Heteromultimetallic Transition Metal Complexes Based on Unsymmetrical Platinum(II) Bis-Acetylides

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The synthesis of a unique series of heteromultinuclear transition metal complexes with up to seven different metal atoms is reported by using consecutive synthesis methodologies including metathesis, dehydrohalogenation, and carbon−carbon cross-coupling reactions. In these compounds the metals Ti, Fe, Ru, Os, Re, Pt, and Cu are connected via carbon-rich bridging units comprising 1,3,5-triethynylbenzene and 2,2′-bipyridyl-5-yl. These molecules have been characterized by elemental analysis, IR and NMR spectroscopy, and ESI-TOF mass spectrometry. The main structural feature of these compounds is an unsymmetrical *trans*-configurated platinum(II) bis-acetylide unit. The structure of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(RcC≡C)PtC≡C]C$_6$H$_3$ (**3**) and 1,3-[(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)OsC≡C]$_2$-5-[(CO)$_3$(Cl)Re(bpyC≡C)]C$_6$H$_3$ (**18**) (Fc = (η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)Fe; Rc = (η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)Ru; ^{t}Bu$_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl; bpy = 2,2′-bipyridyl-5-yl) in the solid state is reported. Both compounds are characterized by the central 1,3,5-triethynylbenzene core, bridging the individual transition metal building blocks. These organometallic fragments show thereby typical structural properties. The appropriate metal acetylide moieties are, as expected, found in a linear arrangement with representative M−C and C≡C bond distances.

Introduction

Due to their active coordination sites, all-carbon ligands, aryldiethynyls, arylethenyls, alkynylthiophenes, etc., are of particular importance in the synthesis of a huge number of rigid-rod-structured carbon-rich π-conjugated homo- and heterometallic transition metal complexes.[1–7] Especially, the 1,3,5-triethynylbenzene core allows the design of organometallics that can be extended in three directions.[8,9] Hitherto, mainly homotrimetallic systems incorporating, for example, [(R$_3$P)Au] and [(η^5-C$_5$Me$_5$)(η^2-dppe)Fe] (dppe = bis(diphenylphosphino)ethane) building blocks exist, while less is known about heterometallic derivatives.[8,9] A short while ago, only one example with three different metal-containing building blocks such as Fc, [(η^2-dppm)$_2$OsCl], and (η^2-dppm)$_2$RuCl] (Fc = (η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)Fe; dppm = bis(diphenylphosphino)methane) was available.[9c] Very recently this family of complexes was enriched by diverse iron, ruthenium, osmium, rhenium, and platinum organometallic termini.[10] One of these molecules is 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(Cl)PtC≡C]C$_6$H$_3$ (^{t}Bu$_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl), which can be used as a suitable starting material in the preparation of heterometallic complexes of higher nuclearity.[10] The Pt−Cl functionality facilitates the formation of unsymmetrical platinum(II) bis-acetylides and consequently the connection to further organic

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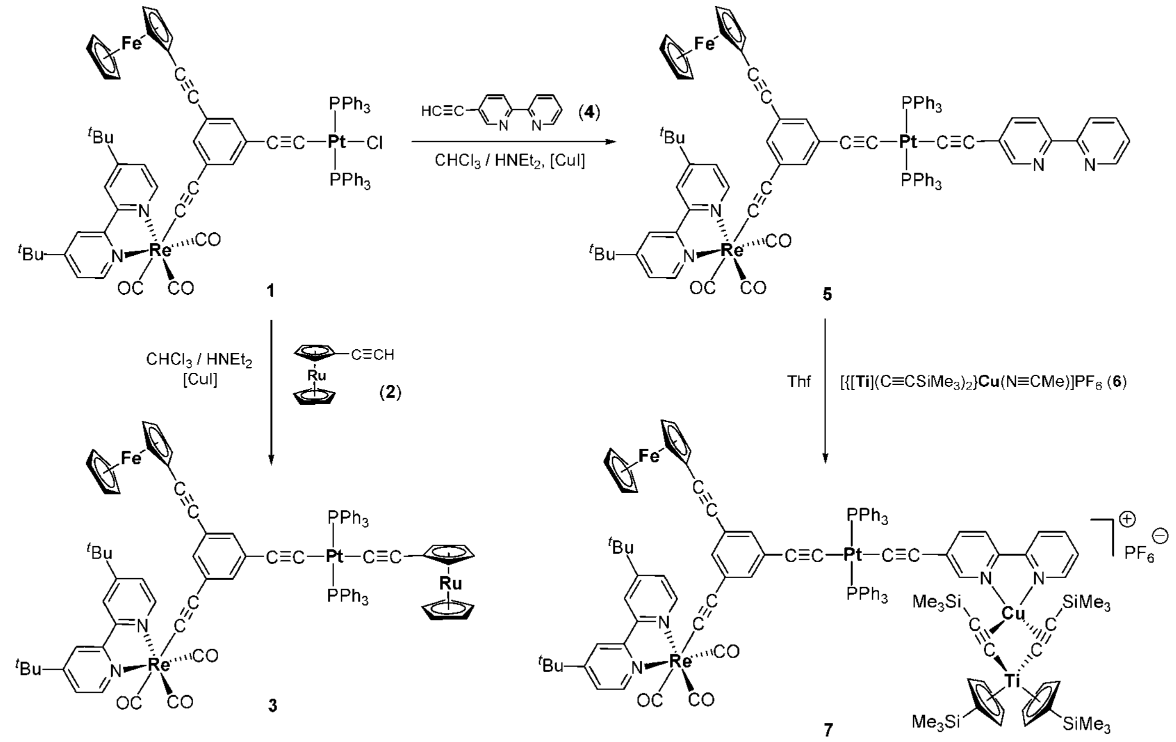
Scheme 1. Reaction Scheme for the Synthesis of Tetrametallic 3 and Pentanuclear 7



and organometallic groups, which additionally can possess pendent coordination sites.

In the frame of our previous work in this field of chemistry, we report herein the consecutive synthesis, characterization, and structure of heterotri- to heteroheptametallic transition metal complexes and, hence, enrich this family of novel compounds in a straightforward way.

Results and Discussion

In order to synthesize heteromultimetallic complexes based on a bis-acetylide platinum(II) connecting unit we choose 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(Cl)PtC≡C]C$_6$H$_3$ (**1**)[10] as key starting material. In general, the preparation of the unsymmetrical Pt(II) bis-acetylides was envisaged by using the dehydrohalogenation methodology introduced by Russo et al.[11] The monoacetylide complex **1** was obtained from 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$-ReC≡C]-5-(HC≡C)C$_6$H$_3$ and *cis*-[(Ph$_3$P)$_2$PtCl$_2$] using chloroform as solvent in the presence of a small amount of diethylamine, which avoided the formation of significant amounts of the corresponding symmetric bis-acetylide complex.[10]

Unsymmetrical 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(RcC≡C)PtC≡C]C$_6$H$_3$ (**3**) and 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(bpyC≡C)PtC≡C]-C$_6$H$_3$ (**5**) (Rc = (η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$)Ru; bpy = 2,2′-bipyridyl-5-yl) were accessible by reacting **1** with 1.5 equiv of ethynylruthenocene (**2**) and 5-ethynyl-2,2′-bipyridyl (**4**), respectively (Scheme 1). It is necessary to add a catalytic quantity of [CuI] to the chloroform−diethylamine reaction medium. After appropriate workup, complexes **3** and **5** could be isolated as yellow- to orange-colored solids in good yield (Experimental Section).

The presence of an N-ligating moiety in **5** allows the complexation of further organometallic complex fragments, and hence, complex **5** was reacted with the organometallic Ti−Cu π-tweezer molecule [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF$_6$ (**6**) ([Ti] = η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti). On replacement of acetonitrile by the 2,2′-bipyridyl ligand, the heteropentametallic molecule **7**, featuring the transition metals Ti, Re, Fe, Pt, and Cu, was obtained as a red material in high yield (Scheme 1).

Multimetallic **3** and **5** are stable both in the solid state and in solution, while **7** slowly starts to decompose in solution over prolonged time.

The identities of **3**, **5**, and **7** have been confirmed by elemental analysis, IR, ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and ESI-TOF mass spectrometry. The structure of **3** in the solid state was additionally determined by single-crystal X-ray structure analysis, thus confirming the structural assignment made from spectroscopic characterization.

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The IR spectra of all complexes are characterized by the $\nu_{C\equiv CPt}$ vibrations in the range of 2097−2106 cm^{-1}; the position of this band is shifted toward lower frequencies compared to monoacetylide **1**.[10,11] The predictable weak $\nu_{C\equiv C}$ vibration at titanium (1925 cm^{-1})[12] in **7** is covered by the three intense carbonyl absorptions typical for the $[(^{t}Bu_2bpy)(CO)_3Re]$ building block (Experimental Section).[4b,9b,13]

In the $^{31}P\{^{1}H\}$ NMR spectra of **3**, **5**, and **7**, when compared to **1**,[10] an upfield shift is observed (**1**: 20.5 ppm; **5**: 17.7 ppm). The magnitude of $^{1}J_{^{31}P^{195}Pt}$ is known to act as a useful probe of the geometry of any present isomer in square-planar Pt(II) complexes.[14] The $^{1}J_{^{31}P^{195}Pt}$ value of **3**, **5**, and **7** is, at 2612−2664 Hz, in agreement with the values found in other square-planar platinum complexes with *trans*-geometry.[11,15]

The consecutive building of higher nuclear heterometallic assemblies from **1** is also confirmed by ^{1}H NMR spectroscopic studies, since the resonance signals for the new introduced organometallic fragments can nicely be seen (Experimental Section). The successful formation of **3** and **5** is best reflected by a significant upfield shift of the Rc and bpy protons adjacent to the alkynyl moiety. For example, the resonance signal of *H4*/bpy is shifted from 7.89 (**4**) to 6.62 (**5**) ppm.

The formation of **3**, **5**, and **7** is additionally evidenced from ESI-TOF mass spectrometric investigations, indicating the presence of molecular ions $[M + H]^{+}$ (**3**, **5**) or $[M - PF_6]^{+}$ (**7**) (Experimental Section).

Single crystals of **3** were obtained from diffusion of *n*-pentane into a dichloromethane/chloroform solution containing **3** at room temperature. The molecular structure of **3** together with selected bond distances (Å) and angles (deg) is presented in Figure 1. The crystal and structure refinement data are summarized in Table 1 (Experimental Section).

Complex **3** represents a heterometallic Fe−Re−Pt−Ru compound in which four different metal building blocks are connected via a 1,3,5-triethynylbenzene core (Figure 1). The structure of **3** shows a somewhat distorted octahedral geometry about Re1 with three carbonyl ligands arranged in a facial fashion. As required by the bite distance exerted by the steric demand of the chelating bipyridyl ligand, the N1−Re1−N2 angle is, at 74.3(2)°, conspicuously smaller than 90° (Figure 1).[13] The Pt1 center with its d^{8}-electron configuration possesses a slightly distorted square-planar coordination geometry (rms deviation 0.0275 Å), as can be seen from the angles around Pt1 with a linear *trans*-oriented C≡C−Pt−C≡C arrangement (Figure 1). The deviation from an ideal square-planar arrangement can be explained by steric interactions between the bulky groups around Pt1. A similar behavior was also observed for, e.g., *trans*-$[(PEt_2Ph)_2(Cl)Pt(C\equiv CPh)]$.[15c] The coordination plane around Pt1 forms an interplanar angle of 32.73(0.22)° with the central phenylene ring. The two cyclopentadienyls of the metallocene units are found in an almost eclipsed conformation (Fc, 1.64(0.43)°; Rc, 7.33(0.71)°). In relation to the central C_6H_3 ring the ferrocene and ruthenocene moieties are located on different sides, whereby the angles between the respective cyclopentadienyl units and the phenyl ring are 34.27(0.37)° (Fc) and 6.59(0.49)° (Rc). The three alkynyl bonds at the phenylene core and the C≡C triple bond in the ethynyl linkage to the ruthenocene unit are in the range 1.201(10)−1.216(11) Å and are comparable to those found for other triethynylbenzene organometallic systems.[8,9]

A further possibility to prepare heteromultimetallic complexes is given by the linkage of two different substituted 1,3,5-triethynylbenzene molecules via a platinum atom. For this purpose we choose 1-(FcC≡C)-3-$[(^{t}Bu_2bpy)(CO)_3ReC\equiv C]$-5-$[$*trans*-$(Ph_3P)_2(Cl)PtC\equiv C]C_6H_3$ (**1**). The synthesis methodology of the second building block to be introduced, 1-$[(Ph_3P)_2(\eta^{5}$-$C_5H_5)OsC\equiv C]$-3-(bpyC≡C)-5-(HC≡C)C_6H_3 (**13**), is displayed in Scheme 2.

For the overall synthesis of **13** 1-iodo-3,5-dibromobenzene (**8**) was used as suitable starting material because the more reactive aryl−iodo bond allowed a selective introduction of a 5-ethynyl-2,2′-bipyridyl moiety following the Sonogashira cross-coupling protocol.[16] Thus formed **9** further reacted with an excess of trimethylsilylacetylene under similar reaction condi-

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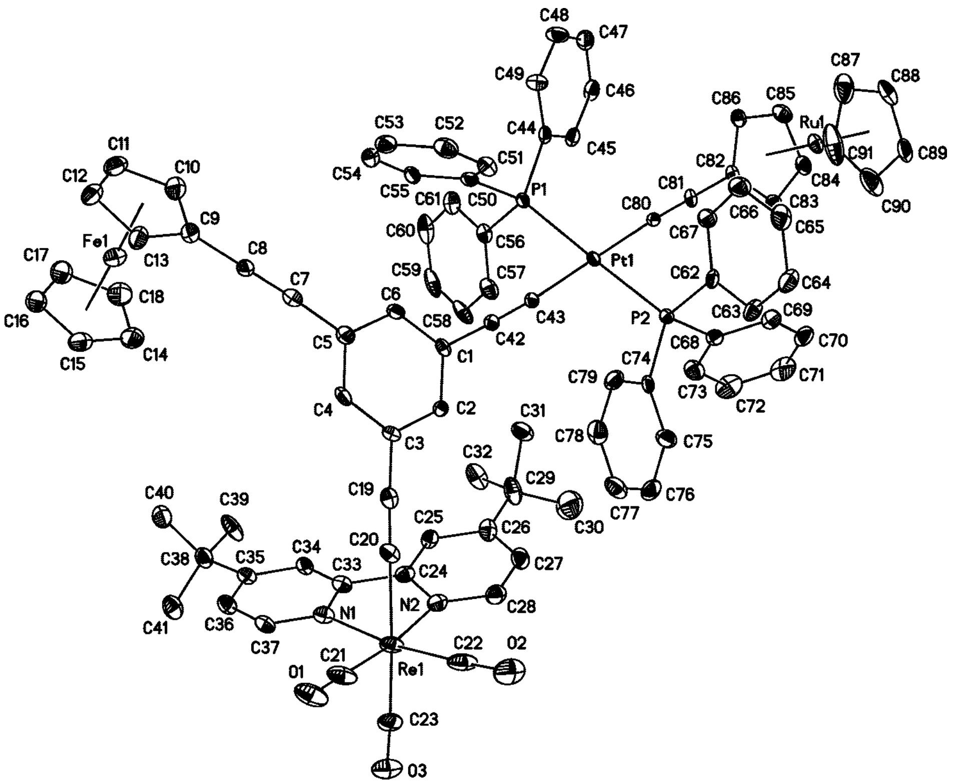

Figure 1. Perspective drawing of complex **3**. Thermal ellipsoids are shown at the 30% probability level. The hydrogen atoms, three molecules of chloroform, one dichloromethane, and one molecule of water are omitted for clarity. Selected bond distances (Å) and angles (deg): C7−C8, 1.215(11); Fe1−D1, 1.639(4); Fe1−D2, 1.650(4); C19−C20, 1.216(11); Re1−C20, 2.111(8); Re1−N1, 2.176(6); Re1−N2, 2.163(7); Re1−C21, 1.922(10); Re1−C22, 1.896(9); Re1−C23, 1.925(9); C21−O1, 1.157(11); C22−O2, 1.171(11); C23−O3, 1.180(10); C42−C43, 1.201(10); Pt1−C43, 1.993(7); Pt1−C80, 2.003(7); C80−C81, 1.212(10); Pt1−P1, 2.3110(18); Pt1−P2, 2.3030(18); Ru1−D1, 1.812(4); Ru1−D2, 1.819(4); C5−C7−C8, 173.4(9); C7−C8−C9, 178.8(10); C3−C19−C20, 174.3(8); C19−C20−Re1, 166.1(6); N1−Re1−N2, 74.3(2); C20−Re1−C23, 172.0(3); Re1−C21−O1, 179.2(8); Re1−C22−O2, 176.6(9); Re1−C23−O3, 177.6(8); C1−C42−C43, 176.6(8); C42−C43−Pt1, 175.6(6); C43−Pt1−C80, 178.9(3); Pt1−C80−C81, 176.7(6); C80−C81−C82, 177.1(8); P1−Pt1−P2, 177.95(6); (D1 = centroid of C9−C13; D2 = centroid of C14−C18; D3 = centroid of C82−C86; D4 = centroid of C87−C91).

tions to produce **10**, whose desilylation with [^{n}Bu$_4$N]F gave **11** as a colorless solid (Scheme 2). The last step in the preparation of **13** included the dehydrohalogenation of **11** with [(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)OsBr] (**12**) in the presence of [NH$_4$]PF$_6$ followed by deprotonation of the intermediate formed osmium vinylidene species by addition of sodium to the methanolic solution. Within this reaction, compound **13** was produced together with dinuclear **14** (Scheme 2), which could be separated by column chromatography (Experimental Section).

Combining molecule **1** with **13** under similar reaction conditions described in the synthesis of **3** and **5** (vide supra) gave heterotetrametallic **15**, which, after appropriate workup, could be isolated as fairly stable orange-colored solid in 72% yield (Scheme 3). Complex **15** bears a free 2,2′-bipyridyl entity, which can be further reacted with the organometallic π-tweezer molecule **6** to form complex **16**, in which six different transition metals are held together by two 1,3,5-triethynylbenzene connecting units (Scheme 3).

Since homodinuclear **14** also features a noncoordinated 2,2′-bipyridyl unit, this molecule was treated with equimolar amounts of [Re(CO)$_5$Cl] (**17**) to give the trimetallic Os$_2$Re species **18** (eq 1, Experimental Section).

Single crystals of **18** suitable for X-ray crystallography were obtained from slow diffusion of *n*-pentane into a dichloromethane solution containing **18** at 25 °C (Figure 2, Table 1).

In **18** a triethynylbenzene moiety connects two [(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)Os] fragments with one [(bpy)(CO)$_3$ClRe] building block. As typical for **3** (Figure 1) the rhenium atom in **18** adopts a somewhat distorted octahedral coordination sphere with facial oriented carbonyl ligands. The bond distances and angles of this unit are characteristic for this type of organometallic fragment.[9b,13] The bpy−Re plane (rms deviation 0.0105 Å) forms an interplanar angle of 19.73(0.33)° with the central phenylene ring. The osmium atoms are pseudotetrahedral coordinated as commonly found in other piano-stool-structured complexes.[17] The bond angles of Os1−C8−C7 (175.6(8)°), C1−C7−C8 (173.5(10)°), Os2−C51−C50 (173.3(8)°), and C3−C50−C51 (175.8(10)°) specify only slightly distorted linear arrangements, as anticipated for the sp hybridization of the alkynyl carbon atoms. All other bond lengths and angles are typical as found in other metal−alkynyl complexes.[13,17]

Complexes **9**−**11**, **13**−**16**, and **18** were characterized by elemental analysis, NMR (^{1}H, ^{31}P{^{1}H}), and IR spectroscopy. Furthermore, ESI-TOF mass spectrometric investigations were carried out.

In the IR spectra of these complexes the CO and C≡C stretching vibrations are very diagnostic and represent a useful

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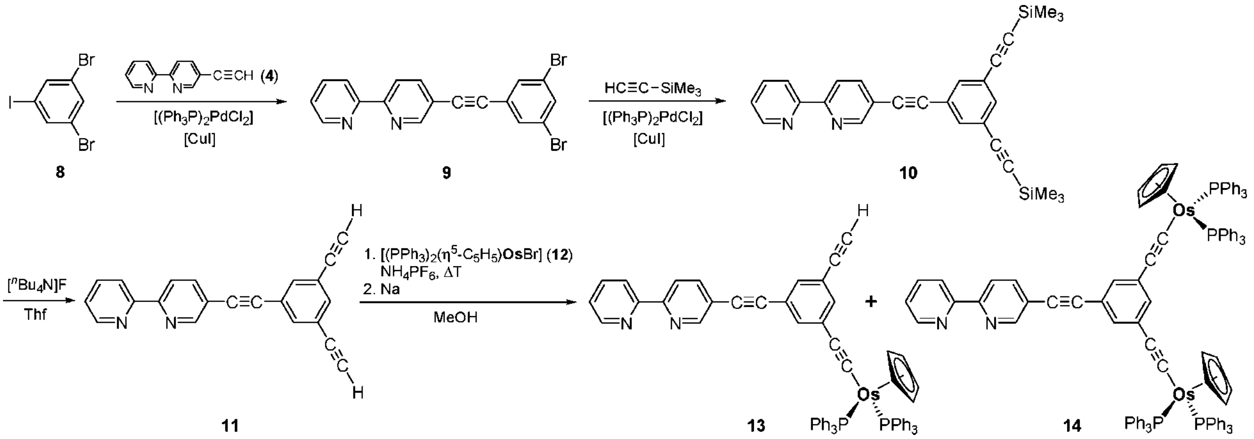
Table 1. Crystal and Intensity Collection Data for 3 and 18

	3 × 3 $CHCl_3$ × CH_2Cl_2 × H_2O	**18** × 2 $CHCl_3$
fw	2305.73	2406.40
chemical formula	$C_{95}H_{82}Cl_{11}FeN_2O_4P_2PtReRu$	$C_{109}H_{82}Cl_7N_2O_3Os_2P_4Re$
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.6644(5)	9.7379(9)
b (Å)	18.1424(10)	20.428(2)
c (Å)	23.1605(13)	26.946(3)
α (deg)	101.209(5)	75.718(10)
β (deg)	100.387(4)	80.444(9)
γ (deg)	100.602(4)	82.966(9)
V (Å^3)	4605.5(4)	5103.7(10)
ρ_{calc} (g cm^{-3})	1.663	1.566
F(000)	2276	2360
cryst dimens (mm^3)	0.2 × 0.2 × 0.2	0.15 × 0.05 × 0.05
Z	2	2
max., min. transmn	1.00000, 0.83410	1.00000, 0.56339
absorp coeff (μ, mm^{-1})	3.545	9.543
scan range (deg)	2.83 to 26.06	3.42 to 60.51
index ranges	$-14 \leq h \leq 14$ $-22 \leq k \leq 22$ $-28 \leq l \leq 28$	$-10 \leq h \leq 9$ $-23 \leq k \leq 23$ $-30 \leq l \leq 30$
total no. of reflns	45 217	39 189
no. of unique reflns	17 964	14 947
R(int)	0.0293	0.0356
no. of data/restraints/params	17 964/21/1085	14 947/81/1023
goodness-of-fit on F^2	1.091	1.038
R1,[a] wR2[a] [$I \geq 2\sigma(I)$]	0.0475, 0.1309	0.0559, 0.1573
R1,[a] wR2[a] (all data)	0.0724, 0.1501	0.0764, 0.1709
max., min. peak in final Fourier map (e Å^{-3})	3.864, −2.294	3.273, −2.401

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

Scheme 2. Synthesis of 13 and 14



monitoring tool (for example, **18**: 1894, 1918, 2019 (ν_{CO}), 2059 ($\nu_{C\equiv COs}$), 2203 ($\nu_{C\equiv Cbpy}$)) along with the appearance and disappearance of the $\nu_{\equiv C-H}$ absorption. Noteworthy is that the intensity of the $\nu_{C\equiv C}$ stretching vibrations can vary, and in some of the complexes not all of the expected bands are observed (Experimental Section).

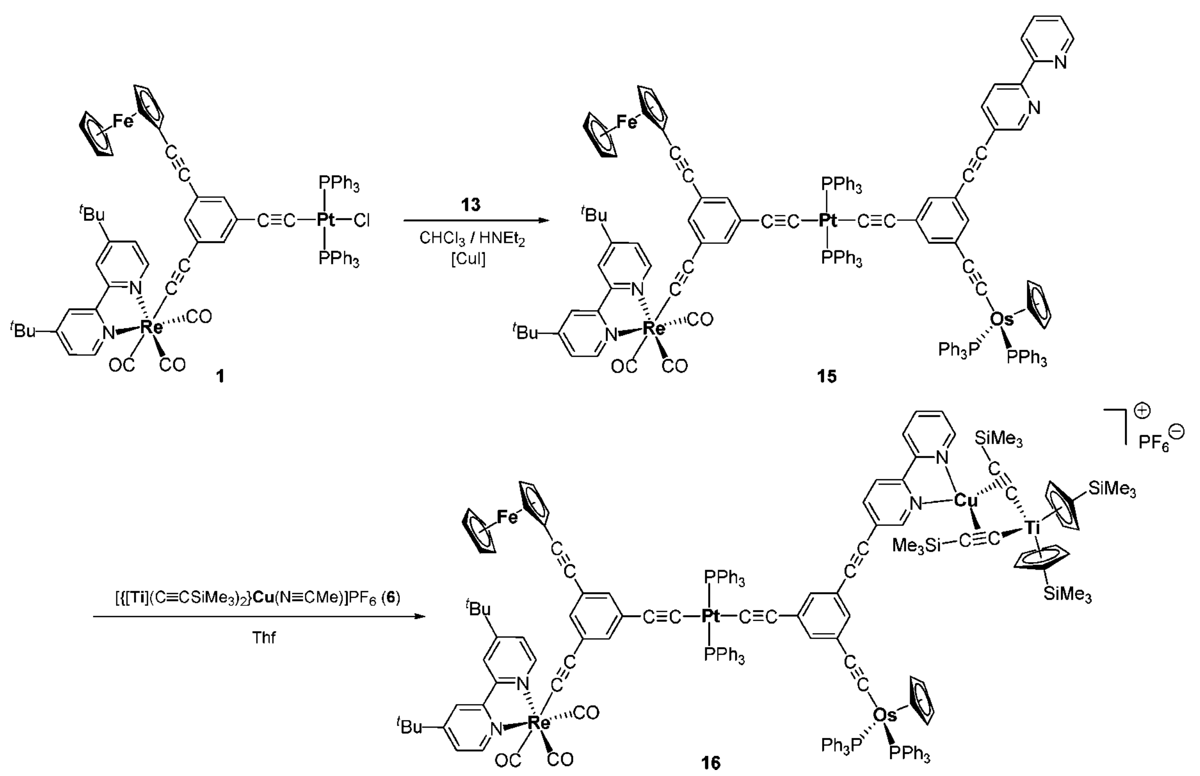
The $^{31}P\{^1H\}$ NMR spectra of **13**−**16** and **18** display one resonance signal at ca. 0.5 ppm due to the presence of the $[(Ph_3P)_2(\eta^5\text{-}C_5H_5)Os]$ unit(s) and a signal centered at 17.5 ppm for the unsymmetrical bis(triphenylphosphine) platinum(II) bis-acetylide moiety. As in **3**, **5**, and **7** the platinum atom in **15** and **16** possesses a *trans*-configuration as derived from the $^1J_{^{31}P^{195}Pt}$ coupling constant (2645, 2650 Hz). However, coordination of the 2,2′-bipyridyl ligand to the transition metal fragments in **16** and **18** does not influence the position of these signals (Experimental Section).

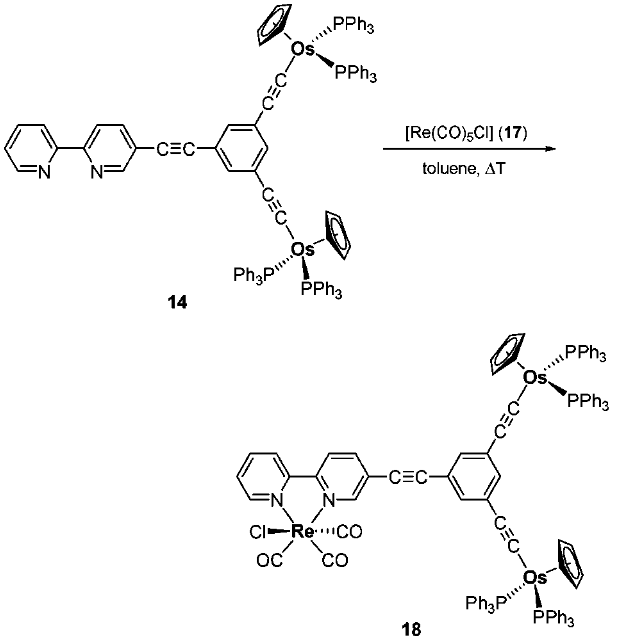
The ^1H NMR spectra of **13**−**16** and **18** are consistent with their formulation as heteromultimetallic 1,3,5-triethynylbenzene-based complexes and reflect the resonance signals for each individual organic and organometallic building block (Experimental Section).

For **15**, **16**, and **18** ESI-TOF mass spectrometry indicated the presence of molecular ions with characteristic isotope distributions patterns, verifying the structural composition of the appropriate organometallic assemblies (Experimental Section).

Using the latter synthesis approach (Scheme 3) also unique heteroheptametallic transition metal complexes should be available upon replacement of one mononuclear fragment in **16** by a heterobimetallic building block. One possibility to realize this is given by the substitution of the ferrocenyl unit by the heterobimetallic fragment $[(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)Ru]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene). To implement this synthesis approach first heterotetrametallic Fe−Ru−Re−Pt (**26**) had to be prepared by applying the consecutive reaction sequence shown in Scheme 4.

Scheme 3. Synthesis of 15 and 16 from 1, 6, and 13





(1)

The three-step synthesis procedure to **26** includes the metathesis of monolithiated triethynylbenzene (**19-Li**) with $[(^t\mathrm{Bu}_2\mathrm{bpy})(\mathrm{CO})_3\mathrm{ReCl}]$ (**20**) and the subsequent dehydrohalogenation of 1-$[(^t\mathrm{Bu}_2\mathrm{bpy})(\mathrm{CO})_3\mathrm{ReC{\equiv}C}]$-3,5-$(\mathrm{HC{\equiv}C})_2\mathrm{C}_6\mathrm{H}_3$ (**21**) with $[(\eta^2\text{-dppf})(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{RuCl}]$ (**22**), followed by treatment of thus formed 1-$[(^t\mathrm{Bu}_2\mathrm{bpy})(\mathrm{CO})_3\mathrm{ReC{\equiv}C}]$-3-$[(\eta^2\text{-dppf})(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{RuC{\equiv}C}]$-5-$(\mathrm{HC{\equiv}C})\mathrm{C}_6\mathrm{H}_3$ (**23**) with *cis*-$[(\mathrm{Ph}_3\mathrm{P})_2\mathrm{PtCl}_2]$ (**25**) (Scheme 4, Experimental Section). For the preparation of **21** a straightforward procedure was used that includes the reaction of $[(^t\mathrm{Bu}_2\mathrm{bpy})(\mathrm{CO})_3\mathrm{ReCl}]$ (**20**) with the in situ prepared lithium acetylide species in refluxing toluene. Compared to the literature, this approach increased the yield of **21**, while the reaction time decreased.[9b] Furthermore it must be noted that, when **21** is reacted with **22**, even in a 1:1 stoichiometry, next to **23** the organometallic $\mathrm{Ru}_2\mathrm{Fe}_2\mathrm{Re}$ compound 1-$[(^t\mathrm{Bu}_2\mathrm{bpy})(\mathrm{CO})_3\mathrm{ReC{\equiv}C}]$-3,5-$[(\eta^2\text{-dppf})(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{RuC{\equiv}C}]_2\mathrm{C}_6\mathrm{H}_3$ (**24**) is formed, in which two $[(\eta^2\text{-dppf})(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{Ru}]$ moieties and a $[(^t\mathrm{Bu}_2\mathrm{bpy})(\mathrm{CO})_3\mathrm{Re}]$ fragment are bridged via a triethynylbenzene core (Experimental Section).

As in the modular synthesis of hexametallic **16**, the linking of two triethynylbenzene molecules is possible, as it could be demonstrated by treatment of **26** with 1-$[(\mathrm{Ph}_3\mathrm{P})_2(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)\mathrm{OsC{\equiv}C}]$-3-$(\mathrm{bpyC{\equiv}C})$-5-$(\mathrm{HC{\equiv}C})\mathrm{C}_6\mathrm{H}_3$ (**13**) under similar reaction conditions producing pentametallic **27** (Scheme 5).

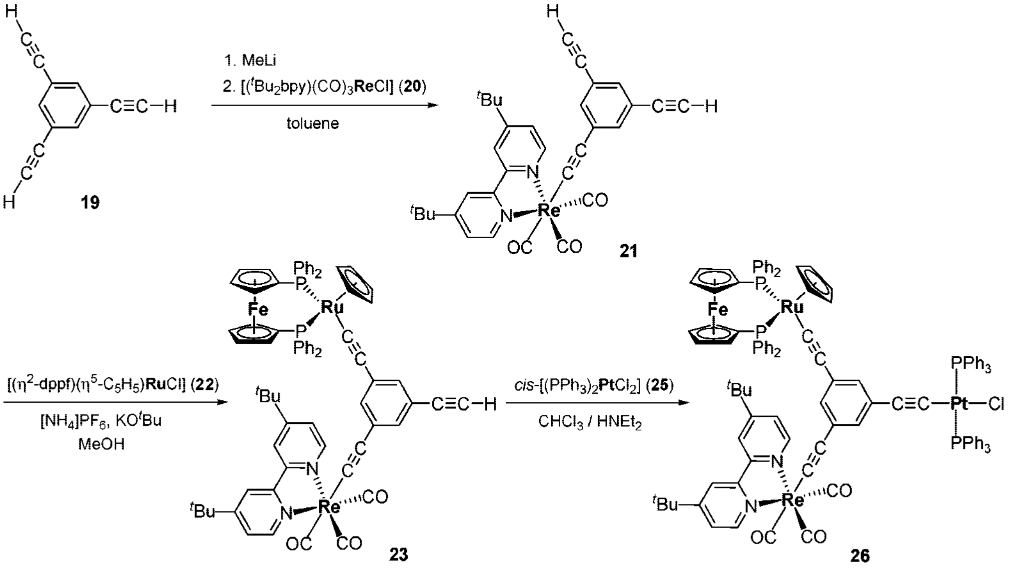
Organometallic **27** further reacts with the Ti−Cu tweezer molecule **6** to give novel **28** (Scheme 5), which, after appropriate workup, could be isolated as an orange solid in high yield.

Complex **28** is the first example of a heteroheptametallic organometallic molecule in which the metal atoms Fe, Ru, Os, Re, Pt, Cu, and Ti are bridged by carbon-rich organic units. Within the structure of **28** two different heterotrimetallic triethynylbenzene entities are connected via a *trans*-$[(\mathrm{Ph}_3\mathrm{P})_2\mathrm{Pt}]$ group, thus generating an unsymmetrical bis-acetylide platinum central core. Molecule **28** is surprisingly very stable in the solid state, while solutions show the tendency to decompose during a longer period of time. Nevertheless, a relative fast decomposition is observed, when solutions containing **28** were exposed to air.

The synthesis protocol developed to prepare heteromultinuclear **27** and **28** (Scheme 5) is directed to the use of modular-shaped organometallic building blocks (vide supra). In this respect, IR and NMR (^{1}H, ^{31}P{^{1}H}) spectroscopy allowed the monitoring of the progress of the reactions and verified the structure and composition of the corresponding organometallic multinuclear assemblies (Experimental Section). In addition, ESI-TOF mass spectrometric studies were carried out with **26** and **28**.

Most characteristic in the IR spectra of **27** and **28** is the appearance of $\nu_{\mathrm{C{\equiv}C}}$ (2064 ($\nu_{\mathrm{C{\equiv}COs(Ru)}}$), 2102 ($\nu_{\mathrm{C{\equiv}CPt}}$), 2210 cm^{-1} ($\nu_{\mathrm{C{\equiv}Cbpy}}$)), and ν_{CO} (1894, 1901, 2003 cm^{-1}) vibrations as

Scheme 4. Synthesis of Complexes 23 and 26, Respectively



typical for the individual σ-alkynyl organometallic transition metal fragments.

In the $^{31}P\{^{1}H\}$ NMR spectrum of **27** three resonance signals at 54.0 (Ru dppf), 17.3 (Ph_3P Pt), and 0.4 ppm (Ph_3P Os) can be found (Figure 3). The signal for the $[(Ph_3P)_2Pt]$ entity shows an additional coupling to ^{195}Pt ($^{1}J_{^{31}P^{195}Pt} = 2659$ Hz), emphasizing a *trans*-configurated bis-acetylide platinum coordination. The heptanuclear complex **28** shows in addition to these signals a resonance signal for the PF_6^- counterion, which is split into a septet ($^{1}J_{PF} = 713$ Hz).

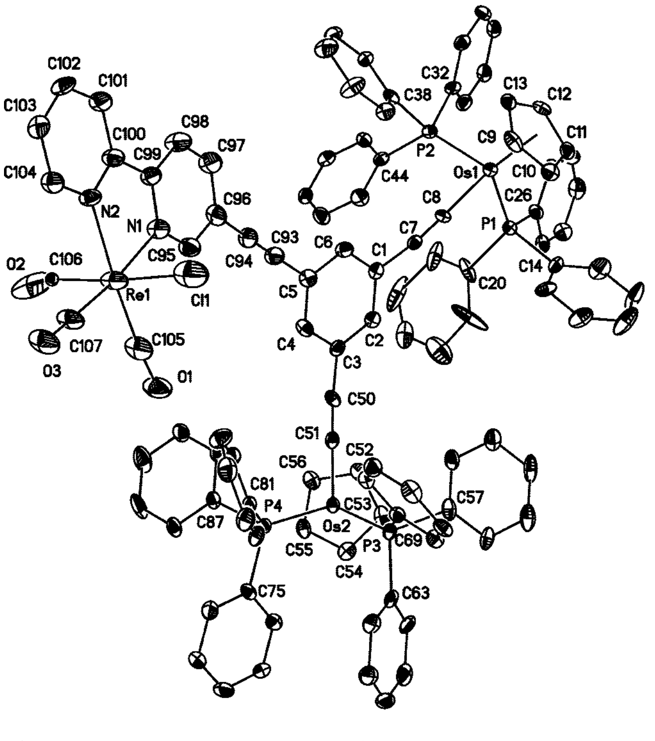


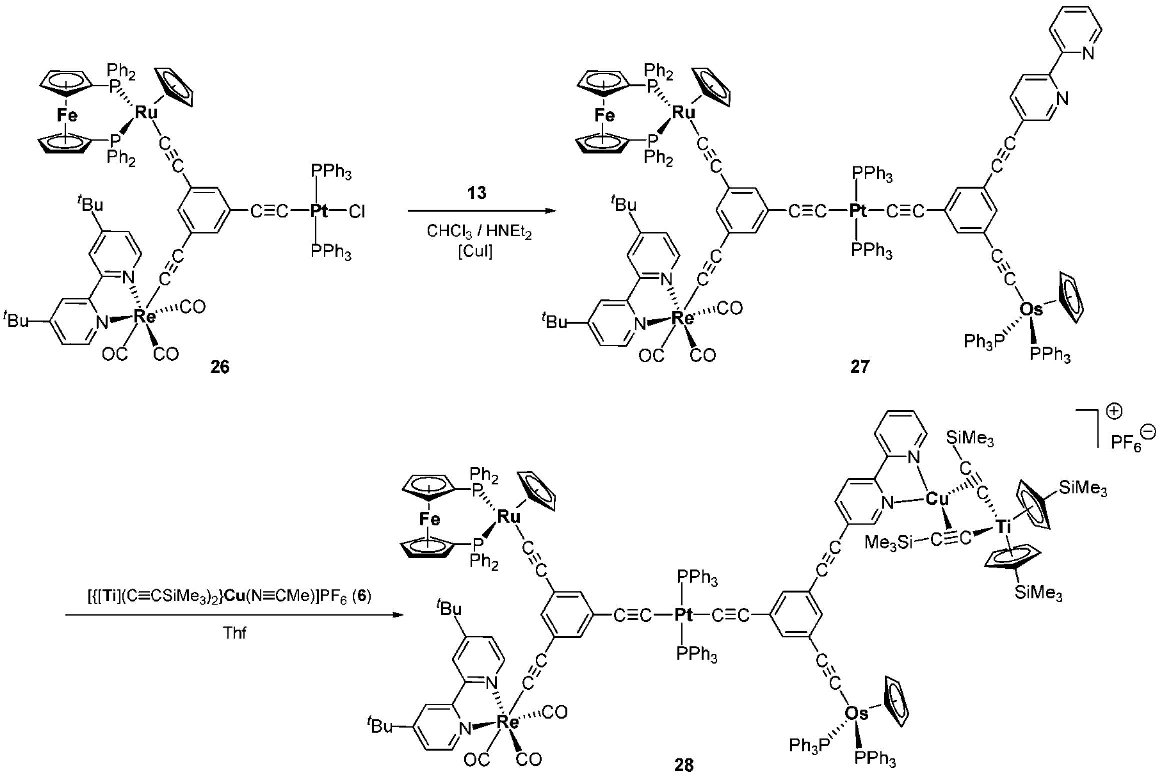
Figure 2. Perspective drawing of **18** with the atom-numbering scheme (only the *ipso*-carbons of the phenyl rings are labeled). Hydrogen atoms and two molecules of chloroform are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles (deg): C7−C8, 1.200(13); Os1−C8, 2.025(9); Os1−P1, 2.296(2); Os1−P2, 2.307(3); Os1-D1, 1.885(4); C50−C51, 1.205(14); Os2−C51, 2.007(10); Os2−P3, 2.285(2); Os2−P4, 2.279(2); Os2−D2, 1.899(4); C93−C94, 1.182(15); Re1−N1, 2.159(8); Re1−N2, 2.170(8); Re1−Cl1, 2.339(6); Os1−C8−C7, 175.6(8); C1−C7−C8, 173.5(10); P1−Os1−P2, 104.39(8); Os2−C51−C50, 173.3(8); C3−C50−C51, 175.8(10); P3−Os2−P4, 99.07(9); C5−C93−C94, 176.5(13); C93−C94−C96, 178.7(14); N1−Re1−N2, 74.6(3); (D1 = centroid of C9−C13, D2 = centroid of C52−C56).

The ^{1}H NMR spectroscopic properties of **27** and **28** nicely correlate with their formulation as heteromultinuclear molecules based on 1,3,5-triethynylbenzene cores showing the respective resonance signal patterns for the organic units. Most distinctive in the proton NMR spectra of both complexes is the appearance of six separated resonance signals for the central phenylene ring protons, confirming the different substitution pattern at the two triethynylbenzene cores (Figure 4). The upfield shift of the C_6H_3 signals, especially those next to the platnum acetylide moieties, may be suggestive of the electron-richness of the corresponding transition metal building blocks, leading to a reduced electron donation from the alkynyl unit. Furthermore, an influence of the ring current of the PPh_3 phenyl rings cannot be excluded.

All other units show the expected resonance signals characteristic for the appropriate organic and organometallic building blocks. Upon coordination of the 2,2′-bipyridyl moiety to copper(I) as given in **28**, the separated and well-resolved signals of this moiety evince up- and downfield shifts forming broad multiplets. Most expressive for the formation of **28** is the high-field shift of the $Me_3SiC{\equiv}C$ protons in comparison to **6**[22] upon coordination of the bipyridyl unit to the organometallic π-tweezer-stabilized copper(I) center, which can be explained by the ring current of the chelating bipyridyl. In addition, as a result of the different chemical environment, the spectrum of **28** reveals two separated singlets for the cyclopentadienyl-bonded $SiMe_3$ groups.

The identitiy of **28** was additionally evidenced from mass spectrometric investigations. The electrospray ionization mass spectrum (ESI-MS) of **28** shows a ion peak at a mass-to-charge ratio (*m*/*z*) of 3790.2, which corresponds to $[M - PF_6]^+$, confirming the elemental composition and charge state (Figure 5). A further peak at *m*/*z* = 1895.6 could be identified as the corresponding 2-fold positive charged complex. The base peak at 809.3 and the one at 749.0 can be assigned to the fragments $[(PPh_3)_2(C_5H_5)Os(CO)]^+$ and $[(dppf)(C_5H_5)Ru(CO)]^+$, which are

Scheme 5. Synthesis of 27 and 28



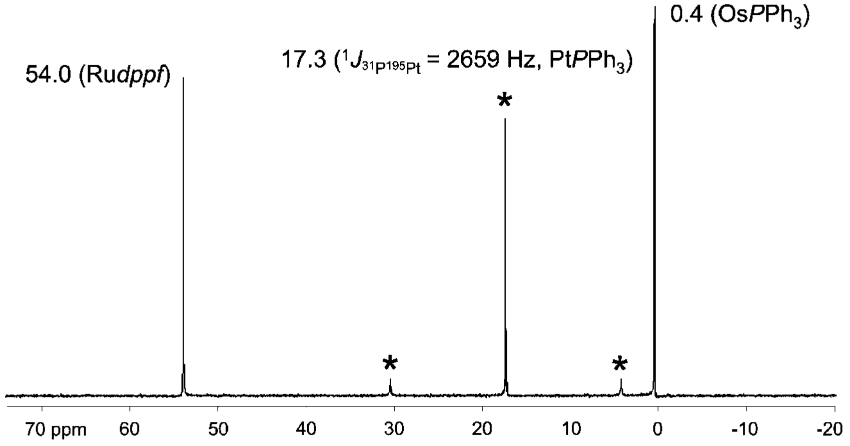


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of heteropentametallic **27**.

typical products of the decomposition of the respective acetylide complexes in the presence of water and air.[18]

Experimental Section

General Data. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran, toluene, and *n*-pentane were purified by distillation from sodium/benzophenone ketyl; dichloromethane and chloroform were purified by distillation from calcium hydride. Diethylamine and diisopropylamine were distilled from KOH; absolute methanol was obtained by distillation from magnesium.

Instruments. Infrared spectra were recorded with a Perkin-Elmer FT-IR Spectrum 1000 spectrometer. 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 (δ = 0.00 ppm) with the solvent as the reference signal ($CDCl_3$: ^{1}H NMR, δ = 7.26; $^{13}C\{^1H\}$ NMR, δ = 77.16).[19] $^{31}P\{^1H\}$ NMR spectra were recorded at 101.255 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard (δ = 139.0, rel to H_3PO_4 (85%) with δ = 0.00 ppm). ESI-TOF mass spectra were recorded using a Mariner biospectrometry workstation 4.0 (Applied Biosystems). Microanalyses were performed with a C,H,N-analyzer of type FlashAE 1112 (Thermo).

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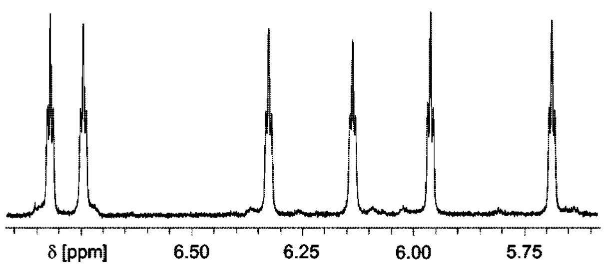

Figure 4. Part of the ^{1}H NMR spectrum (in $CDCl_3$) of heteropentametallic **27** displaying the 6 pseudotriplets (J_{HH} = 1.6 Hz) for the central phenylene ring protons.

Reagents. 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$-(Cl)PtC≡C]C$_6$H$_3$,[10] ethynylruthenocene,[20] 5-ethynyl-2,2′-bipyridyl,[21] [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF$_6$,[22] 1-iodo-3,5-dibromobenzene,[23] trimethylsilylacetylene,[24] [(PPh$_3$)$_2$(η^5-C$_5$H$_5$)OsBr],[25] [Re(CO)$_5$Cl],[26] 1,3,5-triethynylbenzene,[27] [(^{t}Bu$_2$bpy)(CO)$_3$ReCl],[28] [(η^2-dppf)(η^5-C$_5$H$_5$)RuCl],[29] and *cis*-[(PPh$_3$)$_2$PtCl$_2$][30] were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

Synthesis of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(RcC≡C)PtC≡C]C$_6$H$_3$ (3). To 60 mg (0.037 mmol) of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(Cl)PtC≡C]C$_6$H$_3$ (**1**) and 15 mg (0.059 mmol) of ethynylruthenocene (**2**) dissolved in 10 mL of chloroform and 10 mL of diethylamine was added 1 mg of [CuI]. The resulting reaction mixture was stirred for 4 h between 40 and 50 °C. After cooling to room temperature all volatiles were removed in an oil-pump vacuum, and the residue was purified by column chromatography on silica gel using a mixture of dichloromethane/toluene (5:1, v/v) as eluent. After removal of the solvents under reduced pressure, the title compound was obtained as an orange solid. Yield: 50 mg (0.027 mmol, 73% based on **1**).

Anal. Calcd for $C_{91}H_{75}FeN_2O_3P_2PtReRu$ (1844.75): C, 59.25; H, 4.10; N, 1.52. Found: C, 59.20; H, 4.60; N, 1.37. IR (KBr, cm^{-1}): 1899, 2004 (s, ν_{CO}), 2101 (m, $\nu_{C\equiv CPt}$), 2212 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, $CDCl_3$): 1.43 (s, 18 H, ^{t}Bu), 3,86 (pt, J_{HH} = 1.6 Hz, 2 H, C$_5$*H*$_4$/Rc) 4.16 (s, 5 H, C$_5$*H*$_5$), 4.17 (s, 7 H, C$_5$*H*$_4$ + C$_5$*H*$_5$), 4.18 (pt, J_{HH} = 1.9 Hz, 2 H, C$_5$*H*$_4$/Fc), 4.37 (pt, J_{HH} = 1.9 Hz, 2 H, C$_5$*H*$_4$/Fc), 5.95 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.00 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.55 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 7.29 − 7.45 (m, 22 H, C$_6$*H*$_5$ + *H5*/^{t}Bu$_2$bpy), 7.69−7.80 (m, 10 H, C$_6$*H*$_5$), 8.05 (d, J_{HH} = 1.7 Hz, *H3*/^{t}Bu$_2$bpy), 8.96 (d, J_{HH} = 5.8 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR ($CDCl_3$): 17.1 ($^1J_{^{31}P^{195}Pt}$ = 2664 Hz, Pt *P*Ph$_3$). MS (ESI-TOF, *m*/*z*): 1845.45 [M + H]$^+$.

Synthesis of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(bpyC≡C)PtC≡C]C$_6$H$_3$ (5). To 80 mg (0.049 mmol) of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(Cl)PtC≡C]C$_6$H$_3$ (**1**) and 13 mg (0.072 mmol) of 5-ethynyl-2,2′-bipyridyl (**4**) dissolved in 10 mL of chloroform and 10 mL of diethylamine was added 1 mg of [CuI]. The resulting reaction mixture was stirred for 3 h between 40 and 50 °C. After cooling it to room temperature all volatile materials were removed under reduced pressure and the residue was purified by column chromatography on silica gel using a mixture of dichloromethane/toluene (5:1, v/v) as eluent. Evaporation of the solvents under reduced pressure gave the title compound as an orange solid. Yield: 61 mg (0.034 mmol, 70% based on **1**).

Anal. Calcd for $C_{91}H_{73}FeN_4O_3P_2PtRe$ (1769.68): C, 61.76; H, 4.16; N, 3.17. Found: C, 62.22; H, 4.45; N, 2.96. IR (KBr, cm^{-1}): 1895, 2003 (s, ν_{CO}), 2106 (m, $\nu_{C\equiv CPt}$), 2215 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, $CDCl_3$): 1.43 (s, 18 H, ^{t}Bu), 4.17 (s, 5 H, C$_5$*H*$_5$), 4.19 (pt, J_{HH} = 1.9 Hz, 2 H, C$_5$*H*$_4$), 4.37 (pt, J_{HH} = 1.9 Hz, 2 H, C$_5$*H*$_4$), 5.95 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 5.98 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.51 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.62 (dd, $^3J_{H4H3}$ = 8.2 Hz, $^4J_{H4H6}$ = 2.0 Hz, 1 H, *H4*/bpy), 7.19 (ddd, $^3J_{H5'H4'}$ = 7.8 Hz, $^3J_{H5'H6'}$ = 4.8 Hz, $^4J_{H5'H3'}$ = 1.0 Hz, 1 H, H5′/bpy), 7.30−7.48 (m, 20 H (C$_6$*H*$_5$) + 2 H (*H5*/^{t}Bu$_2$bpy)), 7.63 − 7.85 (m, 10 H (C$_6$*H*$_5$) + 2 H (*H4*,*H4′*/bpy)), 7.92 (d, $^3J_{H3H4}$ = 8.4 Hz, 1 H, *H3*/bpy), 8.05 (d, J_{HH} = 1.7 Hz, *H3*/^{t}Bu$_2$bpy), 8.21 (ddd, $^3J_{H3'H4'}$ = 7.8 Hz, $^4J_{H3'H5'}$ = 1.0 Hz, $^5J_{H3'H6'}$ = 1.0 Hz, 1 H, *H3′*/bpy), 8.59 (ddd, $^3J_{H6'H5'}$ = 4.8 Hz, $^4J_{H6'H4'}$ = 1.8 Hz, $^5J_{H6'H3'}$ = 1 Hz, 1 H, *H6′*/bpy), 8.97 (d, J_{HH} = 5.8 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR ($CDCl_3$): 17.7 ($^1J_{^{31}P^{195}Pt}$ = 2629 Hz, Pt*P*Ph$_3$). MS (ESI-TOF, *m*/*z*): 1770.71 [M + H]$^+$.

Synthesis of [1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$({[Ti](μ-σ,π-C≡C-SiMe$_3$)$_2$}Cu-bpyC≡C)PtC≡C]C$_6$H$_3$]-PF$_6$ (7). To a solution of **5** (50 mg, 0.028 mmol) in 15 mL of degassed tetrahydrofuran was added [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF$_6$ (**6**) (22 mg, 0.029 mmol) in a single portion. The reaction solution was allowed to stir for 2.5 h at 25 °C, whereby the color of the solution changed from orange to red. Afterward, the solvent was removed under reduced pressure. The remaining residue was redissolved in 2 mL of dichloromethane, and addition of *n*-hexane (15 mL) caused the precipitation of **7**. After removal of the supernatant solution, the precipitate was washed twice with 10 mL portions of diethyl ether and dried in an oil-pump vacuum to afford **7** as an orange-red solid. Yield: 59 mg (0.024 mmol, 85% based on **5**).

Anal. Calcd for $C_{117}H_{117}CuF_6FeN_4O_3P_3PtReSi_4Ti$ (2495.04): C, 56.32; H, 4.73; N, 2.25. Found: C, 55.97; H, 4.74; N, 2.15. IR (KBr, cm^{-1}): 1892, 1900, 2002 (s, ν_{CO}), 2107 (m, $\nu_{C\equiv CPt}$), 2212 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, $CDCl_3$): −0.56 (s, 18 H, SiMe$_3$), 0.24 (s, 9 H, SiMe$_3$), 0.28 (s, 9 H, SiMe$_3$), 1.43 (s, 18 H, ^{t}Bu), 4.17 (s, 5 H, C$_5$*H*$_5$), 4.18 (pt, J_{HH} = 1.9 Hz, 2 H, C$_5$*H*$_4$), 4.36 (pt, J_{HH} = 1.9 Hz, 2 H, C$_5$*H*$_4$), 5.91 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 5.95 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.13−6.20 (m, 4 H, C$_5$*H*$_4$Si), 6.24 (s, 4 H, C$_5$*H*$_4$Si), 6.51 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.79 (dd, $^3J_{H4H3}$ = 8.2 Hz, $^4J_{H4H6}$ = 1.8 Hz, 1 H, *H4*/bpy), 7.27−7.41 (m, 20 H, C$_6$*H*$_5$), 7.43 (dd, $^3J_{H5H6}$ = 6 Hz, $^4J_{H5H3}$ = 1.8 Hz, 2 H, *H5*/^{t}Bu$_2$bpy), 7.53−7.60 (m, 2 H, bpy), 7.68−7.79 (m, 10 H, (C$_6$*H*$_5$) + 1 H (bpy)), 8.02−8.17 (m, 2 H, bpy), 8.06 (d, $^4J_{H3H5}$ = 1.8 Hz, 2 H, *H3*/^{t}Bu$_2$bpy), 8.35−8.42 (m, 2 H, bpy), 8.96 (d, $^3J_{H6H5}$ = 6 Hz, 2 H, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR ($CDCl_3$): −145.1 (septet, $^1J_{PF}$ = 713 Hz, *P*F$_6$), 17.8 ($^1J_{^{31}P^{195}Pt}$ = 2612 Hz, Pt *P*Ph$_3$). MS (ESI-TOF, *m*/*z*): 2349.9 [M − PF$_6$]$^+$, 1175.9 [M − PF$_6$]$^{2+}$.

Synthesis of 1,3-Br$_2$-5-(bpyC≡C)C$_6$H$_3$ (9). To 800 mg (2.21 mmol) of 1-iodo-3,5-dibromobenzene (**8**) and 380 mg (2.11 mmol) of 5-ethynyl-2,2′-bipyridine (**4**) dissolved in 50 mL of degassed diisopropylamine were added 45 mg of [(PPh$_3$)$_2$PdCl$_2$] and 20 mg of [CuI] at 0 °C. The resulting reaction mixture was stirred for 2 h at this temperature, followed by stirring overnight at 35 °C. After cooling it to room temperature the suspension was filtered through

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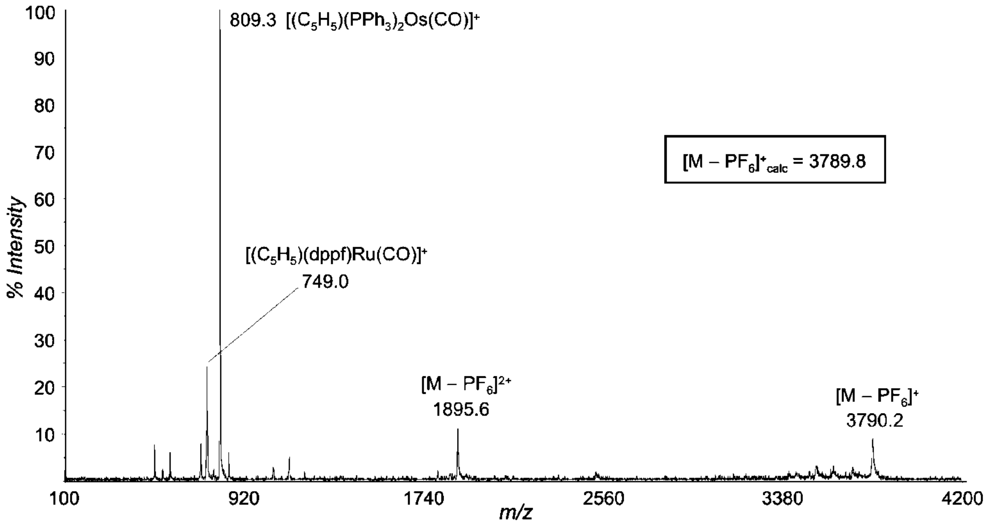

Figure 5. ESI-MS spectra of heteroheptanuclear **28**.

a pad of Celite and the filtrate was evaporated to dryness. The residue was purified by column chromatography on silica gel using a mixture of diethyl ether and petroleum ether (1:1, v/v) as eluent. After removal of the solvents under reduced pressure compound **9** was obtained as a colorless solid. Yield: 680 mg (1.64 mmol, 77% based on **4**).

Anal. Calcd for $C_{18}H_{10}Br_2N_2$ (414.10): C, 52.21; H, 2.43; N, 6.77. Found: C, 51.91; H, 2.11; N, 7.13. Mp: 152 °C. IR (KBr, cm^{-1}): 2221 (w, $\nu_{C\equiv C}$). ^1H NMR (δ, $CDCl_3$): 7.33 (ddd, $^3J_{H5'H4'} = 7.6$ Hz, $^3J_{H5'H6'} = 4.7$ Hz, $^4J_{H5'H3'} = 1.0$ Hz, 1 H, *H5'*/bpy), 7.65 (d, $^4J_{HH} = 1.6$ Hz, 2 H, C_6H_3), 7.67 (t, $^4J_{HH} = 1.6$ Hz, 1 H, C_6H_3), 7.84 (ddd, $^3J_{H4'H3'} = 8.0$ Hz, $^3J_{H4'H5'} = 7.6$ Hz, $^4J_{H4'H6'} = 1.8$ Hz, 1 H, *H4'*/bpy), 7.92 (dd, $^3J_{H4H3} = 8.2$ Hz, $^4J_{H4H6} = 2.0$ Hz, 1 H, *H4*/bpy), 8.43 (ddd, $^3J_{H3'H4'} = 8.0$ Hz, $^4J_{H3'H5'} = 1.0$ Hz, $^5J_{H3'H6'} = 1.0$ Hz, 1 H, *H3'*/bpy), 8.44 (dd, $^3J_{H3H4} = 8.2$ Hz, $^5J_{H3H6} = 1.0$ Hz, 1 H, *H3*/bpy), 8.70 (ddd, $^3J_{H6'H5'} = 4.7$ Hz, $^4J_{H6'H4'} = 1.8$ Hz, $^5J_{H6'H3'} = 1.0$ Hz, 1 H, *H6'*/bpy), 8.79 (dd, $^4J_{H6H4} = 2.0$ Hz, $^5J_{H6H3} = 1.0$ Hz, 1 H, *H6*/bpy). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 89.0 ($C\equiv C$), 90.4 ($C\equiv C$), 119.4 (*C5*/bpy), 120.5 (*C3*/bpy), 121.6 (*C3'*/bpy), 122.9 (C^i/C_6H_3), 124.2 (*C5'*/bpy), 126.1 (C^i/C_6H_3), 133.2 (CH/C_6H_3), 134.6 (CH/C_6H_3), 137.1 (*C4'*/bpy), 139.6 (*C4*/bpy), 149.5 (*C6'*/bpy), 151.8 (*C6*/bpy), 155.4 (C^i/bpy), 155.6 (C^i/bpy).

Synthesis of 1,3-(Me_3 $SiC\equiv C)_2$-5-(bpy$C\equiv C)C_6H_3$ (10). To 600 mg (1.45 mmol) of 1,3-Br_2-5-(bpy$C\equiv C)C_6H_3$ (**9**) dissolved in 50 mL of degassed diisopropylamine were added 380 mg (3.88 mmol) of trimethylsilylacetylene followed by 50 mg of $[(PPh_3)_2PdCl_2]$ and 25 mg of [CuI]. The resulting reaction mixture was stirred overnight at 50 °C. After cooling it to room temperature the suspension was filtered through a pad of Celite and the filtrate was evaporated to dryness. The residue was purified by column chromatography on alumina using a mixture of diethyl ether/petroleum ether (10:1, v/v) as eluent. The product was obtained as a colorless solid. Yield: 510 mg (1.14 mmol, 78% based on **9**).

Anal. Calcd for $C_{28}H_{28}N_2Si_2$ (448.72): C, 74.95; H, 6.29; N, 6.24. Found: C, 74.88; H, 6.76; N, 6.26. Mp: 143 °C. IR (KBr, cm^{-1}): 2158 (s, $\nu_{C\equiv CSi}$), 2220 (w, $\nu_{C\equiv Cbpy}$). ^1H NMR (δ, $CDCl_3$): 0.25 (s, 18 H, Si Me_3), 7.32 (ddd, $^3J_{H5'H4'} = 7.6$ Hz, $^3J_{H5'H6'} = 4.7$ Hz, $^4J_{H5'H3'} = 1.0$ Hz, 1 H, *H5'*/bpy), 7.55 (t, $^4J_{HH} = 1.6$ Hz, 1 H, C_6H_3), 7.60 (d, $^4J_{HH} = 1.6$ Hz, 2 H, C_6H_3), 7.83 (ddd, $^3J_{H4'H3'} = 8.0$ Hz, $^3J_{H4'H5'} = 7.6$ Hz, $^4J_{H4'H6'} = 1.8$ Hz, 1 H, *H4'*/bpy), 7.90 (dd, $^3J_{H4H3} = 8.2$ Hz, $^4J_{H4H6} = 2.0$ Hz, 1 H, *H4*/bpy), 8.39−8.44 (m, 2 H, *H3*,*H3'*/bpy), 8.69 (ddd, $^3J_{H6'H5'} = 4.7$ Hz, $^4J_{H6'H4'} = 1.8$ Hz, $^5J_{H6'H3'} = 1.0$ Hz, 1 H, *H6'*/bpy), 8.78 (dd, $^4J_{H6H4} = 2.0$ Hz, $^5J_{H6H3} = 1.0$ Hz, 1 H, *H6*/bpy). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 87.5 ($C\equiv Cbpy$), 91.8 ($C\equiv Cbpy$), 96.0 ($C\equiv CSi$), 103.1 ($C\equiv CSi$), 119.8 (*C5*/bpy), 120.4 (*C3*/bpy), 121.4 (*C3'*/bpy), 123.2 (C^i/C_6H_3), 124.0 (*C5'*/bpy), 124.0 (C^i/C_6H_3), 134.7 (CH/C_6H_3), 135.3 (CH/C_6H_3), 137.0 (*C4'*/bpy), 139.4 (*C4*/bpy), 149.4 (*C6'*/bpy), 151.7 (*C6*/bpy), 155.2 (C^i/bpy), 155.4 (C^i/bpy).

Synthesis of 1,3-($HC\equiv C)_2$-5-(bpy$C\equiv C)C_6H_3$ (11). To 450 mg (1.00 mmol) of 1,3-($Me_3SiC\equiv C)_2$-5-(bpy$C\equiv C)C_6H_3$ (**10**) dissolved in 40 mL of tetrahydrofuran was added 2.2 mL (2.20 mmol) of $[^nBu_4N]F$ (1 M solution in tetrahydrofuran) over a period of 10 min at 0 °C. After stirring this solution for 1 h at ambient temperature all volatiles were removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel using a mixture of diethyl ether/tetrahydrofuran (20:1, v/v) as eluent. The solvents were removed under reduced pressure, giving a colorless solid identified as **11**. Yield: 260 mg (0.86 mmol, 85% based on **10**).

Anal. Calcd for $C_{22}H_{12}N_2$ (304.35): C, 86.82; H, 3.97; N, 9.20. Found: C, 86.32; H, 4.09; N, 9.40. Mp: 168 °C. IR (KBr, cm^{-1}): 2109 (w, $\nu_{C\equiv CH}$), 2208 (w, $\nu_{C\equiv Cbpy}$), 3284 (s, $\nu_{\equiv C-H}$). ^1H NMR (δ, $CDCl_3$): 3.13 (s, 2 H, $\equiv C$ *H*), 7.32 (ddd, $^3J_{H5'H4'} = 7.6$ Hz, $^3J_{H5'H6'} = 4.7$ Hz, $^4J_{H5'H3'} = 1.0$ Hz, 1 H, *H5'*/bpy), 7.58 (t, $^4J_{HH} = 1.6$ Hz, 1 H, C_6H_3), 7.65 (d, $^4J_{HH} = 1.6$ Hz, 2 H, C_6H_3), 7.86 (ddd, $^3J_{H4'H3'} = 8.0$ Hz, $^3J_{H4'H5'} = 7.6$ Hz, $^4J_{H4'H6'} = 1.8$ Hz, 1 H, *H4'*/bpy), 7.92 (dd, $^3J_{H4H3} = 8.2$ Hz, $^4J_{H4H6} = 2.2$ Hz, 1 H, *H4*/bpy), 8.40−8.45 (m, 2 H, *H3*,*H3'*/bpy), 8.69 (ddd, $^3J_{H6'H5'} = 4.7$ Hz, $^4J_{H6'H4'} = 1.8$ Hz, $^5J_{H6'H3'} = 1.0$ Hz, 1 H, *H6'*/bpy), 8.80 (dd, $^4J_{H6H4} = 2.2$ Hz, $^5J_{H6H3} = 0.8$ Hz, 1 H, *H6*/bpy). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$): 78.9 ($C'\equiv CH$), 81.8 ($C\equiv CH$), 87.9 ($C\equiv Cbpy$), 91.5 ($C\equiv Cbpy$), 119.7 (*C5*/bpy), 120.5 (*C3*/bpy), 121.5 (*C3'*/bpy), 123.2 (C^i/C_6H_3), 123.5 (C^i/C_6H_3), 124.1 (*C5'*/bpy), 135.3 (CH/C_6H_3), 135.6 (CH/C_6H_3), 137.0 (*C4'*/bpy), 139.5 (*C4*/bpy), 149.4 (*C6'*/bpy), 151.8 (*C6*/bpy), 155.3 (C^i/bpy), 155.4 (C^i/bpy).

Synthesis of 1-[$(Ph_3P)_2(\eta^5$-$C_5H_5)OsC\equiv C$]-3-(bpy$C\equiv C$)-5-($HC\equiv C)C_6H_3$ (13) and 1,3-[$(Ph_3P)_2(\eta^5$-$C_5H_5)OsC\equiv C]_2$-5-(bpy-$C\equiv C)C_6H_3$ (14). A mixture of 320 mg (0.37 mmol) of $[(PPh_3)_2(\eta^5$-$C_5H_5)OsBr]$ (**12**), 150 mg (0.49 mmol) of 1,3-($HC\equiv C)_2$-5-(bpy$C\equiv C)C_6H_3$ (**11**), and 70 mg (0.43 mmol) of $[NH_4]PF_6$ was stirred in 60 mL of methanol for 3 h at reflux. During that time the orange suspension turned into a clear red solution, which was afterward cooled to room temperature. Then 20 mg (0.87 mmol) of sodium metal was added with stirring, forming a yellow precipitate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on alumina, eluting with diethyl ether/petroleum ether (3:1, v/v). At first, unreacted **11** was eluted. The following main fraction contained **13**. Finally complex **14** was isolated from the third band. Compounds **13** and **14** were isolated as pale yellow solids. Yield: **13**, 175 mg (0.16 mmol, 44% based on **12**); **14**, 160 mg (0.086 mmol, 46% based on **12**).

13: Anal. Calcd for $C_{63}H_{46}N_2OsP_2$ (1083.25): C, 69.85; H, 4.28; N, 2.59. Found: C, 69.74; H, 4.47; N, 2.58. IR (KBr, cm^{-1}): 2116 (w, $\nu_{C\equiv CH}$), 2061 (s, $\nu_{C\equiv COs}$), 2209 (w, $\nu_{C\equiv Cbpy}$), 3302 (m, $\nu_{\equiv C-H}$). ^{1}H NMR (δ, $CDCl_3$): 3.04 (s, 1 H, $\equiv C$ *H*), 4.42 (s, 5 H, C_5H_5), 7.07−7.24 (m, 20 H, C_6H_5), 7.28 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.32 (ddd, $^3J_{H5'H4'}$ = 7.5 Hz, $^3J_{H5'H6'}$ = 4.7 Hz, $^4J_{H5'H3'}$ = 1.0 Hz, 1 H, *H5′*/bpy), 7.34−7.43 (m, 10 H (C_6H_5) + 2 H (C_6H_3)), 7.83 (ddd, $^3J_{H4'H3'}$ = 8.0 Hz, $^3J_{H4'H5'}$ = 7.5 Hz, $^4J_{H4'H6'}$ = 1.7 Hz, 1 H, *H4′*/bpy), 7.94 (dd, $^3J_{H4H3}$ = 8.4 Hz, $^4J_{H4H6}$ = 2.2 Hz, 1 H, *H4*/bpy), 8.43 (dd, $^3J_{H3H4}$ = 8.4 Hz, $^5J_{H3H6}$ = 0.8 Hz, 1 H, *H3*/bpy), 8.44 (ddd, $^3J_{H3'H4'}$ = 8.0 Hz, $^4J_{H3'H5'}$ = 1.0 Hz, $^5J_{H3'H6'}$ = 1.0 Hz, 1 H, *H3′*/bpy), 8.70 (ddd, $^3J_{H6'H5'}$ = 4.7 Hz, $^4J_{H6'H4'}$ = 1.7 Hz, $^5J_{H6'H3'}$ = 1.0 Hz, 1 H, *H6′*/bpy), 8.82 (dd, $^4J_{H6H4}$ = 2.2 Hz, $^5J_{H6H3}$ = 0.8 Hz, 1 H, *H6*/bpy). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 0.8 (Os *P*Ph$_3$).

14: Anal. Calcd for $C_{104}H_{80}N_2Os_2P_4$ (1862.15): C, 67.08; H, 4.33; N, 1.50. Found: C, 67.12; H, 4.63; N, 1.83. IR (KBr, cm^{-1}): 2063 (s, $\nu_{C\equiv COs}$), 2209 (w, $\nu_{C\equiv Cbpy}$). ^{1}H NMR (δ, $CDCl_3$): 4.41 (s, 10 H, C_5H_5), 6.93 (d, J_{HH} = 1.6 Hz, 2 H, C_6H_3), 7.03−7.17 (m, 40 H, C_6H_5), 7.31 (ddd, $^3J_{H5'H4'}$ = 7.6 Hz, $^3J_{H5'H6'}$ = 4.7 Hz, $^4J_{H5'H3'}$ = 1.0 Hz, 1 H, *H5′*/bpy), 7.38−7.50 (m, 20 H (C_6H_5) + 1 H (C_6H_3)), 7.83 (ddd, $^3J_{H4'H3'}$ = 7.9 Hz, $^3J_{H4'H5'}$ = 7.6 Hz, $^4J_{H4'H6'}$ = 1.7 Hz, 1 H, *H4′*/bpy), 7.96 (dd, $^3J_{H4H3}$ = 8.2 Hz, $^4J_{H4H6}$ = 2.2 Hz, 1 H, *H4*/bpy), 8.42 (dd, $^3J_{H3H4}$ = 8.2 Hz, $^5J_{H3H6}$ = 0.8 Hz, 1 H, *H3*/bpy), 8.44 (ddd, $^3J_{H3'H4'}$ = 7.9 Hz, $^4J_{H3'H5'}$ = 1.0 Hz, $^5J_{H3'H6'}$ = 1.0 Hz, 1 H, *H3′*/bpy), 8.70 (ddd, $^3J_{H6'H5'}$ = 4.7 Hz, $^4J_{H6'H4'}$ = 1.7 Hz, $^5J_{H6'H3'}$ = 1.0 Hz, 1 H, *H6′*/bpy), 8.86 (dd, $^4J_{H6H4}$ = 2.2 Hz, $^5J_{H6H3}$ = 0.8 Hz, 1 H, *H6*/bpy). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 0.5 (Os *P*Ph$_3$).

Synthesis of *trans*-[(PPh$_3$)$_2$Pt{1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(C≡C)C$_6$H$_3$}{1-[(Ph$_3$ P)$_2$(η^5-C$_5$H$_5$)OsC≡C]-3-(bpyC≡C)-5-(C≡C)C$_6$H$_3$}] (15). To 50 mg (0.031 mmol) of 1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-[*trans*-(Ph$_3$P)$_2$(Cl)PtC≡C]C$_6$H$_3$ (**1**) and 40 mg (0.037 mmol) of 1-[(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)OsC≡C]-3-(bpyC≡C)-5-(HC≡C)C$_6$H$_3$ (**13**) dissolved in 10 mL of chloroform and 10 mL of diethylamine was added 1 mg of [CuI]. The resulting reaction mixture was stirred for 3.5 h between 30 and 40 °C. After cooling the mixture to room temperature all volatiles were removed in an oil-pump vacuum and the residue was purified by column chromatography on silica gel using a mixture of dichloromethane/toluene (3:1, v/v) as eluent. Complex **15** was obtained as an orange powder. Yield: 60 mg (0.022 mmol, 72% based on **1**).

Anal. Calcd for $C_{142}H_{111}FeN_4O_3OsP_4PtRe$ (2672.72): C, 63.81; H, 4.19; N, 2.10. Found: C, 63.55; H, 4.29; N, 1.90. IR (KBr, cm^{-1}): 1895, 1905, 2004 (s, ν_{CO}), 2065 (m, $\nu_{C\equiv COs}$), 2097 (m, $\nu_{C\equiv CPt}$), 2212 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, $CDCl_3$): 1.43 (s, 18 H, ^{t}Bu), 4.18 (s, 5 H, C_5H_5/Fc), 4.19 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 4.37 (s, 5 H, C_5H_5/Os), 4.38 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 5.96 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 5.99 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.01 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.33 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.55 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.80 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 7.00−7.17 (m, 20 H, C_6H_5), 7.24−7.45 (m, 30 H (C_6H_5) + 2 H (*H5*/^{t}Bu$_2$bpy) + 1 H (*H5′*/bpy)), 7.71 − 7.86 (m, 10 H (C_6H_5) + 1 H (*H4′*/bpy)), 7.90 (dd, $^3J_{H4H3}$ = 8.4 Hz, $^4J_{H4H6}$ = 2.2 Hz, 1 H, H4/bpy) 8.05 (d, $^4J_{H3H5}$ = 1.7 Hz, *H3*/^{t}Bu$_2$bpy), 8.41 (dd, $^3J_{H3H4}$ = 8.2 Hz, $^5J_{H3H6}$ = 1.0 Hz, 1 H, *H3*/bpy), 8.43 (ddd, $^3J_{H3'H4'}$ = 8.0 Hz, $^4J_{H3'H5'}$ = 1.0 Hz, $^5J_{H3'H6'}$ = 1.0 Hz, 1 H, *H3′*/bpy), 8.70 (ddd, $^3J_{H6'H5'}$ = 4.8 Hz, $^4J_{H6'H4'}$ = 1.7 Hz, $^5J_{H6'H3'}$ = 1.0 Hz, 1 H, *H6′*/bpy), 8.80 (dd, $^4J_{H6H4}$ = 2.2 Hz, $^5J_{H6H3}$ = 1.0 Hz, 1 H, *H6*/bpy), 8.97 (d, $^3J_{H6H5}$ = 5.8 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 0.4 (Os *P*Ph$_3$), 17.5 ($^1J_{^{31}P^{195}Pt}$ = 2650 Hz, Pt *P*Ph$_3$). MS (ESI-TOF, *m*/*z*): 2674.1 [M + H]$^+$, 809.4 [(PPh$_3$)$_2$(C$_5$H$_5$)Os(CO)]$^+$.

Synthesis of *trans*-[(PPh$_3$)$_2$Pt{1-(FcC≡C)-3-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-5-(C≡C)C$_6$H$_3$}{1-[(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)OsC≡C]-3-[{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu-bpyC≡C]-5-(C≡C)C$_6$H$_3$}]PF$_6$ (16). To a stirred solution of [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF$_6$ (**6**) (15 mg, 0.019 mmol) in 20 mL of degassed tetrahydrofuran was added **15** (50 mg, 0.019 mmol) in a single portion. During 2.5 h of stirring at 25 °C the color of the reaction solution changed from orange to red. Afterward all volatiles were removed under reduced pressure and the residue was redissolved in 2 mL of dichloromethane. Complex **16** was precipitated from this solution by the addition of 20 mL of *n*-hexane. After removal of the supernatant solution the remaining solid was washed twice with 10 mL portions of diethyl ether and dried in an oil-pump vacuum to afford an orange-red solid. Yield: 56 mg (0.016 mmol, 84% based on **15**).

Anal. Calcd for $C_{168}H_{155}CuF_6FeN_4O_3OsP_5PtReSi_4Ti \times CH_2Cl_2$ (3482.96): C, 58.28; H, 4.54; N, 1.61. Found: C, 58.26; H, 4.53; N, 1.61. IR (KBr, cm^{-1}): 1900, 2003 (s, ν_{CO}), 2064 (m, $\nu_{C\equiv COs}$), 2095 (m, $\nu_{C\equiv CPt}$), 2207 (w, $\nu_{C\equiv CFc}$). ^{1}H NMR (δ, $CDCl_3$): −0.46 (s, 18 H, Si *Me*$_3$), 0.26 (s, 9 H, Si *Me*$_3$), 0.29 (s, 9 H, Si *Me*$_3$), 1.43 (s, 18 H, ^{t}Bu), 4.17 (s, 5 H, C_5H_5/Fc), 4.18 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 4.36 (s, 5 H, C_5H_5/Os), 4.37 (pt, J_{HH} = 1.9 Hz, 2 H, C_5H_4), 5.30 (s, 2 H, C *H*$_2$Cl$_2$), 5.94 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 5.99 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.03 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.30 (br s, 8 H, C_5H_4Si), 6.38 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.53 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.82 (pt, J_{HH} = 1.6 Hz, 1 H, C_6H_3), 6.99 − 7.14 (m, 20 H, C_6H_5), 7.25−7.45 (m, 30 H (C_6H_5) + 2 H (*H5*/^{t}Bu$_2$bpy)), 7.70 − 7.80 (m, 10 H (C_6H_5) + 1 H (*H5′*/bpy)), 8.06 (d, $^4J_{H3H5}$ = 1.7 Hz, *H3*/^{t}Bu$_2$bpy), 8.18−8.30 (m, 2 H, *H4*,*H4′*/bpy), 8.49−8.67 (m, 4 H, *H3*,*H3′*,*H6*,*H6′*/bpy), 8.96 (d, $^3J_{H6H5}$ = 6.0 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −145.1 (septet, $^1J_{PF}$ = 713 Hz, *P*F$_6$), 0.4 (Os *P*Ph$_3$), 17.6 ($^1J_{^{31}P^{195}Pt}$ = 2645 Hz, Pt *P*Ph$_3$). MS (ESI-TOF, *m*/*z*): 3253.6 [M − PF$_6$]$^+$, 1627.7 [M − PF$_6$]$^{2+}$, 809.4 [(PPh$_3$)$_2$(C$_5$H$_5$)Os(CO)]$^+$.

Synthesis of 1,3-[(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)OsC≡C]$_2$-5-[(CO)$_3$ ClRe(bpyC≡C)]C$_6$H$_3$ (18). To a solution of 20 mg (0.055 mmol) of [Re(CO)$_5$Cl] (**17**) in 30 mL of degassed toluene was added **14** (120 mg, 0.064 mmol) in a single portion. The resulting reaction mixture was heated to 50 °C, and stirring was continued for 5 h at this temperature, whereby the color of the solution turned from yellow to dark red and the desired product partly precipitated. After cooling the reaction solution to ambient temperature the solvent was removed under vacuum and the remaining residue was subjected to column chromatography on alumina. Eluting with dichloromethane/toluene (1:1, v/v) gave an excess of **14**. Changing the eluent to acetone/toluene (1:1, v/v) gave the title complex **18** as a red-brown solid. Yield: 80 mg (0.037 mmol, 67% based on **17**).

Anal. Calcd for $C_{107}H_{80}ClN_2O_3Os_2P_4Re \times 1/2C_7H_8$ (2213.88): C, 59.95; H, 3.82; N, 1.27. Found: C, 59.79; H, 3.79; N, 1.24. IR (KBr, cm^{-1}): 1894, 1918, 2019 (s, ν_{CO}), 2059 (s, $\nu_{C\equiv COs}$), 2203 (w, $\nu_{C\equiv Cbpy}$). ^{1}H NMR (δ, $CDCl_3$): 2.35 (s, 1.5 H, C*H*$_3$/C$_7$H$_8$), 4.43 (s, 10 H, C_5H_5), 6.92 (d, J_{HH} = 1.6 Hz, 2 H, C_6H_3), 7.04−7.23 (m, 40 H (C_6H_5) + 2.5 H (C_7H_8)), 7.32 (ddd, $^3J_{H5'H4'}$ = 7.6 Hz, $^3J_{H5'H6'}$ = 4.7 Hz, $^4J_{H5'H3'}$ = 1.2 Hz, 1 H, *H5′*/bpy), 7.40−7.51 (m, 20 H (C_6H_5) + 1 H (C_6H_3)), 7.90 (ddd, $^3J_{H4'H3'}$ = 8.0 Hz, $^3J_{H4'H5'}$ = 7.6 Hz, $^4J_{H4'H6'}$ = 1.6 Hz, 1 H, *H4′*/bpy), 7.97−8.07 (m, 3 H, H3,H3′,H4/bpy), 8.93 (ddd, $^3J_{H6'H5'}$ = 4.7 Hz, $^4J_{H6'H4'}$ = 1.6 Hz, $^5J_{H6'H3'}$ = 1.0 Hz, 1 H, *H6′*/bpy), 9.13 (dd, $^4J_{H6H4}$ = 2.0 Hz, $^5J_{H6H3}$ = 0.8 Hz, 1 H, *H6*/bpy). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 0.6 (Os *P*Ph$_3$). MS (ESI-TOF, *m*/*z*): 2169.74 [M + H]$^+$, 809.3 [(PPh$_3$)$_2$(C$_5$H$_5$)Os(CO)]$^+$.

Modified Synthesis of 1-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-3,5-(HC≡C)$_2$-C$_6$H$_3$ (21).[9b] To a solution of 1,3,5-triethynylbenzene (**19**) (160 mg, 1.067 mmol) in 30 mL of toluene was added 0.65 mL (1.04 mmol) of methyllithium (1.6 M in diethyl ether) at −20 °C. This reaction solution was then allowed to warm to 25 °C and [(^{t}Bu$_2$-bpy)(CO)$_3$ReCl] (**20**) (200 mg, 0.348 mmol) was added in a single portion. The resulting reaction mixture was subsequently heated to reflux under an inert atmosphere of nitrogen for 5 h. After cooling to 25 °C all volatiles were removed under reduced pressure. The remaining material was subjected to column chromatography on silica gel using a mixture of diethyl ether/petroleum ether (3:1, v/v) as the eluent. After removal of the first band, which contained unreacted 1,3,5-triethynylbenzene, the second band was collected to give complex **21** as a yellow solid. Yield: 125 mg (0.182 mmol, 52% based on **20**). *Please note: The analytical data of **21** correspond to literature values.*[9b]

Synthesis of 1-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-3-[(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C]-5-(HC≡C)C$_6$H$_3$ (23) and 1-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-3,5-[(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C]$_2$C$_6$H$_3$ (24). To 220 mg (0.291 mmol) of [(η^2-dppf)(η^5-C$_5$H$_5$)RuCl] (**22**) and 200 mg (0.291 mmol) of **21** dissolved in 25 mL of dichloromethane and 25 mL of methanol were successively added [NH$_4$]PF$_6$ (55 mg, 0.337 mmol) and KO^{t}Bu (40 mg, 0.357 mmol). The reaction mixture was stirred for 4 h at ambient temperature. After removal of the solvent under reduced pressure the residue was purified by column chromatography on alumina, eluting with diethyl ether/*n*-hexane (4:1, v/v). First unreacted **21** was eluted. The following main fraction contained the dinuclear complex **23**, and finally complex **24** was isolated from the third band. Compounds **23** and **24** were isolated as orange solids. Yield: **23**, 170 mg (0.121 mmol, 41% based on **21**); **24**, 155 mg (0.079 mmol, 25% based on **21**).

23: Anal. Calcd for $C_{72}H_{61}FeN_2O_3P_2ReRu$ (1407.35): C, 61.45; H, 4.37; N, 1.99. Found: C, 61.69; H, 4.72; N, 1.89. IR (KBr, cm^{-1}): 1895, 2003 (s, ν_{CO}), 2062 (m, $\nu_{C\equiv CRu}$), 2103 (w, $\nu_{C\equiv CRe}$), 3307 (m, $\nu_{\equiv C-H}$). ^{1}H NMR (δ, CDCl$_3$): 1.46 (s, 18 H, ^{t}Bu), 2.86 (s, 1 H, 'C *H*), 3.94 (dpt, J_{HP} = 1.2 Hz, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 4.17 (br s, 2 H, C$_5$*H*$_4$), 4.24 (s, 5 H, C$_5$*H*$_5$), 4.26 (br s, 2 H, C$_5$*H*$_4$), 5.24 (br s, 2 H, C$_5$*H*$_4$), 6.55 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.96 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 7.07 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 7.24−7.53 (m, 16 H, C$_6$*H*$_5$), 7.46 (dd, $^3J_{H5H6}$ = 6.0 Hz, $^4J_{H5H3}$ = 2.0 Hz, *H5*/^{t}Bu$_2$bpy), 7.71−7.81 (m, 4 H, C$_6$*H*$_5$), 8.09 (d, $^4J_{H3H5}$ = 2.0 Hz, *H3*/^{t}Bu$_2$bpy), 9.00 (d, $^3J_{H6H5}$ = 6.0 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 53.9 (dppf).

24: Anal. Calcd for $C_{111}H_{93}Fe_2N_2O_3P_4ReRu_2$ (2126.90): C, 62.68; H, 4.41; N, 1.32. Found: C, 63.25; H, 4.81; N, 1.23. IR (KBr, cm^{-1}): 1891, 1902, 2002 (s, ν_{CO}), 2065 (m, $\nu_{C\equiv CRu}$), 2102 (w, $\nu_{C\equiv CRe}$). ^{1}H NMR (δ, CDCl$_3$): 1.40 (s, 18 H, ^{t}Bu), 3.89 (dpt, J_{HP} = 1.2 Hz, J_{HH} = 2.4 Hz, 4 H, C$_5$*H*$_4$), 4.07 (br s, 4 H, C$_5$*H*$_4$), 4.23 (br s, 4 H, C$_5$*H*$_4$), 4.25 (s, 10 H, C$_5$*H*$_5$), 5.43 (br s, 4 H, C$_5$*H*$_4$), 6.82 (d, J_{HH} = 1.6 Hz, 2 H, C$_6$*H*$_3$), 6.96 (t, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 7.12−7.53 (m, 32 H (C$_6$*H*$_5$) + 2 H (*H5*/^{t}Bu$_2$bpy)), 7.76−7.85 (m, 8 H, C$_6$*H*$_5$), 8.09 (d, $^4J_{H3H5}$ = 1.7 Hz, *H3*/^{t}Bu$_2$bpy), 9.06 (d, $^3J_{H6H5}$ = 6.0 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 53.9 (dppf).

Synthesis of 1-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-3-[(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C]-5-[*trans*-(Ph$_3$P)$_2$(Cl)PtC≡C]C$_6$H$_3$ (26). To 100 mg (0.071 mmol) of **23** and 70 mg (0.089 mmol) of *cis*-[(PPh$_3$)$_2$PtCl$_2$] (**25**) dissolved in 20 mL of chloroform was added 0.5 mL of diethylamine. The resulting reaction mixture was heated to reflux for 5 h. After cooling to room temperature and removal of the solvents under reduced pressure, preparative TLC of the residue (alumina, dichloromethane/toluene, 3:1, v/v) gave a major orange band, from which complex **26** was obtained as an orange powder. Yield: 90 mg (0.042 mmol, 58% based on **23**).

Anal. Calcd for $C_{108}H_{90}ClFeN_2O_3P_4PtReRu$ (2162.44): C, 59.99; H, 4.20; N, 1.30. Found: C, 60.07; H, 4.52; N, 1.23. IR (KBr, cm^{-1}): 1891, 1900, 2002 (s, ν_{CO}), 2067 (m, $\nu_{C\equiv CRu}$), 2096 (w, $\nu_{C\equiv CRe}$), 2119 (w, $\nu_{C\equiv CPt}$). ^{1}H NMR (δ, CDCl$_3$): 1.39 (s, 18 H, ^{t}Bu), 3.89 (dpt, J_{HP} = 1.2 Hz, J_{HH} = 2.4 Hz, 2 H, C$_5$*H*$_4$), 3.99 (br s, 2 H, C$_5$*H*$_4$), 4.20 (s, 5 H, C$_5$*H*$_5$), 4.22 (br s, 2 H, C$_5$*H*$_4$), 5.26 (br s, 2 H, C$_5$*H*$_4$), 5.49 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 5.94 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.67 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 7.12−7.47 (m, 32 H (C$_6$*H*$_5$) + 2 H (*H5*/^{t}Bu$_2$bpy)), 7.67−7.77 (m, 18 H, C$_6$*H*$_5$), 8.06 (d, $^4J_{H3H5}$ = 2.0 Hz, *H3*/^{t}Bu$_2$bpy), 9.01 (d, $^3J_{H6H5}$ = 6.0 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 20.3 ($^1J_{^{31}P^{195}Pt}$ = 2669 Hz, Pt *P*Ph$_3$), 53.9 (dppf). MS (ESI-TOF, *m*/*z*): 2164.9 [M + H]$^+$, 749.2 [(dppf)(C$_5$H$_5$)Ru(CO)]$^+$.

Synthesis of *trans*-[(PPh$_3$)$_2$Pt{1-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-3-[(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C]-5-(C≡C)C$_6$H$_3$}{1-[(Ph$_3$P)$_2$(η^5-C$_5$H$_5$)OsC≡C]-3-(bpyC≡C)-5-(C≡C)C$_6$H$_3$}] (27). To 70 mg (0.032 mmol) of complex **26** and 45 mg (0.042 mmol) of **13** dissolved in 10 mL of chloroform and 10 mL of diethylamine was added 1 mg of [CuI]. The resulting reaction mixture was stirred for 4 h at 30 °C. Afterward all volatiles were removed in an oil-pump vacuum and the residue was purified by column chromatography on alumina using a mixture of dichloromethane/toluene (5:1, v/v) as eluent. Complex **27** was obtained as an orange solid. Yield: 65 mg (0.02 mmol, 63% based on **26**).

Anal. Calcd for $C_{171}H_{135}FeN_4O_3OsP_6PtReRu$ (3208.25): C, 64.02; H, 4.24; N, 1.75. Found: C, 64.52; H, 4.13; N, 1.69. IR (KBr, cm^{-1}): 1894, 1901, 2003 (s, ν_{CO}), 2064 (m, $\nu_{C\equiv COs(Ru)}$), 2102 (m, $\nu_{C\equiv CPt}$), 2210 (w, $\nu_{C\equiv Cbpy}$). ^{1}H NMR (δ, CDCl$_3$): 1.39 (s, 18 H, ^{t}Bu), 3.90 (br s, 2 H, C$_5$*H*$_4$), 4.04 (br s, 2 H, C$_5$*H*$_4$), 4.21 (s, 5 H, C$_5$*H*$_5$/Ru), 4.23 (br s, 2 H, C$_5$*H*$_4$), 4.38 (s, 5 H, C$_5$*H*$_5$/Os), 5.32 (br s, 2 H, C$_5$*H*$_4$), 5.70 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 5.97 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.14 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.32 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.73 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.81 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 7.02 − 7.48 (m, 52 H (C$_6$*H*$_5$) + 2 H (*H5*/^{t}Bu$_2$bpy) + 1 H (*H5′*/bpy)), 7.70−7.84 (m, 18 H (C$_6$*H*$_5$) + 1 H (*H4′*/bpy)), 7.91 (dd, $^3J_{H4H3}$ = 8.2 Hz, $^4J_{H4H6}$ = 2.2 Hz, 1 H, *H4*/bpy), 8.06 (d, $^4J_{H3H5}$ = 1.7 Hz, *H3*/^{t}Bu$_2$bpy), 8.42 (dd, $^3J_{H3H4}$ = 8.2 Hz, $^5J_{H3H6}$ = 0.8 Hz, 1 H, *H3*/bpy), 8.43 (ddd, $^3J_{H3'H4'}$ = 8.0 Hz, $^4J_{H3'H5'}$ = 1.0 Hz, $^5J_{H3'H6'}$ = 1.0 Hz, 1 H, *H3′*/bpy), 8.70 (ddd, $^3J_{H6'H5'}$ = 4.7 Hz, $^4J_{H6'H4'}$ = 1.7 Hz, $^5J_{H6'H3'}$ = 1.0 Hz, 1 H, *H6′*/bpy), 8.81 (dd, $^4J_{H6H4}$ = 2.2 Hz, $^5J_{H6H3}$ = 0.8 Hz, 1 H, *H6*/bpy), 9.02 (d, $^3J_{H6H5}$ = 6.0 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 0.4 (Os *P*Ph$_3$), 17.3 ($^1J_{^{31}P^{195}Pt}$ = 2659 Hz, Pt*P*Ph$_3$), 54.0 (dppf).

Synthesis of *trans*-[(PPh$_3$)$_2$Pt{1-[(^{t}Bu$_2$bpy)(CO)$_3$ReC≡C]-3-[(η^2-dppf)(η^5-C$_5$H$_5$)RuC≡C]-5-(C≡C)C$_6$H $_3$}{1-[(Ph$_3$ P)$_2$(η^5-C$_5$H$_5$)OsC≡C]-3-[{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu-bpyC≡C]-5-(C≡C)C$_6$H$_3$}]PF$_6$ (28). To a stirred solution of **27** (45 mg, 0.014 mmol) in 15 mL of degassed tetrahydrofuran was added [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(N≡CMe)]PF$_6$ (**6**) (11 mg, 0.014 mmol) in a single portion at 25 °C. During the reaction time of 2.5 h a color change from orange to red was observed. Subsequently, all volatiles were removed under reduced pressure and the residue was redissolved in 2 mL of dichloromethane. Precipitation of the title complex **28** was achieved by addition of *n*-hexane (15 mL). The supernatant solution was removed, and the precipitate was washed twice with 10 mL portions of diethyl ether. Drying in an oil-pump vacuum provided complex **28** as an orange-red solid. Yield: 50 mg (0.013 mmol, 91% based on **27**).

Anal. Calc for $C_{197}H_{179}CuF_6FeN_4O_3OsP_7PtReRuSi_4Ti$ (3933.61): C, 60.15; H, 4.59; N, 1.42. Found: C, 59.67; H, 4.69; N, 1.42. IR (KBr, cm^{-1}): 1899, 2002 (s, ν_{CO}), 2062 (m, $\nu_{C\equiv COs(Ru)}$), 2101 (m, $\nu_{C\equiv CPt}$), 2207 (w, $\nu_{C\equiv Cbpy}$). ^{1}H NMR (δ, CDCl$_3$): −0.45 (s, 18 H, SiMe$_3$), 0.26 (s, 9 H, SiMe$_3$), 0.29 (s, 9 H, SiMe$_3$), 1.38 (s, 18 H, ^{t}Bu), 3.89 (br s, 2 H, C$_5$*H*$_4$/dppf), 4.01 (br s, 2 H, C$_5$*H*$_4$/dppf), 4.20 (s, 5 H, C$_5$*H*$_5$/Ru), 4.23 (br s, 2 H, C$_5$*H*$_4$/dppf), 4.37 (s, 5 H, C$_5$*H*$_5$/Os), 5.29 (br s, 2 H, C$_5$*H*$_4$/dppf), 5.67 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.01 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.10 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.30 (s, 8 H, C$_5$*H*$_4$Si), 6.37 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.70 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.81 (pt, J_{HH} = 1.6 Hz, 1 H, C$_6$*H*$_3$), 6.98 − 7.48 (m, 52 H (C$_6$*H*$_5$) + 2 H (*H5*/^{t}Bu$_2$bpy)), 7.68−7.82 (m, 18 H (C$_6$*H*$_5$) + 1 H (*H5′*/bpy)), 8.07 (d, $^4J_{H3H5}$ = 1.8 Hz, *H3*/^{t}Bu$_2$bpy), 8.18−8.30 (m, 2 H, *H4*,*H4′*/bpy), 8.48−8.67 (m, 4 H, *H3*,*H3′*,*H6*,*H6′*/bpy), 9.01 (d, $^3J_{H6H5}$ = 5.8 Hz, *H6*/^{t}Bu$_2$bpy). ^{31}P{^{1}H} NMR (δ, CDCl$_3$): −145.1 (septet, $^1J_{PF}$ = 713 Hz, *P*F$_6$), 0.4 (Os *P*Ph$_3$), 17.4 ($^1J_{^{31}P^{195}Pt}$ = 2652 Hz, Pt *P*Ph$_3$), 53.9 (dppf). MS (ESI-TOF, *m*/*z*): 3790.2 [M−PF$_6$]$^+$, 1895.6 [M−PF$_6$]$^{2+}$, 809.3 [(PPh$_3$)$_2$(C$_5$H$_5$)Os(CO)]$^+$, 749.0 [(dppf)(C$_5$H$_5$)Ru(CO)]$^+$, 579.2 [{[Ti](C≡CSiMe$_3$)$_2$}Cu]$^+$.

Crystal Structure Determinations. Crystal data for **3** and **18** are presented in Table 1. The data for **3** and **18** were collected on a Oxford Gemini S diffractometer with graphite-monochromatized Mo Kα (λ = 0.71073 Å, **3**) or Cu Kα radiation (λ = 1.54184 Å, **18**) at 100(2) K using oil-coated shock-cooled crystals.[31] The

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structures were solved by direct methods using SHELXS-97[32] or SIR-92[33] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[34] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, angles, torsion angles, and anisotropic displacement parameters for **3** and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800232M

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