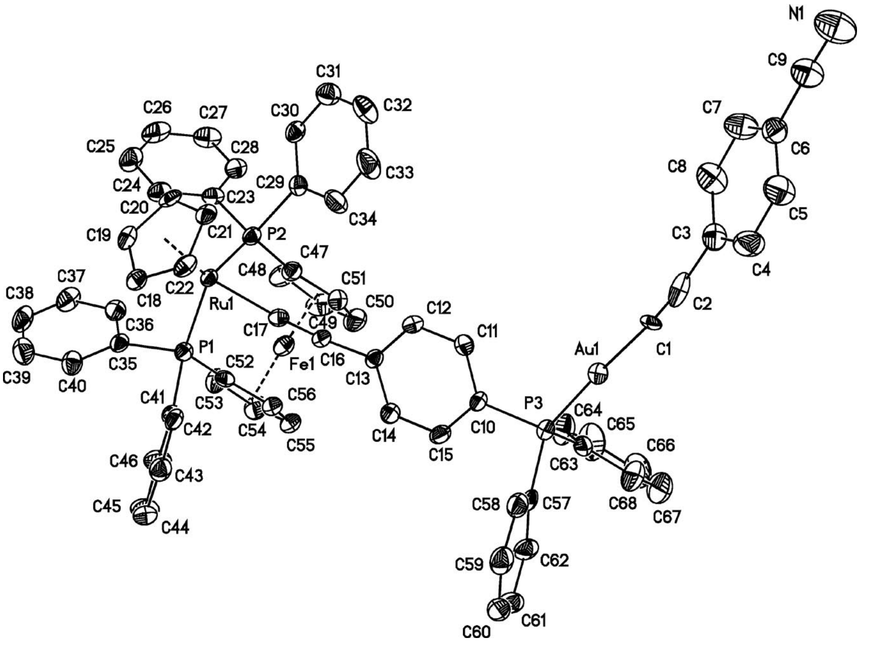

Figure 3. The molecular structure (ORTEP, 50% probability level) of one of the two crystallographically independent molecules of **11b** with atomic numbering scheme; hydrogen atoms and the solvent molecule acetone are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Ru1–C17 2.017(4), C16–C17 1.215(5), Ru1–P1 2.2676(10), Ru1–P2 2.2915(10), Ru1–D3 1.888(2), Fe1–D1 1.639(2), Fe1–D2 1.646(2), P3–Au1 2.2767(10), Au1–C1 2.088(5), C1–C2 1.066(5), C9–N1 1.139(5); P1–Ru1–P2 97.86(4), Ru1–C17–C16 173.2(3), C13–C16–C17 175.3(4), P3–Au1–C1 177.16(12), C1–C2–C3 173.7(5), C6–C9–N1 178.4(5) (D1 = centroid of C47–C51, D2 = centroid of C52–C56, D3 = centroid of C18–C22).

In general, the chelating dppf unit in **9**, **11b**, and **11c** (Figures 3, 4, and 5) exists, as typical for other mono- and polynuclear dppf-containing complexes, in the synperiplanar eclipsed conformation with τ = 2.0 (**9**), 0.5 (**11c**), or 1.2/6.1° (**11b**).[15g,15h] Other intramolecular interactions usually observed for this building block have not been observed in **9**, **11b**, and **11c**.[15g,15h]

Single crystals of the tricarbonyl(diimine)rhenium(I) complex **12a** suitable for X-ray structure analysis were obtained by diffusion of *n*-pentane into a chloroform solution containing **12a**. Compound **12a** crystallizes in the monoclinic space group $P2_1/c$ with one molecule of chloroform. Figure 5 depicts the perspective drawing of **12a** with the atomic numbering scheme and selected bond lengths and angles. The Re1 atom shows a slightly distorted octahedral geometry with three carbonyl ligands in a facial fashion. The N1–Re1–N2 angle is less than 90°, as required by the bite distance exerted by the steric demand of the chelating bipyridyl ligand. The Re1–Cl1 separation is found to be 2.4770(11) Å, which is characteristic for this type of molecule.

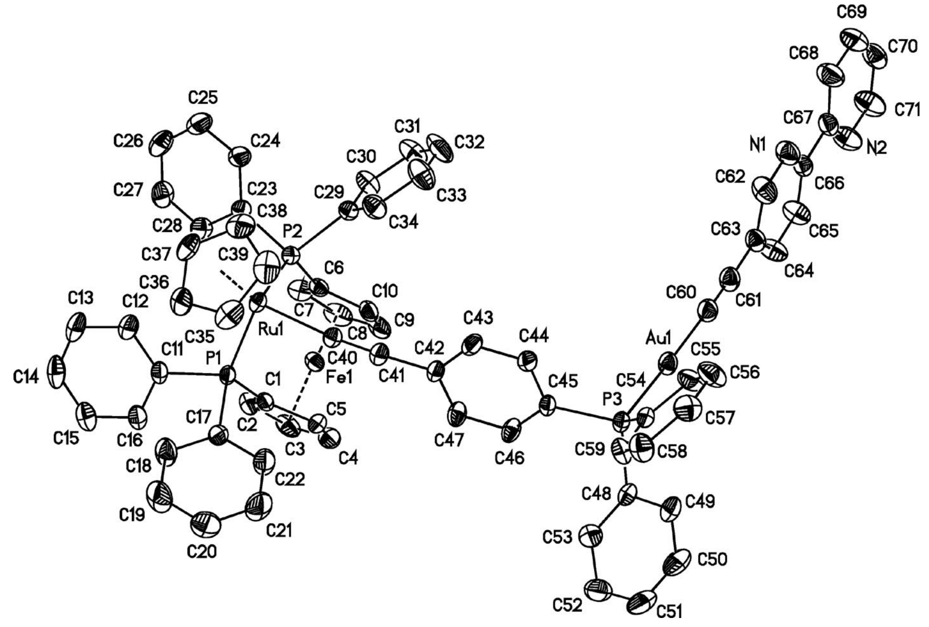

Figure 4. ORTEP diagram of **11c** (30% probability level) with atomic numbering scheme; hydrogen atoms and the disordered *n*-pentane molecule are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Ru1–C40 1.998(3), C40–C41 1.208(4), Ru1–P1 2.2727(9), Ru1–P2 2.2691(8), Ru1–D3 1.884(1), Fe1–D1 1.633(2), Fe1–D2 1.641(2), P3–Au1 2.2771(8), Au1–C60 2.025(4), C60–C61 1.158(5); P1–Ru1–P2 97.58(3), Ru1–C40–C41 171.0(9), C40–C41–C42 176.9(3), P3–Au1–C60 176.33(11), Au1–C60–C61 176.4(4), C60–C61–C63 178.4(4) (D1 = centroid of C1–C5, D2 = centroid of C6–C10, D3 = centroid of C35–C39).

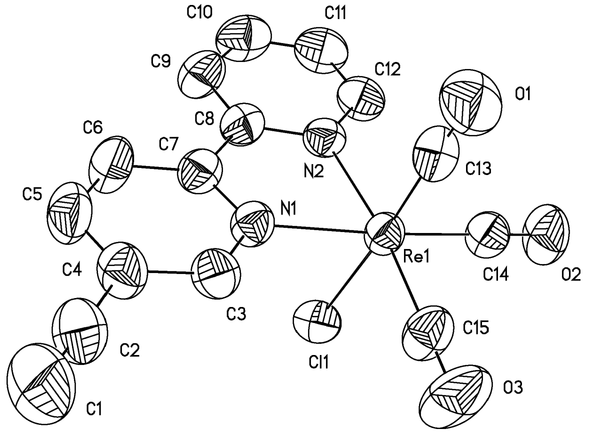

Figure 5. ORTEP diagram of **12a** with 50% probability level of ellipsoids and atomic numbering scheme; hydrogen atoms and one chloroform molecule are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Re1–N1 2.171(3), Re1–N2 2.160(3), Re1–Cl1 2.4770(11), Re1–C13 1.904(5), Re1–C14 1.911(4), Re1–C15 1.914(4), C1–C2 1.154(7); N1–Re1–N2 74.73(11), C14–Re1–C15 87.64(18), C13–Re1–Cl1 176.59(13), C1–C2–C4 179.0(6).

Electrochemistry

The electrochemical responses of complexes **3**, **9**, **11c**, **12**, **13**, **15**, **17**, and **18** were examined by cyclic voltammetry. Their electrochemical data are summarized in Table 1. All complexes containing the (η^2-dppf)(η^5-C_5H_5)Ru acetylide building block show irreversible [Ru^{II}]/[Ru^{III}] oxidations. The reversible [Fe^{II}]/[Fe^{III}] oxidation of the appendant dppf ligand is found at ca. 0.52 V. In addition, the appropriate organometallic fragment gives rise to two further oxidations that may originate from oxidations at the ruthenium atom, which can be verified by comparison with other complexes containing $(PPh_3)_2$(η^5-C_5H_5)Ru or (η^2-dppf)(η^5-C_5H_5)Ru termini.[17] However, both processes could not be detected for all of the investigated complexes. The iron potentials are not notably affected by the coordination of the pendant phosphorus atom to an AuCl (**9**) or AuC≡Cbpy (**11c**) moiety (Table 1). In contrast, the potentials [Ru^{II}/Ru^{III}] differ in the range 0.04–0.17 V, whereby coordination of the Ph_2P group to a gold(I) fragment induces a shift to higher values (**3**: $E_{p,ox}$ = 0.04 V; **9**, **11c**, **12a**, **13**, **15**, **17a**, **17b**, **18**: 0.12–0.17 V) (Table 1). This indicates that from the phosphorus atom electron density is transferred to Au^I, and, hence, the oxidation of Ru^{II} is more difficult. [Au^I]/[Au^0] reductions could not be observed in dichloromethane solution.

The cyclic voltammogram of the mononuclear complex [(HC≡C-bpy)Re(CO)$_3$Cl] (**12a**) displays next to the irreversible one-electron oxidation of the rhenium(I) building block at $E_{p,ox}$ = 1.04 V two reduction waves, which can be assigned to bipyridyl-centered processes and can be explained by the unsymmetrical substitution pattern, because this behavior was also observed for the free 5-ethynyl-2,2′-bipyridyl molecule as well as other bpy-containing species.[18] The introduction of a gold(I) entity at the alkynyl unit, as given in tetranuclear **13**, leads to a facilitation of the [Re^I]/[Re^{II}] oxidation (**12a**: $E_{p,ox}$ = 1.04 V; **13**: $E_{p,ox}$ = 0.95 V). Additionally, the bpy-centered reduction of this complex is shifted to more negative values so that in the electrochemical window only one reduction wave could be observed for **13**.

The same observation was found by comparison of (HC≡C-bpy)Mo(CO)$_4$ (**12b**) with **15**. Whereas for **12b** an oxidation peak could be detected at $E_{p,ox}$ = 0.26 V, which

Table 1. Electrochemical data for selected complexes.[a]

Compd.	Reduction			Oxidation			
	[bpy]/[bpy$^{\cdot-}$] E_0 (ΔE_p)	[M^I]/[M^0] $E_{p,red}$/E_0 (ΔE_p)	[Ti^{IV}]/[Ti^{III}] E_0 (ΔE_p)	[Ru^{II}]/[Ru^{III}] $E_{p,ox}$	[Fe^{II}]/[Fe^{III}] E_0 (ΔE_p)	[M^n]/[M^{n+1}] $E_{p,ox}$/E_0 (ΔE_p)	$E_{p,ox}$[g]
3	–	–	–	0.04	0.52 (0.12)	–	0.47
9	–	–	–	0.15	0.52 (0.15)	–	0.45 0.80
11c		–	–	0.14	0.49 (0.18)	–	0.85
12a	–1.66 (0.13) –1.99 (0.16)	–	–	–	–	1.04[e]	–
12b	–1.88 (0.12)	–	–	–	–	0.26 (0.13)[f]	1.38[h]
13	–1.81 (0.12)	–	–	0.14	0.53 (0.18)	0.95[e]	0.47 0.79
15	–2.03 (0.18)	–	–	0.12	0.52 (0.13)	0.21[f]	1.39[h]
17a		–1.50 (0.10)[b]	–1.62 (0.09) –1.83 (0.15)[d]	0.14	0.48 (0.13)	–	0.85
17b		–1.36[c]	[i]	0.17	0.54 (0.14)	–	0.43 0.81
18		–1.42[b]	[i]	0.16	0.54 (0.15)	–	0.46 0.82

[a] CVs from 10^{-3} M solutions in dichloromethane at 25 °C with [nBu$_4$N]PF$_6$ (0.1 M) as the supporting electrolyte, scan rate = 0.10 V s^{-1}. All potentials are given in V and are referenced to the FcH/FcH$^+$ redox couple [FcH = (η^5-C$_5$H$_5$)$_2$Fe] with E_0 = 0.00 V (ΔE_p = 0.10 V);[20,21] $\Delta E_p = E_{p,ox} - E_{p,red}$. [b] M = Cu. [c] M = Ag. [d] From [Ti](C≡CSiMe$_3$)$_2$. [e] M^n = Re^I. [f] M^n = Mo^0. [g] Irreversible or quasi-reversible processes that may result from the oxidation of the ruthenium atom.[17] [h] Irreversible oxidation at the molybdenum atom. [i] Not observed.

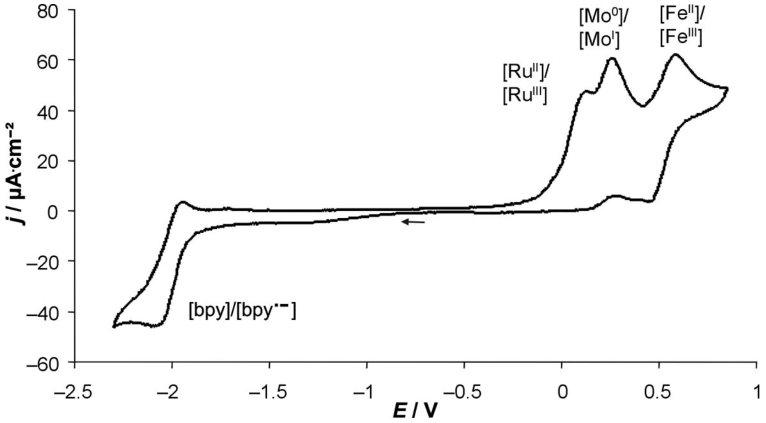

Figure 6. Cyclic voltammogram of **15**; 10^{-3} M solution in dichloromethane at 25 °C with (nBu$_4$N)PF$_6$ (0.1 M) as the supporting electrolyte, scan rate = 0.10 V s^{-1}; all potentials are referenced to the FcH/FcH$^+$ redox couple [FcH = (η^5-C$_5$H$_5$)$_2$Fe] with E_0 = 0.00 V (ΔE_p = 0.10 V).[20,21]

can be referred to a molybdenum-centered one-electron oxidation,[19] this process reveals a slight cathodic shift in **15** (Table 1, Figure 6). For the reduction of the 2,2′-bipyridyl ligand only one reduction process at –1.88 V is observed, whereby this process is cathodically shifted by 0.15 V upon σ-bonding of the alkynyl entity to the gold atom as given in **15**.

The coordination of the bipyridyl ligand in **11c** to a bis(alkynyl)titanocene–copper(I) or –silver(I) fragment as given in complexes **17a** and **17b** does not influence the redox potentials of ruthenium(II) and iron(II). The characteristic [bpy]/[bpy$^{\cdot-}$] reduction could not be detected for these complexes, because this process takes place at more negative potentials.[18] The organometallic π-tweezer part in **17a** gives rise to two reductions. The chelate coordination of the bipyridyl ligand to copper(I) causes a reduction of Cu^I followed by a partial reoxidation, obviously without any structural change of the molecule involved.[22] In addition, the cathodic range displays two reductions resulting from the [Ti^{IV}]/[Ti^{III}] redox couple of intact **17a** and the free tweezer molecule [Ti](C≡CSiMe$_3$)$_2$.[23] In contrast, the reduction of Ag^I to Ag^0 in **17b** is unequivocally irreversible. A similar behavior is found for other Ti–Cu(Ag) π-tweezer complexes, i.e. [FcPPh$_2$Au-C≡C-bpy({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M)]X (M = Cu, X = PF$_6$; M = Ag, X = ClO$_4$).[23] The expected [Ti^{IV}]/[Ti^{III}] reduction wave of [Ti](C≡CSiMe$_3$)$_2$ could, however, not be observed. The electrochemical behavior of pentametallic **18**, in which a monodentate-bonded pyridyl unit is present at the copper(I) atom, is similar to that of **17b**. At $E_{p,red}$ = –1.42 V a reduction current peak is observed that can be assigned to an irreversible [Cu^I]/[Cu^0] process.[18]

Conclusions

A series of heteromultimetallic complexes of type [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2] [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene], [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-{Rh}] [{Rh} = (cod)RhCl, (η^5-C_5Me_5)-$RhCl_2$], [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-AuCl] and [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡CR] {R = C_5H_4N-4, C_6H_4-4-C≡N, 2,2′-bipyridyl-5-yl (= bpy), bpy[Re(CO)$_3$Cl], bpy[Mo(CO)$_4$], bpy([{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M]X) (M = Cu, X = PF_6; M = Ag, X = ClO_4), C_5H_4N([{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu])OTf} have been synthesized in a straightforward manner. In these molecules two, three, four, or even five different transition-metal atoms, such as titanium, molybdenum, rhenium, iron, ruthenium, rhodium, copper, and gold are connected by carbon-rich bridging units based on alkynyl groups. Complex [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡C-bpy({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu)]PF_6 is an example of a transition-metal system containing five different metal atoms linked by carbon-rich organic units such as cyclopentadienyl, diphenylphosphane, alkynyl, benzene, and bipyridyl, respectively.

Selected complexes have been subjected to cyclovoltammetric studies showing that there is no significant interaction between the corresponding metal atoms along the organic backbone.

Experimental Section

General Comments: All reactions were carried out under nitrogen by using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, benzene, and *n*-hexane were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride. Methanol was purified by distillation from magnesium and diethylamine by distillation from KOH. Celite (purified and annealed, Erg. B.6, Riedel–de Haën) was used for filtrations.

Instruments: Infrared spectra were recorded with a Perkin–Elmer FT-IR spectrometer Spectrum 1000. ^{1}H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; ^{13}C{^{1}H} NMR spectra were recorded at 62.860 MHz. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane with the solvent as reference signal [^{1}H NMR: $CDCl_3$, δ = 7.26; ^{13}C{^{1}H} NMR: $CDCl_3$, δ = 77.16 ppm].[24] ^{31}P{^{1}H} NMR spectra were recorded at 101.255 MHz in $CDCl_3$ with P(OMe)$_3$ as the external standard [δ = 139.0 ppm, rel. to H_3PO_4 (85%) with δ = 0.00 ppm]. ESI-TOF mass spectra were recorded with a Mariner biospectrometry workstation 4.0 (Applied Biosystems). Cyclic voltammograms were recorded in a dried cell purged with purified argon. Platinum wires served as the working electrode and the counter electrode. A saturated calomel electrode in a separate compartment served as the reference electrode. For ease of comparison, all electrode potentials are converted by using the redox potential of the ferrocene/ferrocenium couple FcH/FcH$^+$ [FcH = (η^5-C_5H_5)$_2$Fe, E_0 = 0.00 V] as reference.[20,21] Electrolyte solutions were prepared from tetrahydrofuran or dichloromethane and (nBu$_4$N)PF_6 (Fluka, dried in an oil-pump vacuum). The appropriate organometallic complexes were added at c = 1.0 mM. Cyclic voltammograms were recorded with a Voltalab 3.1 potentiostat (Radiometer) equipped with a digital electrochemical analyzer DEA 101 and an electrochemical interface IMT 102. Microanalyses were performed partly by the Institute of Organic Chemistry, Chemnitz Technical University, Chemnitz, Germany.

Starting Materials: [(dppf)(η^5-C_5H_5)RuCl],[25] 1-(diphenylphosphanyl)-4-ethynylbenzene,[5] 5-ethynyl-2,2′-bipyridine,[12,26] 4-ethynylpyridine,[27] 4-ethynylbenzonitrile,[28] [(tht)AuCl],[29] [(cod)-RhCl]$_2$,[30] [(η^5-C_5Me_5)RhCl$_2$]$_2$,[31] [Re(CO)$_5$Cl],[32] [(nbd)Mo-(CO)$_4$],[33] [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF_6,[34] [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu]OTf,[34] and [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Ag]-OClO$_3$[35] were prepared according to published procedures. All other chemicals were purchased by commercial suppliers and were used without further purification.

[(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2] (3): Complex [(η^2-dppf)(η^5-C_5H_5)RuCl] (**1**) (200 mg, 0.265 mmol) was heated to reflux in methanol for 20 min to give a yellow-orange suspension to which HC≡C-C_6H_4-4-PPh_2 (**2**) (90 mg, 0.314 mmol) was added. The reaction mixture was heated to reflux for 20 min. During that time the mixture became a clear orange-red solution. The solution was cooled to room temperature, and addition of 2 equiv. of sodium resulted in rapid precipitation of a yellow solid. Stirring was continued for 1 h, and then all the volatiles were removed under reduced pressure. The residue was filtered through a pad of Celite by using dichloromethane as solvent. The solvent was removed, and the crude material was purified by column chromatography on silica gel by using petroleum ether/diethyl ether (3:1) as eluent. Yield: 215 mg (0.214 mmol, 80%). $C_{59}H_{47}FeP_3Ru$ (1005.86): calcd. C 70.45, H 4.71; found C 70.45, H 5.08. IR (KBr): $\tilde{\nu}$ = 2068 (m, $\nu_{C\equiv CRu}$) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.99 (dpt, J_{HP} = 1.2, J_{HH} = 2.4 Hz, 2 H, C_5H_4), 4.17 (br. s, 2 H, C_5H_4), 4.30 (br. s, 2 H, C_5H_4), 4.31 (s, 5 H, C_5H_5), 5.30 (br. s, 2 H, C_5H_4), 7.15–7.42 (m, 26 H, C_6H_5), 7.49–7.58 (m, 4 H, C_6H_4), 7.82–7.93 (m, 4 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 68.0 (pt, J_{CP} = 2.4 Hz, CH/C_5H_4), 71.5 (pt, J_{CP} = 2.9 Hz, CH/C_5H_4), 73.2 (CH/C_5H_4), 76.6 (pt, J_{CP} = 5.0 Hz, CH/C_5H_4), 84.8 (t, J_{CP} = 1.9 Hz, C_5H_5), 88.7 (pt, J_{CP} = 25 Hz, C_i/C_5H_4), 112.8 (RuC≡C), 121.3 (t, J_{CP} = 26 Hz, RuC≡C), 127.2 [pt, J_{CP} = 4.8 Hz, CH/C_6H_5 (dppf)], 127.4 [pt, J_{CP} = 4.8 Hz, CH/C_6H_5 (dppf)], 128.4 (d, J_{CP} = 6.5 Hz, CH/C_6H_5), 128.5 (CH/C_6H_5), 128.7 [CH/C_6H_5 (dppf)], 129.2 [CH/C_6H_5 (dppf)], 130.1 (d, J_{CP} = 8.2 Hz, C_i/C_6H_4), 130.9 (d, J_{CP} = 8.1 Hz, CH/C_6H_4), 131.2 (C_i/C_6H_4), 133.8 (d, J_{CP} = 19 Hz, CH/C_6H_5), 133.9 [pt, J_{CP} = 5.8 Hz, CH/C_6H_5 (dppf)], 134.3 [pt, J_{CP} = 5.8 Hz, CH/C_6H_5 (dppf)], 138.2 (d, J_{CP} = 11 Hz, C_i/C_6H_5), 140.9 [pt, J_{CP} = 22 Hz, C_i/C_6H_5 (dppf)], 142.1 [dd, J_{CP} = 23 Hz, C_i/C_6H_5 (dppf)] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –6.7 (PPh_2), 53.9 (dppf) ppm.

[(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-{Rh(cod)Cl}] (5): To [Rh(cod)Cl]$_2$ (32 mg, 0.065 mmol) (**4**) dissolved in toluene (20 mL) was added [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2] (**3**) (135 mg, 0.134 mmol) in a single portion. The resulting yellow reaction solution was stirred at 50 °C for 2 h. After cooling to room temperature, the solution was reduced in volume to 5 mL. The product was precipitated by addition of *n*-hexane (20 mL), washed twice with *n*-hexane (10-mL portions), and dried in an oil-pump vacuum. Yield: 110 mg (0.088 mmol, 83% based on **4**). $C_{67}H_{59}ClFeP_3RhRu$ (1252.40): calcd. C 64.26, H 4.75; found C 64.26, H 4.85. IR (KBr): $\tilde{\nu}$ = 2062 (s, $\nu_{C\equiv CRu}$) cm–1. ^{1}H NMR ($CDCl_3$): δ = 1.85–2.11 (m, 4 H, CH_2), 2.34–2.45 (m, 4 H, CH_2), 3.17 (br. s, 2 H, CH), 3.98 (dpt, J_{HP} = 1.1, J_{HH} = 2.4 Hz, 2 H, C_5H_4), 4.20 (br. s, 2 H, C_5H_4), 4.30 [br. s, 5 H, (C_5H_5), 2 H (C_5H_4)], 5.26 (br. s, 2 H, C_5H_4), 5.57 (br. s, 2 H, CH), 7.20–7.86 (m, 34 H, C_6H_5, C_6H_4) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 29.0 (d, J_{PRh} = 149 Hz, RhPPh$_2$), 54.0 (dppf) ppm.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-{Rh(η^5-C$_5$Me$_5$)Cl$_2$}] (7): [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$] (**3**) (110 mg, 0.109 mmol) was dissolved in dichloromethane (10 mL) and was then added dropwise to [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ (**6**) (34 mg, 0.055 mmol) dissolved in dichloromethane (10 mL). The resulting red solution was stirred at 25 °C for 1 h. Afterwards, the solution was reduced in volume (3 mL), and the title compound was precipitated by addition of *n*-hexane (20 mL). Removal of the supernatant solution, washing with *n*-hexane, and drying in an oil-pump vacuum afforded **7** as an orange-red microcrystalline solid. Yield: 130 mg (0.099 mmol, 90%). C$_{69}$H$_{62}$Cl$_2$FeP$_3$RhRu (1314.90): calcd. C 63.03, H 4.75; found C 62.75, H 4.98. IR (KBr): ṽ = 2062 (s, $\nu_{C\equiv CRu}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.38 (d, J_{HRh} = 3.5 Hz, 15 H, C$_5$*Me*$_5$), 3.98 (dpt, J_{HP} = 1.1, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 4.16 (br. s, 2 H, C$_5$*H*$_4$), 4.30 (br. s, 2 H, C$_5$*H*$_4$), 4.31 (s, 5 H, C$_5$*H*$_5$), 5.22 (br. s, 2 H, C$_5$*H*$_4$), 7.14–7.65 (m, 26 H, C$_6$*H*$_5$), 7.78–7.93 [m, 4 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$)] ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 28.7 (d, J_{PRh} = 143 Hz, Rh*P*Ph$_2$), 54.0 (dppf) ppm.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-AuCl] (9): A solution of [(tht)AuCl] (**8**) (64 mg, 0.2 mmol) in tetrahydrofuran (10 mL) was slowly added to a cooled (0 °C) solution of [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$] (**3**) (200 mg, 0.2 mmol) in tetrahydrofuran (20 mL). The resulting reaction mixture was stirred at 0 °C for 20 min and then at room temperature for 45 min. The solvent was removed in an oil-pump vacuum, and the residue was purified by column chromatography on silica gel by using dichloromethane as eluent. The product was obtained as a yellow solid. Yield: 220 mg (0.18 mmol, 89%). C$_{59}$H$_{47}$AuClFeP$_3$Ru (1238.28): calcd. C 57.23, H 3.83; found C 57.00, H 4.23. IR (KBr): ṽ = 2065 (m, $\nu_{C\equiv CRu}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.00 (dpt, J_{HP} = 1.2, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 4.19 (br. s, 2 H, C$_5$*H*$_4$), 4.31 (s, 5 H, C$_5$*H*$_5$), 4.32 (br. s, 2 H, C$_5$*H*$_4$), 5.17 (br. s, 2 H, C$_5$*H*$_4$), 7.17–7.59 [m, 26 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$)], 7.77–7.87 (m, 4 H, C$_6$*H*$_5$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 31.4 (Au*P*Ph$_2$), 53.9 (dppf) ppm.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-C$_5$H$_4$N-4] (11a): Complex [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-AuCl] (**9**) (150 mg, 0.121 mmol) was dissolved in dichloromethane (15 mL) and diethylamine (15 mL). To this solution 4-ethynylpyridine (20 mg, 0.194 mmol) and [CuI] (1 mg) were added. After 5 h of stirring at 25 °C, all volatiles were removed in an oil-pump vacuum. The residue was purified by column chromatography on silica gel by using first diethyl ether and then dichloromethane to isolate a yellow band that contained the product. After evaporation of all volatile materials, the title compound **11a** was obtained as a yellow solid. Yield: 120 mg (0.092 mmol, 76%). C$_{66}$H$_{51}$AuFeNP$_3$Ru (1304.94): calcd. C 60.75, H 3.94, N 1.07; found C 60.73, H 4.17, N 0.92. IR (KBr): ṽ = 2062 (s, $\nu_{C\equiv CRu}$), 2120 (w, $\nu_{C\equiv CAu}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.00 (dpt, J_{HP} = 1.2, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 4.19 (br. s, 2 H, C$_5$*H*$_4$), 4.32 (s, 5 H, C$_5$*H*$_5$), 4.33 (br. s, 2 H, C$_5$*H*$_4$), 5.19 (br. s, 2 H, C$_5$*H*$_4$), 7.19–7.61 [m, 26 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$), 2 H (C$_5$*H*$_4$N)], 7.78–7.88 (m, 4 H, C$_6$*H*$_5$), 8.46–8.50 (m, 2 H, C$_5$*H*$_4$N) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 68.2 (pt, J_{CP} = 2.4 Hz, *CH*/C$_5$H$_4$), 71.4 (pt, J_{CP} = 2.4 Hz, *CH*/C$_5$H$_4$), 73.3 (*CH*/C$_5$H$_4$), 76.3 (pt, J_{CP} = 5.3 Hz, *CH*/C$_5$H$_4$), 84.9 (t, J_{CP} = 2.4 Hz, C$_5$H$_5$), 88.5 (pt, J_{CP} = 24 Hz, *C$_i$*/C$_5$H$_4$), 101.5 (d, J_{CP} = 26.5 Hz, AuC≡C), 113.1 (d, J_{CP} = 1.4 Hz, RuC≡*C*), 120.8 (AuC≡C), 121.8 (Ru*C*≡C), 126.7 (*CH*/C$_5$H$_4$N), 127.2 [pt, J_{CP} = 4.8 Hz, *CH*/C$_6$H$_5$ (dppf)], 127.4 [pt, J_{CP} = 4.8 Hz, *CH*/C$_6$H$_5$ (dppf)], 128.4 [*CH*/C$_6$H$_5$ (dppf)], 129.2 (d, J_{CP} = 11.3 Hz, *CH*/C$_6$H$_5$), 129.3 [*CH*/C$_6$H$_5$ (dppf)], 130.5 (d, J_{CP} = 56.5 Hz, *C$_i$*/C$_6$H$_5$), 131.3 (d, J_{CP} = 13 Hz, *CH*/C$_6$H$_4$), 131.4 (*CH*/C$_6$H$_5$), 133.4 (d, J_{CP} = 2 Hz, *C$_i$*/C$_5$H$_4$N), 133.9 [pt, J_{CP} = 5.2 Hz, *CH*/C$_6$H$_5$ (dppf)], 134.1 [pt, J_{CP} = 5.2 Hz, *CH*/C$_6$H$_5$ (dppf)], 134.3 (d, J_{CP} = 13.6 Hz, *CH*/C$_6$H$_5$), 140.7 [pt, J_{CP} = 21 Hz, *C$_i$*/C$_6$H$_5$ (dppf)], 141.8 [pt, J_{CP} = 22 Hz, *C$_i$*/C$_6$H$_5$ (dppf)], 149.5 (*CH*/C$_5$H$_4$N) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.2 (Au*P*Ph$_2$), 53.9 (dppf) ppm.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-C$_6$H$_4$-C≡N] (11b): Complex **11b** was prepared according to the procedure described for **11a**. Experimental details: [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-AuCl] (**9**) (150 mg, 0.121 mmol), 4-ethynylbenzonitrile (20 mg, 0.157 mmol), [CuI] (1 mg). Yield: 130 mg (0.098 mmol, 81%). C$_{68}$H$_{51}$AuFeNP$_3$Ru (1328.96): calcd. C 61.46, H 3.87, N 1.05; found C 61.57, H 4.23, N 1.01. IR (KBr): ṽ = 2061 (s, $\nu_{C\equiv CRu}$), 2115 (w, $\nu_{C\equiv CAu}$), 2224 (w, $\nu_{C\equiv N}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.00 (dpt, J_{HP} = 1.2, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 4.19 (br. s, 2 H, C$_5$*H*$_4$), 4.32 (s, 5 H, C$_5$*H*$_5$), 4.33 (br. s, 2 H, C$_5$*H*$_4$), 5.19 (br. s, 2 H, C$_5$*H*$_4$), 7.20–7.61 [m, 26 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$), 4 H (C$_6$*H*$_4$CN)], 7.79–7.89 (m, 4 H, C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 68.3 (pt, J_{CP} = 2.4 Hz, *CH*/C$_5$H$_4$), 71.4 (pt, J_{CP} = 2.4 Hz, *CH*/C$_5$H$_4$), 73.3 (*CH*/C$_5$H$_4$), 76.3 (pt, J_{CP} = 5.3 Hz, *CH*/C$_5$H$_4$), 84.9 (t, J_{CP} = 2.4 Hz, C$_5$H$_5$), 88.5 (pt, J_{CP} = 25 Hz, *C$_i$*/C$_5$H$_4$), 101.5 (d, J_{CP} = 26.5 Hz, AuC≡C), 109.7 (*C$_i$*/C$_6$H$_4$CN), 113.1 (d, J_{CP} = 1.9 Hz, RuC≡*C*), 119.2 (*C*≡N), 120.8 (AuC≡C), 121.8 (Ru*C*≡C), 127.2 [pt, J_{CP} = 4.8 Hz, *CH*/C$_6$H$_5$ (dppf)], 127.4 [pt, J_{CP} = 4.8 Hz, *CH*/C$_6$H$_5$ (dppf)], 128.8 [*CH*/C$_6$H$_5$ (dppf)], 129.2 (d, J_{CP} = 11.3 Hz, *CH*/C$_6$H$_5$), 129.3 [*CH*/C$_6$H$_5$ (dppf)], 130.4 (d, J_{CP} = 2.8 Hz, *C$_i$*/C$_6$H$_4$CN), 130.5 (d, J_{CP} = 56.0 Hz, *C$_i$*/C$_6$H$_5$), 131.3 (d, J_{CP} = 13 Hz, *CH*/C$_6$H$_4$), 131.4 (*CH*/C$_6$H$_5$), 131.9 (*CH*/C$_6$H$_4$CN), 132.9 (*CH*/C$_6$H$_4$CN), 134.0 [pt, J_{CP} = 5.2 Hz, *CH*/C$_6$H$_5$ (dppf)], 134.1 [pt, J_{CP} = 5.2 Hz, *CH*/C$_6$H$_5$ (dppf)], 134.3 (d, J_{CP} = 13.6 Hz, *CH*/C$_6$H$_5$), 140.7 [pt, J_{CP} = 21 Hz, *C$_i$*/C$_6$H$_5$ (dppf)], 141.8 [pt, J_{CP} = 22 Hz, *C$_i$*/C$_6$H$_5$ (dppf)] ppm. ^{31}P{^{1}H} NMR (: CDCl$_3$): δ = 40.3 (PPh$_2$Au), 53.9 (dppf) ppm.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-bpy] (11c): Complex **11c** was prepared according to the procedure described for **11a**. Experimental details: [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-AuCl] (**9**) (150 mg, 0.121 mmol), 5-ethynyl-2,2′-bipyridine (30 mg, 0.167 mmol), [CuI] (1 mg). Yield: 130 mg (0.094 mmol, 78%). C$_{71}$H$_{54}$AuFeN$_2$P$_3$Ru (1382.03): calcd. C 61.70, H 3.94, N 2.03; found C 61.58, H 4.21, N 1.93. IR (KBr): ṽ = 2062 (s, $\nu_{C\equiv CRu}$), 2116 (w, $\nu_{C\equiv CAu}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.00 (dpt, J_{HP} = 1.2, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 4.20 (br. s, 2 H, C$_5$*H*$_4$), 4.32 [br. s, 5 H (C$_5$*H*$_5$), 2 H (C$_5$*H*$_4$)], 5.19 (br. s, 2 H, C$_5$*H*$_4$), 7.18–7.62 [m, 26 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$), 1 H (*H5′*/bpy)], 7.75–7.87 [m, 4 H (C$_6$*H*$_5$), 1 H (*H4′*/bpy)], 7.91 (dd, $^3J_{H4H3}$ = 8.2, $^4J_{H4H6}$ = 2 Hz, 1 H, *H4*/bpy), 8.30 (dd, $^3J_{H3H4}$ = 8.2, $^5J_{H3H6}$ = 0.8 Hz, 1 H, *H3*/bpy), 8.37 (ddd, $^3J_{H3'H4'}$ = 8, $^4J_{H3'H5'}$ = 1, $^5J_{H3'H6'}$ = 1 Hz, 1 H, *H3′*/bpy), 8.66 (ddd, $^3J_{H6'H5'}$ = 4.8, $^4J_{H6'H4'}$ = 1.8, $^5J_{H6'H3'}$ = 1 Hz, 1 H, *H6′*/bpy), 8.82 (dd, $^4J_{H6H4}$ = 2, $^5J_{H6H3}$ = 0.8 Hz, 1 H, *H6*/bpy) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 68.2 (pt, J_{CP} = 2.8 Hz, *CH*/C$_5$H$_4$), 71.4 (pt, J_{CP} = 2.8 Hz, *CH*/C$_5$H$_4$), 73.3 (pt, J_{CP} = 1.9 Hz, *CH*/C$_5$H$_4$), 76.3 (pt, J_{CP} = 5 Hz, *CH*/C$_5$H$_4$), 84.9 (t, J_{CP} = 1.9 Hz, C$_5$H$_5$), 88.5 (pt, J_{CP} = 24 Hz, *C$_i$*/C$_5$H$_4$), 101.0 (d, J_{CP} = 27 Hz, AuC≡C), 113.1 (d, J_{CP} = 1.5 Hz, RuC≡*C*), 120.2 (*C3*/bpy), 120.9 (AuC≡C), 121.2 (*C3′*/bpy), 121.8 (Ru*C*≡C), 122.3 (d, J_{CP} = 2.8 Hz, *C5*/bpy), 123.5 (*C5′*/bpy), 127.2 [pt, J_{CP} = 4.8 Hz, *CH*/C$_6$H$_5$ (dppf)], 127.4 [pt, J_{CP} = 4.8 Hz, *CH*/C$_6$H$_5$ (dppf)], 128.8 [*CH*/C$_6$H$_5$ (dppf)], 128.9 (d, J_{CP} = 11.3 Hz, *CH*/C$_6$H$_5$), 129.3 [*CH*/C$_6$H$_5$ (dppf)], 130.6 (d, J_{CP} = 56.2 Hz, *C$_i$*/C$_6$H$_5$), 131.3 (d, J_{CP} = 14 Hz, *CH*/C$_6$H$_4$), 131.4 (*CH*/C$_6$H$_5$), 134.0 [pt, J_{CP} = 5.3 Hz, *CH*/C$_6$H$_5$ (dppf)], 134.1 [pt, J_{CP} = 5.3 Hz, *CH*/C$_6$H$_5$ (dppf)], 134.3 (d, J_{CP} = 14 Hz, *CH*/C$_6$H$_5$), 136.9 (*C4′*/bpy), 140.1 (*C4*/bpy), 140.7 [pt, J_{CP} = 21 Hz, *C$_i$*/C$_6$H$_5$ (dppf)], 141.8 [pt, J_{CP} = 23 Hz, *C$_i$*/C$_6$H$_5$ (dppf)], 149.3 (*C6′*/bpy), 152.7 (*C6*/bpy), 153.3 (*C2*/bpy), 156.1 (*C2′*/bpy) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.3 (Au*P*Ph$_2$), 53.9 (dppf) ppm.

[(HC≡C-bpy)(CO)$_3$ReCl] (12a): To [Re(CO)$_5$Cl] (300 mg, 0.83 mmol) dissolved in benzene (80 mL) was added 5-ethynyl-2,2′-bipyridine (180 mg, 1 mmol) at 60 °C. The resulting yellow solution was stirred at this temperature for 8 h and afterwards concentrated to dryness. The residue was redissolved in dichloromethane (5 mL). The title complex **12a** was precipitated by addition of *n*-hexane (30 mL), washed twice with diethyl ether (15-mL portions), and was then dried in an oil-pump vacuum to give an orange solid. Yield: 375 mg (0.77 mmol, 93%). $C_{15}H_8ClN_2O_3Re$ (485.90): calcd. C 37.08, H 1.66, N 5.77; found C 37.43, H 1.63, N 5.73. IR (KBr): $\tilde{\nu}$ = 1895, 1919, 2020 (s, ν_{CO}), 2105 (w, $\nu_{C\equiv C}$), 3184 (m, $\nu_{\equiv C-H}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 3.53 (s, 1 H, ≡C*H*), 7.57 (ddd, $^3J_{H5'H4'}$ = 7.8, $^3J_{H5'H6'}$ = 4.8, $^4J_{H5'H3'}$ = 1 Hz, 1 H, *H5′*/bpy), 8.05–8.20 (m, 4 H, *H3*,*H3′*,*H4*,*H4′*/bpy), 9.08 (ddd, $^3J_{H6'H5'}$ = 4.8, $^4J_{H6'H4'}$ = 1.8, $^5J_{H6'H3'}$ = 1 Hz, 1 H, *H6′*/bpy), 9.12 (dd, $^4J_{H6H4}$ = 2.4, $^5J_{H6H3}$ = 0.6 Hz, 1 H, *H6*/bpy) ppm.

[(HC≡C-bpy)Mo(CO)$_4$] (12b): A solid sample of 5-ethynyl-2,2′-bipyridine (50 mg, 0.278 mmol) was added to a solution of [(nbd)-Mo(CO)$_4$] (70 mg, 0.233 mmol) in dichloromethane/tetrahydrofuran (5:1) (20 mL). The reaction solution was stirred at 25 °C for 15 h, whereby the solution changed from yellow to deep red. Afterwards, the solution was reduced in volume to ca. 3 mL, and addition of *n*-hexane (20 mL) caused the precipitation of complex **12b**. After removal of the supernatant solution, the precipitate was washed three times with diethyl ether/*n*-hexane (1:1) (10-mL portions) and dried in an oil-pump vacuum to afford a dark red solid. Yield: 65 mg (0.167 mmol, 72%). $C_{16}H_8MoN_2O_4$·1/3thf (412.13): calcd. C 50.50, H 2.61, N 6.80; found C 50.76, H 2.50, N 7.17. IR (KBr): $\tilde{\nu}$ = 1806, 1869, 1910, 2012 (s, ν_{CO}), 2116 (w, $\nu_{C\equiv C}$), 3285 (s, $\nu_{\equiv C-H}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 3.45 (s, 1 H, ≡C*H*), 7.41 (ddd, $^3J_{H5'H4'}$ = 7.8, $^3J_{H5'H6'}$ = 4.8, $^4J_{H5'H3'}$ = 1 Hz, 1 H, *H5′*/bpy), 7.90–8.13 (m, 4 H, *H3*,*H3′*,*H4*,*H4′*/bpy), 9.16 (ddd, $^3J_{H6'H5'}$ = 4.8, $^4J_{H6'H4'}$ = 1.8, $^5J_{H6'H3'}$ = 1 Hz, 1 H, *H6′*/bpy), 9.23 (dd, $^4J_{H6H4}$ = 2.4, $^5J_{H6H3}$ = 0.6 Hz, 1 H, *H6*/bpy) ppm.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-bpy(Re(CO)$_3$-Cl)] (13): To a solution of [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-AuCl] (**9**) (70 mg, 0.057 mmol) and [(HC≡C-bpy)(CO)$_3$ReCl] (**12a**) (30 mg, 0.062 mmol) in tetrahydrofuran (15 mL) was added diethylamine (10 mL) and [CuI] (1 mg). The reaction mixture was stirred at 25 °C for 3 h. Afterwards, all volatiles were removed under reduced pressure, and the remaining material was subjected to column chromatography on alumina by using a mixture of dichloromethane/toluene (5:1) as eluent. The title complex was isolated as an orange solid. Yield: 30 mg (0.018 mmol, 30%). $C_{74}H_{54}AuClFeN_2O_3P_3ReRu$ (1687.72): calcd. C 52.66, H 3.22, N 1.66; found C 52.05, H 3.56, N 1.90. IR (KBr): $\tilde{\nu}$ = 1894, 1914, 2019 (s, ν_{CO}), 2060 (m, $\nu_{C\equiv CRu}$), 2120 (w, $\nu_{C\equiv CAu}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.01 (dpt, J_{HP} = 1.2, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 4.20 (br. s, 2 H, C$_5$*H*$_4$), 4.32 [br. s, 5 H (C$_5$*H*$_5$), 2 H (C$_5$*H*$_4$)], 5.19 (br. s, 2 H, C$_5$*H*$_4$), 7.20–7.63 [m, 26 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$), 1 H (*H5′*/bpy)], 7.78–7.87 (m, 4 H, C$_6$*H*$_5$), 7.91–8.09 (m, 4 H, *H3*,*H3′*,*H4*,*H4′*/bpy), 9.00 (ddd, $^3J_{H6'H5'}$ = 5.5, $^4J_{H6'H4'}$ = 1.6, $^5J_{H6'H3'}$ = 0.6 Hz, 1 H, *H6′*/bpy), 9.12 (dd, $^4J_{H6H4}$ = 2, $^5J_{H6H3}$ = 0.6 Hz, 1 H, *H6*/bpy) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 39.9 (Au*P*Ph$_2$), 53.9 (dppf) ppm. MS (ESI-TOF): *m/z* (%) = 1688.9 [M + H]$^+$, 749.0 [(dppf)(C$_5$H$_5$)Ru(CO)]$^+$.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-bpy(Mo-(CO)$_4$)] (15): To [(nbd)Mo(CO)$_4$] (**14**) (18 mg, 0.060 mmol) dissolved in a mixture of dichloromethane (25 mL) and tetrahydrofuran (5 mL), [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-bpy] (**11c**) (80 mg, 0.058 mmol) was added in a single portion. The reaction mixture was stirred at 25 °C for 8 h whereby the solution changed from yellow to deep red. The solution was reduced to 3 mL, and the title compound was precipitated by addition of diethyl ether (25 mL). The precipitate was washed twice with diethyl ether (10-mL portions) and dried in an oil-pump vacuum to afford complex **15** as a dark red solid. Yield: 65 mg (0.041 mmol, 71%). $C_{75}H_{54}AuFeMoN_2O_4P_3Ru$ (1590.01): calcd. C 56.66, H 3.42, N 1.76; found C 56.92, H 3.59, N 1.67. IR (KBr): $\tilde{\nu}$ = 1830, 1875, 1898, 2012 (s, ν_{CO}), 2060 (m, $\nu_{C\equiv CRu}$), 2118 (w, $\nu_{C\equiv CAu}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 4.01 (dpt, J_{HP} = 1.2, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 4.20 (br. s, 2 H, C$_5$*H*$_4$), 4.32 [br. s, 5 H (C$_5$*H*$_5$), 2 H (C$_5$*H*$_4$)], 5.18 (br. s, 2 H, C$_5$*H*$_4$), 7.20–7.63 [m, 26 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$), 1 H (*H5′*/bpy)], 7.79–8.04 [m, 4 H (C$_6$*H*$_5$), 4 H (*H3*,*H3′*,*H4*,*H4′*/bpy)], 9.11 (ddd, $^3J_{H6'H5'}$ = 5.5, $^4J_{H6'H4'}$ = 1.6, $^5J_{H6'H3'}$ = 0.6 Hz, 1 H, *H6′*/bpy), 9.24 (dd, $^4J_{H6H4}$ = 1.7, $^5J_{H6H3}$ = 0.6 Hz, 1 H, *H6*/bpy) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.0 (Au*P*Ph$_2$), 53.9 (dppf) ppm. MS (ESI-TOF): *m/z* (%) = 1590.4 [M + H]$^+$, 749.2 [(dppf)C$_5$H$_5$)Ru(CO)]$^+$.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-bpy-Cu-{(Me$_3$SiC≡C)$_2$[Ti]}]PF$_6$ (17a): To [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}-Cu(N≡CMe)]PF$_6$ (**16a**) (55 mg, 0.072 mmol) dissolved in tetrahydrofuran (30 mL) was added [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-bpy] (**11c**) (100 mg, 0.072 mmol) in a single portion. The reaction solution was stirred at 25 °C for 2 h. During this time, the solution changed from orange to red. Afterwards, the solution was reduced in volume (3 mL), and the product was precipitated with *n*-pentane (20 mL). Removal of the supernatant solution, washing twice with *n*-pentane (10 mL), and drying in an oil-pump vacuum afforded the title compound as an orange-red solid. Yield: 140 mg (0.066 mmol, 92%). $C_{97}H_{98}AuCuF_6FeN_2P_4RuSi_4Ti$ (2107.39): calcd. C 55.28, H 4.69, N 1.33; found C 54.53, H 4.86, N 0.95. IR (KBr): $\tilde{\nu}$ = 1924 (w, $\nu_{C\equiv CTi}$), 2060 (m, $\nu_{C\equiv CRu}$), 2117 (w, $\nu_{C\equiv CAu}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = –0.50 (s, 18 H, Si*Me*$_3$), 0.27 (s, 9 H, Si*Me*$_3$), 0.29 (s, 9 H, Si*Me*$_3$), 4.00 (br. s, 2 H, C$_5$*H*$_4$/dppf), 4.17 (br. s, 2 H, C$_5$*H*$_4$/dppf), 4.31 (s, 5 H, C$_5$*H*$_5$), 4.32 (br. s, 2 H, C$_5$*H*$_4$/dppf), 5.17 (br. s, 2 H, C$_5$*H*$_4$/dppf), 6.25–6.31 (m, 8 H, C$_5$*H*$_4$Si), 7.19–7.61 [m, 26 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$)], 7.69 (dd, $^3J_{H5'H4'}$ = 8, $^3J_{H5'H6'}$ = 5 Hz, 1 H, *H5′*/bpy), 7.78–7.87 (m, 4 H, C$_6$*H*$_5$), 8.15 (dd, $^3J_{H4H3}$ = 8.5, $^4J_{H4H6}$ = 2 Hz, 1 H, *H4*/bpy), 8.24 (pt, J_{HH} = 8 Hz, *H4′*/bpy), 8.38 (d, $^3J_{H3H4}$ = 8.5 Hz, *H3*/bpy), 8.48–8.56 (m, 3 H, *H3′*,*H6*,*H6′*/bpy) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.0 (Au*P*Ph$_2$), 53.9 (dppf), –145.1 (sept, J_{PF} = 708 Hz, *P*F$_6$) ppm. MS (ESI-TOF): *m/z* (%) = 1963.4 [M – PF$_6$]$^+$, 1890.3 [M – PF$_6$ – SiMe$_3$]$^+$, 749.1 [(dppf)(C$_5$H$_5$)Ru(CO)]$^+$, 581.1 [{[Ti](C≡CSiMe$_3$)$_2$}-Cu]$^+$.

[(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-bpy-Ag{(Me$_3$-SiC≡C)$_2$[Ti]}]ClO$_4$ (17b): Complex **17b** was prepared in the same way as described for **17a**. Experimental details: {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}AgOClO$_3$ (**16b**) (38 mg, 0.053 mmol), [(η^2-dppf)(η^5-C$_5$H$_5$)Ru-C≡C-C$_6$H$_4$-4-PPh$_2$-Au-C≡C-bpy] (**11c**) (75 mg, 0.054 mmol). Yield: 95 mg (0.045 mmol, 85%). $C_{97}H_{98}AgAuClFeN_2O_4P_3RuSi_4Ti$ (2106.19): calcd. C 55.32, H 4.69, N 1.33; found C 55.33, H 4.53, N 1.16. IR (KBr): $\tilde{\nu}$ = 1955 (w, $\nu_{C\equiv CTi}$), 2058 (m, $\nu_{C\equiv CRu}$), 2116 (w, $\nu_{C\equiv CAu}$) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = –0.30 (s, 18 H, Si*Me*$_3$), 0.29 (s, 18 H, Si*Me*$_3$), 4.00 (br. s, 2 H, C$_5$*H*$_4$/dppf), 4.17 (br. s, 2 H, C$_5$*H*$_4$/dppf), 4.31 (s, 5 H, C$_5$*H*$_5$), 4.32 (br. s, 2 H, C$_5$*H*$_4$/dppf), 5.17 (br. s, 2 H, C$_5$*H*$_4$/dppf), 6.41–6.49 (m, 8 H, C$_5$*H*$_4$Si), 7.19–7.68 [m, 26 H (C$_6$*H*$_5$), 4 H (C$_6$*H*$_4$), 1 H (*H5′*/bpy)], 7.77–7.87 (m, 4 H, C$_6$*H*$_5$), 8.10 (dd, $^3J_{H4H3}$ = 8.5, $^4J_{H4H6}$ = 2 Hz, 1 H, *H4*/bpy), 8.17 (pt, J_{HH} = 8 Hz, *H4′*/bpy), 8.27 (d, J_{H3H4} = 8.5 Hz, *H3*/bpy), 8.38 (d, $J_{H3'H4'}$ = 8 Hz, H3′/bpy), 8.60 (ddd, $^3J_{H6'H5'}$ = 5.5, $^4J_{H6'H4'}$ = 1.6, $^5J_{H6'H3'}$ = 0.6 Hz, 1 H, *H6′*/bpy), 8.64 (d, $^4J_{H6H4}$ = 1.7 Hz, 1 H, *H6*/bpy) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 40.0 (Au*P*Ph$_2$), 53.9 (dppf) ppm. MS

(ESI-TOF): *m*/*z* (%) = 2006.5 [M – ClO_4]$^+$, 749.1 [(dppf)(C_5H_5)Ru(CO)]$^+$.

[(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡C-C_5H_4N-Cu-{(Me_3SiC≡C)$_2$[Ti]}]OTf (18): To [(η^2-dppf)(η^5-C_5H_5)Ru-C≡C-C_6H_4-4-PPh_2-Au-C≡C-C_5H_4N-4] (**11a**) (55 mg, 0.042 mmol) dissolved in toluene (5 mL) was added dropwise a solution of {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}CuOTf (**16c**) (40 mg, 0.055mmol) in diethyl ether (20 mL). The resulting reaction mixture was stirred at 25 °C for 1 h. Afterwards, the supernatant solution was removed from the formed precipitate which was subsequently washed three times with diethyl ether/*n*-pentane (1:1) (10-mL portions) and dried in an oil-pump vacuum. The title complex was isolated as an orange solid. Yield: 50 mg (0.025 mmol, 58 %). $C_{93}H_{95}AuCuF_3FeNO_3P_3RuSSi_4Ti$ (2034.4): calcd. C 54.91, H 4.71, N 0.69; found C 54.19, H 4.67, N 0.56. IR (KBr): $\tilde{\nu}$ = 1918 (w, $\nu_{C\equiv CTi}$), 2060 (m, $\nu_{C\equiv CRu}$), 2118 (w, $\nu_{C\equiv CAu}$) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.06 (s, 18 H, Si*Me*$_3$), 0.26 (s, 18 H, Si*Me*$_3$), 4.01 (br. s, 2 H, C_5H_4/dppf), 4.18 (br. s, 2 H, C_5H_4/dppf), 4.31 (s, 5 H, C_5H_5), 4.33 (br. s, 2 H, C_5H_4/dppf), 5.18 (br. s, 2 H, C_5H_4/dppf), 6.24–6.32 (m, 8 H, C_5H_4Si), 7.17–7.62 [m, 26 H (C_6H_5), 4 H (C_6H_4), 2 H (C_5H_4N)], 7.76–7.88 (m, 4 H, C_6H_5), 8.48–8.54 (m, 2 H, C_5H_4N) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 39.9 (Au*P*Ph$_2$), 53.9 (dppf) ppm. MS (ESI-TOF): *m*/*z* (%) = 1885.7 [M – OTf]$^+$, 749.2 [(dppf)(C_5H_5)Ru(CO)]$^+$, 579.3 [{[Ti](C≡CSiMe$_3$)$_2$}Cu]$^+$.

X-ray Crystallography: The data for **9** and **11c** were collected with a Bruker Smart CCD 1k diffractometer and for **11b** and **12** with an Oxford Gemini S diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å) at 293(2) K (**9**, **11c**, **12a**) or 160(2) K (**11b**) by using oil-coated shock-cooled crystals.[36] The structures were solved by direct methods using SHELXS-97[37] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[38] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. For crystal and intensity collection data of **9**, **11b**, **11c**, and **12a** see Table 2. CCDC-686774 (**11b**), -686775 (**9**), -686776 (**11c**), and -686777 (**12a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 2. Crystal and intensity collection data for **9**, **11b**, **11c**, and **12a**.

	9·$CHCl_3$·0.5CH_2Cl_2	**11b**·0.5(CH_3)CO	**11c**·C_5H_{12}	**12a**·$CHCl_3$
Empirical formula	$C_{60.5}H_{49}AuCl_5FeP_3Ru$	$C_{69.5}H_{54}AuFeNO_{0.5}P_3Ru$	$C_{76}H_{66}AuFeN_2P_3Ru$	$C_{16}H_9Cl_4N_2O_3Re$
Formula weight	1400.04	1357.93	1454.10	605.25
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	11.3926(9)	10.9962(7)	10.5220(12)	10.6541(16)
b [Å]	35.591(3)	19.3738(11)	14.1097(16)	15.076(2)
c [Å]	15.0094(12)	27.1517(10)	23.238(3)	12.8412(19)
α [°]	90	91.853(4)	107.271(2)	90
β [°]	111.8930(10)	91.469(4)	96.600(2)	101.291(3)
γ [°]	90	103.965(5)	100.724(2)	90
V [Å^3]	5647.0(8)	5607.1(5)	3183.2(6)	2022.6(5)
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.647	1.609	1.517	1.988
F(000)	2764	2704	1460	1144
Crystal dimensions [mm]	0.4 × 0.3 × 0.3	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.2	0.4 × 0.4 × 0.3
Z	4	4	2	4
Max./min. transmission	0.99999/0.74869	1.00000/0.73879	0.99999/0.79573	0.99999/0.52466
Absorption coefficient [μ (mm^{-1})]	3.469	3.262	2.878	6.554
Scan range [°]	1.57–26.38	2.90–27.56	1.55–26.41	1.95–26.28
Index ranges	$-14 \le h \le 13$	$-14 \le h \le 10$	$-13 \le h \le 12$	$-13 \le h \le 13$
	$0 \le k \le 44$	$-15 \le k \le 25$	$-17 \le k \le 16$	$0 \le k \le 18$
	$0 \le l \le 18$	$-35 \le l \le 34$	$0 \le l \le 29$	$0 \le l \le 15$
Total reflections	64465	33978	24693	23004
Unique reflections	11763	24621	12933	4258
R(int)	0.0288	0.0268	0.0244	0.0271
Data/restraints/parameters	11539/1/658	24621/0/1384	12927/171/807	4081/0/235
Goodness-of-fit on F^2	1.128	0.881	1.023	1.047
R_1,[a] wR_2[a] [$I \ge 2\sigma(I)$]	0.0404, 0.1049	0.0329, 0.0573	0.0278, 0.0602	0.0217, 0.0526
R_1,[a] wR_2[a] (all data)	0.0450, 0.1072	0.0685, 0.0625	0.0444, 0.0651	0.0283, 0.0560
Max./min. peak in final Fourier map [e Å^{-3}]	1.251/–1.094	1.315/–0.946	0.603/–0.446	0.518/–0.609

[a] $R_1 = [\Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|]$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)\}^{1/2}$. $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$; n = number of reflections, p = parameters used.

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