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Mixed-Transition-Metal Acetylides: Synthesis and Characterization of Complexes with up to Six Different Transition Metals Connected by Carbon-Rich Bridging Units

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Abstract: The synthesis and reaction chemistry of heteromultimetallic transition-metal complexes by linking diverse metal-complex building blocks with multifunctional carbon-rich alkynyl-, benzene-, and bipyridyl-based bridging units is discussed. In context with this background, the preparation of $[1\text{-}\{(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{RuC}{\equiv}\text{C}\}\text{-}3\text{-}\{(t\text{Bu}_2\text{bpy})(\text{CO})_3\text{ReC}{\equiv}\text{C}\}\text{-}5\text{-}(\text{PPh}_2)\text{-}\text{C}_6\text{H}_3]$ (**10**) (dppf = 1,1′-bis(diphenylphosphino)ferrocene; $t\text{Bu}_2\text{bpy}$ = 4,4′-di-*tert*-butyl-2,2′-bipyridyl; Ph = phenyl) is described; this complex can react further, leading to the successful synthesis of heterometallic complexes of higher nuclearity. Heterotetrametallic transition-metal compounds were formed when **10** was reacted with $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2\}_2]$ (**18**), $[(\text{Et}_2\text{S})_2\text{PtCl}_2]$ (**20**) or $[(\text{tht})\text{AuC}{\equiv}\text{C-bpy}]$ (**24**) (Me = methyl; Et = ethyl; tht = tetrahydrothiophene; bpy = 2,2′-bipyridyl-5-yl). Complexes $[1\text{-}\{(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{RuC}{\equiv}\text{C}\}\text{-}3\text{-}\{(t\text{Bu}_2\text{bpy})(\text{CO})_3\text{ReC}{\equiv}\text{C}\}\text{-}5\text{-}\{\text{PPh}_2\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}\text{C}_6\text{H}_3]$ (**19**), $[\{1\text{-}[(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{RuC}{\equiv}\text{C}]\text{-}3\text{-}[(t\text{Bu}_2\text{bpy})(\text{CO})_3\text{ReC}{\equiv}\text{C}]\text{-}5\text{-}(\text{PPh}_2)\text{C}_6\text{H}_3\}_2\text{PtCl}_2]$ (**21**), and $[1\text{-}\{(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{RuC}{\equiv}\text{C}\}\text{-}3\text{-}\{(t\text{Bu}_2\text{bpy})(\text{CO})_3\text{ReC}{\equiv}\text{C}\}\text{-}5\text{-}\{\text{PPh}_2\text{AuC}{\equiv}\text{C-bpy}\}\text{C}_6\text{H}_3]$ (**25**) were thereby obtained in good yield. After a prolonged time in solution, complex **25** undergoes a transmetallation reaction to produce $[(t\text{Bu}_2\text{bpy})(\text{CO})_3\text{ReC}{\equiv}\text{C-bpy}]$ (**26**). Moreover, the bipyridyl building block in **25** allowed the synthesis of Fe-Ru-Re-Au-Mo- (**28**) and Fe-Ru-Re-Au-Cu-Ti-based (**30**) assemblies on addition of $[(\text{nbd})\text{Mo}(\text{CO})_4]$ (**27**), (nbd = 1,5-norbornadiene), or $[\{[\text{Ti}](\mu\text{-}\sigma,\pi\text{-C}{\equiv}\text{CSiMe}_3)_2\}\text{Cu}(\text{N}{\equiv}\text{CMe})][\text{PF}_6]$ (**29**) ($[\text{Ti}] = (\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$) to **25**. The identities of **5**, **6**, **8**, **10–12**, **14–16**, **19**, **21**, **25**, **26**, **28**, and **30** have been confirmed by elemental analysis and IR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. From selected samples ESI-TOF mass spectra were measured. The solid-state structures of **8**, **12**, **19** and **26** were additionally solved by single-crystal X-ray structure analysis, confirming the structural assignment made from spectroscopy.

Keywords: heterometallic complexes · mass spectrometry · solid-state structures · transition metals

Introduction

The linkage of transition-metal complexes to give (hetero)-multimetallic species is, from the viewpoint of synthetic chemistry, a challenge, since the molecular design of such assemblies requires the accessibility of multitopic bridging units featuring diverse reactive coordination sites.[1,2] In this respect, metal-containing alkynyls have been studied extensively due to their rigid structures, their stability, and, for example, their rich spectroscopic, photophysical, and electrochemical properties.[2] To control the structure and composition of multimetallic complexes, a prior synthesis of multifunctional bridging ligands is necessary that allows the stepwise metal coordination. Examples of such connectivities are 1,4-diethynylbenzene,[3,4] 1,3,5-triethynylbenzene,[5,6] 1-ethynyl-4-diphenylphosphinobenzene,[7] 5-ethynyl-2,2′-bipyridyl,[8] and 2,5-bis(alkynyl) thiophenes.[9,10] Based on these cores, mainly homometallic transition-metal compounds have been synthesized, while less is known about heteromultimetallic molecules. Recently, Long and Yam reported a series of phenylenethynyl-bridged di- and trinuclear complexes featuring Re–Pt, Re–Pd_2, and Fe–Ru–Os metal

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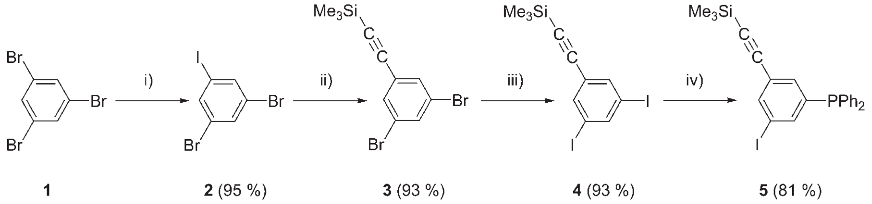
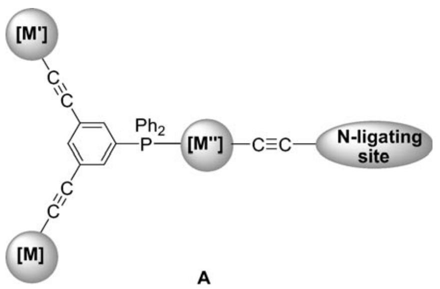
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains a description of the structure of complex **26** in the solid state (Figure S1) and discussion of the 2D layers formed by π–π interactions (Figures S2 and S3), including the crystallographic data (Table S1).

atoms.[4a,6b,c] Electrochemical and luminescence studies were carried out on these rigid-rod-structured compounds.



Scheme 1. Synthesis of **5**: i) 1. *n*BuLi, Et$_2$O, -90°C; 2. I$_2$, Et$_2$O/Thf, $-90\rightarrow25$°C; ii) HC≡CSiMe$_3$, [(Ph$_3$P)$_2$PdCl$_2$]/[CuI], Thf/NEt$_3$, 0°C; iii) 1. *t*BuLi, Et$_2$O, -80°C; 2. I$_2$, Et$_2$O, $-80\rightarrow25$°C; iv) 1. *n*BuLi, Et$_2$O, -80°C; 2. ClPPh$_2$, Et$_2$O, $-80\rightarrow25$°C.

Very recently, we reported on the synthesis of heterodi-[11] and heterotrimetallic compounds[8a,12] in which early and late transition-metal atoms are spanned by carbon-rich π-conjugated connectivities. These molecules showed a novel reactivity and reaction chemistry compared with that of related mononuclear complexes. Within these studies, heterotetrametallic[12a,b,13] and even heteropentametallic[7b,c] transition-metal complexes could be synthesized and structurally characterized by our group for the first time. As multitopic linking units, for example, 5-ethynyl-2,2′-bipyridyl and 1-ethynyl-4-diphenylphosphino benzene were used. Extending the core into three directions (e.g., a type **A** molecule) is of interest, since such species should serve as versatile building blocks allowing carbon-rich molecules of higher nuclearity to be synthesized.



A

In particular, molecule **A** should be able to exploit the electron-based cooperation between individual transition-metal subunits of molecular assemblies with a delocalized π-backbone. This may allow diverse applications in material sciences to be found.

Here, we describe a series of novel heteromultimetallic complexes with up to six different transition metals (Ti, Re, Fe, Ru, Cu, and Au) based on the 1,3-bis(ethynyl)-5-diphenylphosphinobenzene core as a linking unit.

Results and Discussion

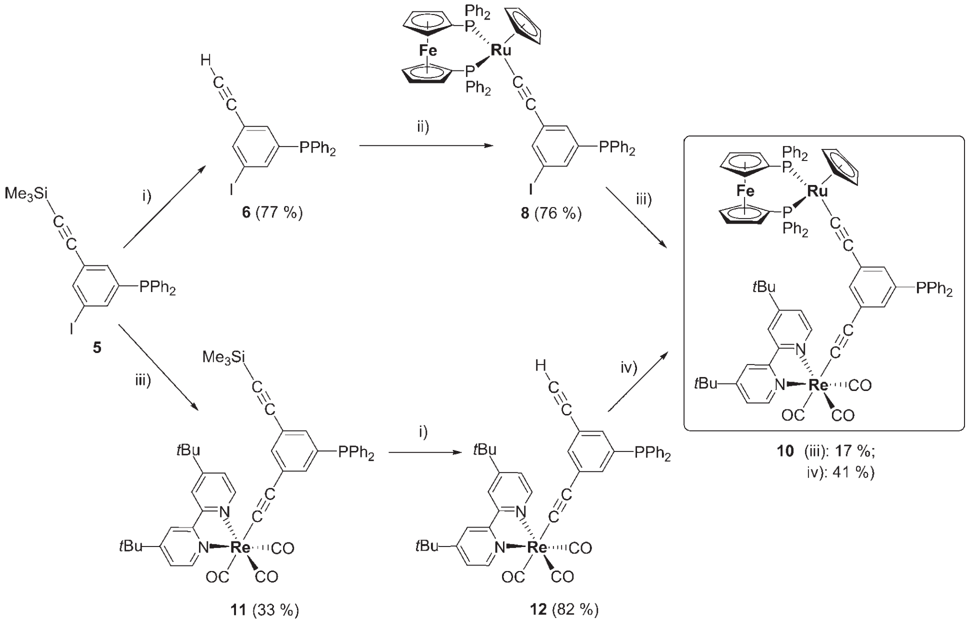
Synthesis and spectroscopic analysis: Scheme 1 shows the transformation of compound **1** through **2**–**4** to give the starting material 1-trimethylsilylethynyl-3-iodo-5-diphenylphosphinobenzene (**5**). In detail, compound **5** was synthesized from 1,3-diiodo-5-trimethylsilylethynylbenzene (**4**), which was accessible by using consecutive reactions including halide exchange reactions (synthesis of **2** and **4**) and Sonogashira carbon–carbon cross coupling of **2** with trimethylsilylacetylene (synthesis of **3**; Scheme 1).[5j] Lithiation of **4** with *n*BuLi and treatment of Li-**4** with equimolar amounts of chlorodiphenylphosphine gave **5** in good yield (Scheme 1).

Scheme 2 shows the reaction scheme involving compounds **5**–**9** to successfully give [1-{(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C}-3-{(*t*Bu$_2$bpy)(CO)$_3$ReC≡C}-5-(PPh$_2$)C$_6$H$_3$] (**10**) (dppf = 1,1′-bis(diphenylphosphino)ferrocene; *t*Bu$_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; Ph = phenyl). Desilylation of **5** afforded 1-ethynyl-3-iodo-5-diphenylphosphinobenzene (**6**), which was further treated with [(η^2-dppf)(η^5-C$_5$H$_5$)RuCl] (**7**) in refluxing methanol followed by the addition of sodium metal to give **8** (Scheme 2). This procedure, adapted from that of Field et al.,[14] was preferred over the method using [NH$_4$]PF$_6$ and DBU (DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene), because this last reaction gave lower yields of **8**. Reacting **8** with [(*t*Bu$_2$bpy)(CO)$_3$ReC≡CH] (**9**) under typical Sonogashira cross-coupling reaction conditions produced orange heterotrimetallic **10** (Scheme 2).

After the appropriate workup, complex **10** could be isolated in very low yield. The limiting step in the synthesis of **10** is the low turnover of the Sonogashira carbon–carbon cross-coupling reaction and the thereby partial decomposition of **8** under the reaction conditions used (i.e., refluxing triethylamine). Since **10** is the key metal precursor for the synthesis of higher heteromultimetallic molecules [see Eq. (1)] and Scheme 4 below) another and, hence, more efficient and straightforward way to prepare this compound had to be developed.

The better synthetic approach used to synthesize **10** is based on the reaction sequence **5**→**11**→**12**→**10** as depicted in Scheme 2. It was found that the reaction of organic **5** with **9** gave somewhat better yields than with **8** with **9**. Desilylation of **11** with [*n*Bu$_4$N]F (Bu = butyl) afforded **12** in almost quantitative yield. On the other hand, the introduction of the [(η^2-dppf)(η^5-C$_5$H$_5$)Ru] fragment by using [NH$_4$]PF$_6$ and DBU (see above) produced **10** only in moderate yield. In summary, the over-all yield of the second reaction route was admittedly better then the first one, but still not satisfactory.

The choice of these two reaction routes finally leading to **10** was determined by the desire to prevent side products, because the respective reactions should preferentially give the postulated compounds. The introduction of the rhenium(I) acetylide building block by a carbon–carbon cross-coupling reaction by using **9** as the alkyne could be demon-

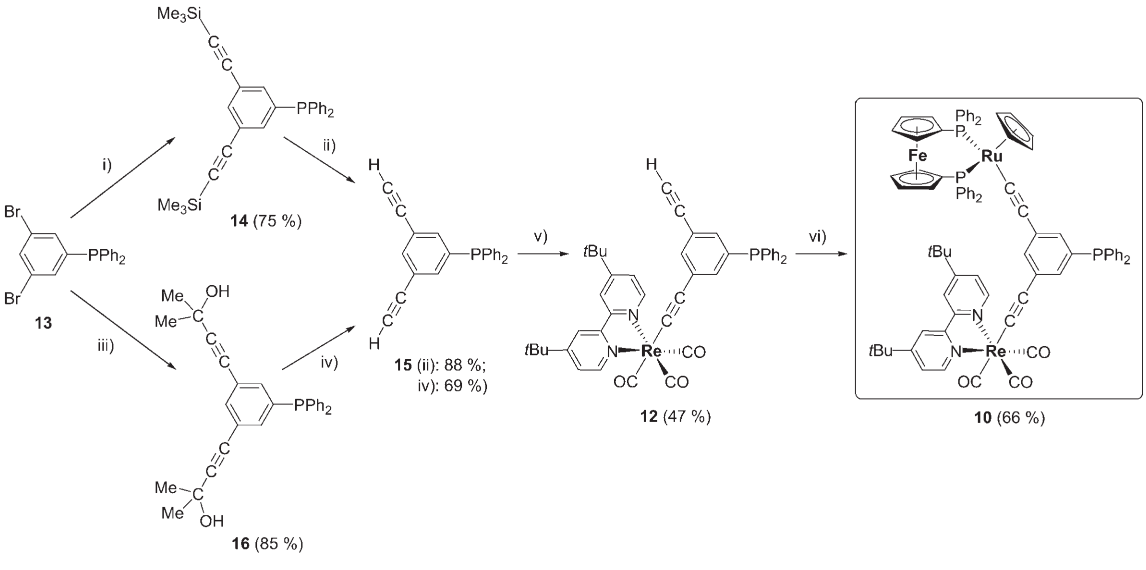


Scheme 2. Synthesis of trimetallic **10** from **5**: i) $[nBu_4N]F$, Thf, 25 °C; ii) 1. $[(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)RuCl]$ (**7**), MeOH, reflux; 2. Na, MeOH, 25 °C; iii) $[(tBu_2bpy)(CO)_3ReC{\equiv}CH]$ (**9**), $[(Ph_3P)_2PdCl_2]/[CuI]$, Thf/NEt_3, reflux; iv) 1. $[(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)RuCl]$ (**7**), $[NH_4]PF_6$, CH_2Cl_2/MeOH, 25 °C; 2. DBU, CH_2Cl_2/MeOH, 25 °C.

strated to be possible, but, unfortunately, proved to be unsuitable in this case because of very low yields obtained under the reaction conditions used.

In contrast, the most straightforward and efficient methodology to synthesize **10** starts from the reaction of 1,3-dibromo-5-diphenylphosphino-benzene (**13**) with trimethylsilylacetylene (formation of **14**) under typical Sonogashira cross-coupling conditions to give 1,3-bis(ethynyl)-5-diphenylphosphino benzene (**15**) (Scheme 3). Alternatively, the reaction of **13** with 2-methyl-3-butyn-2-ol (formation of **16**) under typical Sonogashira cross-coupling conditions also gave **15** (Scheme 3).[15] Desilylation of **14** was achieved by addition of $[nBu_4N]F$. The de-protection of the propargylic group in **16** was carried out with powdered potassium hydroxide in toluene. Both reactions produced **15** as a colorless solid in good yield.

The introduction of the first transition-metal building block in **15** succeeded by mono-lithiation of **15** with one equivalent of $LiN(SiMe_3)_2$ (Me = methyl) in toluene at room temperature followed by addition of $[(tBu_2bpy)(CO)_3ReCl]$ (**17**) and heating the reaction mixture to reflux (Scheme 3). This new procedure allowed the isolation of **12** in about 45 % yield. Nevertheless, this reaction did not take place when diethyl ether, tetrahydrofuran, or mixtures of both were used.[16] This behavior is most probably attributed to the low solubility of **17** in diethyl ether and to the observation that Li-**15** decomposed quite fast in tetrahydrofuran. Also the methods introduced by Yam et al. and Pérez et al. using the reaction of the rhenium chloride precursor with terminal acetylides in the presence of [AgOTf] (OTf =



Scheme 3. Synthesis of **10** from **13**: i) $HC{\equiv}CSiMe_3$, $[(Ph_3P)_2PdCl_2]/[CuI]$, $HNiPr_2$, reflux; ii) $[nBu_4N]F$, Thf, 25 °C; iii) $HC{\equiv}CCMe_2OH$, $[(Ph_3P)_2PdCl_2]/[CuI]$, $HNiPr_2$, reflux; iv) KOH, toluene, 80 °C; v) 1. $LiN(SiMe_3)_2$, toluene, 25 °C; 2. $[(tBu_2bpy)(CO)_3ReCl]$ (**17**), toluene, reflux; vi) $[(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)RuCl]$ (**7**), $[NH_4]PF_6$, KOtBu, CH_2Cl_2/MeOH, 25 °C.

trifluoromethanesulfonate) and NEt$_3$ (Et = ethyl) in refluxing tetrahydrofuran and the reaction of [(bpy)(CO)$_3$Re(thf)][BPh$_4$] with the in situ lithiated alkyne, respectively, were not successful.[6b,17] An optimized route to **10** is the reaction of **12** with [(η^2-dppf)(η^5-C$_5$H$_5$)RuCl] (**7**) in a 1:1 dichloromethane/methanol mixture with the simultaneous addition of [NH$_4$]PF$_6$ and the base KO*t*Bu (O*t*Bu = *tert*-butanolate).

Complex **10** is an air-stable, orange solid that dissolves nicely in polar organic solvents. However, in solution it is observed that **10** is easier to oxidize at the phosphorus atom than, for example, triphenylphosphine, giving the appropriate phosphinoxide. Due to this, oxygen must strictly be excluded during the workup procedure.

The Fe-Ru-Re compound **10** bears a free PPh$_2$ group that is able to react with a fourth transition-metal fragment to form heterotetranuclear molecules in which four different metals are connected by the bis(alkynyl)diphenylphosphinobenzene core.

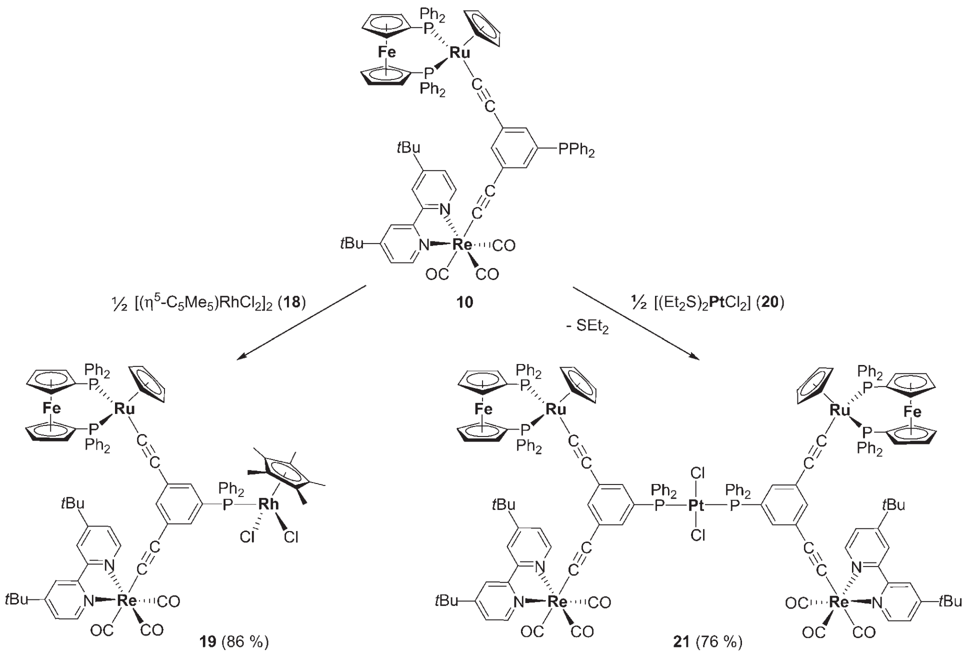
Cleavage of the chloride-bridged dimer [{(η^5-C$_5$Me$_5$)RhCl$_2$}$_2$] (**18**) upon addition of **10** in dichloromethane at 25 °C leads to the formation of [1-{(η^2-dppf)(η^5-C$_5$H$_5$)RuC$\equiv$C}-3-{(*t*Bu$_2$bpy)(CO)$_3$ReC$\equiv$C]-5-[PPh$_2$RhCl$_2$(η^5-C$_5$Me$_5$)}C$_6$H$_3$] (**19**) (Scheme 4). Pure **19** was obtained as a red crystalline material in 86 % yield by precipitation from dichloromethane with *n*-hexane.

The reaction of **10** with 0.5 equivalents of [(Et$_2$S)$_2$PtCl$_2$] (**20**) produced, upon replacement of both diethylsulfide ligands with the tertiary phosphine **10**, the heptametallic complex **21** which possesses a *trans*-configuration (Scheme 4). A small amount (ca. 5 %) of the isomer containing the *cis*-[Pt(PR$_3$)$_2$Cl$_2$] fragment was evidenced from ^{31}P{^{1}H} NMR spectroscopy and also from ^{1}H NMR studies due to a second set of resonance signals.

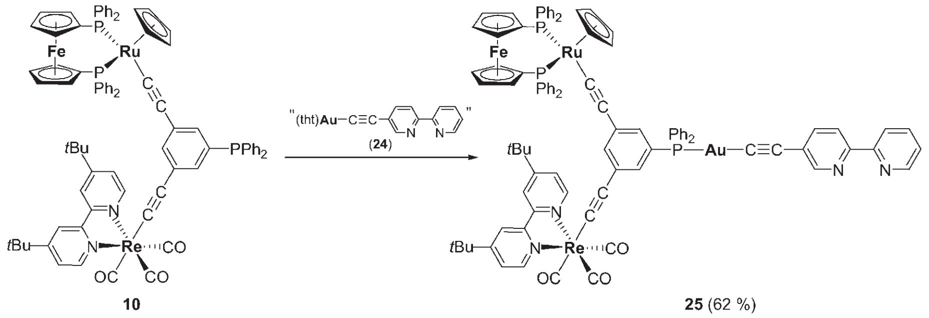
A possibility to introduce a transition-metal fragment with a further coordination site allowing the incorporation of other metal building blocks should be possible using the successive reaction of **10** with [(tht)AuCl] (tht = tetrahydrothiophene) (**22**) and 5-ethynyl-2,2′-bipyridyl (**23**).[13a,18] Thus, **10** was treated with **22** in tetrahydrofuran. After the appropriate workup, including column chromatography, [(*t*Bu$_2$bpy)(CO)$_3$ReCl] could be isolated as the only unequivocally characterized molecule including X-ray structure analysis.[16b] This observation corresponds to an unexpected transmetallation reaction between the gold and rhenium atoms.

Another widely used method for the preparation of new phosphine gold(I) acetylide complexes centers on the depolymerization reaction of neutral homoleptic gold(I) polymers of the type [{AuC$\equiv$CR}$_n$] upon addition of tertiary phosphines. Such reactions enabled the synthesis of a high number of neutral[19] and ionic gold(I) alkynyl derivatives.[20,21] In this context, we tried to prepare [{AuC$\equiv$C−bpy}$_n$] by reacting 5-ethynyl-2,2′-bipyridyl (**23**) with [(tht)AuCl] (**22**) in the presence of triethylamine. However, this reaction did not result in the precipitation of the desired polymeric species. Furthermore, the addition of catalytic amounts of CuI only led to the decomposition and formation of elemental gold.

For this reason we treated [(tht)AuCl] (**22**) with 5-ethynyl-2,2′-bipyridyl (**23**) in a tetrahydrofuran/diethylamine mixture. The addition of catalytic amounts of CuI to this reaction mixture led to a turbidity, which was attributed to the formation of HNEt$_2$ × HCl. However, attempts to isolate the formed product failed due to its instability, which was not unexpected since thioether-substituted gold(I) acetylides have not been reported so far. Nevertheless, we suggest the main product to be [(tht)AuC$\equiv$C-bpy] (**24**). Another possibility is that in this reaction the alkynyl ligand and the amine itself replace both the tht and the chloride ligand, forming [(HNEt$_2$)AuC$\equiv$C-bpy], which could be shown by Vicente et al. for [(HNEt$_2$)AuC$\equiv$CR] (R = SiMe$_3$, *t*Bu).[21] Since **24** could not be isolated this assumption could not be confirmed. Thus, in situ prepared **24** was reacted with the tertiary phosphine **10** to give the desired Fe-Ru-Re-Au transition-metal complex **25** after column chromatography in good yield [Eq. (1)].



Scheme 4. Synthesis of **19** and **21** from **10**.



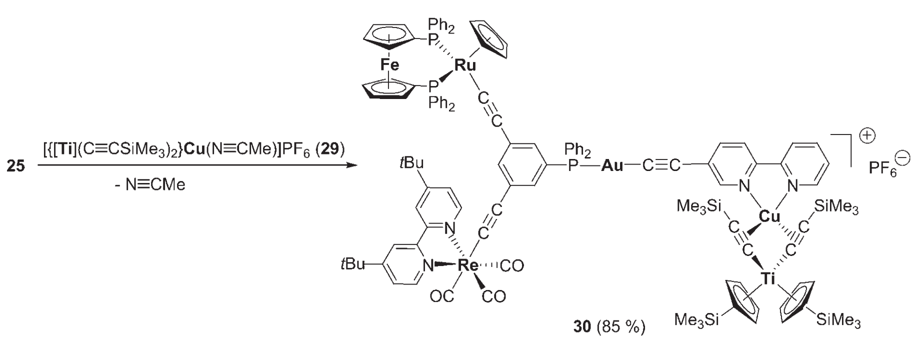
(1)

When trying to crystallize **25** by diffusion of *n*-hexane into a solution of **25** in dichloromethane, it appeared that this complex was not stable for a long period of time. Complex **25** decomposed to produce [(*t*Bu$_2$bpy)(CO)$_3$ReC≡C-bpy] (**26**) along with an insoluble yellow precipitate, which does not dissolve in common organic solvents. This observation again underlies an unexpected transmetallation reaction between the Re and Au alkynyls. The transmetallation product was indisputably characterized by single-crystal X-ray diffraction studies. The insoluble precipitate probably evinces a polymeric structure formed by the remaining phosphine gold(I) acetylide building block.

Nevertheless, complex **25** with its four different transition-metal atoms is the key starting material for the synthesis of organometallic molecules of higher nuclearity, due to the presence of a pendant 2,2′-bipyridyl entity as a further N-ligating site. Thus, complex **25** was reacted with equimolar amounts of [(nbd)Mo(CO)$_4$] (**27**) (nbd = 2,5-norbornadiene) in a 5:1 mixture of dichloromethane/tetrahydrofuran at 25 °C to obtain the respective heteropentanuclear Fe-Ru-Re-Au-Mo compound. Admittedly, the expected complex [1-{(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C}-3-{(*t*Bu$_2$bpy)(CO)$_3$ReC≡C}-5-[PPh$_2$AuC≡C-bpy{Mo(CO)$_4$}]C$_6$H$_3$] (**28**) could not be isolated in a pure form; this fact is attributed to the partial decomposition of **25** during the long reaction time of 15 h. In contrast, when **25** was treated with the organometallic π-tweezer [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF$_6$ (**29**) in tetrahydrofuran heterohexanuclear **30** was formed in a straightforward manner, that is, the acetonitrile is substituted by the bipyridyl ligand [Eq. (2)]. In this reaction, the coordination number at copper is changed from three (planar) to four (tetrahedral).[8a,11]

The identities of **5**, **6**, **8**, **10**–**12**, **14**–**16**, **19**, **21**, **25**, **26**, **28**, and **30** have been confirmed by elemental analysis, infrared (IR) spectroscopy, and ^{1}H, ^{31}P{^{1}H} and partly by ^{13}C{^{1}H} NMR spectroscopy. From selected samples the electrospray ionization time of flight (ESI-TOF) mass spectra were measured. The solid-state structures of **8**, **12**, **19** and **26** were additionally solved by single-crystal X-ray structure analysis, thus confirming the structural assignment made from spectroscopic analysis.

Most characteristic in the IR spectra of all complexes are the $\nu_{C\equiv C}$ and ν_{CO} vibrations which are diagnostic and represent a useful monitoring tool. However, it should be noted that the intensity of the $\nu_{C\equiv C}$ vibrations can vary so that in some of the complexes not all of the expected bands can be detected. As an example, this is shown for the series **5**→**8**→**10**→**25**→**30**. While the $\nu_{C\equiv C}$ absorption band for **5** is found at 2150 cm^{-1}, it is shifted to 2055 and 2065 cm^{-1} in **8** and **10**, respectively. This observation nicely reflects the introduction of a ruthenium(II) entity and is representative in transition-metal–acetylide chemistry.[22] The difference of the $\nu_{C\equiv C}$ bands in **8** and **10** by 10 cm^{-1} mirrors a weak interaction between the ruthenium and rhenium atoms through the carbon-rich connectivity. The ReC≡C stretching frequency, however, overlaps with the RuC≡C band. In **25** an additional vibration is found at 2116 cm^{-1} for the AuC≡C unit.[19–21] The [(*t*Bu$_2$bpy)Re(CO)$_3$] fragment is evidenced by the presence of three intense carbonyl stretching modes between 1900–2005 cm^{-1} as expected for a [M(CO)$_3$] building block in a facial arrangement.[6b,16] Due to this, the predictable weak $\nu_{C\equiv C}$ vibration at titanium (expected at ca. 1925 cm^{-1})[8a,11] in **30** is covered.



(2)

The $^{31}P\{^1H\}$ NMR spectra of **5**, **6**, **11**, **12**, and **14**–**16** indicate the presence of a single phosphorus environment. In all other complexes in which the $\{(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)Ru\}$ unit is present, a second resonance signal is observed at about 54 ppm.[23] The chemical shift of the benzene-bonded PPh_2 entity is almost independent (−5 to −6 ppm) of the appropriate substitution pattern of the benzene core, while a representative shift to lower field takes place upon coordination to a transition-metal fragment as given in **19**, **21**, **25**, **28**, and **30**. For example, the coordination of the tertiary phosphine **10** to a $\{RhCl_2(\eta^5\text{-}C_5Me_5)\}$ fragment is best reflected by a downfield shift to 29.8 ppm (**19**). The resonance signal thereby shows a characteristic coupling with ^{103}Rh ($I = ^1\!/_2$, 100% abundance) giving a doublet with a typical $^1J(^{31}P,^{103}Rh)$ coupling constant of 144 Hz.[24]

The consecutive building of higher nuclear heterometallic molecules from **5** and **15** is also confirmed by ^1H and partly by $^{13}C\{^1H\}$ NMR spectroscopic studies, since after each individual synthesis step the resonance signals for the newly introduced organometallic fragments can be seen nicely. The ^1H NMR spectra of **6**, **12**, and **15** reveal a singlet at about 3.10 (**6**, **15**) and 2.94 ppm (**12**) corresponding to the acetylenic protons that disappear upon coordination of the alkynyl units to ruthenium(II) and rhenium(I). The aryl protons on the 2-, 4-, and 6-positions of the central phenylene ring show an upfield shift upon the coordination of the alkynyl groups to Re^I and Ru^{II}. Such a shift to a higher field in the C_6H_3 resonance signals in **10**–**12** compared with that in **6** and **15** may be suggestive of the electron richness of the respective transition-metal building blocks $\{(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)Ru\}$ and $\{(t\text{Bu}_2\text{bpy})Re(CO)_3\}$ leading to a reduced electron donation from the alkynyl units. The ^1H NMR spectrum of **30** also confirms the successful formation of this compound, giving two signals for the cyclopentadienyl bonded $SiMe_3$ groups, which arises from their unsymmetrical environment in the final assembly. Furthermore, when compared to **29**, the resonance signal for the acetylene bonded $SiMe_3$ entity undergoes an upfield shift of 0.75 ppm, which can be explained by the ring current of the chelating bipyridyl.

The identity of the heterometallic complexes **10**, **19**, **21**, **25**, **28**, and **30** were additionally evidenced from mass spectrometric investigations. The electrospray ionization mass spectra (ESI-MS) of **10**, **19**, **21**, **25**, and **28** show ion peaks at a mass-to-charge ratio (m/z) which correspond to $[M+H]^+$. For example, the ESI MS spectrum of heterohexametallic **30** is shown in Figure 1. It exhibits a prominent ion peak at $m/z = 2524.7$, which, according to the mass and isotope distribution pattern, is $[\mathbf{30}-PF_6]^+$, and confirms the elemental composition and charge state. Further assigned peaks are at m/z 2452.6 $[\mathbf{30}-PF_6-SiMe_3]^+$, 1262.9 $[\mathbf{30}-PF_6]^{2+}$, 749.1 $[(C_5H_5)(PPh_3)_2Ru(CO)]^+$,[25] and 579.2 $[[Ti](C{\equiv}CSiMe_3)_2Cu]^+$ (Figure 1).

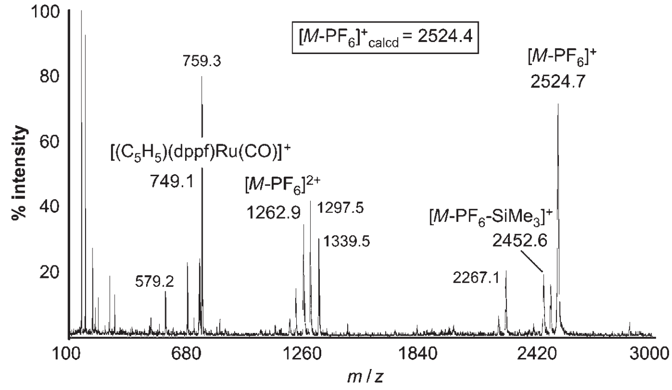


Figure 1. ESI MS spectrum of heterohexametallic **30**.

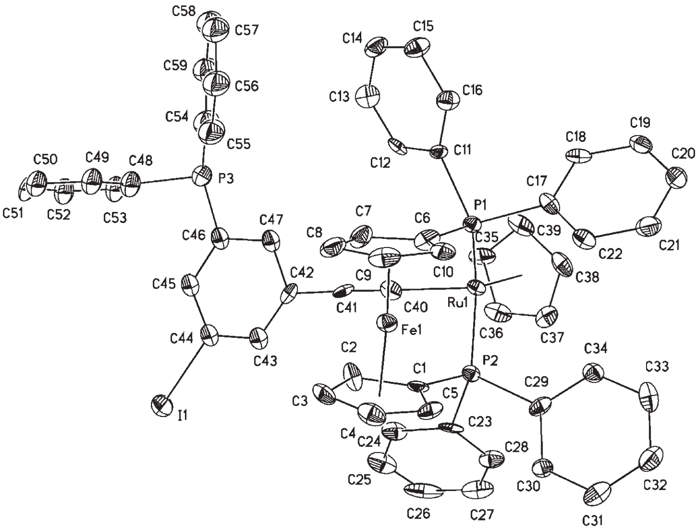


Figure 2. ORTEP drawing of **8**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1−P1 2.272(2), Ru1−P2 2.267(2), Ru1−D3 1.885(1), Ru1−C40 2.009(9), C40−C41 1.198(11), C41−C42 1.455(12), C44−I1 2.102(13), Fe1−D1 1.637(4), Fe1−D2 1.643(4); P1-Ru1-P2 96.90(8), Ru1-C40-C41 168.5(7), C40-C41-C42 174.9(8), C46-P3-C48 102.0(7), C46-P3-C54 102.9(8), C48-P3-C54 103.9(7) (D1 = centroid of C1−C5; D2 = centroid of C6−C10; D3 = centroid of C35−C39).

X-ray crystallography: The solid-state structures of **8**, **12**, **19**, and **26** have been determined by single-crystal X-ray analysis. Suitable crystals of **8**, **12**, **19**, and **26** were obtained at room temperature from diffusion of n-pentane into the respective dichloromethane or chloroform solutions. The solid-state structures together with selected bond lengths (Å) and angles (°) are presented in Figures 2–4. The crystallographic data are given in Table 1. While complexes **8** and **26** crystallize in the monoclinic space group $P2_1/n$, compound **12** is found in the monoclinic space group $P2_1/a$, and **19** crystallizes in the triclinic space group $P\bar{1}$. In the solid-state structure of **8**, a part of the molecule is disordered and has been refined to split occupancies of 0.50/0.50 (I1, P3 and C43–C59). In the packing network, phenyl rings are found close together, but due to the disorder (0.50/0.50) no intermolecular contact is present. There are two independent molecules per asymmetric unit found in **12**, of which only

Table 1. Crystal and intensity collection data for **8**, **12**, and **19**.

	8	**12**	**19**·4 CH_2Cl_2
formula	$C_{59}H_{46}FeIP_3Ru$	$C_{86}H_{74}N_4O_6P_2Re_2$	$C_{96}H_{87}Cl_{10}FeN_2O_3P_3ReRhRu$
M_r	1131.69	1693.83	2210.12
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/a$	$P\bar{1}$
a [Å]	10.1173(3)	22.4784(10)	14.2510(9)
b [Å]	31.9585(7)	11.5220(5)	18.6426(9)
c [Å]	17.0011(4)	29.1985(10)	19.0689(8)
α [°]	90	90	97.161(4)
β [°]	94.956(2)	99.824(3)	98.847(5)
γ [°]	90	90	109.849(5)
V [Å^3]	5476.5(2)	7451.4(5)	4622.4(4)
ρ_{calcd} [g cm^{-3}]	1.373	1.510	1.588
$F(000)$	2272	3384	2212
crystal size [mm^3]	0.1×0.08×0.02	0.7×0.4×0.1	0.4×0.3×0.2
Z	4	4	2
μ [mm^{-1}]	1.227	3.346	2.186
Θ range [°]	2.82 to 26.00	3.02 to 25.00	2.89 to 24.00
index ranges	$-12\leq h\leq 12$	$-26\leq h\leq 26$	$-16\leq h\leq 16$
	$-39\leq k\leq 39$	$-13\leq k\leq 13$	$-21\leq k\leq 21$
	$-20\leq l\leq 20$	$-34\leq l\leq 34$	$-21\leq l\leq 21$
reflns collected	50382	48673	30066
independent reflns	10712	12547	13556
R(int)	0.0947	0.0248	0.0652
data/restraints/parameters	10712/443/748	12547/0/901	13556/0/1063
GOF on F^2	1.033	1.148	0.934
$R1$[a]/$wR2$[a] [$I\geqq 2\sigma(I)$]	0.0771/0.1948	0.0382/0.0845	0.0509/0.1202
$R1$[a]/$wR2$[a] (all data)	0.1420/0.2249	0.0515/0.0875	0.0902/0.1317
largest peak/hole [e Å^{-3}]	2.222/−0.781	2.629/−1.678	1.844/−1.564

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

one is depicted in Figure 3. The difference between these two molecules is revealed by a different orientation of the alkynyl ligand formed by rotation around the acetylide unit.

Complexes **8** and **19** contain a {(η^2-dppf)(η^5-C_5H_5)Ru}–acetylide building block with Ru1 in a pseudo-tetrahedral surrounding. The 1,1′-bis(diphenylphosphino)ferrocene unit is in an eclipsed geometry (**8**: 2.09(29)°; **19**: 3.76(16)°), and the cyclopentadienyl rings are inclined at an angle of 6.56(49)° (**8**) and 2.10(28)° (**19**). Notable is the dppf bite angle P-Ru-P which is with 96.90(8)° (**8**) and 98.59(8)° (**19**) slightly smaller than those ones found in [{(Ph_3P)$_2$(η^5-C_5H_5)Ru}–σ-acetylide] complexes (99.01(6)–101.17(7)°), but similar to related [{(η^2-dppf)(η^5-C_5H_5)Ru}-acetylide] systems.[23] The ruthe-

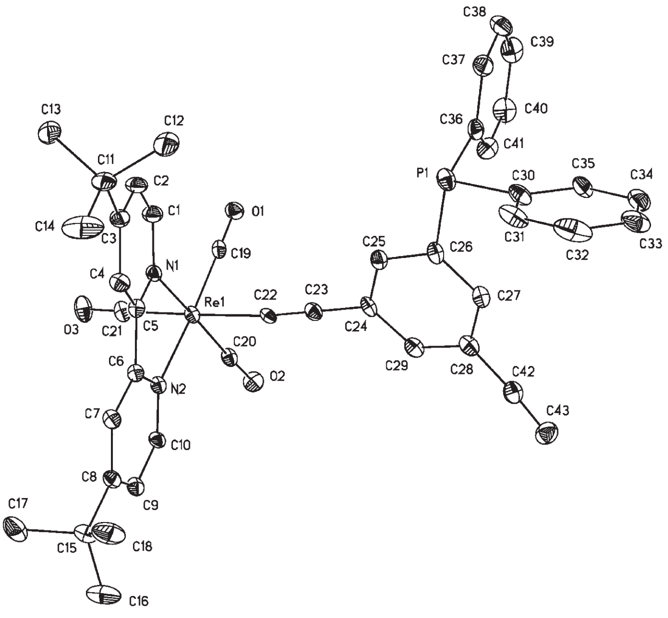


Figure 3. ORTEP drawing of **12**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Re1–N1 2.158(5), Re1–N2 2.162(5), Re1–C19 1.903(7), Re1–C20 1.915(6), Re1–C21 1.954(7), C19–O1 1.149(7), C20–O2 1.152(7), C21–O3 1.144(8), Re1–C22 2.121(6), C22–C23 1.212(9), C42–C43 1.182(10); N1-Re1-N2 73.92(18), Re1-C22-C23 174.7(5), C22-C23-C24 179.7(8), C28-C42-C43 175.8(8), C26-P1-C30 102.7(3), C26-P1-C36 100.5(3), C30-P1-C36 101.8(3).

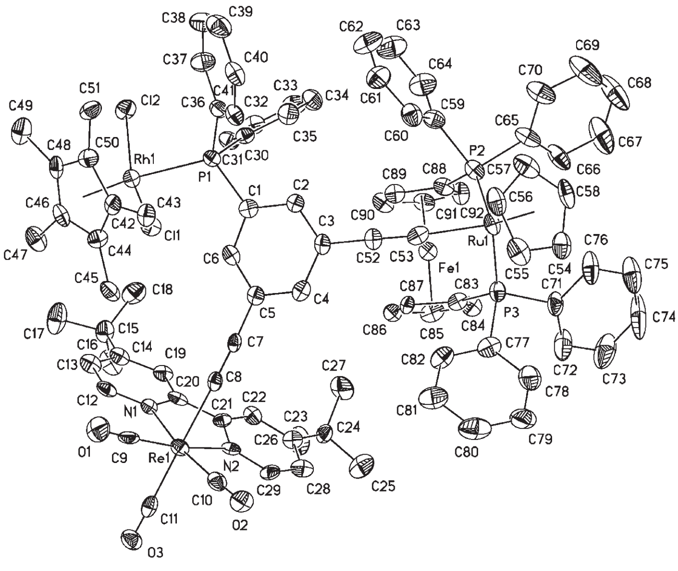


Figure 4. ORTEP drawing of **19**. Thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms and four dichloromethane molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Re1–N1 2.180(6), Re1–N2 2.173(7), Re1–C9 1.919(10), Re1–C10 1.915(9), Re1–C11 1.960(10), Re1–C8 2.123(9), C7–C8 1.209(11), Ru1–P2 2.253(2), Ru1–P3 2.266(2), Ru1–D1 1.881(4), Ru1–C53 2.004(9), C52–C53 1.213(11), Rh1–P1 2.334(2), Rh1–Cl1 2.406(2), Rh1–Cl2 2.381(2), Rh1–D2 1.810(4), Fe1–D3 1.648(4), Fe1–D4 1.647(4); N1-Re1-N2 75.2(2), Re1-C8-C7 176.5(7), C5-C7-C8 176.7(8), P2-Ru1-P3 98.59(8), Ru1-C53-C52 175.7(7), C3-C52-C53 169.7(8), C1-P1-C30 104.1(4), C1-P1-C36 105.9(4), C30-P1-C36 102.1(4), Cl1-Rh1-Cl2 93.23(8), Cl1-Rh1-P1 92.94(8), Cl2-Rh1-P1 87.56(8) (D1 = centroid of C_5H_5; D2 = centroid of C_5Me_5; D3 = centroid of C83–C87; D4 = centroid of C88–C92).

nium–phosphorus and ruthenium–carbon distances are as expected and are in accordance with those found in related complexes.[22,23] The ruthenium–σ-acetylide unit is essentially linear with angles between 168.5(7)° and 175.7(7)° and the distance of the C≡C bond is with 1.198(11) (**8**) and 1.213(11) Å (**19**) typical for terminal metal σ-coordinated carbon–carbon triple bonds.[22,23]

The structures of complexes **12** and **19** show a slightly distorted octahedral geometry around Re1 with three facial arranged carbonyl ligands. The Re−C≡C−C units are as expected essentially linear with bond angles of 174.7(5)–179.7(8)° and C≡C distances typical for metal–alkynyl systems.[6b,16] The Re1−C22 (2.121(6) Å) (**12**) and Re1−C8 (2.123(9) Å) (**19**) bonds are somewhat longer when compared to the other Re−CO separations (1.903(7)–1.960(10) Å) and are indicative for little or no significant metal-to-ligand π-back-bonding to the acetylide unit. Similar Re−C bond lengths are reported for related tricarbonyldiiminealkynylrhenium(I) complexes.[6b,16] In both compounds the N1-Re1-N2 bond angles (**12**, 73.92(18)°; **19**, 75.2(2)°) are less than 90°, as required by the bite distance exerted by the steric demand of the chelating bipyridine ligand.

Coordination of the diphenylphosphino group to $\{RhCl_2(\eta^5\text{-}C_5Me_5)\}$ in complex **19** results in a tetrahedral surrounded phosphorus atom, which in turn slightly increases the C-P-C angles. The coordination sphere around the rhodium(III) ion shows noticeable deformations, which apparently results from the steric demand of the phosphine building block.

All other bond lengths and angles require no further discussion because they agree well with those parameters described for related transition-metal complexes.[16,22,23,26]

The structure of the transmetallation product **26** in the solid state was determined (Supporting Information). The main structural feature is the distorted octahedral geometry around Re1 with three carbonyl ligands arranged in a facial fashion as typical for Re^I–tricarbonyl–diimine systems.[6b,16] In the solid state, the molecules of complex **26** are involved in π–π interactions, including all pyridine rings, and, hence, 2D layers along the crystallographic *b* and *c* axes are formed (Supporting Information).

Conclusion

This report describes the synthesis of a series of heteromultimetallic complexes featuring two, three, four, five, or even six different transition metals, including titanium, molybdenum, rhenium, iron, ruthenium, rhodium, copper, and gold, which are connected by carbon-rich organic bridging units based on the 1,3-bis(ethynyl)-5-diphenylphosphinobenzene core. The consecutive synthesis procedure allowed the straightforward preparation of a series of such complexes that should enable us to systematically develop the field of heteromultimetallic molecules, which is up to now only rarely investigated. Complex $[1\text{-}\{(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)RuC{\equiv}C\}\text{-}3\text{-}\{(tBu_2bpy)(CO)_3ReC{\equiv}C\}\text{-}5\text{-}\{PPh_2\text{-}AuC{\equiv}C\text{-bpy}(\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu)\}C_6H_3][PF_6]$ is the first example of a transition-metal system containing six different metals linked by π-conjugated organic units. X-ray structure analyses show the solid-state structure of four representative molecules.

Experimental Section

General procedure: 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 over sodium/benzophenone ketyl; dichloromethane was purified by distillation over calcium hydride. Amines were distilled over potassium hydroxide. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations.

Measurements: Infrared spectra were recorded with a Perkin Elmer FTIR spectrometer Spectrum 1000. NMR spectra were recorded with a Bruker Avance 250 spectrometer (^{1}H NMR at 250.12 MHz and $^{13}C\{^1H\}$ NMR at 62.86 MHz) in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane ($\delta=0.00$ ppm) with the solvent as the reference signal ($CDCl_3$: ^{1}H NMR, $\delta=7.26$ ppm; $^{13}C\{^1H\}$ NMR, $\delta=77.16$ ppm).[31] $^{31}P\{^1H\}$ NMR spectra were recorded at 101.255 MHz in $CDCl_3$ with $P(OMe)_3$ as an external standard ($\delta=139.0$ ppm, relative 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 Inorganic Chemistry and partly by the Institute of Organic Chemistry, Chemnitz, Technical University.

Materials: Trimethylsilylacetylene,[32] 1,3-diiodo-5-trimethylsilylethynyl benzene (**4**),[5j] $[(tBu_2bpy)(CO)_3ReCl]$ (**17**),[16b] $[(tBu_2bpy)(CO)_3ReC{\equiv}CH]$ (**9**),[33] $[(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)RuCl]$ (**7**),[34] 1,3-dibromo-5-diphenylphosphino benzene (**13**),[35] $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (**18**),[36] $[(Et_2S)_2PtCl_2]$ (**20**),[37] [(tht)AuCl] (**22**),[38] 5-ethynyl-2,2′-bipyridyl (**23**),[39] $[(nbd)Mo(CO)_4]$ (**27**)[40] and $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu(N{\equiv}CMe)][PF_6]$ (**29**)[41] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

Preparation of 1-trimethylsilylethynyl-3-iodo-5-diphenylphosphinobenzene (5): *n*-Butyllithium (2.20 mL, 1.6 M in *n*-hexane, 3.52 mmol) was slowly added to a solution of compound **4** (1.50 g 3.52 mmol) in diethyl ether (60 mL) at −80 °C. The reaction mixture was stirred for 60 min at this temperature. Then chlorodiphenylphosphine (0.90 g, 4.08 mmol) was slowly added with a syringe and stirring was continued for 10 min at −80 °C. After warming the reaction solution to room temperature over 30 min with stirring, it was filtered through a pad of Celite and all volatile materials were removed from the filtrate to give a clear viscous oil which was purified by column chromatography on silica gel. Complex **5** was eluted with petroleum ether/diethyl ether (10:1 v/v). After removal of the solvents using an oil-pump vacuum, a colorless solid remained. Yield: 1.38 g (2.85 mmol, 81 %); m.p. 124 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta=0.22$ (s, 9H; $SiMe_3$), 7.27–7.40 (m, 10H (C_6H_5) + 1H (C_6H_3)), 7.50 (dpseudo-t, $J_{HP}=6.4$ Hz, $J_{HH}=1.5$ Hz, 1H; C_6H_3), 7.79 ppm (pseudo-t, $J_{HH}=1.5$ Hz, 1H; C_6H_3); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta=-0.1$ ($SiMe_3$), 94.5 (d, $J_{CP}=6.2$ Hz, Ci/C_6H_3), 96.6 (C≡C), 103.0 (C≡C), 125.4 (d, $J_{CP}=4.3$ Hz, Ci/C_6H_3), 128.9 (d, $J_{CP}=7.2$ Hz, CH/C_6H_5), 129.3 (CH/C_6H_5), 134.0 (d, $J_{CP}=20.1$ Hz, CH/C_6H_5), 136.0 (d, $J_{CP}=21.4$ Hz, CH/C_6H_3), 136.0 (d, $J_{CP}=11$ Hz, Ci/C_6H_5), 140.8 (CH/C_6H_3), 140.8 (d, $J_{CP}=17.8$ Hz, Ci/C_6H_3), 141.9 ppm (d, $J_{CP}=18.9$ Hz, CH/C_6H_3); $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C): $\delta=-5.5$ ppm (s, PPh_2); IR (KBr): $\tilde{\nu}=2163\ cm^{-1}$ (m, C≡C); elemental analysis calcd (%) for $C_{23}H_{22}IPSi$ (484.39): C 57.03, H 4.58; found: C 57.43, H 4.87.

Preparation of 1-ethynyl-3-iodo-5-diphenylphosphinobenzene (6): $[nBu_4N]F$ (1 M in THF, 1.70 mL, 1.70 mmol) was added to a solution of compound **5** (0.75 g, 1.55 mmol) in THF (30 mL). The dark solution was stirred for 1 h at 25 °C and afterwards the solvent was removed under reduced pressure. The residue was purified by column chromatography on alumina using a mixture of petroleum ether/diethyl ether (2:1, v/v) as eluent. After removing all volatiles under reduced pressure, compound **6** was obtained as a colorless solid. Yield: 0.49 g (1.19 mmol, 77 %); m.p. 136 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 3.08$ (s, 1H; $=CH$), 7.27–7.40 (m, 10H (C_5H_6) + 1H (C_6H_3)), 7.58 (dpseudo-t, $J_{HP} = 6.6$ Hz, $J_{HH} = 1.5$ Hz, 1H; C_6H_3), 7.80 ppm (pseudo-t, $J_{HH} = 1.5$ Hz, 1H; C_6H_3); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 79.1$ ($C\equiv CH$), 81.8 ($C\equiv CH$), 94.5 (d, $J_{CP} = 6.5$ Hz, Ci/C_6H_3), 124.4 (d, $J_{CP} = 6.7$ Hz, Ci/C_6H_3), 128.9 (d, $J_{CP} = 7.2$ Hz, CH/C_6H_5), 129.4 (CH/C_6H_5), 133.9 (d, $J_{CP} = 20$ Hz, CH/C_6H_5), 135.8 (d, $J_{CP} = 11$ Hz, Ci/C_6H_5), 136.1 (d, $J_{CP} = 19.2$ Hz, CH/C_6H_3), 140.8 (CH/C_6H_3), 141.1 (d, $J_{CP} = 18.1$ Hz, Ci/C_6H_3), 142.3 ppm (d, $J_{CP} = 20.8$ Hz, CH/C_6H_3); $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C): $\delta = -5.7$ ppm (s, PPh_2); IR (KBr): $\tilde{\nu} = 3288$ cm^{-1} (s, $\equiv C{-}H$); elemental analysis calcd (%) for $C_{20}H_{14}IP$ (412.2): C 58.28, H 3.42; found: C 58.81, H 3.56.

Preparation of 1,3-bis(trimethylsilylethynyl)-5-diphenylphosphinobenzene (14): Trimethylsilylacetylene (0.75 g, 7.65 mmol), [$(PPh_3)_2PdCl_2$] (80 mg), and CuI (40 mg) were added To compound **13** (0.80 g, 1.90 mmol) dissolved in degassed diisopropylamine (40 mL). The resulting reaction mixture was heated to 50 °C and stirred 48 h. After cooling to 25 °C, the reaction mixture was filtered through a pad of Celite and all volatiles were removed under reduced pressure. The remaining material was subjected to column chromatography on silica gel using a mixture of petroleum ether/diethyl ether (5:1, v/v) as eluent. Compound **14** was isolated as a colorless solid after evaporation of all volatile materials under reduced pressure. Yield: 650 mg (1.430 mmol, 75 %); m.p. 132 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 0.25$ (s, 18H; $SiMe_3$), 7.30–7.40 (m, 10H; C_6H_5), 7.41 (dd, $J_{HP} = 7$ Hz, $J_{HH} = 1.6$ Hz, 2H; C_6H_3), 7.62 ppm (t, $J_{HH} = 1.6$ Hz, 1H; C_6H_3); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 0.0$ ($SiMe_3$), 95.7 ($C\equiv C$), 103.9 ($C\equiv C$), 123.8 (d, $J_{CP} = 7.7$ Hz, Ci/C_6H_3), 128.8 (d, $J_{CP} = 7$ Hz, CH/C_6H_5), 129.1 (CH/C_6H_5), 133.9 (d, $J_{CP} = 19.8$ Hz, CH/C_6H_5), 135.9 (CH/C_6H_3), 136.2 (d, $J_{CP} = 10.9$ Hz, Ci/C_6H_5), 136.6 (d, $J_{CP} = 20.2$ Hz, CH/C_6H_3), 138.5 ppm (d, $J_{CP} = 15.2$ Hz, Ci/C_6H_3); $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C): $\delta = -6.2$ ppm (s, PPh_2); IR (KBr): $\tilde{\nu} = 2161$ cm^{-1} (m, $C\equiv C$); elemental analysis calcd (%) for $C_{28}H_{31}PSi_2$ (454.70): C 73.96, H 6.87; found: C 73.82, H 6.78.

Preparation of 1,3-($C\equiv C{-}C(CH_3)_2OH)_2$-5-diphenylphosphinobenzene (16): 2-Methyl-3-butyn-2-ol (0.64 g, 7.61 mmol),[$(PPh_3)_2PdCl_2$] (80 mg), and CuI (40 mg) were added to compound **13** (0.80 g, 1.90 mmol) dissolved in degassed diisopropylamine (50 mL) . The resulting reaction mixture was refluxed for 20 h. After cooling to 25 °C, it was filtered through a pad of Celite, and all volatiles were removed under reduced pressure. The remaining material was purified by column chromatography on silica gel using a mixture of petroleum ether/diethyl ether (1:5, v/v) as eluent. After removing all solvents under reduced pressure, compound **16** was obtained as a colorless solid. Yield: 690 mg (1.618 mmol, 85 %); m.p. 133 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 1.55$ (s, 12H; CH_3), 2.44 (brs, 2H; OH), 7.24–7.38 (m, 10H (C_6H_5) + 2H (C_6H_3)), 7.45 ppm (t, $J_{HH} = 1.6$ Hz, 1H; C_6H_3); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 31.5$ (CH_3), 65.6 (C-OH), 81.1 ($C\equiv C$), 95.1 ($C\equiv C$), 123.4 (d, $J_{CP} = 7.7$ Hz, Ci/C_6H_3), 128.8 (d, $J_{CP} = 6.8$ Hz, CH/C_6H_5), 129.2 (CH/C_6H_5), 133.9 (d, $J_{CP} = 19.6$ Hz, CH/C_6H_5), 135.2 (CH/C_6H_3), 136.07 (d, $J_{CP} = 19.1$ Hz, CH/C_6H_3), 136.13 (d, $J_{CP} = 11.1$ Hz, Ci/C_6H_5), 138.5 ppm (d, $J_{CP} = 14.9$ Hz, Ci/C_6H_3); $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C): $\delta = -6.3$ ppm (s, PPh_2); IR (KBr): $\tilde{\nu} = 3341$ cm^{-1} (s, O–H); elemental analysis calcd (%) for $C_{28}H_{27}O_2P$ (426.49): C 78.85, H 6.38; found: C 78.38, H 6.74.

Preparation of 1,3-bis(ethynyl)-5-diphenylphosphinobenzene (15)

*Preparation from **14***: [nBu_4N]F (1.0 M in THF, 1.5 mL, 1.50 mmol) was slowly added to a solution of **14** (600 mg, 1.32 mmol) in THF (30 mL). The resulting reaction solution was stirred for 1 h at 25 °C. Afterwards all volatiles were removed under reduced pressure, and the remaining material was purified by column chromatography on silica gel. Eluting with a mixture of diethyl ether/petroleum ether (1:1, v/v) gave compound **15** as a colorless solid. Yield: 360 mg (1.160 mmol, 88 %).

*Preparation from **16***: KOH (420 mg, 7.50 mmol) was added to **16** (640 mg 1.50 mmol) dissolved in toluene (30 mL), and the resulting reaction mixture was heated to 80 °C for 5 h. After cooling to 25 °C it was filtered through a pad of Celite and all volatiles were removed under reduced pressure. The remaining orange oil was subjected to column chromatography on silica gel using a mixture of diethyl ether/petroleum ether (1:1, v/v) as eluent. After removal of all volatile materials under reduced pressure compound **15** could be isolated as a colorless solid. Yield: 320 mg (1.031 mmol, 69 %).

*Data for **15***: M.p. 143 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 3.08$ (s, 2H; $\equiv CH$), 7.30–7.42 (m, 10H; C_6H_5), 7.45 (dd, $J_{HP} = 7.1$ Hz, $J_{HH} = 1.6$ Hz, 2H; C_6H_3), 7.63 ppm (t, $J_{HH} = 1.6$ Hz, 1H; C_6H_3); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 78.7$ ($C\equiv CH$), 82.4 ($C\equiv CH$), 122.8 (d, $J_{CP} = 7.4$ Hz, Ci/C_6H_3), 128.8 (d, $J_{CP} = 7.2$ Hz, CH/C_6H_5), 129.3 (CH/C_6H_5), 133.9 (d, $J_{CP} = 20$ Hz, CH/C_6H_5), 135.8 (CH/C_6H_3), 136.0 (d, $J_{CP} = 10.8$ Hz, Ci/C_6H_5), 137.1 (d, $J_{CP} = 19.8$ Hz, CH/C_6H_3), 139.0 ppm (d, $J_{CP} = 15.5$ Hz, Ci/C_6H_3); $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C): $\delta = -6.4$ ppm (s, PPh_2); IR (KBr): $\tilde{\nu} = 3289$ (s, $\equiv C{-}H$); elemental analysis calcd (%) for $C_{22}H_{15}P$ (310.33): C 85.15, H 4.87; found: C 84.80, H 5.02.

Preparation of [1-{(η^2-dppf)(η^5-C_5H_5)$RuC\equiv C$}-3-I-5-(PPh_2)C_6H_3] (8): Complex [(η^2-dppf)(η^5-C_5H_5)RuCl] (200 mg, 0.265 mmol) was heated to reflux in methanol (30 mL) for 20 min to give a yellow orange suspension to which a single portion of **6** (130 mg, 0.315 mmol) was added. The reaction mixture was then refluxed for 30 min. During that time it became a clear orange-red solution, which afterwards was cooled to room temperature. Addition of two equivalents (10 mg) of sodium resulted in the rapid precipitation of a yellow solid. Stirring was continued for 1 h, and then all volatile materials were removed under reduced pressure. The residue was filtered through a pad of Celite using dichloromethane as solvent. The solvent was removed, and the remaining material was purified by column chromatography on silica gel using a mixture of petroleum ether/THF (4:1, v/v) as eluent. After removal of all volatiles under reduced pressure, compound **8** could be isolated as a yellow solid. Yield: 230 mg (0.203 mmol, 76 %); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 3.98$ (dpseudo-t, $J_{HP} = 1.2$ Hz, $J_{HH} = 2.4$ Hz, 2H; C_5H_4), 4.10 (brs, 2H; C_5H_4), 4.29 (s, 5H; C_5H_5), 4.30 (brs, 2H; C_5H_4), 5.12 (brs, 2H; C_5H_4), 7.14–7.57 (m, 26H (C_6H_5) + 3H (C_6H_3))), 7.72–7.81 ppm (m, 4H; C_6H_5); $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25 °C): $\delta = 68.2$ (pseudo-t, $J_{CP} = 2.4$ Hz, CH/C_5H_4), 71.4 (pseudo-t, $J_{CP} = 2.8$ Hz, CH/C_5H_4), 73.2 (pseudo-t, $J_{CP} = 2.0$ Hz, CH/C_5H_4), 76.6 (pseudo-t, $J_{CP} = 4.8$ Hz, CH/C_5H_4), 84.9 (pseudo-t, $J_{CP} = 2.4$ Hz, C_5H_5), 88.4 (pseudo-t, $J_{CP} = 24.3$ Hz, Ci/C_5H_4), 95.1 (d, $J_{CP} = 8.8$ Hz, C-I/C_6H_3), 111.4 ($RuC\equiv C$), 124.8 (t, $J_{CP} = 25.0$ Hz, $RuC\equiv C$), 127.2 (pseudo-t, $J_{CP} = 4.8$ Hz, CH/C_6H_5(dppf)), 127.4 (pseudo-t, $J_{CP} = 4.8$ Hz, CH/C_6H_5(dppf)), 128.6 (d, $J_{CP} = 7.0$ Hz, CH/C_6H_5), 128.8 (CH/C_6H_5(dppf)), 128.9 (CH/C_6H_5), 129.2 (CH/C_6H_5(dppf)), 132.4 (d, $J_{CP} = 6.3$ Hz, Ci/C_6H_3), 133.8 (pseudo-t, $J_{CP} = 5.7$ Hz, CH/C_6H_5(dppf)), 133.9 (d, $J_{CP} = 19.8$ Hz, CH/C_6H_5), 134.2 (pseudo-t, $J_{CP} = 5.7$ Hz, CH/C_6H_5(dppf)), 134.9 (d, $J_{CP} = 16.8$ Hz, CH/C_6H_3), 136.8 (d, $J_{CP} = 23.0$ Hz, CH/C_6H_3), 137.2 (d, $J_{CP} = 11.0$ Hz, Ci/C_6H_5), 139.1 (d, $J_{CP} = 14.5$ Hz, Ci/C_6H_3), 140.1 (CH/C_6H_3), 140.8 (pseudo-t, $J_{CP} = 23.0$ Hz, Ci/C_6H_5(dppf)), 141.9 ppm (pseudo-t, $J_{CP} = 22.8$ Hz, Ci/C_6H_5(dppf); $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C): $\delta = -5.1$ (s, PPh_2), 53.7 ppm (s, dppf); IR (KBr): $\tilde{\nu} = 2055$ cm^{-1} (m, $\nu C\equiv CRu$); elemental analysis calcd (%) for $C_{59}H_{46}FeIP_3Ru$ (1131.75): C 62.62, H 4.10; found: C 62.62, H 4.49.

Preparation of [1-($Me_3SiC\equiv C$)-3-{(tBu_2bpy)$(CO)_3ReC\equiv C$}-5-(PPh_2)C_6H_3] (11): [$(PPh_3)_2PdCl_2$] (8 mg) and CuI (4 mg) were added to **9** (130 mg, 0.231 mmol) and **5** (120 mg, 0.248 mmol) dissolved in degassed triethylamine (30 mL). The resulting reaction mixture was heated to reflux overnight. After cooling to 25 °C, all volatiles were removed using an oil-pump vacuum, and the remaining residue was subjected to column chromatography on silica gel using a mixture of diethyl ether/*n*-hexane (1:1, v/v) as eluent. Complex **11** was obtained as a yellow solid. Yield: 70 mg (0.076 mmol, 33 % based on **9**); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 0.15$ (s, 9H; $SiMe_3$), 1.45 (s, 18H; *t*Bu), 6.90–7.03 (m, 3H; C_6H_3), 7.14–7.30 (m, 10H; C_6H_5), 7.44 (dd, $J_{H5H6} = 6$ Hz, $J_{H5H3} = 1.9$ Hz, *H5*/tBu_2bpy), 8.07 (d, $J_{H3H5} = 1.9$ Hz, *H3*/tBu_2bpy), 8.94 ppm (d, $J_{H6H5} = 6$ Hz, *H6*/tBu_2bpy); $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C): $\delta = -6.0$ ppm (s, PPh_2); IR (KBr): $\tilde{\nu} = 1900$, 2004 (s, CO), 2088 cm^{-1} (w, $C\equiv CRe$), 2156 (w, $C\equiv CSi$); elemental analysis calcd (%) for $C_{46}H_{46}N_2O_3PReSi$ (920.15): C 60.04, H 5.04, N 3.04; found: C 59.67, H 5.15, N 2.89.

Preparation of [1-($HC\equiv C$)-3-{(tBu_2bpy)$(CO)_3ReC\equiv C$}-5-(PPh_2)C_6H_3] (12)

*Preparation from **11***: [nBu$_4$N]F (1.0 M in THF, 0.1 mL, 0.10 mmol) was added to a solution of **11** (60 mg 0.065 mmol) in THF (15 mL). After 1 h of stirring at 25 °C, all volatiles were removed under vacuum, and the residual material was purified by column chromatography on silica gel using a mixture of diethyl ether/n-hexane (2:1, v/v) as eluent. Complex **12** was obtained as a yellow solid. Yield: 45 mg (0.053 mmol, 82 %).

*Preparation from **15***: LiN(SiMe$_3$)$_2$ (160 mg, 0.956 mmol) was added to a cooled (0 °C) solution of (**15**) (300 mg, 0.967 mmol) in toluene (50 mL). The resulting reaction mixture was stirred for 3 h at 0 °C. Afterwards **17** (200 mg, 0.348 mmol) was added, and the reaction mixture was refluxed for 5 h. After cooling to room temperature, the toluene was removed by rotary evaporation, and the residue was subjected to column chromatography on silica gel. A diethyl ether/n-hexane mixture of ratio 2:1 (v/v) was used as eluent, eluting first the excess of 1,3-bis(ethynyl)-5-diphenylphosphinobenzene followed by compound **12** and finally unreacted **17**. Complex **12** was obtained as a yellow powder. Yield: 140 mg (0.165 mmol, 47 % based on **17**). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.45 (s, 18H; tBu), 2.94 (s, 1H; $\equiv$CH), 6.93 (dpseudo-t, $^3J_{\mathrm{HP}}$ = 6.5 Hz, $^4J_{\mathrm{HH}}$ = 1.6 Hz, 1H; C$_6H_3$), 6.95 (pseudo-t, $^4J_{\mathrm{HH}}$ = 1.6 Hz, 1H; C$_6H_3$), 7.07 (dpseudo-t, $^3J_{\mathrm{HP}}$ = 9 Hz, J_{HH} = 1.6 Hz, 1H; C$_6H_3$), 7.16–7.31 (m, 10H; C$_6H_5$), 7.44 (dd, $^3J_{\mathrm{H5H6}}$ = 5.8 Hz, $^4J_{\mathrm{H5H3}}$ = 1.9 Hz, 2H; *H5*/tBu$_2$bpy), 8.08 (d, J_{H3H5} = 1.9 Hz, 2H; *H3*/tBu$_2$bpy), 8.95 ppm (d, J_{H6H5} = 5.8 Hz, 2H; *H6*/tBu$_2$bpy); ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$, 25 °C): δ = 30.5 (CH$_3$), 35.6 (C(CH$_3$)$_3$), 76.9 (C$\equiv$CH), 83.6 ($C\equiv$CH), 104.6 (ReC$\equiv$C), 119.4 (*CH*/tBu$_2$bpy), 121.6 (d, J_{CP} = 6.8 Hz, *Ci*/C$_6$H$_3$), 124.2 (*CH*/tBu$_2$bpy), 128.3 (d, J_{CP} = 9.5 Hz, *Ci*/C$_6$H$_3$), 128.6 (d, J_{CP} = 7 Hz, *CH*/C$_6$H$_5$), 128.8 (*CH*/C$_6$H$_5$), 133.1 (d, J_{CP} = 15.8 Hz, *CH*/C$_6$H$_3$), 133.8 (d, J_{CP} = 19.6 Hz, *CH*/C$_6$H$_5$), 136.1 (*CH*/C$_6$H$_3$), 136.6 (d, J_{CP} = 9.5 Hz, *Ci*/C$_6$H$_5$), 136.8 (d, J_{CP} = 12.4 Hz, *Ci*/C$_6$H$_3$), 137.3 (d, J_{CP} = 24.9 Hz, *CH*/C$_6$H$_3$), 152.9 (*CH*/tBu$_2$bpy), 155.8 (*Ci*/tBu$_2$bpy), 162.9 (*Ci*/tBu$_2$bpy), 192.9 (CO), 198.3 ppm (CO); ^{31}P{^{1}H} NMR (101.25 MHz, CDCl$_3$, 25 °C): δ = −6.3 ppm (s, PPh$_2$); IR (KBr): $\tilde{\nu}$ = 1884, 1901, 2004 (s, CO), 2092 (w, C$\equiv$CRe), 3299 cm^{-1} (m, $\equiv$C−H); elemental analysis calcd (%) for $C_{43}H_{38}N_2O_3PRe$ (847.97): C 60.91, H 4.52, N 3.30; found: C 60.76, H 4.84, N 3.18.

Preparation of [1-{(η^2-dppf)(η^5-C$_5$H$_5$)RuC$\equiv$C}-3-{(tBu$_2$bpy)(CO)$_3$ReC$\equiv$C}-5-(PPh$_2$)C$_6$H$_3$] (10)

*Preparation from **8***: [(PPh$_3$)$_2$PdCl$_2$] (5 mg) and CuI (3 mg) were added to **8** (150 mg, 0.133 mmol) and **9** (75 mg, 0.133 mmol) dissolved in a degassed mixture of THF (10 mL) and triethylamine (20 mL). The reaction mixture was heated to reflux for 8 h. Afterwards all volatiles were removed using an oil pump vacuum, and the residual material was subjected to column chromatography over alumina. Using diethyl ether as eluent gave first unreacted starting materials, followed by the homo-coupled product, and finally an orange red band from which complex **10** could be isolated as an orange solid. Yield: 35 mg (0.022 mmol, 17 %).

*Preparation from **12**—method A*: [NH$_4$]PF$_6$ (20 mg, 0.12 mmol) were added to **7** (80 mg, 0.11 mmol) and **12** (100 mg, 0.12 mmol) dissolved in dichloromethane and methanol (30 mL, ratio 1:1) . The reaction solution was stirred for 5 h at 25 °C, followed by the addition of DBU (25 mg, 0.164 mmol). Stirring was continued for 1 h. Then all volatiles were removed using an oil pump vacuum, and the residue was purified by column chromatography on silica gel. Excess **12** was removed with toluene/dichloromethane (10:1, v/v) and compound **10** was eluted with toluene/THF (20:1, v/v). After precipitation from a concentrated solution in dichloromethane by the addition of n-hexane, complex **10** was isolated as an orange solid. Yield: 70 mg (0.045 mmol, 41 % based on **7**).

*Preparation from **12**—method B*: [NH$_4$]PF$_6$ (20 mg, 0.12 mmol) and KOtBu (15 mg, 0.13 mmol) were simultaneously added to **7** (80 mg, 0.11 mmol) and **12** (100 mg, 0.12 mmol) dissolved in dichloromethane/methanol (1:1, 30 mL). The resulting solution was stirred for 4 h at 25 °C until compound **7** was completely consumed, which was proven by ^{31}P{^{1}H} NMR spectroscopy. Subsequently, all volatiles were removed under reduced pressure. The workup method was identical to that described above. Yield: 110 mg (0.070 mmol, 66 % based on **7**).

*Data for **10***: ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.42 (s, 18H; tBu), 3.90 (dpseudo-t, J_{HP} = 1.3 Hz, J_{HH} = 2.4 Hz, 2H; C$_5H_4$), 3.98 (brs, 2H; C$_5H_4$), 4.20 (s, 5H; C$_5H_5$), 4.22 (brs, 2H; C$_5H_4$), 5.12 (brs, 2H; C$_5H_4$), 6.74 (dpseudo-t, J_{HP} = 10.7 Hz, J_{HH} = 1.6 Hz, 1H; C$_6H_3$), 6.80 (dpseudo-t, J_{HP} = 7.1 Hz, J_{HH} = 1.6 Hz, 1H; C$_6H_3$), 7.10–7.52 (m, 26H (C$_6H_5$) + 1H (C$_6H_3$)), 7.42 (dd, $^3J_{\mathrm{H5H6}}$ = 5.8 Hz, $^4J_{\mathrm{H5H3}}$ = 1.9 Hz, 2H; *H5*/tBu$_2$bpy), 7.65–7.74 (m, 4H; C$_6H_5$), 8.06 (d, $^4J_{\mathrm{H3H5}}$ = 1.9 Hz, 2H; *H3*/tBu$_2$bpy), 8.98 ppm (d, $^3J_{\mathrm{H6H5}}$ = 5.8 Hz, 2H; *H6*/tBu$_2$bpy); ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$, 25 °C): δ = 30.5 (CH$_3$), 35.6 (C(CH$_3$)$_3$), 67.7 (pseudo-t, J_{CP} = 2.4 Hz, *CH*/C$_5$H$_4$), 71.5 (pseudo-t, J_{CP} = 2.8 Hz, *CH*/C$_5$H$_4$), 72.9 (pseudo-t, J_{CP} = 2.0 Hz, *CH*/C$_5$H$_4$), 76.9 (pseudo-t, J_{CP} = 4.8 Hz, *CH*/C$_5$H$_4$), 84.7 (pseudo-t, J_{CP} = 2.4 Hz, C$_5$H$_5$), 88.5 (pseudo-t, J_{CP} = 24.3 Hz, *Ci*/C$_5$H$_4$), 105.7 (ReC$\equiv$C), 112.2 (RuC$\equiv$C), 117.3 (t, J_{CP} = 26.5 Hz, Ru$C\equiv$C), 119.3 (*CH*/tBu$_2$bpy), 124.1 (*CH*/tBu$_2$bpy), 125.2–129.2 (C$_6$H$_5$ + C$_6$H$_3$), 132.2–135.0 (C$_6$H$_5$ + C$_6$H$_3$), 138.1 (d, J_{CP} = 11.1 Hz, *Ci*/C$_6$H$_5$), 140.8 (pseudo-t, J_{CP} = 21.0 Hz, *Ci*/C$_6$H$_5$(dppf)), 142.3 (pseudo-t, J_{CP} = 22.8 Hz, *Ci*/C$_6$H$_5$(dppf), 153.0 (*CH*/tBu$_2$bpy), 155.8 (*Ci*/tBu$_2$bpy), 162.7 (*Ci*/tBu$_2$bpy), 193.1 (CO), 198.6 ppm(CO); ^{31}P{^{1}H} NMR (101.25 MHz, CDCl$_3$, 25 °C): δ = −5.3 (s, PPh$_2$), 53.7 ppm (s, dppf); IR (KBr): $\tilde{\nu}$ = 1892, 1901, 2003 (s, CO), 2065 cm^{-1} (m, C$\equiv$CRu); MS (ESI-TOF): m/z: 1568.9 [M+H]$^+$, 749.3 [(C$_5$H$_5$)(dppf)Ru(CO)]$^+$; elemental analysis calcd (%) for $C_{82}H_{70}FeN_2O_3P_3ReRu$ (1567.51): C 62.83, H 4.50, N 1.79; found: C 63.33, H 4.91, N 1.50.

Preparation of [1-{(η^2-dppf)(η^5-C$_5$H$_5$)RuC$\equiv$C}-3-{(tBu$_2$bpy)(CO)$_3$ReC$\equiv$C}-5-{PPh$_2$Rh(η^5-C$_5$Me$_5$)Cl$_2$}C$_6$H$_3$] (19): Complex (**10**) (80 mg, 0.051 mmol) was dissolved in dichloromethane (10 mL) and was then added dropwise to **18** (15 mg, 0.024 mmol) dissolved in dichloromethane (10 mL). The resulting red solution was stirred for 1 h at 25 °C. Afterwards, the solvent was reduced in volume to about 3 mL and compound **19** was precipitated by addition of n-hexane (20 mL) and washed with n-hexane (2 × 15 mL) to give an orange red solid. Yield: 78 mg (0.042 mmol, 86 % based on **18**).; ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.34 (d, $^4J_{\mathrm{HRh}}$ = 3.4 Hz, 15H; C$_5Me_5$), 1.42 (s, 18H; tBu), 3.89 (brs, C$_5H_4$), 3.93 (brs, C$_5H_4$), 4.22 (s, C$_5H_5$), 4.23 (brs, C$_5H_4$), 5.03 (brs, C$_5H_4$), 6.99 (dpseudo-t, J_{HP} = 9.5 Hz, J_{HH} = 1.5 Hz, 1H; C$_6H_3$), 7.05–7.56 (m, 22H (C$_6H_5$) + 2H (*H5*/tBu$_2$bpy) + 2H (C$_6H_3$)), 7.64–7.80 (m, 8H; C$_6H_5$), 8.06 (d, J_{HH} = 1.6 Hz, 2H; *H3*/tBu$_2$bpy), 8.99 ppm (d, J_{HH} = 6 Hz, 2H; *H6*/tBu$_2$bpy); ^{31}P{^{1}H} NMR (101.25 MHz, CDCl$_3$, 25 °C): δ = 29.8 (d, J_{PRh} = 144 Hz, RhPPh$_2$), 53.9 ppm (s, dppf); IR (KBr): $\tilde{\nu}$ = 1896, 2003 (s, CO), 2063 cm^{-1} (m, C$\equiv$CRu); MS (ESI-TOF): m/z: 1877.9 [M+H]$^+$, 749.2 [(C$_5$H$_5$)(dppf)Ru(CO)]$^+$; elemental analysis calcd (%) for $C_{92}H_{85}Cl_2FeN_2O_3P_3ReRhRu$ (1876.55): C 58.89, H 4.56, N 1.49; found: C 58.99, H 4.68, N 1.40.

Preparation of *trans*-[{1-[(η^2-dppf)(η^5-C$_5$H$_5$)RuC$\equiv$C]-3-[(tBu$_2$bpy)(CO)$_3$ReC$\equiv$C]-5-(PPh$_2$)C$_6$H$_3$}$_2$PtCl$_2$] (21): A solution of **20** (12 mg, 0.027 mmol) in dichloromethane (20 mL) was treated with **10** (90 mg, 0.057 mmol) and stirred for 2 h at 25 °C. Subsequently, the solvent was reduced in volume to 3 mL and addition of n-hexane (20 mL) caused the precipitation of complex **21**, which was washed with n-hexane (2 × 10 mL) and dried using an oil pump vacuum. Yield: 70 mg (0.021 mmol, 76 % based on **20**); ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.35 (s, 36H; tBu), 3.87 (brs, 4H; C$_5H_4$), 3.96 (brs, 4H; C$_5H_4$), 4.16 (brs, 4H; C$_5H_4$), 4.19 (s, 10H; C$_5H_5$), 5.17 (brs, 4H; C$_5H_4$), 6.76–6.85 (m, 2H; C$_6H_3$), 7.04–7.51 (m, 4H (C$_6H_3$) + 4H (*H5*/tBu$_2$bpy) + 40H (C$_6H_5$)), 7.59–7.75 (m, 20H; C$_6H_5$), 8.01 (d, J_{H3H5} = 1.7 Hz, 4H; *H3*/tBu$_2$bpy), 8.90 ppm (d, J_{H6H5} = 5.8 Hz, 4H; *H6*/tBu$_2$bpy); ^{31}P{^{1}H} NMR (101.25 MHz, CDCl$_3$, 25 °C): δ = 19.1 (s, J_{PPt} = 2643 Hz, PtPPh$_2$), 53.8 ppm (s, dppf); IR (KBr): $\tilde{\nu}$ = 1892, 1903, 2003 (s, CO), 2062 cm^{-1} (m, C$\equiv$CRu); MS (ESI-TOF): m/z: 3401.5 [M+H]$^+$, 749.1 [(C$_5$H$_5$)(dppf)Ru(CO)]$^+$; elemental analysis calcd (%) for $C_{164}H_{140}Cl_2Fe_2N_4O_6P_6PtRe_2Ru_2$ (3401.0): C 57.92, H 4.15, N 1.65; found: C 57.76, H 4.20, N 1.50.

Preparation of [1-{(η^2-dppf)(η^5-C$_5$H$_5$)RuC$\equiv$C}-3-{(tBu$_2$bpy)(CO)$_3$ReC$\equiv$C}-5-(PPh$_2$AuC$\equiv$C-bpy)C$_6$H$_3$] (25): Compound **23** (15 mg, 0.083 mmol) and CuI (1 mg) were added to **22** (20 mg, 0.063 mmol) dissolved in THF (10 mL) and diethylamine (10 mL). The solution was stirred at 25 °C for 30 min. The resulting turbid reaction mixture was filtered using a cannula into a stirred solution of **10** (105 mg, 0.067 mmol) in THF (10 mL) and stirred for 1 h. After removal of all volatiles, the remaining residue was subjected to column chromatography on silica gel. As eluent a mixture of toluene/THF (20:1, v/v) was used. The first orange band contained unreacted **10** and the second band yielded complex **25** as a yellow solid. Yield: 75 mg (0.039 mmol, 62 % based on **22**);

^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.43 (s, 18 H; *t*Bu), 3.92 (dpseudo-t, J_{HP} = 1.1 Hz, J_{HH} = 2.4 Hz, 2 H; C$_5$*H*$_4$), 4.03 (brs, 2 H; C$_5$*H*$_4$), 4.22 (s, 5 H; C$_5$*H*$_5$), 4.24 (brs, 2 H; C$_5$*H*$_4$), 5.02 (brs, 2 H; C$_5$*H*$_4$), 6.78 (dpseudo-t, J_{HP} = 11.8 Hz, J_{HH} = 1.6 Hz, 1 H; C$_6$*H*$_3$), 6.96 (dpseudo-t, J_{HP} = 15.8 Hz, J_{HH} = 1.6 Hz, 1 H; C$_6$*H*$_3$), 7.07–7.52 (m, 26 H (C$_6$*H*$_5$) + 1 H (*H5'*/bpy) + 2 H (*H5*/*t*Bu$_2$bpy) + 1 H (C$_6$*H*$_3$)), 7.63–7.74 (m, 4 H; C$_6$*H*$_5$), 7.80 (ddd, $^{3}J_{\mathrm{H4'H3'}}$ = 7.8 Hz, $^{3}J_{\mathrm{H4'H5'}}$ = 7.8 Hz, $^{4}J_{\mathrm{H4'H6'}}$ = 1.8 Hz, 1 H; *H4'*/bpy), 7.87 (dd, $^{3}J_{\mathrm{H4H3}}$ = 8.2 Hz, $^{4}J_{\mathrm{H4H6}}$ = 2.2 Hz, 1 H; *H4*/bpy), 8.30 (dd, $^{3}J_{\mathrm{H3H4}}$ = 8.2 Hz, $^{5}J_{\mathrm{H3H6}}$ = 0.8 Hz, 1 H; *H3*/bpy), 8.37 (ddd, $^{3}J_{\mathrm{H3'H4'}}$ = 7.8 Hz, $^{4}J_{\mathrm{H3'H5'}}$ = 1.0 Hz, $^{5}J_{\mathrm{H3'H6'}}$ = 1.0 Hz, 1 H; *H3'*/bpy), 8.42 (d, $^{4}J_{\mathrm{H3H5}}$ = 1.7 Hz, 2 H; *H3*/*t*Bu$_2$bpy), 8.66 (ddd, $^{3}J_{\mathrm{H6'H5'}}$ = 4.9 Hz, $^{4}J_{\mathrm{H6'H4'}}$ = 1.8 Hz, $^{5}J_{\mathrm{H6'H3'}}$ = 1.0 Hz, 1 H; *H6'*/bpy), 8.79 (dd, $^{4}J_{\mathrm{H6H4}}$ = 2.2 Hz, $^{5}J_{\mathrm{H6H3}}$ = 0.8 Hz, 1 H; *H6*/bpy), 8.97 ppm (d, $^{3}J_{\mathrm{H6H5}}$ = 6.0 Hz, 2 H; *H6*/*t*Bu$_2$bpy); ^{31}P{^{1}H} NMR (101.25 MHz, CDCl$_3$, 25 °C): δ = 41.2 (s, Au*P*Ph$_2$), 53.8 ppm (s, dppf); IR (KBr): $\tilde{\nu}$ = 1895, 1904, 2004 (s, CO), 2060 cm^{-1} (m, C≡CRu), 2116 (w, C≡CAu); MS (ESI-TOF) *m*/*z*: 1944.7 [*M*+H]$^+$, 749.2 [(C$_5$H$_5$)(dppf)Ru(CO)]$^+$; elemental analysis calcd (%) for C$_{94}$H$_{77}$AuFeN$_4$O$_3$P$_3$ReRu (1943.68): C 58.09, H 3.99, N 2.88; found: C 58.52, H 4.29, N 2.60.

Preparation of [(*t*Bu$_2$bpy)(CO)$_3$ReC≡C-bpy] (26): Complex **25** was dissolved in dichloromethane and left for 3 days at room temperature. The formed precipitate was filtered off and from the filtrate pure **26** could be isolated. Crystallization was achieved by diffusion of *n*-pentane into a dichloromethane solution containing **26**. ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.46 (s, 18 H; *t*Bu), 7.19 (ddd, $^{3}J_{\mathrm{H5'H4'}}$ = 7.6 Hz, $^{3}J_{\mathrm{H5'H6'}}$ = 4.7 Hz, $^{4}J_{\mathrm{H5'H3'}}$ = 1.0 Hz, 1 H; *H5'*/bpy), 7.36 (dd, $^{3}J_{\mathrm{H4H3}}$ = 8.2 Hz, $^{4}J_{\mathrm{H4H6}}$ = 2.2 Hz, 1 H; *H4*/bpy), 7.48 (dd, J_{H5H6} = 5.8 Hz, J_{H5H3} = 1.9 Hz, *H5*/*t*Bu$_2$bpy), 7.71 (ddd, $^{3}J_{\mathrm{H4'H3'}}$ = 8.0 Hz, $^{3}J_{\mathrm{H4'H5'}}$ = 7.6 Hz, $^{4}J_{\mathrm{H4'H6'}}$ = 1.7 Hz, 1 H; *H4'*/bpy), 8.03 (dd, $^{3}J_{\mathrm{H3H4}}$ = 8.2 Hz, $^{5}J_{\mathrm{H3H6}}$ = 1.0 Hz, 1 H; *H3*/bpy), 8.10 (d, J_{H3H5} = 1.9 Hz, *H3*/*t*Bu$_2$bpy), 8.15 (dd, $^{4}J_{\mathrm{H6H4}}$ = 2.2 Hz, $^{5}J_{\mathrm{H6H3}}$ = 1.0 Hz, 1 H; *H6*/bpy), 8.22 (ddd, $^{3}J_{\mathrm{H3'H4'}}$ = 8.0 Hz, $^{4}J_{\mathrm{H3'H5'}}$ = 1.0 Hz, $^{5}J_{\mathrm{H3'H6'}}$ = 1.0 Hz, 1 H; *H3'*/bpy), 8.58 (ddd, $^{3}J_{\mathrm{H6'H5'}}$ = 4.7 Hz, $^{4}J_{\mathrm{H6'H4'}}$ = 1.7 Hz, $^{5}J_{\mathrm{H6'H3'}}$ = 1.0 Hz, 1 H; *H6'*/bpy), 9.00 ppm (d, J_{H6H5} = 5.8 Hz, 2 H; *H6*/*t*Bu$_2$bpy); IR (NaCl): $\tilde{\nu}$ = 1888, 1903, 2003 (s, CO), 2091 cm^{-1} (m, C≡CRe).

Preparation of 1-[(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C]-3-[(*t*Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[PPh^{2}AuC≡C-bpy(Mo(CO)$_4$)]C$_6$H$_3$ (28): A single portion of **27** (7 mg, 0.023 mmol) was added to a solution of **25** (45 mg, 0.023 mmol) in a mixture of dichloromethane/THF (5:1, 10 mL). The resulting solution was stirred for 15 h at ambient temperature. Subsequently, the solvent was reduced in volume to about 2 mL. On addition of diethyl ether (10 mL), a red solid precipitated, which was washed with diethyl ether (2×10 mL) and was then dried using an oil pump vacuum. Please note that NMR spectroscopic investigations showed that **28** partly decomposed. For this reason complex **28** could not be obtained in pure form, but could be unequivocally identified. ^{31}P{^{1}H} NMR (101.25 MHz, CDCl$_3$, 25 °C): δ = 40.8 (Au*P*Ph$_2$), 53.7 ppm (dppf); MS (ESI-TOF): *m*/*z*: 2152.8 [*M*+H]$^+$, 749.2 [(C$_5$H$_5$)(dppf)Ru(CO)]$^+$; elemental analysis calcd (%) for C$_{98}$H$_{77}$AuFeMoN$_4$O$_7$P$_3$ReRu (2151.66): C 54.71, H 3.61, N 2.60; found: C 54.08, H 3.67, N 2.39.

Preparation of [1-{(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C}-3-{(*t*Bu$_2$bpy)(CO)$_3$ReC≡C}-5-{PPh$_2$AuC≡C-bpy({[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu)}C$_6$H$_3$][PF$_6$] (30): A single portion of **25** (60 mg, 0.031 mmol) was added to **29** (25 mg, 0.033 mmol) dissolved in THF (25 mL). The resulting reaction solution was stirred for 2 h at 25 °C, whereby the color of the solution changed from orange to red. Subsequently, the solvent was reduced in volume under reduced pressure and the product **30** was precipitated by addition of *n*-hexane (20 mL). The precipitate was washed with *n*-hexane (2×10 mL) and was then dried using an oil pump vacuum. Complex **30** could be obtained as an orange red solid. Yield:70 mg (0.026 mmol, 85 %). ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = −0.50 (s, 18 H; Si*Me*$_3$), 0.27 (brs, 18 H; Si*Me*$_3$), 1.41 (s, 18 H; *t*Bu), 3.93 (dpseudo-t, J_{HP} = 1 Hz, J_{HH} = 2.4 Hz, 2 H; C$_5$*H*$_4$), 4.02 (bs, 2 H; C$_5$*H*$_4$), 4.20 (s, 5 H; C$_5$*H*$_5$), 4.25 (bs, 2 H; C$_5$*H*$_4$), 5.00 (brs, 2 H; C$_5$*H*$_4$), 6.23–6.30 (m, 8 H; C$_5$*H*$_4$/CpTMS), 6.83 (dpseudo-t, J_{HP} = 12.8 Hz, J_{HH} = 1.5 Hz, 1 H; C$_6$*H*$_3$), 7.00 (dpseudo-t, J_{HP} = 15 Hz, J_{HH} = 1.5 Hz, 1 H; C$_6$*H*$_3$), 7.06–7.53 (m, 26 H (C$_6$*H*$_5$) + 1 H (C$_6$*H*$_3$) + 2 H (*H5*/*t*Bu$_2$bpy)), 7.62–7.75 (m, 4 H (C$_6$*H*$_5$) + 1 H (*H5'*/bpy)), 8.12 (dd, $^{3}J_{\mathrm{H4H3}}$ = 8.4 Hz, $^{4}J_{\mathrm{H4H6}}$ = 2.0 Hz, *H4*/bpy), 8.18–8.27 (m, 3 H; *H3*/*t*Bu$_2$bpy + *H4'*/bpy), 8.42 (d, $^{3}J_{\mathrm{H3H4}}$ = 8.4 Hz, 1 H; *H3*/bpy), 8.49–8.58 (m, 3 H; *H3'*,*H6*,*H6'*/bpy), 8.97 ppm (d, $^{3}J_{\mathrm{H6H5}}$ = 6.0 Hz, 2 H; *H6*/*t*Bu$_2$bpy); ^{31}P{^{1}H} NMR (101.25 MHz, CDCl$_3$, 25 °C): δ = −145.1 (septet, J_{PF} = 713 Hz, *P*F$_6$), 40.8 (Au*P*Ph$_2$), 53.7 ppm (dppf); IR (KBr): $\tilde{\nu}$ = 1893, 1904, 2003 (s, CO), 2060 (m, C≡CRu), 2117 cm^{-1} (w, C≡CAu); MS (ESI-TOF): *m*/*z*: 2524.7 [*M*−PF$_6$]$^+$, 2452.6 [*M*−PF$_6$−SiMe$_3$]$^+$, 1262.9 [*M*−PF$_6$]$^{2+}$, 749.1 [(C$_5$H$_5$)(dppf)Ru(CO)]$^+$; elemental analysis calcd (%) for C$_{120}$H$_{121}$AuCuF$_6$FeN$_4$O$_3$P$_4$ReRuSi$_4$Ti (2669.03): C 54.00, H 4.57, N 2.10; found: C 54.76, H 4.80, N 2.04.

X-ray data collection and structure determinations of 8, 12, 19, and 26: Crystal data for **8**, **12**, and **19** are summarized in Table 1 (for **26** see Supporting information). All data were collected on an Oxford Gemini S diffractometer with graphite-monochromatized Mo$_{\mathrm{K}\alpha}$ radiation (λ = 0.71073 Å) at 293(2) K (**12**, **26**) and 100 K (**8**, **19**) with oil-coated shock-cooled crystals.[42] The structures were solved by direct methods by using SHELXS-97[43] or SIR-92[44] and refined by full-matrix least-square procedures on F^2 with SHELXL-97.[45] All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions.

CCDC-669322 (**8**), 669323 (**12**), 669324 (**19**), and 669325 (**26**) 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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