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Reviews

Organometallic *π*-Tweezers, NCN Pincers, and Ferrocenes as Molecular “Tinkertoys” in the Synthesis of Multiheterometallic Transition-Metal Complexes

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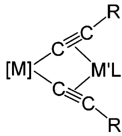
This review describes the synthesis, reaction chemistry, structures, and bonding of early−late heterodi-, heterotri-, and heterotetrametallic transition-metal complexes by applying the molecular “Tinkertoy” approach. As connecting units between the different metal atoms, *π*-conjugated carbon-rich organic and/or inorganic groups can be used. The electrochemical behavior of such one-dimensional molecular wire molecules, coordination polymers, starlike structures, and dendritic oriented transition-metal species, respectively, is presented as well.

Introduction

Recently, bis(alkynyl) transition-metal complexes of the type RC≡C−[M]−C≡CR with [M] = 14−16-valence-electron complex fragment and R = singly bound organic or organometallic group[1] have come into use as organometallic *π*-tweezers (organometallic bidentate chelating ligands) for the stabilization of many diverse low-valent metal fragments $M'L_n$ (M′ = element of groups 1, 2, and 4−12 of the periodic table of the elements; L = neutral or ionic organic or inorganic 2-electron-donor ligand; $n = 1{-}4$).[2] In the thus accessible heterobimetallic $\{[M](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}M'L_n$ tweezer molecules the alkynyl groups RC≡C act as *σ*-donors to M and as *π*-donors to M′ and hold the metals M (preferably an early-transition-metal atom, such as Ti, Zr, or Hf) and M′ (vide supra) in close proximity to each other.[2] Synergistic and cooperative effects between M and M′ are observed, and apparently, these complexes show versatile applications.[2,3]



Another extensively investigated chelating ligand in organometallic chemistry is the potentially η^3-chelating, monoanionic diaminoaryl pincer NCN (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$).[4] Together with related diphosphino− and disulfido−aryl anions, many pincer metal complexes are accessible, which possess a remarkable stability and at the same time show excellent catalytic properties.[5] Recently, this approach was successfully extended to synthesize pincer main-group-element compounds (Chart 1).[6]

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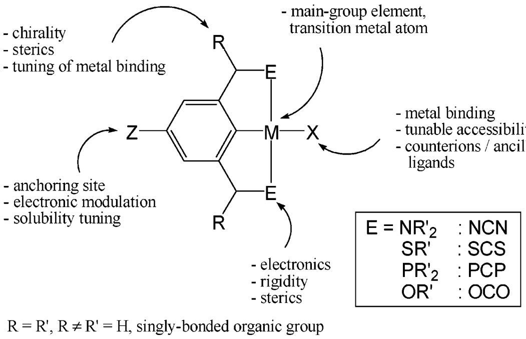
10.1021/om058042p CCC: $33.50

Chart 1



R = R', R ≠ R' = H, singly-bonded organic group

Functionalized ferrocenes can act as bidentate chelating ligands toward many diverse transition-metal and main-group-element entities.[7] In addition, the ferrocene moiety is an exceptional building block in the preparation of, for example, multimetallic coordination complexes which provide interesting electronic, optical and/or magnetic properties.[8] Although ferrocene celebrated its 50th anniversary 5 years ago,[9] it still is a fountain of youth for the synthesis of new types of transition-metal complexes with specific properties.

The concept of molecular "Tinkertoys" was independently established by Michl[10] and Stoddart.[11] Individual functionalized inorganic, organic, and/or organometallic molecules can be considered as molecular "Tinkertoys" and can be assembled according to a specific building design to give new complexes with novel chemical head structures. This construction process should be reversible. The parts thus prepared can be maintained until the next molecular "Tinkertoy" process starts anew.

In context with this background, we focus here on the use of mainly mono- and bis(alkynyl) transition-metal complexes, ferrocenes, NCN pincer molecules, functionalized acetylenes, carboxylates, halides, and pseudohalides as molecular "Tinkertoys" in the modular synthesis of heteroatomic multinuclear assemblies. This review is divided into three sections: (i) recent developments in organometallic π-tweezer chemistry, (ii) coordination polymers, and, particularly, (iii) multimetallic transition-metal complexes. In all multiheterometallic species different transition metals are spanned by π-conjugated organic and/or inorganic units, allowing electronic communication between the metals along the bridging entities. However, clusters or (linear) transition-metal complexes with direct metal−metal interactions will not be considered.[12]

Recent Developments in Organometallic π-Tweezer Chemistry

Bis(alkynyl) transition-metal complexes of the structural type $RC\equiv C-[M]-C\equiv CR$ (type **A** molecule; [M] = 14−16-valence-electron complex fragment, R = singly bound organic or organometallic group)[1] act toward different metal fragments (electron rich or electron poor) as organometallic bidentate chelating ligands (organometallic π-tweezers) to give alkynyl-bridged heterobimetallic species of structural types **B**−**G** (Scheme 1).[1,2]

The structures adopted by the bis(alkynyl) (hetero)bimetallic complexes **B**−**G** (Scheme 1) strongly depend on the relative affinity of the metals M and M′ for electron density. If one metal atom (e.g., M) is significantly more electrophilic than the other (M′), then the alkynyl ligands $RC_\beta\equiv C_\alpha$ will preferentially bind to the electrophilic metal M through the C_α carbon atoms. This results in structural type **B** complexes in which both alkynyl ligands are σ-bound to M and π-coordinated to the second metal M′. This is the preferred structure for many early−late heterobimetallic complexes.[2] In most type **B** complexes, for example, $\{[Ti](\mu-\sigma,\pi\text{-}C\equiv CR)_2\}M'X$ ([Ti] = $(\eta^5\text{-}C_5H_5)_2Ti$, $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$, ...; M′ = Cu, Ag, Au, ..., X = neutral or ionic inorganic or organic 2-electron donor; M′ = Ni, Co, X = CO,

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(5) For example, see: (a) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317. (b) Loeb, S. J.; Shimizu, G. K. H.; Wisner, J. H. *Organometallics* **1998**, *17*, 2324. (c) Vigalok, A.; Rybtchinski, B.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *18*, 895. (d) Back, S.; Gossage, R. A.; Lang, H.; van Koten, G. *Eur. J. Inorg. Chem.* **2000**, 1457. (e) Back, S.; Lutz, M.; Spek, A. L.; Lang, H.; van Koten, G. *J. Organomet. Chem.* **2001**, *620*, 227 and references cited therein. (f) Back, S.; Gossage, R. A.; Lutz, M.; del Rio, I.; Spek, A. L.; Lang, H.; van Koten, G. *Organometallics* **2000**, *19*, 3296. (g) Olsson, D.; Nilsson, P.; El Masnaouy, M.; Wendt, O. F. *Dalton Trans.* **2005**, *11*, 1924. (h) Medici, S.; Gagliardo, M.; Williams, S. B.; Chase, P. A.; Gladiali, S.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Helv. Chim. Acta* **2005**, *88*, 694. (i) Gupta, A. K.; Kim, K. S.; Oh, C. H. *Synlett* **2005**, *3*, 457. (j) Slagt, M. Q.; van Zwieten, D. A. P.; Moerkerk, A. J. C. M.; Gebbink, R. J. M.; van Koten, G. *Coord. Chem. Rev.* **2004**, *248*, 2275. (k) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759. (l) Jensen, C. M. *Chem. Commun.* **1999**, *24*, 2443. (m) van Koten, G.; Jastrzebski, J. T. B. H. *J. Mol. Catal. A: Chem.* **1999**, *146*, 317.

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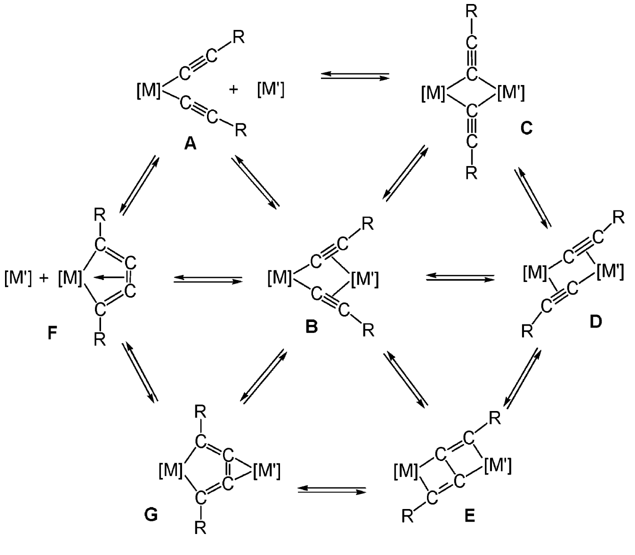
Scheme 1. Interconversion of Alkynyl Coordination Modes in Type A−G Molecules[1,2]



PR$_3$, ...), the respective metals M′ within the tweezer framework are tricoordinate and possess a planar environment.[2,13]

If the metals M and M′ are competitive in their affinities toward the alkynyl ligands, or if steric factors prevent the formation of a type **B** tweezer complex, then structural type **C** or **D** molecules are formed. In these molecules, the alkynyl ligands are more evenly shared, either with both metals, σ-bonded by both alkynyl ligands (type **C**), or with each metal σ-bonded by one alkynyl unit and π-coordinated to the other (type **D**).[2,13]

Since the two alkynyl ligands in type **B** molecules are held in close proximity by the [M] connecting unit, coupling reactions between the two $RC\equiv C$ ligands are possible, forming molecules of structural types **E** and **G**.[2,13] Subtle steric and electronic effects appear to play an important role in determining the feasibility of the carbon−carbon bond-forming reactions, as small changes in the alkynyl substituents R or in the ancillary ligands of M and M′ can induce or prevent these reactions.

Scheme 1 represents the state of the art in the field of organometallic π-tweezer chemistry up to 2000, and many examples to date confirm this picture.[2,13] While we have in the beginning of this chemistry been attracted to the use of type **A** molecules as organometallic chelating ligands for the stabilization of low-valent transition-metal fragments [M′] (structural type **B** molecules), in their manifold reaction chemistry and in their structural aspects,[2] we recently became more and more interested in the application of such systems to study electron

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transfer,[14] to create self-assembled monolayers (SAMs),[15] to prepare one-dimensional molecular wires and to use them in molecular electronics to span metal surfaces/electrodes,[15] and, finally, to synthesize coordination polymers.[2e−g,16]

With regard to these topics, special attention was drawn to alkynyl-stabilized organocopper(I) and -silver(I) species.[2] While the use of alkyne-stabilized inorganic and organic group 11 metal fragments has lately been reviewed in detail,[2] we focus here on recent results obtained in the field of electron transfer based on organometallic π-tweezers.[14]

Since the early work of Creutz and Taube,[17] there has been a rapidly growing interest in the synthesis and chemical and physical properties of homo- and heterobimetallic transition-metal complexes in which a π-conjugated organic ligand spans the two transition-metal atoms.[18,19]

A series of redox-active model compounds have been synthesized, such as $(\eta^5\text{-}C_5Me_5)(dppe)Fe{-}C{\equiv}CC{\equiv}C{-}Fe(\eta^5$-

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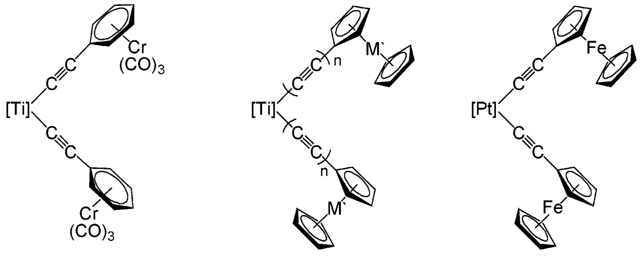
$C_5Me_5)(dppe)$[18t] and $[(\eta^5\text{-}C_5Me_5)(NO)(Ph_3P)Re{=}C{=}C{=}C{=}C{=}C{=}Mn(\eta^5\text{-}C_5Cl_5)(CO)_2]^+$,[19p] in which a molecular wire consisting of an all-carbon C_4 or C_5 chain bridges the two metal center Fe/Fe or Re/Mn, giving rise to an electronic coupling through five or six bonds. Further examples of molecular wires are $[\mathit{trans}\text{-}(R\text{-}4\text{-}C_6H_4)(Ph_3P)_2Pd{\leftarrow}N^\frown N{\rightarrow}Pd(PPh_3)_2(C_6H_4\text{-}4\text{-}R)]^{n+}$ ($N^\frown N$ = 4,4′-bipy, $C_6H_4\text{-}1,4\text{-}(C{\equiv}N)_2$, $(C_6H_4\text{-}4\text{-}C{\equiv}N)_2$, $C_5H_4NCH{=}CHC_6H_4CH{=}CHC_5H_4N$, ...; R = Me(O)CS, n = 2; R = Ph_3P, n = 4) and $[(R\text{-}4\text{-}C_6H_2(CH_2NMe_2)_2\text{-}2,6)\text{-}Pt{\leftarrow}N^\frown N{\rightarrow}Pt(C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}4\text{-}R)]^{2+}$, in which the group 10 redox termini can be adjusted at variable distances to each other by the bidentate connecting units $N^\frown N$.[15]


1
[Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$

2
M\` = Fe, Ru; n = 1, 2

3
[Pt] = (bipy)Pt
cis-$(PPh_3)_2Pt$

Figure 1. Organometallic π-tweezer molecules with (benzene tricarbonyl) chromium (**1**), ferrocenyl (**2**, **3**), and ruthocenyl (**2**) (redox-active) termini.[2,14a,b,20−23]

In addition to these late−late transition-metal complexes, also a number of early−late species, e.g. $(\eta^5\text{-}C_5H_5)(Me_3P)_2Ru{-}C{\equiv}C{-}Zr(\eta^5\text{-}C_5H_5)_2(Cl)$, are known.[19l] Further examples of this family are depicted in Figure 1. Complexes **1**−**3** are suited to transport electrons along the organic π-system between the redox-active metal termini.

Cyclic voltammetric studies of **1** showed a quasi-reversible wave at $E_0 = -1.6$ V (ΔE = 100 mV), which can be assigned to the Ti(IV)/Ti(III) redox couple.[20] For the half-sandwich $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ unit the appearance of irreversible oxidation waves is typical.[24] Replacement of the $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ fragment in **1** by more weakly electron withdrawing groups such as ferrocenyl or ruthenocenyl affords the organometallic π-tweezers $[Ti][(C{\equiv}C)_mMc][(C{\equiv}C)_nM'c]$ (**2a**, $m = n = 1$, Mc = M′c = Fc; **2b**, $m = n = 1$, Mc = M′c = Rc; **2c**, $m = n = 2$, Mc = M′c = Fc; **2d**, [Ti] = $(\eta^5\text{-}C_5H_5)_2Ti$, $m = n = 2$, Mc = M′c = Fc; **2e**, $m = n = 2$, Mc = Fc, M′c = Rc; **2f**, $m = 1$, $n = 2$, Mc = M′c = Fc; **2g**, $m = 1$, $n = 2$, Mc = Rc, M′c = Fc; Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$, Rc = $(\eta^5\text{-}C_5H_4)Ru(\eta^5\text{-}C_5H_5)$) (Figure 1).[14a,b,21] Oxidation of **2** leads to an instantaneously oxidative coupling of the acetylide−ferrocenyl or −ruthenocenyl entities $Mc(C{\equiv}C)_m$ and $M'c(C{\equiv}C)_n$ to give the respective all-carbon

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complexes by an electron transfer from Ti$-$C$_{C\equiv C}$ to Mc or M′c across the π-conjugated acetylides (C≡C)$_m$ and (C≡C)$_n$, respectively. The oxidatively induced coupling of the Mc(C≡C)$_m$ and M′c(C≡C)$_n$ moieties is not even averted when the alkynyl ligands in **2** are η^2-coordinated to an additional transition-metal fragment as given in, for example, {[Ti](μ-σ,π-C≡CFc)$_2$}CuBr and {[Ti](μ-σ,π-C≡CFc)$_2$}PdPPh$_3$.[14c,d]

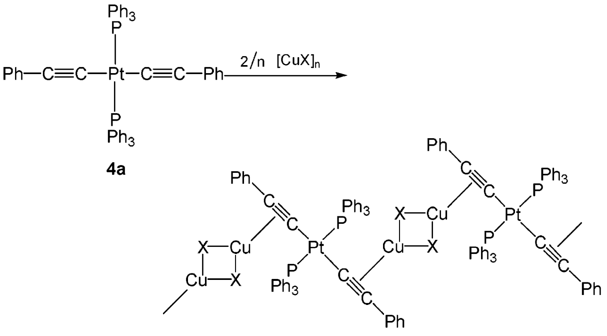
To prevent the metal$-$carbon cleavage in **2**, the titanocene moiety [Ti] was replaced by [Pt], because platinum$-$carbon bonds are more stable than Ti$-$C ones. In *cis*-[Pt](C≡CFc)$_2$ (**3a**, [Pt] = (bipy)Pt; **3b**, [Pt] = (Ph$_3$P)$_2$Pt; bipy = 2,2′-bipyridine) a d^8 square-planar coordination of the Pt(II) ion is present. The electrochemical response of **3a** and **3b** shows two reversible one-electron oxidations centered on the Fc moieties at $E_0 = -0.1$ V (ΔE = 180 mV) and +0.05 V (ΔE = 115 mV) for **3a** and $E_0 = +0.1$ V (ΔE = 200 mV) and +0.17 V (ΔE = 200 mV) for **3b**. This indicates a moderate electronic interaction between the iron cores through the connecting organic chain and the platinum atom. Nevertheless, the electronic interaction found in **3a** and **3b** is stronger than in all-carbon Fc-C≡CC≡C$-$Fc.[22,23] In addition to the two reversible oxidation processes, two irreversible one-electron reductions are found at -1.55 and -2.19 V for **3b** and at -1.46 V for **3a**, which can be assigned to the stepwise reduction of Pt(II) to Pt(0). The second reduction wave for **3a** (Pt(I)/Pt(0)) is covered by the reversible reduction of the 2,2′-bipyridine ligand (bipy/bipy$^-$, -1.78 V (ΔE = 140 mV); bipy$^-$/bipy^{2-}, -2.47 V (ΔE = 180 mV)).[22]

Extending the idea of connecting early- and late-transition-metal building blocks from all-carbon to other carbon-rich μ-σ,π-conjugated organic groups enabled the synthesis of a large variety of early$-$late transition-metal complexes by applying the molecular "Tinkertoy" approach (see below).

Coordination Polymers

Recently, the reaction chemistry of *cis*-[Pt](C≡CPh)$_2$ ([Pt] = (bipy)Pt, (bipy′)Pt; bipy′ = 4,4′-dimethyl-2,2′-bipyridine) towards different group 11 metal salts [M′X] (M′ = Cu, Ag; X = inorganic ligand) to give heterobimetallic or oligomeric complexes was reported.[2g,f,16a,b] In contrast, *trans*-L$_2$Pt(C≡CR)$_2$ (**4a**, L = PPh$_3$, R = Ph; **4b**, L = PMe$_2$Ph, R = ^{t}Bu; **4c**, L = PMe$_2$Ph, R = H) produced with various [M′X] salts in a 1:1 or 1:2 molar ratio novel linear coordination polymers.[16f−i] For coordination polymers with transition metals other than platinum and copper or platinum and silver see refs 16j$-$s.

Coordination polymers **5a** and **5b**, which are based on *trans*-L$_2$Pt(C≡CR)$_2$ and CuX, can be synthesized by the reaction of **4a** with 2 equiv of [CuX] (X = Cl, Br) (eq 1).[16a]



4a

(1)

5a: X = Cl
5b: X = Br

In **5a** and **5b** a linear polymeric structure is adopted by *trans*-Pt(μ-σ,π-C≡CPh)$_2$ and Cu$_2$X$_2$ building blocks.[16a] A similar polymer, [{*trans*-(PhMe$_2$P)$_2$Pt(C≡C^{t}Bu)$_2$}Cu$_2$(μ-Cl)$_2$]$_n$ (**5c**), is accessible by the linear copolymerization of **4b** with [CuCl] in the presence of NEt$_2$H.[16f,g]

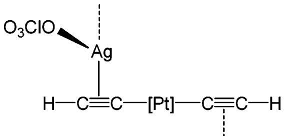
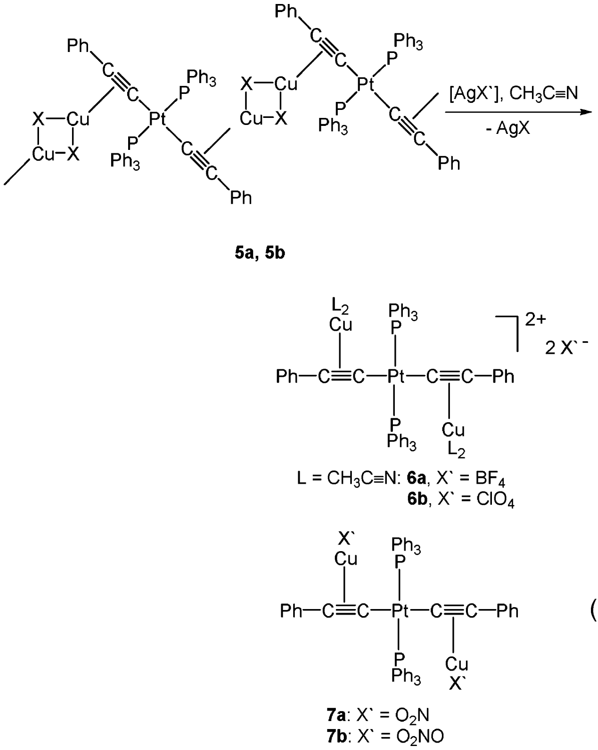


Figure 2. Schematic representation of the monomeric part of polymeric **8** ([Pt] = (PhMe$_2$P)$_2$Pt).[16h]

Depolymerization of **5** can be initiated by the addition of [AgX′] (X′ = BF$_4$, ClO$_4$, NO$_2$, NO$_3$, ...), whereby trinuclear **6** and **7** are formed (eq 2).[16a]



5a, 5b

L = CH$_3$C≡N: **6a**, X` = BF$_4$
6b, X` = ClO$_4$

(2)

7a: X` = O$_2$N
7b: X` = O$_2$NO

Complexes isostructural with **7** can be obtained, when **4a** is reacted with [AgX] (X = NO$_2$, NO$_3$).[16a] When silver salts with X = OTf, BF$_4$, ClO$_4$ are used, then platinum$-$silver coordination polymers are available.[2g,16b,c,25] One of the first examples was reported by Yamazaki and co-workers, who obtained polymeric {[*trans*-(PhMe$_2$P)$_2$Pt(C≡CH)$_2$]AgClO$_4$}$_n$ (**8**) by treatment of **4c** with [AgClO$_4$] in a 1:1 molar ratio.[16h] In **8**, PtC≡CH units are π-bound to a AgOClO$_3$ building block (Figure 2).

However, when **4a**, instead of **4c**, is treated with a twofold excess of [AgClO$_4$], then coordination polymers **9**$-$**11** are formed (Figure 3).[16b,25]

In **9**, *trans*-(Ph$_3$P)$_2$Pt(C≡CPh)$_2$ units are linked by [Ag(μ-OCl(O)$_2$O)]$_2$ rings.[16b,25,26] The silver(I) ion is additionally η^2-coordinated to one phenyl group of a triphenylphosphine ligand to result in a pseudotetrahedral coordination sphere at silver. The structure of **9** is dominated by the parallel orientation of individual Pt(C≡CPh)$_2$ units (Figure 3).

In **10** and **11** the perchlorates are σ-bound to Ag(I). To achieve coordination number 4 at silver, additional η^2-coordina-

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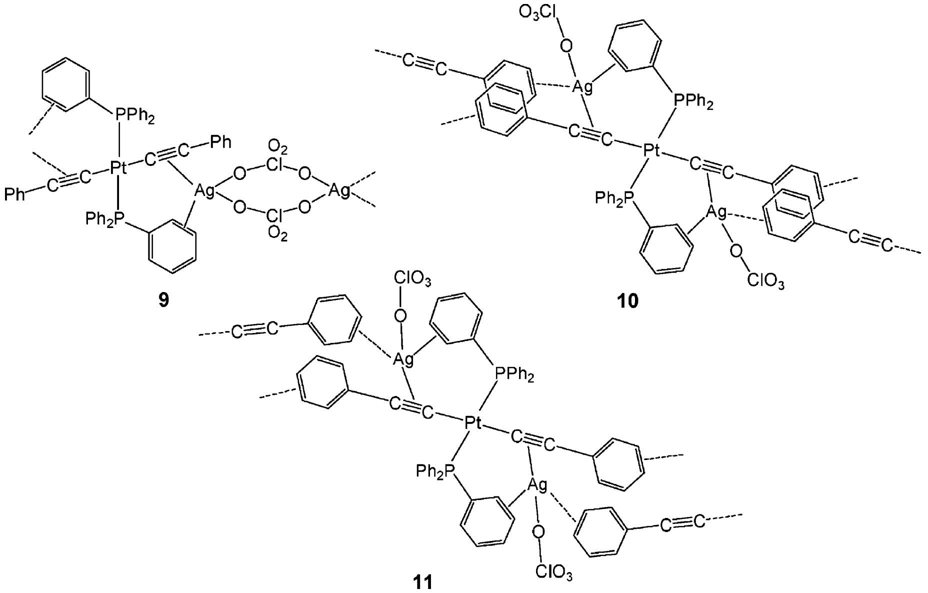

9 **10** **11**

Figure 3. Schematic representations of **9**−**11**.[16b,25]

tion of the PhC≡C alkynyl and one of the three PPh_3 phenyl groups and the PhC≡C phenyl unit must occur (Figure 3). While in **10** the Pt(C≡CPh)$_2$ moieties are oriented parallel to each other, in **11** the silver ion has slipped along the surface of the phenyl ring and, apparently, a zigzag arrangement is characteristic (Figure 3).

The structural motif of **10** and **11** is also verified in {[*trans*-$(Ph_3P)_2Pt(C{\equiv}CPh)_2]AgBF_4\}_n$ (**12**).[2e,g,25,27]

In contrast, the reaction of **4a** with 2 equiv of [AgOTf] produces {[*trans*-$(Ph_3P)_2Pt(C{\equiv}CPh)_2]AgOTf\}_n$ (**13**), in which the polymeric zigzag chain is set up by Pt(μ-σ:η^2-C≡CPh)$_2$ and eight-membered $(AgOTf)_2$ units, of which the latter moiety is the linking entity.[2e,g,16b,25]

Further polynuclear complexes containing platinum and silver atoms, based on $[(C_6F_5)_2Pt(C{\equiv}CR)_2Ag_2]_n$ (**14**), were synthesized by the Forniés group.[28]

Following the molecular "Tinkertoys" approach, coordination polymers **8**−**14** can be broken down to monomeric or heterobimetallic species on addition of Lewis bases, such as acetonitrile, pyridine, and bipyridine, respectively.[2e,g,25]

Multimetallic Transition-Metal Complexes

Multimetallic transition metal complexes can be synthesized by molecular manufacturing. In this respect, transition metals and organic and/or inorganic building blocks can be considered as molecular "Tinkertoys". The modular preparation of molecular wires in which two, three, or even four different redox-active early−late or late−late transition metals are spanned by π-conjugated organic units is possible. This idea can be extended even to penta- to nonametallic systems featuring two, three, or four different metal ions.

Thus, in this section we focus on the synthesis and reaction chemistry of multimetallic complexes based mainly on titanocene−, ferrocene−, platinum− and/or gold alkynyl and/or NCN pincer (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$), carboxylate, and nitrogen containing heterocyclic building blocks.

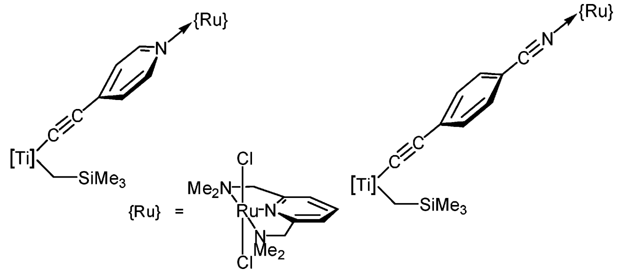

Figure 4. Complexes **15** (left) and **16** (right).[29]

(Hetero)bimetallic Transition-Metal Complexes. Besides early−late organometallic π-tweezer complexes of structural type **B** (Scheme 1),[2] titanocene monoacetylides have also enabled the synthesis of a series of heterobimetallic transition-metal species (Figure 4).[29]

Replacement of the $C_5H_4N{\rightarrow}\{Ru\}$ and C_6H_4-4-C≡N→{Ru} moieties in **15** and **16** by a Fc unit (Fc = (η^5-C_5H_4)Fe(η^5-C_5H_5)) leads to [Ti](CH_2SiMe_3)(C≡CFc) (**17**).[29,30] Complex **17** represents a further example of a mixed early−late transition-metal compound with reasonable electron transfer between the reducible [Ti] and oxidizable Fc groups via a C≡C connecting unit.

Likewise, {Pt}(C≡CC_6H_4-4-C≡N) (**18**) ({Pt} = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$Pt) can be used as starting material for the synthesis of rigid-rod-structured bimetallic {Pt}−C≡CC_6H_4-4-C≡N→M′L (**19a**, M′L = {Pt}BF_4; **19b**, M′L = {Ru}; **19c**, M′L = AuCl).[31]

A series of heterobimetallic complexes based on Fc moieties is accessible by applying different synthetic strategies. Sonogashira cross-coupling of ethynylferrocene (**20**) with 4-bromobenzonitrile and 5-bromo-2,2′-bipyridine afforded Fc−C≡C-C_6H_4-4-C≡N (**21**) and Fc−C≡C-bipy (**22**), respectively. Treatment of **21** and **22** with {Pt}BF_4, {Ru}N≡N{Ru}, (nbd)Mo$(CO)_4$ (nbd = norbornadiene), $Mn(CO)_5Br$, $Ru(bipy)_2Cl_2$, and $(Et_2S)PtCl_2$ gave the respective complexes Fc−C≡CC_6H_4-4-C≡N→M′L (**23a**, M′L = {Pt}BF_4; **23b**, M′L = {Ru}) and Fc−

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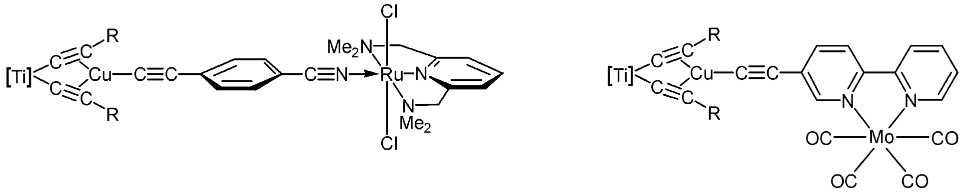
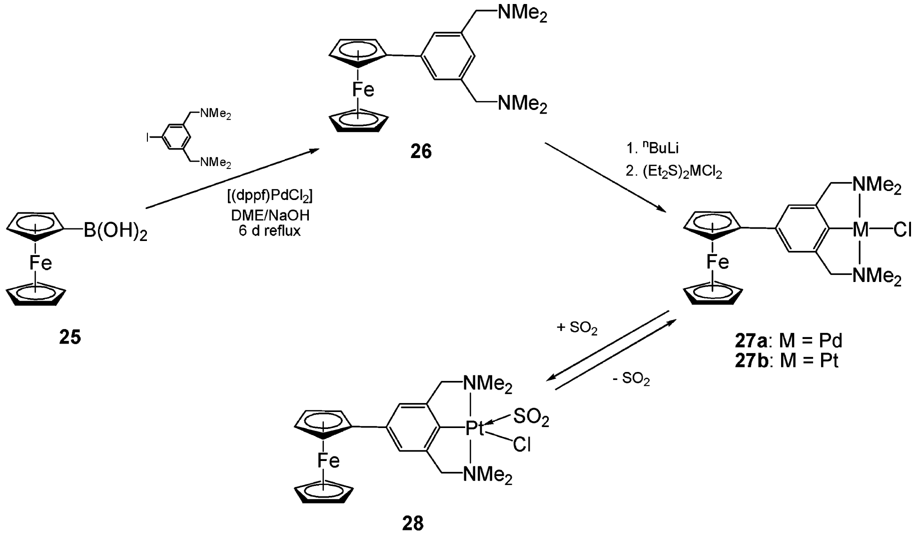


Figure 5. Trimetallic **34** (left) and **35** (right) (R = $SiMe_3$, ^tBu).[32,35b]

Scheme 2. Synthesis of Heterobimetallic 27a and 27b[33,34]



C≡C-bipy(M′L) (**24a**, M′L = $Mo(CO)_4$; **24b**, M′L = $Mn(CO)_3Br$; **24c**, M′L = $Ru(bipy)_2(PF_6)_2$; **24d**, M′L = $PtCl_2$).[20b,32]

Heterobimetallic iron−platinum and iron−palladium complexes based on the pincer-functionalized ferrocene Fc−NCNH (NCN = $[4\text{-}C_6H_2(CH_2NMe_2)_2\text{-}2,6]^-$) are available by the synthesis protocol shown in Scheme 2.[33,34]

Compound **27b** possesses the ability to reversibly bind sulfur dioxide and, hence, can successfully be used as a gas sensor for the detection of SO_2 (Scheme 2).[33,34]

The related compound Fc−C≡CNCNH (**29**), in which the NCNH and the Fc moieties are separated by an acetylide, is accessible from **20** by applying the Sonogashira cross-coupling reaction. Lithiation of **29** and reaction of **29**•Li with $[(Et_2S)_2MCl_2]$ (M = Pd, Pt) produced Fc−C≡CNCN−MCl (**30a**, M = Pd; **30b**, M = Pt).[33,34]

The introduction of a PdI entity into ferrocene−pincer molecules is possible by oxidative addition of the carbon−iodide bond in Fc−NCN−I or Fc−C≡CNCN−I to palladium (for example, $[Pd_2(dba)_3]$, dba = dibenzylideneacetone). The complexes Fc−NCN−PdI (**27c**) and Fc−C≡CNCN−PdI (**30c**) are thereby formed in good yields.[33,34]

The influence of the connecting alkynyl−aromatic moieties has been considered through electrochemical measurements of closely related complexes (vide supra) with a metal−ligand combination and a range of ethynyl−aromatic bridging entities.[33,34]

(Hetero)trimetallic Transition-Metal Complexes. Recent work of our group has been concerned with (hetero)trimetallic complexes derived from the organometallic π-tweezers $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}M'X$ (type **B** molecules).[2] Within these studies a closely related series of diverse complexes with interesting properties could be prepared.

An approach to transition-metal complexes with linear heterotrimetallic assemblies is given by starting from $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}CuCH_3$ (**31a**, R = $SiMe_3$; **31b**, R = ^tBu). Reaction of **31a** and **31b** with equimolar amounts of **20** produces, upon loss of methane, $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}CuC{\equiv}CFc$ (**32**).[3,4i,35] Compounds similar to **32** can be obtained when **31** is reacted with 4-ethynylbenzonitrile or 5-ethynyl-2,2′-bipyridine. The $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}CuC{\equiv}CR'$ (**33a**, R′ = C_6H_4-4-C≡N; **33b**, R′ = bipy) thus formed can be further reacted with, for example, {Ru}N≡N{Ru} and $(nbd)Mo(CO)_4$ to afford **34** and **35**, respectively (Figure 5).[32,35b]

In **34** and **35** three different transition metals (TiCuRu, TiCuMo) are connected via σ,π-bound acetylides and datively bound to benzonitrile (**34**) or 2,2′-bipyridine (**35**) ligands. A further example of a similar compound is $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu{-}C{\equiv}N{\rightarrow}Cr(CO)_5$ (**37**), which is accessible by treatment of $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}CuC{\equiv}N$ (**36a**) with $Cr(CO)_5(thf)$.[36] However, complex **37** could only be characterized spectroscopically, due to its great instability at room temperature.

A further effort to include metal centers within organic connecting moieties is possible by treatment of $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M'X$ (**38a**, M′X = $Cu(N{\equiv}CMe)BF_4$; **38b**, M′X = $AgFBF_3$) with $Ph_3PAuC{\equiv}N$ in a 1:1 molar ratio.[36] Complex **38a** affords, upon elimination of MeC≡N, cationic **39** (Figure 6), in which the linear Cu−N≡C−Au−P assembly is stabilized by the chelating effect of the organometallic π-tweezer $[Ti](C{\equiv}CSiMe_3)_2$. However, when **38b** is reacted with the same gold(I) precursor, then heterotrimetallic **40** is obtained (Figure 6).[36]

In contrast to **39**, with its tricoordinate planar copper(I) center adding up to 16 valence electrons, in **40** the coordination number of silver(I) expands and an 18-valence-electron fragment is

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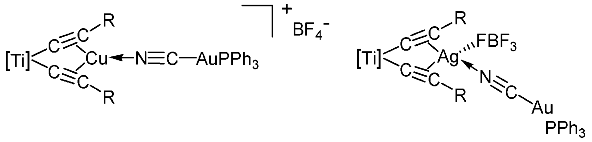


Figure 6. Complexes **39** (left) and **40** (right) (R = $SiMe_3$).[36]

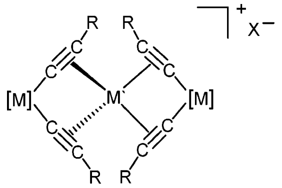
Table 1. [{[M](μ-σ,π-C≡CR)$_2$}$_2$M′][X] Complexes (41−44)

compd	[M]	R	M′	X	ref
41a	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Ph	Cu	BF_4	38, 39
41b	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Ph	Cu	PF_6	38, 39
41c	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Fc	Cu	BF_4	39
42a	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Ph	Ag	BF_4	38, 39
42b	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Ph	Ag	PF_6	38, 39
42c	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Ph	Ag	ClO_4	38, 39
42d	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Fc[a]	Ag	PF_6	21c
42e	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Fc[a]	Ag	ClO_4	39
42f	(η^5-C_5H_5)$_2$Ti	C≡CFc[a]	Ag	PF_6	21c
42g	(η^5-$C_5H_4SiMe_3$)$_2$Ti	C≡CFc[a]	Ag	PF_6	21c
42h	(η^5-$C_5H_4SiMe_3$)$_2$Ti	Rc[b]	Ag	PF_6	21c
43a	(bipy)Pt[c]	Ph	Cu	BF_4	25a, 40
43b	(bipy′)Pt[d]	Ph	Cu	BF_4	25a, 40
43c	(dppe)Pt[e]	Ph	Cu	BF_4	25a, 40
43d	(bppz)Pt[f]	$SiMe_3$	Cu	BF_4	25a, 40
43e	(bipy)Pt[c]	Fc[a]	Cu	Br	22
43f	(bipy)Pt[c]	Fc[a]	Cu	BF_4	22
43g	(dppf)Pt[g]	Ph	Cu	BF_4	25c
44a	(bipy)Pt[c]	Ph	Ag	BF_4	25a, 40
44b	(bipy)Pt[c]	Ph	Ag	PF_6	25a, 40
44c	(bipy)Pt[c]	Ph	Ag	ClO_4	25a, 40
44d	(bipy′)Pt[d]	Ph	Ag	BF_4	25a, 40
44e	(bipy′)Pt[d]	Ph	Ag	PF_6	25a, 40
44f	(bipy′)Pt[d]	Ph	Ag	ClO_4	25a, 40
44g	(bipy)Pt[c])	Fc[a]	Ag	ClO_4	22
44h	(bppz)Pt[f]	$SiMe_3$	Ag	ClO_4	25a, 40
44i	$(PPh_3)_2$Pt	Ph	Ag	ClO_4	41
44j	$(PEt_3)_2$Pt	Ph	Ag	ClO_4	41
44k	(dppe)Pt[e]	Ph	Ag	ClO_4	41
44l	$(PPh_3)_2$Pt	^{t}Bu	Ag	ClO_4	41
44m	(dppe)Pt[e]	^{t}Bu	Ag	ClO_4	41

[a] Fc = (η^5-C_5H_4)Fe(η^5-C_5H_5). [b] Rc = (η^5-C_5H_4)Ru(η^5-C_5H_5). [c] bipy = 2,2′-bipyridine. [d] bipy′ = 4,4′-dimethyl-2,2′-bipyridine. [e] dppe = 1,2-diphenylphosphinoethane. [f] bppz = 2,5-bis(2-pyridyl)pyrazine. [g] dppf = 1,1′-bis(diphenylphosphino)ferrocene.

formed.[36] Complex **40** displays a *non*linear Ti−Ag−N≡C−Au array, as required by the pseudotetrahedral geometry around silver(I). For the different coordination behaviors of copper(I) and silver(I) toward Lewis bases see refs 2 and 37.

Although the reaction of [M](C≡CR)$_2$ π-tweezers with metal sources in a 1:1 ratio results in the formation of heterobimetallic structural type **B** complexes, an interesting class of oligometallic species is produced when 2 equiv of [M](C≡CR)$_2$ is allowed to react with copper(I) or silver(I) salts, forming compounds of the type [{[M](μ-σ,π-C≡CR)$_2$}$_2$M′]X (**41**−**44**; Table 1). In these complexes a single metal M′ (M′ = Cu, Ag) is tetrahedrally coordinated by two organometallic π-tweezer fragments, as shown. In these compounds, the counterion X must be a poor ligand (such as BF_4^-, ClO_4^-, or PF_6^-) to prevent the formation of structural type **B** molecules.[2] Complexes **41**−**44** are summarized in Table 1.



41 – 44

The solid-state structures of selected species of types **41**−**44** were determined by X-ray structure analysis.[39] The basic structure [{[M](μ-σ,π-C≡CR)$_2$}$_2$M′]$^+$ is set up by two almost orthogonally positioned bis(alkynyl) transition-metal fragments, which are spanned by a d^{10} M′$^+$ ion. Thereby all four RC≡C ligands are η^2-coordinated to M′$^+$, forming a linear M−M′−M array. Very characteristic features of **41**−**44** are the *non*equivalent linkages of C$_\alpha$ and C$_\beta$ to M′ (M−C$_\alpha$≡C$_\beta$), which are even more pronounced than in the case of type **B** molecules.[2]

While in **43c** the copper ion lies only slightly out of the Pt(C≡CC$_{Ph}$)$_2$ plane, to presumably minimize steric interactions between the phenylethynyl ligands and the dppe chelate, in **44b** an asymmetric structure is typical, which means that the silver(I) ion is more closely situated to one Pt(C≡CC$_{Ph}$)$_2$ fragment than to the other (Pt(1)−Ag = 3.384 Å, Pt(2)−Ag = 3.513 Å).[2,16g,30,41]

Further possible ways to synthesize **43a**−**c** are given in Scheme 3 and are based on the stoichiometry of the reactants *cis*-[Pt](C≡CPh)$_2$ and [Cu(N≡CMe)$_4$]X (X = BF_4, PF_6, ClO_4) (Scheme 3).[25a,40]

When *cis*-[Pt](C≡CPh)$_2$ is reacted with [Cu(N≡CMe)$_4$]X in the ratio of 3:2, pentametallic **45** is formed, in which three helically arranged *cis*-[Pt](C≡CPh)$_2$ building blocks are spanned by two copper(I) ions.[2e,g,25a,30,42] In **45** the two outer bis(alkynyl) platinum entities are coordinated by only one copper atom. For this, we reacted **45** with a further type **B** molecule to obtain higher oligomeric structures. Surprisingly, after the appropriate workup, only trimetallic **43** could be isolated.[25a,42]

On the other hand, treatment of *cis*-[Pt](C≡CPh)$_2$ with the copper source [Cu(N≡CMe)$_4$]X in a 2:1 molar ratio at low temperature gives ionic **46**, in which the copper(I) ion is π-bound by one PhC≡C ligand of each of the *cis*-[Pt]C≡CPh)$_2$ units, thus resulting in a linear alkyne−copper−alkyne array (alkyne = midpoint of the C≡C triple bond).[2e,g,25,30,42] Complex **46** can be considered as an intermediate in the formation of **43** (Scheme 3). When it is slowly warmed to 45 °C, **46** smoothly rearranges via the formation of **47** and **48** to give **43**, as could be shown by spectroscopic as well as single-crystal X-ray diffraction studies.[2e,g,25,30,42]

Furthermore, when **43** is reacted with 1 equiv of [Cu(N≡CMe)$_4$]X, the incoming Cu(I) adds to the alkynyl ligands of **43**, resulting in the formation of **49** (Scheme 3). In **49** two bis(alkynyl) platinum entities are linked by copper(I) ions, whereby two PhC≡C units, one associated with each platinum atom, are η^2-coordinated to the group 11 metal.[2e,g,10n,25,30,42]

A further possible way to synthesize trimetallic **44a** (Table 1) is given by treatment of {*cis*-[Pt](μ-σ,π-C≡CPh)$_2$}AgFBF$_3$ (**50**) with *cis*-[Pt](C≡CPh)$_2$ in a 1:1 molar ratio (Scheme 4).[25a,40]

As shown in Scheme 4, the first step in the preparation of **44a** involves the elimination of BF_4^- from **50** upon addition of the organometallic chelate *cis*-[Pt](C≡CPh)$_2$.[2e,g,25a,30,43] Initially formed [{*cis*-[Pt](μ-σ,π-C≡CPh)$_2$}$_2$Ag]BF_4 (**51**) contains two

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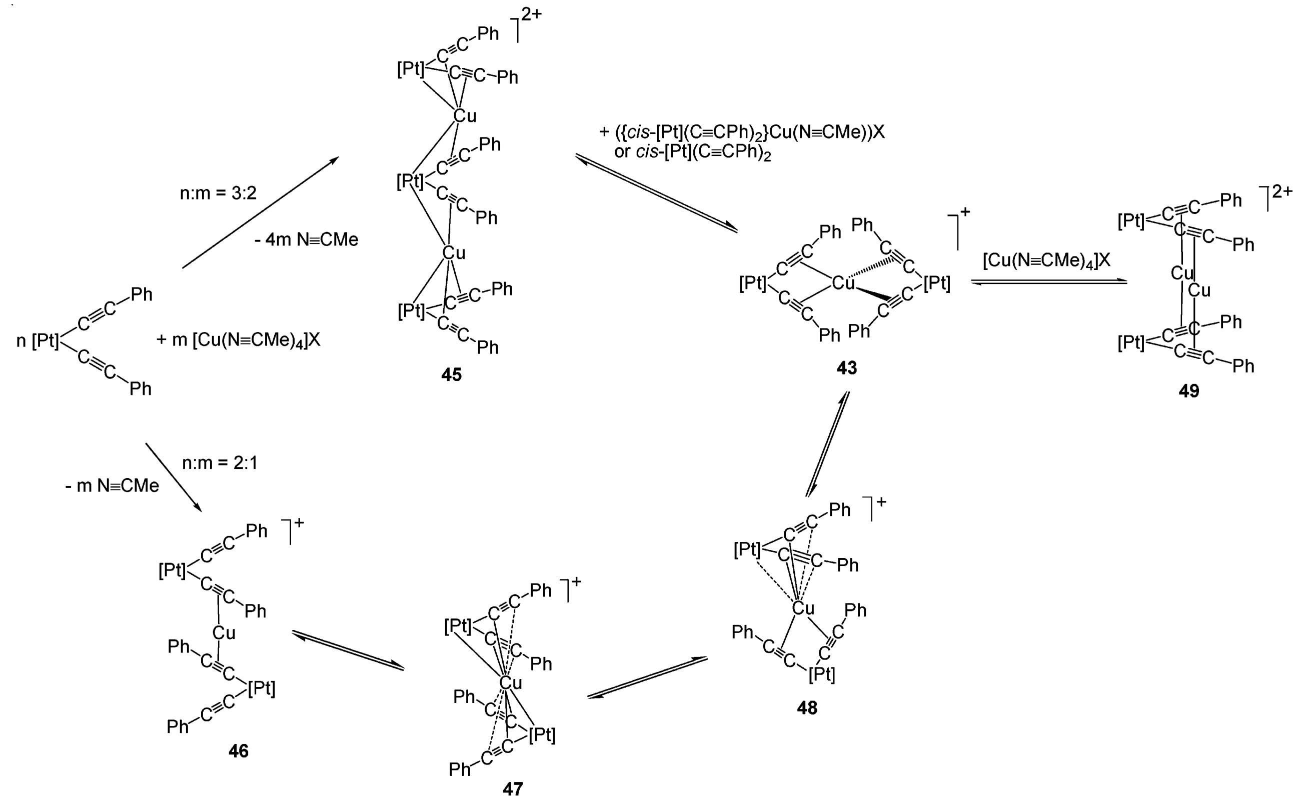
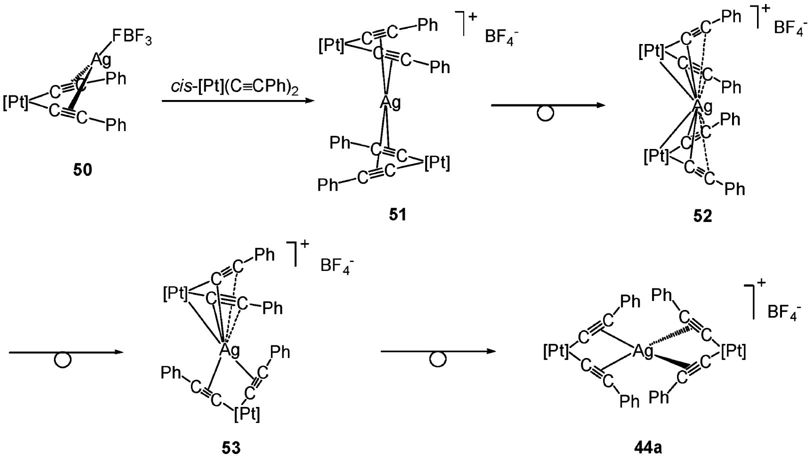
Scheme 3. Reaction Chemistry of *cis*-[Pt](C≡CPh)$_2$ toward [Cu(N≡CMe)$_4$]X[25a,40]



Scheme 4. Synthesis of 44a by Reacting 50 with *cis*-[Pt](C≡CPh)$_2$[25a,40,43]



cis-[Pt](C≡CPh)$_2$ moieties which are η^2-coordinated to a silver(I) cation by all four PhC≡C groups. The two *cis*-[Pt](C≡CPh)$_2$ assemblies are oriented parallel to the platinum atoms on opposite sides.

Complex **51** isomerizes in solution to produce **52** and then **53**, which afterward rearranges to give **44a** (Scheme 4). IR spectroscopic studies gave the first hint for the different bonding modes of the respective alkynyl groups present in **50**−**53** and **44a**. This finding could additionally be confirmed by single-crystal X-ray structure determinations.[2e,g,25a,30,43]

Moreover, trimetallic M$_2$M′ species (M = Fe, M′ = Hg, Pd; M = Pd, Pt, M′ = Fe) can be synthesized in a straightforward manner by applying different synthetic strategies.[44]

Treatment of 2 equiv of **20** with Hg(OAc)$_2$ produces (FcC≡C)$_2$Hg (**54a**). Compounds isostructural with **54a** are accessible when **20**·Li is reacted with MCl$_2$ (M = Cd, Zn). The complexes (FcC≡C)$_2$M (**54b**, M = Cd; **54c**, M = Zn) are thereby obtained in good yield.[44]

A Fe$_2$Pd trinuclear complex of composition [(Fc−C≡CC$_6$H$_4$-4-C≡N)$_2$Pd(PPh$_3$)$_2$](OTf)$_2$ (**55**) is available by the reaction of Fc−C≡CC$_6$H$_4$-4-C≡N (**21**) with Pd(PPh$_3$)$_2$(OTf)$_2$.[45]

Electrochemical studies of **54** and **55** showed that only one reversible redox couple is found for the Fc units. Electron transfer via the connecting metals Hg, Cd, Zn, and Pd, respectively, is not observed.[44,45]

As shown earlier, Fc−NCNH pincer molecules can be used successfully in the synthesis of heterobimetallic complexes. The introduction of a further NCNH unit in Fc−NCNH opens the possibility of preparing the ferrocene-based trimetallic FeM$_2$ complexes **59** and **60** (M = Pd, Pt), as presented in Scheme 5. The reactions depicted there include metalation−transmetalation and oxidative addition processes.[33,46]

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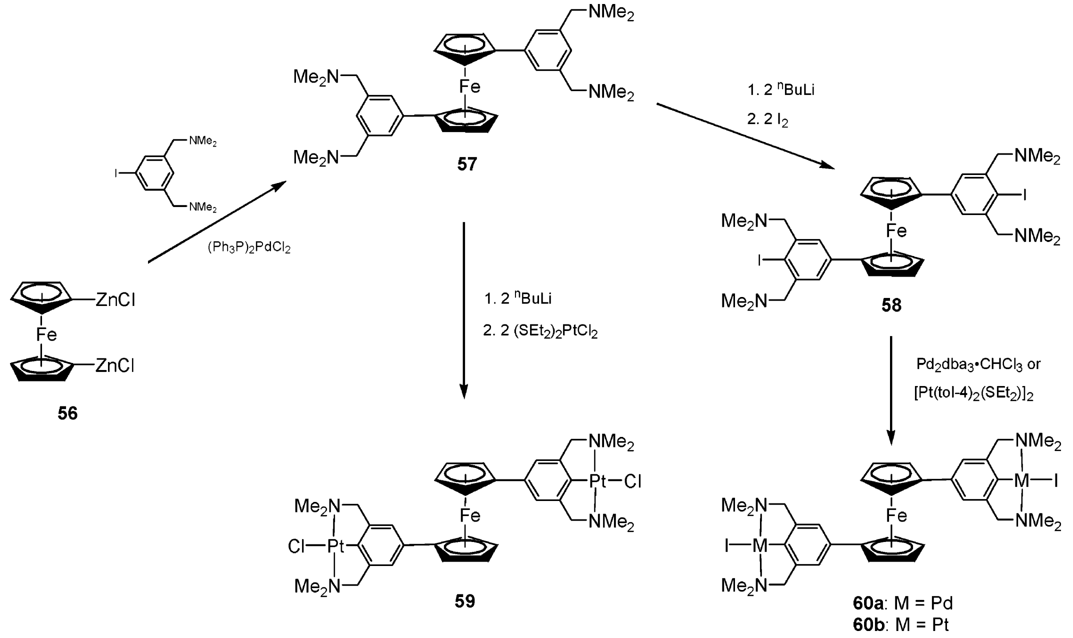
Scheme 5. Synthesis of Complexes 59 and 60[33,46]



Other trimetallic MM'_2 bis(alkynyl) metal complexes are $\{[(\eta^5\text{-}C_5H_4PPh_2)_2CuCl]Ti(\mu\text{-}\sigma,\pi\text{-}C{\equiv}C^tBu)_2\}CuCl$ (**61**), $Pt[(\mu\text{-}\sigma,\pi\text{-}C{\equiv}CPh)CdCl_2]_2$ (**62**), and $Pt[(C{\equiv}CC_6H_4\text{-}2\text{-}C{\equiv}C)_2HgCl_2]_2$ (**63**).[47]

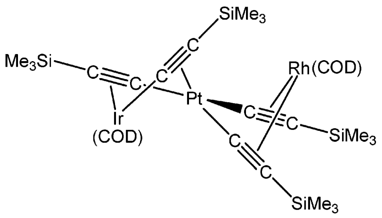
So far, trimetallic molecules with two different transition metals have been discussed. A straightforward synthetic method of preparing heterotrimetallic derivatives is depicted in Scheme 6.[32,48]

Alkynylation of **24d** gives **64**, which produces with $[Cu(N{\equiv}CMe)_4]BF_4$ heterotrimetallic **65** (Scheme 6). In **65** a Fc−C≡C−bipy unit is chelate-bound to a Pt−Cu tweezer moiety. A similar structural motif is found in $[(\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M')bipy{-}C{\equiv}CFc]X$ (**66a**, M′ = Cu, X = PF_6; **66b**, M′ = Ag, X = ClO_4), where the 2,2′-bipyridine entity is coordinated to a $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M'^+$ fragment.[32,48]

Related compounds can be obtained, when the gold(I) acetylide $Ph_3PAu{-}C{\equiv}C{-}bipy$ (**67**) is reacted with the organometallic π-tweezer $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M'X$ (M′X = $Cu(N{\equiv}CMe)PF_6$, $AgClO_4$). After the appropriate workup, $[(\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M')bipy{-}C{\equiv}C{-}AuPPh_3]X$ (**68a**, M′ = Cu, X = PF_6; **68b**, M′ = Ag, X = ClO_4) can be isolated as a red solid in excellent yield.[32] The chemical and physical properties of the latter species correspond to those of other gold(I) acetylides.[36,49]

Another trimetallic complex with a gold(I) acetylide unit is $Ph_3PAu{-}C{\equiv}CNCN{-}Pt{-}C{\equiv}C{-}Fc$ (**70**), which can be obtained by treatment of $Ph_3PAu{-}C{\equiv}CNCN{-}PtCl$ (**69**) with $FcC{\equiv}CSnMe_3$.[5d] Complex **70** represents a rigid-rod-shaped molecular wire molecule in which the transition metals are spanned by acetylide, cyclopentadienyl, and phenyl units.

A heterotrimetallic species featuring Ir, Pt, and Rh metals is **71**, which is accessible by treatment of $(NBu_4)[\{Ir{-}Pt\}(C{\equiv}CSiMe_3)_2]$ with $[Rh(cod)(acetone)_x]^+$ (cod = cyclooctadiene).[50]



71

The solid-state structure of **71** confirms the presence of the heterotrimetallic zwitterion $[(cod)Ir(\mu\text{-}1\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CSiMe_3)(\mu\text{-}$

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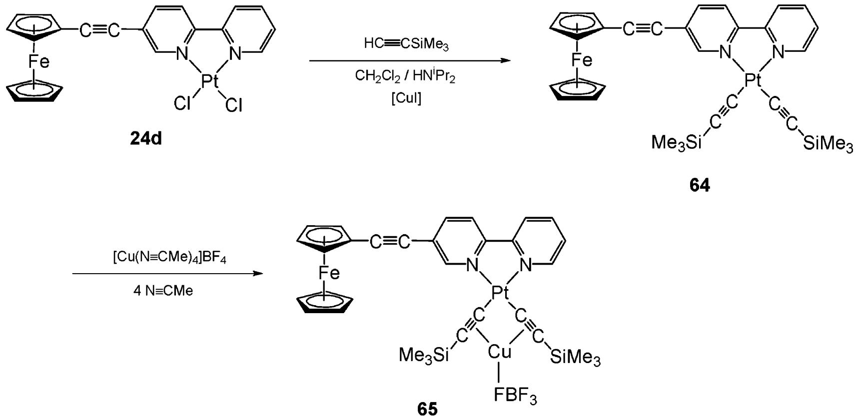
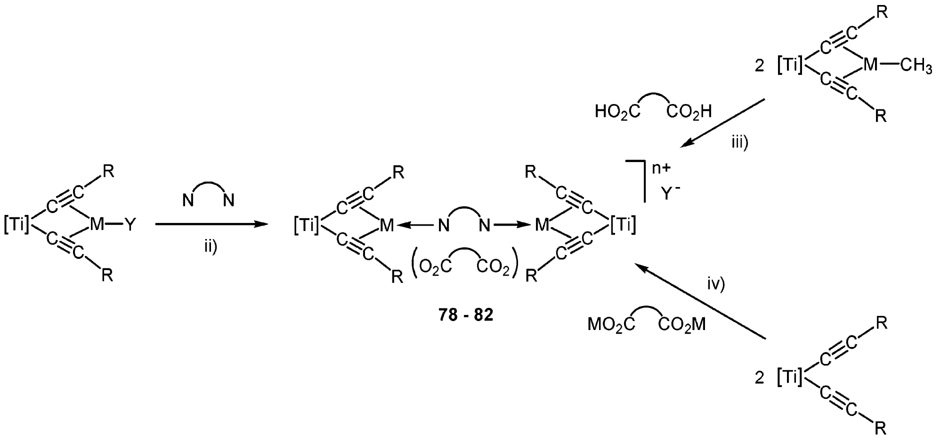
Scheme 6. Synthesis of Heterotrimetallic 65[32,48]



Scheme 7. Synthesis of Tetrametallic 78−82 (Table 2)



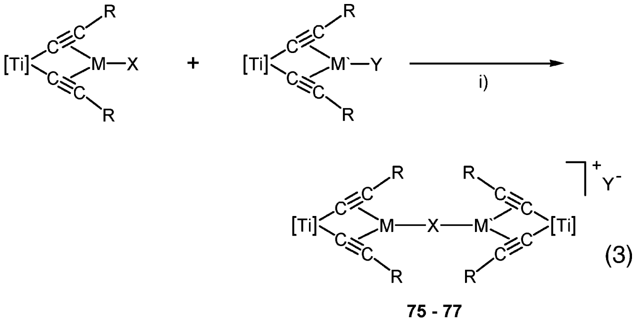
$2\kappa C^{\alpha}$:η^2-C≡CSiMe$_3$)Pt$^-$(μ-$2\kappa C^{\alpha}$:η^2-C≡CSiMe$_3$)$_2$Rh$^+$(cod)], formed by the binuclear anionic fragment [(cod)Ir(μ-$1\kappa C^{\alpha}$:η^2-C≡CSiMe$_3$)(μ-$2\kappa C^{\alpha}$:η^2-C≡CSiMe$_3$)Pt(C≡CSiMe$_3$)$_2$]$^-$, which in its turn acts as a chelating dimetallo bidentate ligand toward the cationic [Rh(cod)]$^+$ building block.[50]

A further series of trinuclear heterometallic complexes could be synthesized on the basis of 1,3,5-triethynylbenzene. Two examples are [1,3-{Cl(PEt$_3$)$_2$PdC≡C}$_2$-5-{(Me$_2$bpy)(CO)$_3$Re-C≡C}C$_6$H$_3$] (**72**) and [1-{Fc-C≡C}-3-{(CO)$_3$Cr(η^6-C$_6$H$_5$C≡C)}-5-{Ph$_3$PAuC≡C}C$_6$H$_3$] (**73**).[51,52] For similar compounds see ref 53.

A heterotrimetallic Fe−Ru−W complex is represented by (dppf)(η^5-C$_5$H$_5$)Ru−C≡CC$_5$H$_4$N→W(CO)$_4$PPh$_3$ (**74**; dppf = 1,1′-bis(diphenylphosphino)ferrocene).[54]

(Hetero)tetrametallic Transition-Metal Complexes. Organometallic type **B** π-tweezers can also successfully be used in the preparation of tetrametallic Ti$_2$M$_a$′M$_b$′ species (M$_a$′ = M$_b$′; M$_a$′ ≠ M$_b$′; M$_a$′, M$_b$′ = Cu, Ag).[2,14g,38,55]

In this respect, halides, pseudohalides (X), dicarboxylates (O$_2$C∩CO$_2$) and, for example, nitrogen-based bidentate molecules (N∩N) have been utilized to connect tweezer-chelated copper(I) and silver(I) centers (eq 3, Scheme 7 and Table 2).



Complexes **75**−**82** may display metal−metal interactions, as the inorganic or organic connecting units permit rapid intramolecular electron transfer.[14g,38,55] The compounds synthesized thus far are summarized in Table 2.

The electrochemistry of selected complexes was studied by cyclic voltammetry. Semiempirical calculations were also carried out.[14g,55,61] The results indicate a strong intramolecular interaction between the group 11 metals held in place by the organometallic bis(alkynyl) π-tweezers.

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Table 2. Synthesis of Complexes $\{[\mathrm{Ti}](\mu\text{-}\sigma,\pi\text{-C}{\equiv}\mathrm{CR})_2\}\mathrm{M{-}L^\frown L{-}M'}\{([\mathrm{Ti}](\mu\text{-}\sigma,\pi\text{-C}{\equiv}\mathrm{CR})_2\}$ ($\mathrm{L^\frown L}$ = X, $\mathrm{N^\frown N}$, $\mathrm{O_2C^\frown CO_2}$)

compd	M/M′	R	X	Y	$\mathrm{O_2C^\frown CO_2/N^\frown N}$	*n*	reacn[a]	ref
75a	Cu	SiMe$_3$	Cl	ClO$_4$			i	14g, 38, 55
75b	Cu	SiMe$_3$	Br	ClO$_4$			i	14g, 38, 55
75c	Cu	SiMe$_3$	I	ClO$_4$			i	14g, 38, 55
75d	Cu	SiMe$_3$	CN	ClO$_4$			i	14g, 38, 55
75e	Cu	SiMe$_3$	NCS	ClO$_4$			i	14g, 38, 55
76a	Cu/Ag	SiMe$_3$	Cl	ClO$_4$			i	14g, 38, 55
76b	Cu/Ag	SiMe$_3$	Br	ClO$_4$			i	14g, 38, 55
76c	Cu/Ag	SiMe$_3$	I	ClO$_4$			i	14g, 38, 55
76d	Cu/Ag	SiMe$_3$	CN	ClO$_4$			i	14g, 38, 55
76e	Cu/Ag	SiMe$_3$	NCS	ClO$_4$			i	14g, 38, 55
77a	Ag	SiMe$_3$	Cl	ClO$_4$			i	14g, 38, 55
77b	Ag	SiMe$_3$	Br	ClO$_4$			i	14g, 38, 55
77c	Ag	SiMe$_3$	I	ClO$_4$			i	14g, 38, 55
77d	Ag	SiMe$_3$	CN	ClO$_4$			i	14g, 38, 55
77e	Ag	SiMe$_3$	SCN	ClO$_4$			i	14g, 38, 55
77f	Ag	SiMe$_3$	OCN	ClO$_4$			i	14g, 38, 55
77g	Ag	SiMe$_3$	SeCN	ClO$_4$			i	14g, 38, 55
78a	Cu	^{t}Bu			$\mathrm{O_2C{-}CO_2}$	0	iii	2, 3b−d, 56
78b	Cu	^{t}Bu			$\mathrm{O_2CC{\equiv}CCO_2}$	0	iii	2, 3b−d, 56
78c	Cu	^{t}Bu			*cis*-$\mathrm{O_2CCH{=}CHCO_2}$	0	iii	2, 3b−d, 56
78d	Cu	^{t}Bu			*trans*-$\mathrm{O_2CCH{=}CHCO_2}$	0	iii	2, 3b−d, 56
78e	Cu	^{t}Bu/SiMe$_3$			*trans*-$\mathrm{O_2CCH{=}CHCO_2}$	0	iii	2, 3b−d, 56
78f	Cu	^{t}Bu			$\mathrm{O_2CC_6H_4CO_2}$-1,4	0	iii	2, 3b−d, 56
78g	Cu	^{t}Bu			$\mathrm{(O_2C)_2C_6H_3}$-1,3-$\mathrm{(CO_2H)}$-5	0	iii	2, 3b−d, 56
78h	Cu	^{t}Bu/SiMe$_3$			$\mathrm{O_2CCH_2C(O)C({=}CH_2)CO_2}$	0	iii	2, 3b−d, 56
78i	Cu	SiMe$_3$			$\mathrm{C_6H_2O_4}$	0	iii	2, 3b−d, 56
78j	Cu	^{t}Bu			$\mathrm{O_2CC{\equiv}C}$	0	iii	2, 3b−d, 56
79a	Ag	Ph			$\mathrm{O_2C{-}CO_2}$	0	iv	2, 3b−d, 56
79b	Ag	SiMe$_3$			*trans*-$\mathrm{O_2CCH{=}CHCO_2}$	0	iv	2, 3b−d, 56
79c	Ag	SiMe$_3$			$\mathrm{O_2CC_6H_4CO_2}$-1,4	0	iv	2, 3b−d, 56
79d	Ag	SiMe$_3$			$\mathrm{C_4O_4}$	0	iv	2, 3b−d, 56
79e	Ag	SiMe$_3$			$\mathrm{C_6H_2O_4}$	0	iv	2, 3b−d, 56
80a	Cu	SiMe$_3$	PF$_6$	PF$_6$	biphenyldicarbonitrile	2	ii	57
80b	Cu	SiMe$_3$	BF$_4$	BF$_4$	biphenyldicarbonitrile	2	ii	57
80c	Cu	SiMe$_3$	PF$_6$	PF$_6$	*p*-phenylendiacetonitrile	2	ii	57
80d	Cu	SiMe$_3$	PF$_6$	PF$_6$	$\mathrm{NC_5H_4CH{=}CHC_5H_4N}$	2	ii	59
81a	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	1,4-pyrazine	2	ii	58
81b	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	4,4′-bipyridine	2	ii	59
81c	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	1,4-dicyanobenzene	2	ii	57
81d	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	bis((4-cyanophenyl)oxy)dimethylsilane	2	ii	57
81e	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	biphenyldicarbonitrile	2	ii	57
81f	Ag	SiMe$_3$	OTf	OTf	biphenyldicarbonitrile	2	ii	57
81g	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	*p*-phenylendiacetonitrile	2	ii	57
81h	Ag	SiMe$_3$	OTf	OTf	*p*-phenylendiacetonitrile	2	ii	57
81i	Ag	Ph	OTf	OTf	biphenyldicarbonitrile	2	ii	57
81j	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	pyridine-4-carbonitrile	2	ii	57
81k	Ag	SiMe$_3$	OTf	OTf	pyridine-4-carbonitrile	2	ii	57
81l	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	fumaronitrile	2	ii	57
81m	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	2,3-bis(2-pyridyl)pyrazine	2	ii	57
81n	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	2,2′:6′,2″-terpyridine	2	ii	57
81o	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	$\mathrm{NC_5H_4CH{=}CHC_5H_4N}$	2	ii	59
81p	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	$\mathrm{NC_5H_4CH{=}C_6H_6O{=}CHC_5H_4N}$	2	ii	59
81q	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	$\mathrm{NC_5H_4C_2N_3HC_5H_4N}$	2	ii	59
81r	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	$\mathrm{NC_5H_4CH{=}NC_6H_4N{=}CHC_5H_4N}$	2	ii	59
81s	Ag	SiMe$_3$	ClO$_4$	ClO$_4$	$\mathrm{NC_5H_4CH{=}C_5H_4O{=}CHC_5H_4N}$	2	ii	59
81t	Ag	SiMe$_3$	OTf	OTf	2,2′-bipyrimidine	2	ii	60
82a	Cu/Ag	SiMe$_3$	PF$_6$	ClO$_4$	pyridine-4-carbonitrile	2	ii	57
82b	Cu/Ag	^{t}Bu/SiMe$_3$		OTf	$\mathrm{C{\equiv}CC{\equiv}N}$	1	*b*	60

[a] The reaction letter refers to the reactions shown in Scheme 7. [b] Reaction of $\{[\mathrm{Ti}](\mu{-}\sigma,\pi\text{-C}{\equiv}\mathrm{CR})_2\}\mathrm{CuC{\equiv}CC{\equiv}N}$ with $\{[\mathrm{Ti}](\mu\text{-}\sigma,\pi\text{-C}{\equiv}\mathrm{CR})_2\}\mathrm{M'(OTf)}$ (M′ = Cu, Ag; R = ^{t}Bu, SiMe$_3$).

Other tetrametallic MM′M″$_2$ species are $\{[\mathrm{M}](\mu\text{-}\sigma,\pi\text{-C}{\equiv}\mathrm{CFc})_2\}\mathrm{M'X}$ ([M] = $(\eta^5\text{-C}_5\mathrm{H_4SiMe_3})_2$Ti: **83a**, M′X = Pd(PPh$_3$); **83b**, M′X = Ni(CO); **83c**, M′X = CuBr; **83d**, M′X = CuCl; **83e**, M′X = CuOTf; **83f**, M′X = CuCl$_2$; **83g**, M′X = ZnCl$_2$; **83h**, M′X = ZnBr$_2$; **83i**, M′X = AgCl; **83j**, M′X = AgBF$_4$; [M] = (bipy)Pt: **84a**, M′X = CuBr; **84b**, M′X = CuOTf; **84c**, M′X = CuBF$_4$; **84d**, M′X = AgNO$_3$; **84e**, M′X = AgClO$_4$; **84f**, M′X = AgO$_2$CCF$_3$; [M] = [(Ph$_2$PCH$_2$PPh$_2$)$_2$Ru: **85**, M′X = CuI).[14,22] They are impressive examples of mixed early−late transition-metal complexes in which both reducible and oxidizable groups are present. Their electrochemical behavior is discussed in detail in refs 14 and 22.

Further heterotetrametallic compounds are **88a** and **88b** (Figure 7), which are accessible in a two-step synthesis, including the Sonogashira cross-coupling reaction of 1,1′-bis(ethynyl) biferrocene (**86**) with I-1-NCN-4-Br and the oxidative addition of 1,1′-(Br-4-NCNC≡C)$_2$bfc (**87**; bfc = biferrocene) to [Pd$_2$(dba)$_3$] and [Pt(tol)$_2$(SEt$_2$)$_2$], respectively.[62]

Cyclic voltammetric studies of **88a** and **88b** show that the ferrocene moieties can be oxidized independently. The differ-

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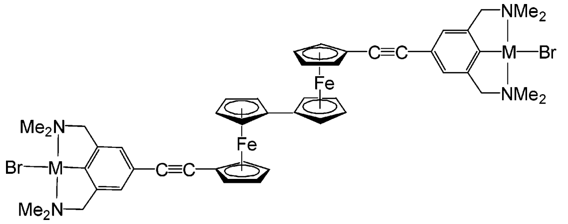


Figure 7. Biferrocene-based molecules **88a** (M = Pd) and **88b** (M = Pt).[62]

ence of the potentials of the Fe(II)/Fe(III) redox couples is 300 mV and is not affected by the NCN transition-metal pincer.[62]

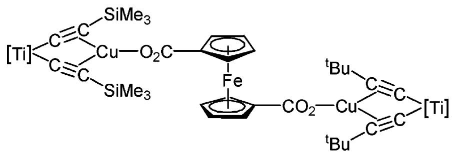
Even heterotetrametallic MM′M″M‴ complexes with four different metals, based on an organometallic π-tweezer, can be obtained by joining heterobimetallic Ti−Cu or Ti−Ag tweezers with Fe−Au- or Fe−Pt-containing molecules (Figure 8). Thus, $HC{\equiv}C{-}\{Pt\}{-}C{\equiv}C{-}Fc$ (**89**) ($\{Pt\} = Pt(C_6H_2(CH_2NMe_2)_2\text{-}2,6)$) gives with $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}C^tBu)_2\}CuCH_3$ (**90**) on loss of CH_4 complex **91**,[4g] while $FcPPh_2Au{-}C{\equiv}C{-}bipy$ (**92**) affords with $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M'X$ ($M'X = Cu(N{\equiv}CMe)PF_6$, $AgClO_4$) tetrametallic **93**.[63]

Complexes **91** and **93** represent the first examples of heterotetrametallic transition-metal complexes in which early and late metals are connected by π-conjugated organic bridging units. A striking feature of **91** is that all metals possess different coordination spheres: Ti shows a pseudotetrahedral environment, Cu possesses a planar environment, Pt has square-planar coordination, and Fe is part of a sandwich structure.[4g]

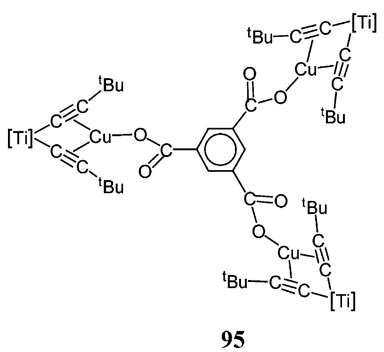
(Hetero)pentametallic to (Hetero)nonametallic Transition-Metal Complexes. Further examples of the molecular "Tinkertoys" approach includes the synthesis of (hetero)penta- to (hetero)nonametallic complexes.

An important family of "Tinkertoys" are halide, pseudohalide, cyanoacetylide, heterocyclic, and/or di- and tricarboxylic acid functionalized transition-metal building blocks.

There are mainly three methods which can successfully be applied for the preparation of the title compounds. The first synthesis protocol includes the reaction of $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}C\,R)_2\}CuCH_3$ with diverse organic and organometallic di- and tricarboxylic acids, owing to the instability of alkyl−copper systems, and is based on the preparation of **94** and **95**.[56,64]



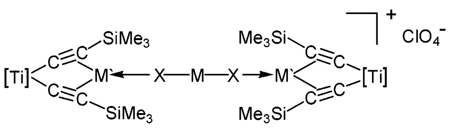
94



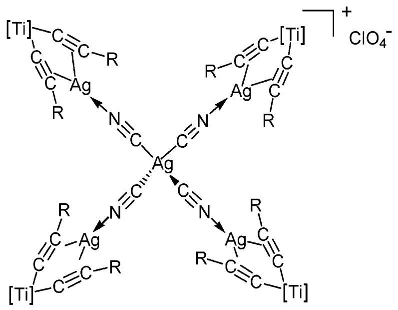
95

In the latter molecules organometallic π-tweezer units are connected by a 1,1′-ferrocenyldicarboxylate (**94**) or a 1,3,5-benzenetricarboxylic entity (**95**). However, electrochemical studies showed that the connecting carboxylates act as an impedance rather than a transmitter.[56,64]

The second and ultimately more straightforward synthetic route to (hetero)multimetallic π-tweezer-based complexes is the reaction of $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M'X$ ($M' = Cu$, Ag; $X = ClO_4$, OTf) with the metal salts $[MX_2]^-$ ($M = Cu$, Ag, Au; $X = C{\equiv}N$, OCN) (synthesis of **96a**−**e**) or $[Ag(C{\equiv}N)_4]^{3-}$ (synthesis of **97**) in the ratios of 2:1 and 4:1, respectively.[2e,g,36,38,55,65]



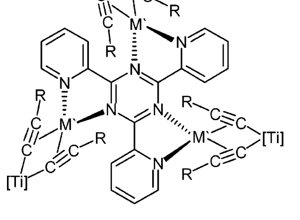
96a – 96e



97

Complexes **96a**−**e** (**96a**, $M = M' = Cu$, $X = C{\equiv}N$; **96b**, $M = M' = Ag$, $X = C{\equiv}N$; **96c**, $M = M' = Ag$, $X = N{=}C{=}O$; **96d**, $M = Ag$, $M' = Cu$, $X = C{\equiv}N$; **96e**, $M = Au$, $M' = Cu$, $X = C{\equiv}N$) have linear structures and contain the features typical for one-dimensional molecular wire molecules. Complex **97** is one of the outstanding examples of a cross-shaped molecule in which four titanium−silver tweezers are linked by a $[Ag(C{\equiv}N)_4]^{3-}$ core. In **97** each cyanide is datively bound to a silver(I) center of an individual π-tweezer fragment. While the inner silver atom possesses a tetrahedral environment, the outer silver(I) ions are coordinated in a planar fashion and, hence, possess coordination number 3.[65]

Multiple π-tweezers can also be linked together by bipyridyl, 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt), or pyridyl functionalized porphyrin connecting units.[57,66] With tpt, complexes **98a**−**d** ($M' = Cu$, $X = PF_6$: **98a**, R = Ph; **98b**, $R = SiMe_3$; $M' = Ag$, $X = ClO_4$: **98c**, R = Ph; **98d**, $R = SiMe_3$) are formed, when $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}M'X$ is reacted with tpt in the stoichiometry of 3:1.



98a – 98d

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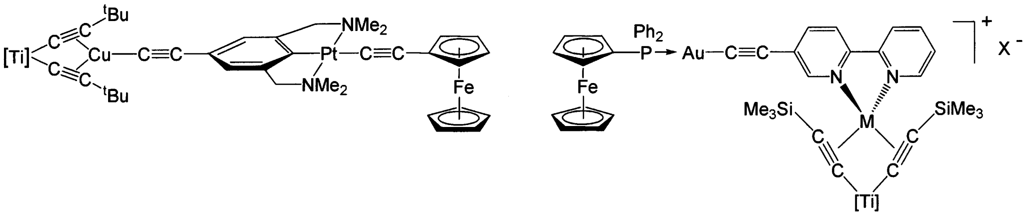
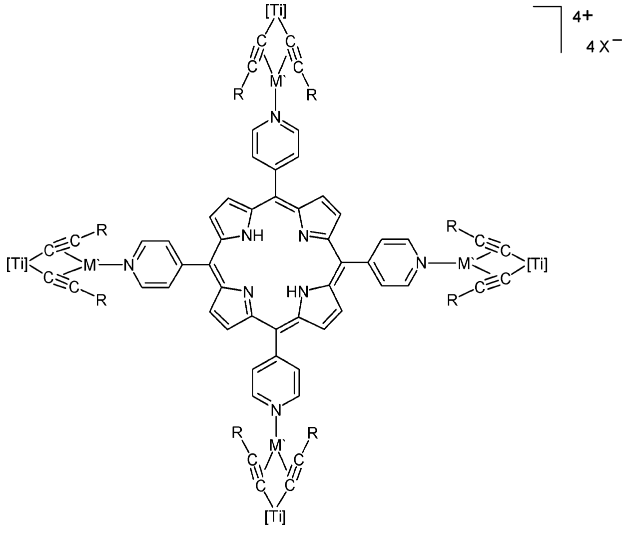


Figure 8. Complexes **91** (left) and **93** (right; **93a**: M = Cu, X = PF_6; **93b**: M = Ag, X = ClO_4).[4g,63]

In a similar manner, the heptametallic $FeAu_2Cu_2Ti_2$ and $FeAu_2Ag_2Ti_2$ molecules Fe((η^5-$C_5H_4PPh_2$)AuC≡C−bipy−M{(μ-σ,π-C≡CSiMe$_3$)$_2$[Ti]})$_2$ (**99**, M = Cu; **100**, M = Ag) are accessible by treatment of Fe((η^5-$C_5H_4PPh_2$)AuC≡Cbipy)$_2$ with 2 equiv of {[Ti]($\mu-\sigma$,π-C≡CSiMe$_3$)$_2$}M′X (M′X = Cu(N≡CMe)PF_6, $AgClO_4$).[52]

Pyridine-functionalized porphyrins allow the linkage of four organometallic π-tweezers as shown in **101a** (M = Cu) and **101b** (M = Ag). However, these molecules show a tendency to decompose in solution with formation of elemental copper or silver along with [Ti](C≡CSiMe$_3$)$_2$ and the porphyrin.[66]



101

A study of the reaction chemistry of **101a** and **101b** toward diverse transition-metal and main-group-element salts is in progress.

Further Fc-based penta- and hexametallic species are [Ph((η^5-C_5H_5)Fe(η^5-C_5H_4))$_2$P]AuC≡CAu[P((η^5-C_5H_5)Fe(η^5-C_5H_4))$_2$Ph] (**102**),[68] (FcC≡CC≡CFc)$_2$Os$_2$(CO)$_6$ (**103**),[67] and (FcC≡C)$_2$Os$_3$(CO)$_9$ (104).[68]

Summary and Outlook

This review addresses the chemistry of mono- and bis(alkynyl) transition-metal complexes, functionalized diaminoaryl NCN pincer molecules (NCN = [$C_6H_2(CH_2NMe_2)_2$-2,6]$^-$) and modified ferrocenes toward diverse metal fragments and serves to understand the manifold and sometimes unexpected reaction behavior of such species. Interesting novel (hetero)bi- to (hetero)nonametallic compounds with often uncommon structural motifs are formed, in which the respective transition-metal building blocks are connected via π-conjugated organic and/or inorganic bridging units. The reactions based on the modular molecular “Tinkertoys” approach depend on the steric and electronic properties of the metal centers and ligands involved. Despite the large quantity of experimental work carried out in this field of chemistry, the exact factors which control the formation and/or interconversion of the structures in the (hetero)multimetallic complexes is still an open question and will continue to stimulate fruitful work in this field. A challenge is the preparation of even larger transition-metal complexes featuring more than four different early−late metal atoms and new functionalities. In addition, it should be possible to use the described (thiol-functionalized) organometallic species as one-dimensional molecular wires to span metal surfaces/electrodes and, hence, such single molecules may function as key components or insulators in future computational devices. This chemistry also opens the possibility for creating new materials with innovative electronic, catalytic, optical, and/or magnetic properties.

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