MIXED TRANSITION METAL ACETYLIDES CONNECTED BY CARBON-RICH BRIDGING UNITS: ON THE WAY TO HETEROHEXAMETALLIC ORGANOMETALLICS

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Dedicated to Dr Karel Mach, a very distinguished scientist and good friend, on the occasion of his 70th birthday and in recognition of his outstanding contributions to the area of organometallic synthesis and catalysis.

This review describes the synthesis, reaction chemistry, structures and bonding of heterotri- to heterohexametallic complexes with early and late transition metal centres by applying the molecular Tinkertoy approach. The use of π-conjugated carbon-rich multifunctional organic units such as alkynyl-functionalized bipyridine, 1,4-di- and 1,3,5-trisubstituted benzene or phosphane moieties connecting the different metal atoms, is highlighted.
Keywords: Heteromultimetallic complexes; Transition metals; Organometallic π-tweezers; Alkyne complexes; Bipyridine ligands; Ferrocene; Half-sandwich complexes; Metallocenes.

The coordinative and covalent linking of modular constructed transition metal building blocks to generate heteromultimetallic assemblies has gained increasing interest in the last few years because such species may find applications in diverse areas, for example, in the fields of electroluminescence, information storage materials and photochemical molecular devices[1]. In addition, polynuclear metal complexes featuring unsaturated bridging ligands are of interest as they may be used as representative model compounds in the fundamental study of electron-transfer and photoinduced energy-transfer processes[1]. One possible design strategy for the preparation of such complexes rests on the principle of molecular manufacturing[2,3]. Generally, this approach requires the prior preparation of multifunctional organic molecules, which allows the stepwise synthesis of multitopic organometallic species. Numerous different functional groups may be used as binding sites within the multifunctional ligand scaffold in-

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cluding moieties such as acetylides, phosphines, and *N*,*N*,(*N*)-donors (*N*,*N*,(*N*) = bi- or tridentate Lewis base) to control the synthesis of multimetallic complexes. 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[4]. Examples of ligands that take advantage of such connectivities include all-carbon alkyne ligands[5,6] and cumulenes[1k,7], aryldiethynyl units[8,9], 1-(diphenylphosphanyl)-4-ethynylbenzene[10], 1,3,5-triethynylbenzene[11,12], 5-ethynyl-2,2′-bipyridine[13], and 2,5-dialkynylthiophenes[14,15]. Based on these cores, mainly homometallic assemblies have been synthesized[5,7,8,10,11,14], although only little is known about heteromultimetallic transition metal species.

In this context we focus here on the synthesis of heterotri- to heterohexametallic transition metal complexes, a hitherto barely explored class of compounds, using multitopic organometallic and organic building blocks. This review is therefore divided into three sections: 1. heterotrimetallic, 2. heterotetrametallic, and 3. heteropentametallic and heterohexametallic transition metal complexes. In all of the heteromultimetallic compounds described here, different early and late transition metals are spanned by π-conjugated carbon-rich organic moieties allowing electronic interactions between the metals along the bridging groups.

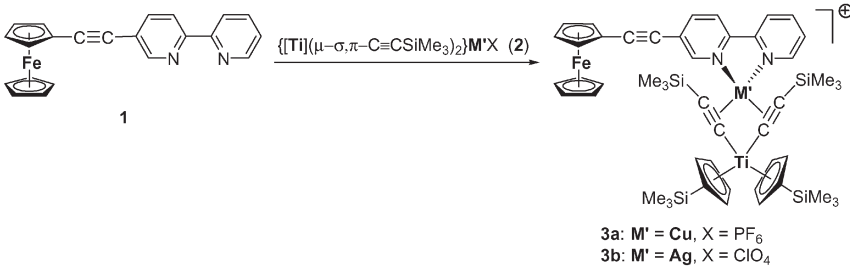
This article is a continued amendment of a recently published review in this field of chemistry by Lang et al., which includes recent developments in organometallic π-tweezer chemistry, i.e. interconversion of alkynyl coordination modes in molecules of the type $\{[M](C{\equiv}CR)_2\}[M']$ ($[M] = Ti(\eta^5\text{-}C_5H_5)_2$, $Ti(\eta^5\text{-}C_5H_4SiMe_3)_2$, ...; $[M'] = M'X$: M' = Cu, Ag, Au, ..., X = neutral or ionic inorganic or organic two-electron donor; M' = Ni, Co, X = CO, PPh_3, ...; $[M'] = M'X_2$: M' = Fe, Co, Ni, ..., X = halide, ...)[16]. In the previous review, the chemistry of mono- and dialkynyl transition metal complexes, functionalized diaminoaryl NCN pincer molecules (NCN = $[2,6\text{-}C_6H_2(CH_2NMe_2)_2]^-$) and modified ferrocenes with diverse metal fragments was addressed and served to understand the numerous and sometimes unexpected reaction behavior of such species[16]. Also a critical review on the concept of connecting early and late transition metal building blocks through all-carbon and other carbon-rich μ-σ,π-conjugated organic and/or inorganic groups, thereby enabling the synthesis of a large variety of mainly heterobimetallic early-late transition metal complexes, by applying the molecular Tinkertoy approach was included[16].

However, in the present review, clusters or (linear) transition metal complexes with direct metal–metal interactions will not be considered.

1. Heterotrimetallic Transition Metal Complexes

There are several methodologies available to synthesize heterotrimetallic complexes that rely on combining appropriate functionalized mononuclear and heterobimetallic transition metal complexes.

One example is the family of [FcC≡C-bipy{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M′]X complexes (**3a**: M′ = Cu, X = PF$_6$; **3b**: M′ = Ag, X = ClO$_4$; [Ti] = Ti(η^5-C$_5$H$_4$SiMe$_3$)$_2$; Fc = Fe(η^5-C$_5$H$_4$)(η^5-C$_5$H$_5$); bipy = 2,2′-bipyridine-5-yl) (Eq. (*1*)) in which the Group 11 metals, copper and silver, are chelated by the organometallic π-tweezer [Ti](C≡CSiMe$_3$)$_2$ and the bipyridine ligand, resulting in tetracoordination at M′. These complexes are accessible by combining the mononuclear ferrocene acetylide FcC≡C-bipy (**1**) with the heterobimetallic building block {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M′X (**2a**: M′X = [Cu(MeCN)]PF$_6$, **2b**: M′X = AgOClO$_3$ [17]. While red **3a** and **3b** are stable in the solid state, they slowly start to decompose in solution on exposure to air, i.e. **3b** gives elemental silver along with **1** and [Ti](C≡CSiMe$_3$)$_2$ (**4**)[17].



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3a: **M' = Cu**, X = PF$_6$
3b: **M' = Ag**, X = ClO$_4$

(1)

For **3a** the solid state structure could be determined by single-crystal X-ray structure analysis (Fig. 1)[17].

Heterotrimetallic **3a** shows a pseudotetrahedral coordination geometry around Cu1 with two η^2-coordinated Me$_3$SiC≡C groups (C23–C24, C28–C29) and the chelated bipy ligand (N1, N2) (Fig. 1). The difference between Cu1–N1 (2.225(4) Å) and Cu1–N2 (2.044(4) Å) which verifies an asymmetrical chelate binding of the bipyridine ligand to Cu1 is noteworthy. The large dissimilarity between Cu1–N1 and Cu1–N2 in **3a** can most probably be ascribed to electronic effects resulting from the electron-rich FcC≡C unit.

A similar structural motif including a {Pt(μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(FBF$_3$) organometallic π-tweezer fragment is found in FcC≡C-bipy-{[Pt(μ-σ,π-C≡CSiMe$_3$)$_2$]Cu(FBF$_3$)} (**7**) that can be prepared successively by alkynylation of FcC≡C-bipy(PtCl$_2$) (**5**) with (trimethylsilyl)acetylene in the presence of diisopropylamine and catalytic amounts of CuI to give FcC≡C-bipy[Pt(C≡CSiMe$_3$)$_2$] (**6**), which produces the trimetallic Fe-Pt-Cu complex **7** on reaction with [Cu(MeCN)$_4$]BF$_4$ ^{17}.

Related compounds can be obtained, when the gold(I) and ruthenium(II) acetylides [Au(C≡C-bipy)(PPh$_3$)] (**8**) and [Ru(C≡C-bipy)(η^5-C$_5$H$_5$)(PPh$_3$)$_2$] (**9**) are reacted with **2a** and **2b**, respectively^{18}. After appropriate work-up, complexes [L$_n$M(C≡C-bipy){[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M′]X (**10a**: L$_n$M = Au(PPh$_3$), M′ = Cu, X = PF$_6$; **10b**: L$_n$M = Au(PPh$_3$), M′ = Ag, X = ClO$_4$; **11a**: L$_n$M = Ru(η^5-C$_5$H$_5$)(PPh$_3$)$_2$, M′ = Cu, X = PF$_6$; **11b**: L$_n$M = Ru(η^5-C$_5$H$_5$)(PPh$_3$)$_2$, M′ = Ag, X = ClO$_4$) can be isolated in excellent yields^{18}. The complexes are fairly stable, both in the solid state and in solution. An approach to similar transition metal complexes in which the Ti-Cu organometallic π-tweezer fragment is bonded by the acetylide unit of 5-ethynyl-2,2′-bipyridine, is obtained from {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(CH$_3$) (**12**)^{18,19}. Reaction of **12** with equimolar amounts of 5-ethynyl-2,2′-bipyridine produces {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(C≡C-bipy) (**13**) upon loss of methane. Further treatment of **13** with [Mo(CO)$_4$(nbd)] (nbd = norbornadiene) gives {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(C≡C-bipy)[Mo(CO)$_4$] (**14**)^{18}. When **12** is reacted with ethynylferrocene under similar reaction conditions, then heterotrimetallic {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(C≡CFc) (**15**) is obtained^{19a}. In **14** and **15**, a heterobimetallic Cu-Mo an Cu-Fe fragment with the copper(I) centre

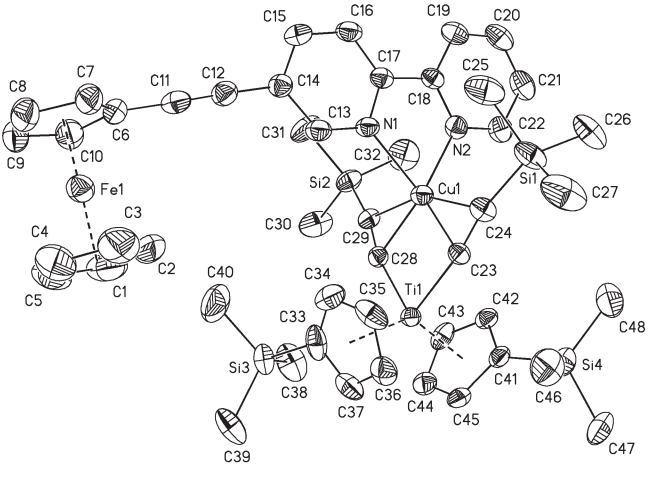
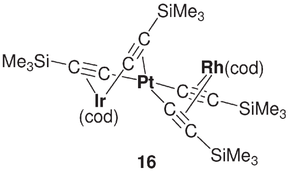


Fig. 1

ORTEP plot (30% probability level) of **3a** with the atom numbering scheme. The hydrogen atoms, the PF$_6^-$ counterion, and the distortion of one Me$_3$Si group are omitted for clarity. For selected bond distances (in Å) and angles (in °) see ref.^{17}

in a planar environment is stabilized by the chelating effect of the organometallic π-tweezer $[Ti](C{\equiv}CSiMe_3)_2$ [19,20]. This coordination behavior is typical in titanium-copper tweezer chemistry with a low-valent copper(I) building block[20].

Compound **16**, featuring Ir, Pt, and Rh metal atoms, is accessible by the reaction of $(Bu_4N)[\{Ir\text{-}Pt\}(C{\equiv}CSiMe_3)_2]$ with $[Rh(cod)(acetone)_x]^+$ (cod = 1,5-cyclooctadiene)[21].



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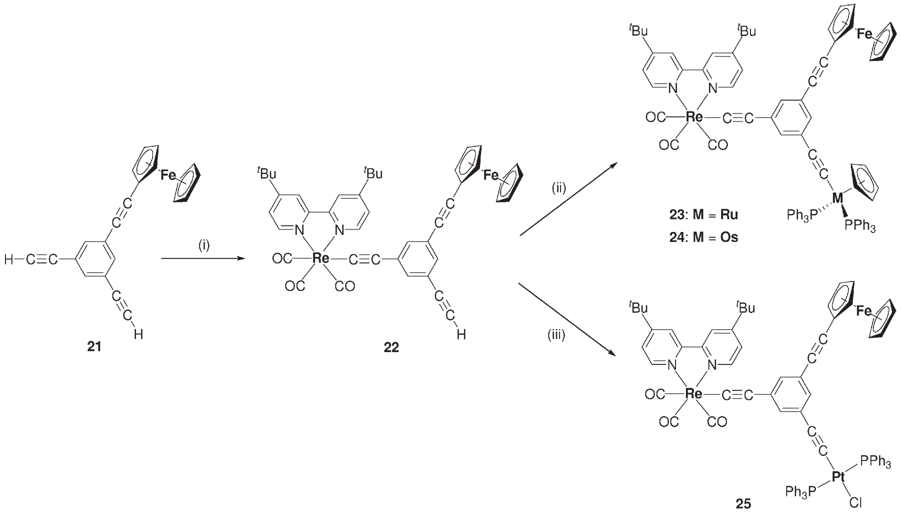
The molecular solid-state structure of **16** proves the presence of the zwitterion $[(cod)Ir(\mu\text{-}1\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)\text{-}Pt^-(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2Rh^+(cod)]$, resulting from the dinuclear anionic fragment $[(cod)Ir(\mu\text{-}1\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)(\mu\text{-}2\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)Pt(C{\equiv}CSiMe_3)_2]^-$ that acts as a chelating dimetallo bidentate ligand towards the cationic $[Rh(cod)]^+$ building block[21].

One more heterotrimetallic complex is represented by $[(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)Ru{-}C{\equiv}C{-}C_5H_4N{\rightarrow}W(CO)_4(PPh_3)]$ (**17**) (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene) in which a linear carbon-rich dimetalla $Ru{-}C{\equiv}C{-}C_5H_4N{-}W$ segment is present[22]. Replacement of the 4-ethynylpyridine by 1-(diphenylphosphanyl)-4-ethynylbenzene gives access to a further series of complexes, i.e. $[(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)Ru{-}C{\equiv}C{-}C_6H_4PPh_2{-}ML_n]$ (ML_n = AuCl (**18**), $RhCl_2(\eta^5\text{-}C_5Me_5)$ (**19**), RhCl(cod) (**20**))[23].

Another possible synthetic route to heterotrinuclear transition metal assemblies utilizes polyethynylbenzenes as bringing units to span the respective metal ions[8,9,11,12,24]. Recently, 1,3,5-triethynylbenzene was introduced as core in organometallic chemistry, leading to the preparation of symmetrical and unsymmetrical bridged transition metal complexes[11,12]. Due to its geometry and active coordination sites, 1,3,5-triethynylbenzene allows one to extend the resulting molecules into three directions by using, e.g., dehydrohalogenation and C–C coupling reactions. In general, there has been considerably more effort expanded on the synthesis of symmetric homosubstituted benzene cores, using iron, iridium, chromium, gold and platinum-containing building blocks[11]. On the other hand, only little is known about unsymmetrical substituted complexes of triethynylbenzene featuring, for example, *trans*-$[RuCl(dppm)_2]$, *trans*-$[OsCl(dppm)_2]$,

$[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (dppm = bis(diphenylphosphanyl)methane), and ferrocenyl end-grafted moieties[12]. These dendritic organometallic systems have attracted much attention because of their interesting electrochemical, catalytic, and energy-transfer properties[11,12]. They are also useful in building supramolecular polymetallic assemblies, nanoarchitectures for materials science, and nanoscale electronic and optical devices for nanotechnology[25]. However, only one example is known in which three different transition metal fragments based on Fe, Ru and Os are arranged around the periphery of the 1,3,5-triethynylbenzene core[12c].

A suitable starting material for the preparation of additional heterotrinuclear σ-alkynyl complexes is the 1,3,5-ethynylbenzene core $1,3\text{-}(HC{\equiv}C)_2\text{-}1\text{-}(FcC{\equiv}C)C_6H_3$ (**21**) because alkynyl ferrocenes are known to be very robust in further reactions[26]. Lithiation of **21** with $LiN(SiMe_3)_2$ followed by treatment with $[ReCl(CO)_3(bipy')]$ (bipy′ = 4,4′-di-*tert*-butyl-2,2′-bipyridine) afforded heterobimetallic $1\text{-}(FcC{\equiv}C)\text{-}3\text{-}[(bipy')(CO)_3Re\text{-}(C{\equiv}C)]\text{-}5\text{-}(HC{\equiv}C)C_6H_3$ (**22**). Complex **22** has the free alkynyl entity as a further reactive site, and, therefore, should have a great potential for introduc-

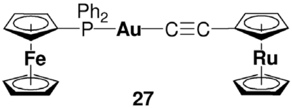


SCHEME 1

Reaction chemistry of **22**. Synthesis of heterotrimetallic **23**–**25** ((i) 1. $LiN(SiMe_3)_2$, toluene, 25 °C, 2 h; 2. $[ReCl(CO)_3(bipy')]$, toluene, reflux, 5 h. (ii) M = Ru: $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$, NH_4PF_6, *t*-BuOK, CH_2Cl_2/MeOH, 5 h; M = Os: 1. $[OsBr(\eta^5\text{-}C_5H_5)(PPh_3)_2]$, NH_4PF_6, MeOH, reflux, 3 h; 2. Na, MeOH, 25 °C, 1 h. (iii) *cis*-$[PtCl_2(PPh_3)_2]$, $CHCl_3/Et_2NH$, reflux, 3 h)[18] ing a third transition metal building block. Thus, the reaction behavior of the disubstituted iron-rhenium assembly **22** towards diverse transition metal complexes was studied. The preferred synthetic method for the preparation of heterotrimetallic species was accomplished by the addition of the organometallic metal chloride [RuCl(η^5-C_5H_5)(PPh_3)$_2$] to **22** in presence of NH_4PF_6 and the base *t*-BuOK (Scheme 1). The analogous osmium(II) complex could be prepared by the reaction of **22** with [OsBr(η^5-C_5H_5)(PPh_3)$_2$] in refluxing methanol in the presence of NH_4PF_6, followed by deprotonation of the vinylidene intermediate by addition of sodium[12d,18]. After appropriate work-up, 1-(FcC≡C)-3-[(bipy′)(CO)$_3$Re(C≡C)]-5-[(η^5-C_5H_5)(Ph_3P)$_2$M(C≡C)]C_6H_3 (**23**: M = Ru, **24**: M = Os) could be isolated as orange powders in good yields[18]. The introduction of a platinum building block was accomplished through the reaction of **22** with *cis*-[PtCl$_2$(PPh_3)$_2$] in refluxing chloroform in the presence of diethylamine (Scheme 1)[18]. To avoid the formation of the corresponding bis(acetylide) platinum complex, the use of an excess of the platinum source *cis*-[PtCl$_2$(PPh_3)$_2$] is required. 1-(FcC≡C)-3-[(bipy′)(CO)$_3$Re-(C≡C)]-5-[Cl(Ph_3P)$_2$Pt(C≡C)]C_6H_3 (**25**) could be isolated as a yellow solid[18].

A further series of trinuclear heterometallic complexes could be synthesized, based on the 1,3,5-triethynylbenzene core, for example, 1-(FcC≡C)-3-[(CO)$_3$Cr(η^6-C_6H_5C≡C)]-5-(Ph_3PAuC≡C)C_6H_3 (**26**)[18].

Heterotrimetallic complexes based on the diphenylphosphanyl ferrocene building block are (FcPPh$_2$)Au–C≡C–Rc (**27**) (Rc = Ru(η^5-C_5H_4)(η^5-C_5H_5), (FcPPh$_2$)Au–C≡C–[Cr(η^6-C_6H_5)(CO)$_3$] (**28**), and (FcPPh$_2$)Au–C≡C–bipy[Mo(CO)$_4$] (**29**)[18,27].



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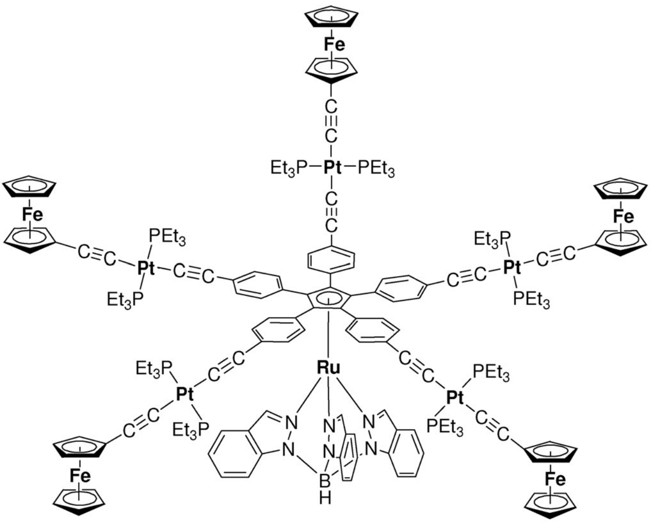
The influence of bridging transition metal atoms by alkynylaromatic moieties has been considered through electrochemical measurements, and is discussed in detail elsewhere[18,27].

The synthesis of the new heteropolytopic penta(4-ethynylphenyl)cyclopentadiene ligand and its complexation through the cyclopentadienyl ring to ruthenium triindazolylborane and through the terminal alkyne groups to five (ferrocenylethynyl)platinum units, yielding the undecanuclear heterotrimetallic complex **30**, was described recently by Rapenne et al.[28]



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2. *Heterotetrametallic Transition Metal Complexes*

Recent work of our group has been concerned with heterotetrametallic complexes derived from the organometallic π-tweezer {[Ti](μ-σ,π-C≡C-SiMe$_3$)$_2$}M′X [20]. Within these studies a closely related series of complexes with interesting properties were prepared. Thus, reaction of HC≡C–{Pt}–C≡C–Fc (**31**) ({Pt} = Pt($C_6H_2(CH_2NMe_2)_2$-2,6)) with {[Ti](μ-σ,π-C≡C–*t*-Bu)$_2$}-Cu(CH_3) (**12**) affords complex {[Ti](μ-σ,π-C≡C–*t*-Bu)$_2$}Cu–C≡C–{Pt}–C≡C–Fc (**32**) on loss of methane[29], while (FcPPh$_2$)Au–C≡C-bipy reacts with {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M′X (M′X = [Cu(MeCN)]PF$_6$, AgOClO$_3$) to give tetrametallic **33** (Fig. 2)[30].

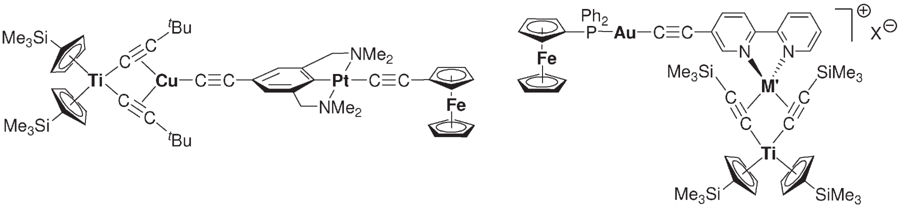
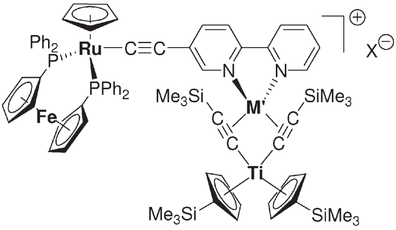


FIG. 2
Complexes **32** (left) and **33** (right; **33a**: M′ = Cu, X = PF$_6$; **33b**: M′ = Ag, X = ClO$_4$)[29,30]

Complexes **32** and **33** represent the first examples of heterotetrametallic transition metal complexes in which early and late transition metal atoms are connected by π-conjugated organic bridging units[29,30]. A striking feature of **32** is that all metals possess different coordination spheres: titanium shows a pseudo-tetrahedral environment, copper a triangular planar vicinity, platinum is square-planar-coordinated and iron is a part of a sandwich structure[29].

When the $(FcPPh_2)Au$ moiety in **33** is replaced by the Ru(η^2-dppf)-(η^5-C_5H_5) building block, related tetranuclear complexes of type [(η^2-dppf)-(η^5-C_5H_5)Ru–C≡C-bipy{[Ti](μ-σ,π-C≡$CSiMe_3$)$_2$}M′]X (**34a**: M′ = Cu, X = PF_6; **34b**: M′ = Ag, X = ClO_4) are accessible[18].



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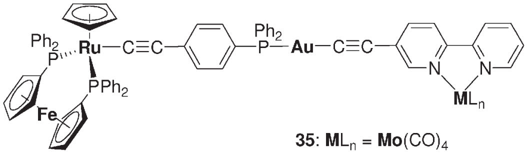
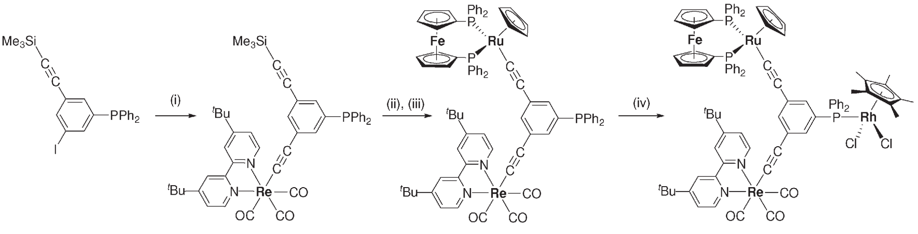
Extending the distance between the remote Fe-Ru and the Ti-M′ fragments in **34** by a (1,4-C≡C–C_6H_4–PPh_2)Au moiety opens the possibility to create stable heteropentametallic transition metal complexes (see Section 3). When the organometallic π-tweezer entity (vide supra) is substituted by mononuclear transition metal building blocks, such as $Mo(CO)_4$ or $ReCl(CO)_3$, then tetrametallic [(η^2-dppf)(η^5-C_5H_5)Ru–(1,4-C≡C–C_6H_4–PPh_2)Au(C≡C-bipy)ML_n] complexes (**35**: ML_n = $Mo(CO)_4$, **36**: $ReCl(CO)_3$)) are formed, in which four different metal atoms are connected by organic carbon-rich bridging units[18].



35: **M**L$_n$ = **Mo**(CO)$_4$
36: **M**L$_n$ = **Re**(CO)$_3$Cl

Compounds of the latter type are formed by combining [(η^2-dppf)(η^5-C_5H_5)Ru–(1,4-C≡C–C_6H_4–PPh_2)Au(C≡C-bipy)] (**38**) with [$Mo(CO)_4$(nbd)] (synthesis of **35**) or treatment of [(η^2-dppf)(η^5-C_5H_5)Ru–(1,4-C≡C–C_6H_4–PPh_2)-AuCl] (**37**) with [$ReCl(CO)_3$(bipy-C≡CH)] (synthesis of **36**)[18].

An elegant approach to novel tetrametallic Fe-Ru-Re-Rh compound **39**, based on the 1-(diphenylphosphanyl)-3,5-diethynylbenzene core, is the use of a consecutive reaction sequence as presented in Scheme 2, including, for example, dehydrohalogenation and carbon–carbon coupling reactions[18].



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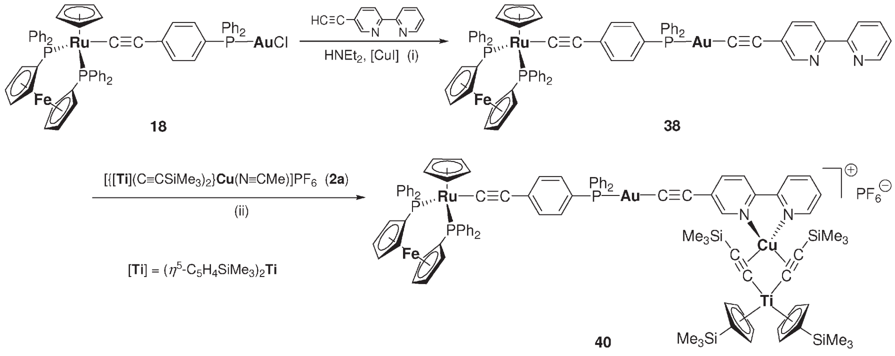
SCHEME 2

Synthesis of heterotetrametallic **39** ((i) [ReCl(C≡CH)$(CO)_3$(bipy′)], [$PdCl_2(PPh_3)_2$], CuI, *i*-Pr_2NH, reflux, 5 h; (ii) Bu_4NF, THF, 25 °C, 1 h; (iii) [RuCl(dppf)(η^5-C_5H_5)], NH_4PF_6, *t*-BuOK, CH_2Cl_2/MeOH, 25 °C, 3 h; (iv) [Rh(η^5-C_5Me_5)(μ-Cl)$_2$]$_2$, CH_2Cl_2, 25 °C, 1 h)[18]

The molecular solid state structure of **39** was solved by single-crystal X-ray structure analysis, thus confirming the structural assignment made from spectroscopic data[18]. An ORTEP drawing of this species is depicted in Fig. 3.

3. Heteropentametallic and Heterohexametallic Transition Metal Complexes

The syntheses of heteropenta- and heterohexametallic complexes with Re, Fe, Ru, Au, Cu and Ti metals is possible. The complex [(η^2-dppf)(η^5-C_5H_5)Ru–(1,4-C≡C–C_6H_4–PPh_2)Au(C≡C-bipy)[{[Ti](μ-σ,π-C≡$CSiMe_3$)$_2$}Cu]PF_6 (**40**) is accessible via a consecutive reaction sequence by using (η^2-dppf)(η^5-C_5H_5)Ru–(1,4-C≡C–C_6H_4–PPh_2)AuCl (**18**) as the key starting material[18,23]. The newly synthesized compounds and the overall synthetic strategy employed are shown in Scheme 3. Compound **18** reacts with 5-ethynyl-2,2′-bipyridine, whereby this compound is added in a 20% excess, in presence of CuI and diethylamine to give [(η^2-dppf)(η^5-C_5H_5)Ru–(1,4-C≡C–C_6H_4–PPh_2)Au–(C≡C-bipy)] (**38**) (Scheme 3, route (i)). This molecule contains a terminal 2,2′-bipyridine moiety which provides an additional *N*-ligating site that can react with stoichiometric amounts of the heterobimetallic tweezer molecule



SCHEME 3

Synthesis of trimetallic **38** and pentametallic **40** (route (i): THF, 25 °C, 3 h; (ii): THF, 25 °C, 2 h)[18,23]

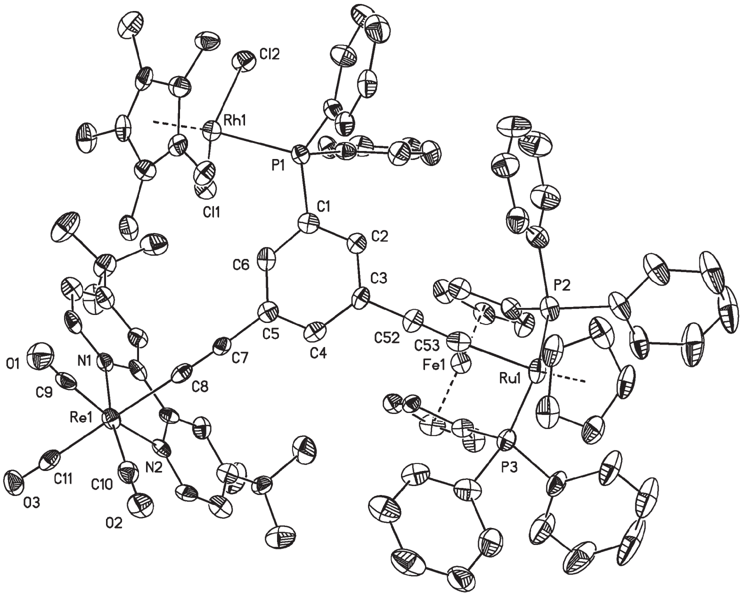


FIG. 3

ORTEP drawing of **39**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (in Å) and angles (in °): C7–C8, 1.209(11); Re1–C8, 2.123(9); Rh1–P1, 2.334(2); C52–C53, 1.213(11); Ru1–C53, 2.004(9); Ru1–P2, 2.253(2); Ru1–P3, 2.266; C5–C7–C8, 176.7(8); C7–C8–Re1, 176.5(7); C3–C52–C53, 169.7(8); C52–C53–Ru1, 175.7(7); C1–P1–Rh1, 112.9(3)[18]

$[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu(MeCN)]PF_6$ (**2a**) (Scheme 3, route (ii)). On replacement of the copper-bonded acetonitrile in **2a** by 2,2′-bipyridine, complex **40** is formed that could be isolated after appropriate work-up in 92% yield[18,23]. Novel **40** is surprisingly a very stable species in which five different transition metals are brought in close proximity to each other by $C_5H_4PPh_2$, C≡C, C_6H_4, and bipyridine bridging units.

The formation of heteropentanuclear **40** was evidenced from spectroscopic studies as well as from ESI-TOF mass spectrometric investigations[18,23]. The ESI-TOF spectrum shows a prominent ion peak at *m/z* 1963.4 (100%) corresponding to [**40**-PF_6]$^+$. Moreover, comparison of the measured isotope pattern of **40** with the calculated one confirms the elemental composition and charge state (Fig. 4).

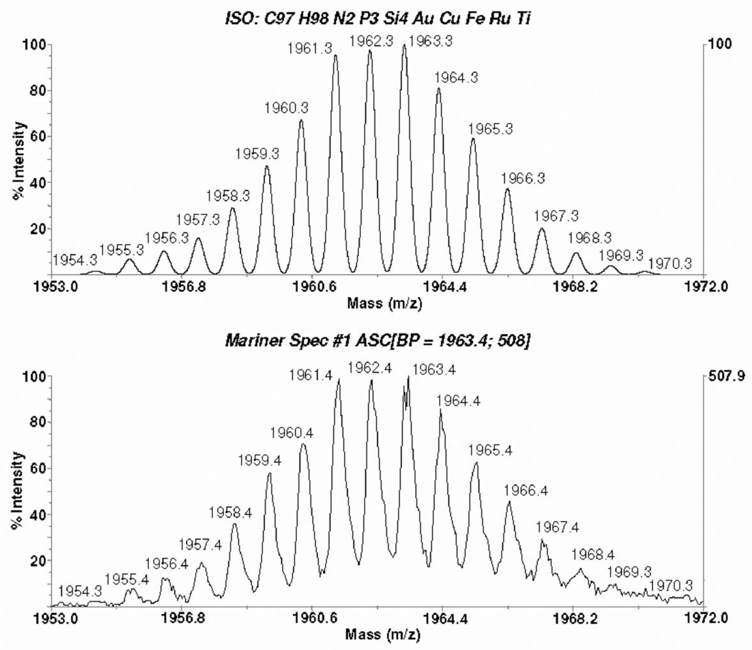
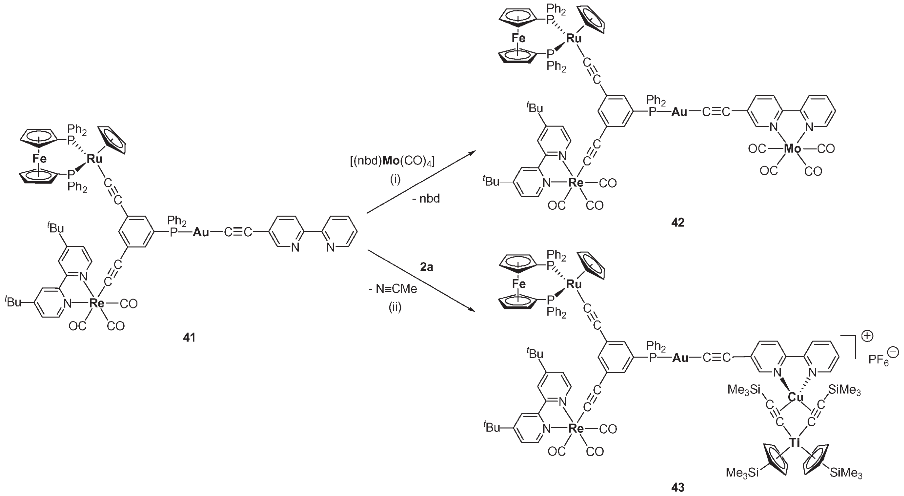


FIG. 4

Comparison of the calculated (top) and measured (bottom) isotope pattern of the ion peak [**40**-PF_6]$^+$ in the ESI-MS spectrum of complex **40** [18,23]

The 2,2′-bipyridine building block in 1-[(η^2-dppf)(η^5-C_5H_5)Ru–(C≡C)]-3-[(bipy′)$(CO)_3$Re(C≡C)]-5-[PPh_2Au(C≡C-bipy)]C_6H_3 (**41**) as bidentate binding site allows the preparation of Fe-Ru-Re-Au-Mo- and even Fe-Ru-Re-Au-Cu-Ti-based assemblies, as outlined in Scheme 4. Addition of [Mo$(CO)_4$-(nbd)] to **41** yields heteropentanuclear **42** upon replacement of nbd by bipy. Heterohexanuclear **43** is formed in a straightforward manner when **41** is treated with stoichiometric amounts of **2a**. In this reaction, the coordination number of copper changes from three (planar trigonal) to four (tetrahedral)[18].



SCHEME 4
Synthesis of heteropentametallic **42** and heterohexanuclear **43** ((i) CH_2Cl_2, THF, 25 °C, 8 h; (ii) THF, 25 °C, 2 h)[18]

The synthetic protocol developed to prepare heteromultinuclear **42** and **43** can also be directed towards the use of modular shaped organometallic building blocks (vide supra). This allowed the syntheses of novel complexes in which acetylene, aromatic and diphenylphosphanyl groups are all used in bridging the respective transition metal atoms within a common core for the first time.

IR and NMR (^{1}H, ^{31}P{^{1}H}) spectroscopies allow to monitor the progress of the reactions and verify the structure and composition of the final assemblies. Most characteristic in the IR spectra of **41**–**43** is the appearance of ν(C≡C) and ν(CO) vibrations typical of the individual σ-alkynyl organometallic transition metal fragments, which are diagnostic and represent a useful monitoring tool. The introduction of the gold acetylide building block at the phosphane is evidenced by the ν(C≡C) absorption at 2117 cm^{-1} typical of phosphanyl-stabilized gold(I) acetylides, which is also found in **42** and **43**.

The $^{31}P\{^1H\}$ NMR spectra of **41**–**43** show the expected resonances. In all complexes, a signal at 54 ppm is observed for the dppf entity bound to ruthenium. Owing to the coordination of the Ph_2P group to gold(I), a representative chemical shift of 41 ppm (**41**) is observed. It is, however, only slightly influenced, due to additional metal coordination as given in **42** and **43**.

The ^1H NMR spectra of **41**–**43** nicely correlate with their formulations as heteromultinuclear assemblies based on the 1-(diphenylphosphanyl)-3,5-diethynylbenzene core, showing the respective resonance patterns for the organic units. Most distinctive for the formation of **42** and **43** is the change in the chemical shifts of the bipy protons. Furthermore, as a result of coordination of the bipyridine unit to the organometallic π-tweezer-stabilized copper(I) centre in **43**, a highfield shift of the $Me_3SiC{\equiv}C$ protons is observed, in contrast to **2a**. This can be explained by the ring current of the bipyridine ligand. In addition, ESI-TOF mass spectrometric studies were carried out, which confirm the structural composition of the respective complexes[18].

The reports on the syntheses of transition metal complexes in which five different metals such as Fe, Ru, Au, Cu and Ti (**40**), Fe, Ru, Re, Au and Mo (**42**) or even six different metal atoms (Fe, Ru, Re, Au, Cu, Ti) (**43**) are spanned by carbon-rich bridging units, demonstrate that such large heteronuclear assemblies can be synthesized in a straightforward manner by using the modular Tinkertoy approach[2,3]. This procedure allows a fair control over the structure and composition of such molecules. A detailed investigation of photophysical properties and electronic interactions between the appropriate metal atoms in **40**, **42**, and **43** is in progress.

The identities of all the complexes described in this review have been confirmed by elemental analyses, IR, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies. From selected samples, ESI-TOF mass spectra were recorded and the solid state structures were determined by single-crystal X-ray structure analyses. IR and NMR (^1H, $^{31}P\{^1H\}$) spectroscopies allow to monitor the progress of the reactions and verify the structure and composition of the final multinuclear assemblies.

CONCLUSION/OUTLOOK

This review addresses for the first time the chemistry of mono- and heterodinuclear transition metal complexes in the modular syntheses of multiheterometallic complexes with up to six different early and late transition metal atoms, including titanium, molybdenum, tungsten, chromium, rhenium, iron, ruthenium, rhodium, iridium, copper, silver and gold. The metal atoms are brought in close (linear) proximity to each other by carbon-rich organic bridging units. The successive synthetic procedures allowed the straightforward preparation of a series of such complexes, which makes it possible to systematically develop the field of the heteromultimetallic assemblies that have been up to now only rarely investigated. The reactions based on the modular molecular Tinkertoys approach depend upon electronic and steric properties of the metal atoms and diverse organic ligands involved. Despite the quantity of experimental work carried out so far in this field of chemistry, the exact factors that control the formation of the structures in the heteromultimetallic complexes, are still an open question and continuously stimulate fruitful work in this field of chemistry. A challenge is the preparation of even larger transition metal complexes featuring more than six different early and late transition metal atoms and new functionalities, as various metals with different redox potentials are combined through conjugated bridging units in one molecule. This chemistry also opens the possibility of creating new materials with envisaged innovative electronic, catalytic, optical and/or magnetic properties.

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