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Bis(alkynyl) transition metal complexes, $R^1C{\equiv}C{-}[M]{-}C{\equiv}CR^2$, as organometallic chelating ligands; formation of $\mu,\eta^{1(2)}$-alkynyl-bridged binuclear and oligonuclear complexes

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Abstract

The reaction chemistry of bis(alkynyl)metal complexes towards different metal centers (electron-rich or electron-poor) to give alkynyl-bridged binuclear and oligonuclear species is described. Different coordination modes of the alkynyl ligands are found in these systems, depending upon the nature of the alkynyl substituents and the metal centers involved. The interconversion of these structures, as well as the factors affecting the preference for one coordination mode over another, is discussed.

Keywords: Bis(alkynyl) transition metal complexes; Organometallic chelating ligands; Alkynyl-bridged binuclear and oligonuclear complexes

1. Introduction

Transition metal alkynyl complexes have been proposed to play an important role in many industrial processes, such as homogeneous and heterogeneous catalysis and have great relevance to fields such as materials science. The wide range of reaction products that can be obtained from these complexes can be attributed to their high degree of unsaturation. In addition to increasing the reactivity of these compounds, the presence of two sets of π-orbitals also allows the alkynyl ligand to bridge two or more metal centers. In this context, transition metal acetylide chemistry has been extensively reviewed [1–3].

In mononuclear systems, the alkynyl group can bind terminally to a main group or transition metal center, acting as a strong σ-donor (type **A** molecule, Fig. 1). In the presence of a second metal center, an alkynyl ligand can bridge the two metals, acting either as a σ-donor to both metals (type **C** molecule) or, more commonly, as a σ-donor to one metal and a π-donor to the other (type **B** and **D** molecules). Depending on the nature of the metal centers and the alkynyl ligands, condensation of the alkynyl building blocks can occur, resulting in the formation of more complex organic ligands, as shown in molecule types **E**, **F** and **G**. In type **E**

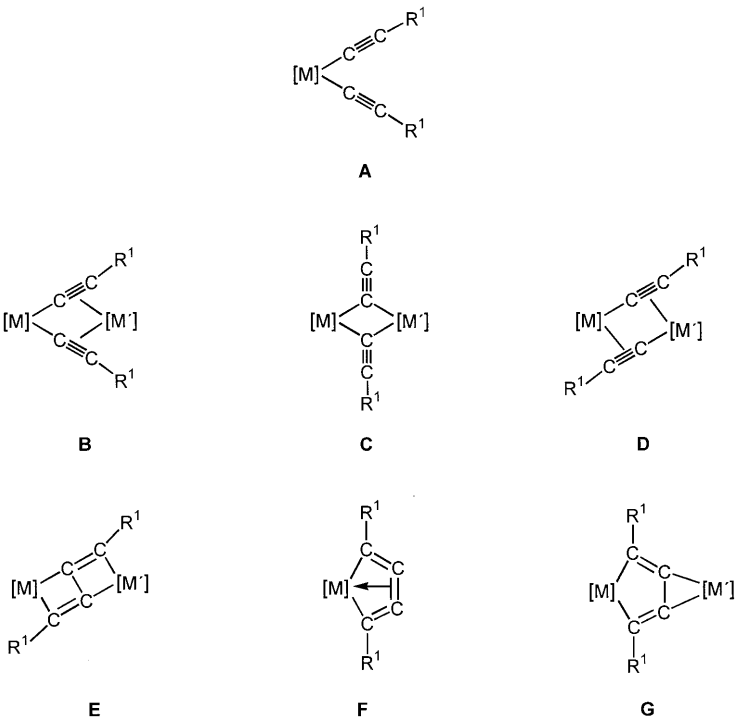


Fig. 1. Different coordination modes of C≡CR[1] units in the coordination sphere of transition metal atoms and/or main group elements [M]/[M′].

Fig. 2. Schematic orientation of the $M(C{\equiv}CR^1)_2$ plane with the metal atom M′ in $\{[M](C{\equiv}CR^1)_2\}[M']$ species (type **B** molecules). (a) π-Tweezer complexes, $M(C{\equiv}CR^1)_2$ and M′ coplanar. (b) Non-planar tweezer molecules, $M(C{\equiv}CR^1)_2$ and M′ not coplanar.

molecules, two alkynyl ligands have condensed to form a tetradehydro-$\eta^{(1,3)}$:$\eta^{(2,4)}$-*trans*,*trans*-butadiene moiety, which acts as a bridging ligand between two metal centers. Coupling of the alkynyl groups can also result in the formation of molecule types **F** and **G**. In these five-membered metallacyclic cumulenes, the central carbon–carbon double bond additionally coordinates to M (type **F** molecule) or to M′ (type **G** molecule).

Compounds of type **B** can be considered as key molecules in the formation of the bridged structural type **C**–**G** species [2–10]. Therefore, this review focuses on the synthesis and reaction chemistry of type **B** molecules and their conversion into compounds of type **C**–**G**. More complex coordination modes, in which the alkynyl ligand bridges three or more metals, will not be discussed in this review [1].

2. Synthesis, chemical behavior, structure and bonding of type B molecules, $\{[M](C{\equiv}CR^1)_2\}[M']$

Compounds of type **A**, $R^1C{\equiv}C{-}[M]{-}C{\equiv}CR^1$ {[M] = transition metal moiety, R = singly bonded organic ligand}, can be considered as bidentate organometallic chelating ligands (organometallic π-tweezers) for the stabilization of various low-valent and mononuclear transition metal moieties [M′] by formation of type **B** molecules, $\{[M](C{\equiv}CR^1)_2\}[M']$ [2]. In these compounds, the [M′] unit is complexed by both alkynyl ligands of the bis(alkynyl) transition metal fragment $[M](C{\equiv}CR^1)_2$.

Type **B** molecules can be further broken down into two classes: π-tweezer complexes, in which the chelated metal center M′ and the $M(C{\equiv}CR^1)_2$ fragment are coplanar (Fig. 2(a)); and non-planar complexes, in which the M′ center is displaced from the plane defined by the M center and the alkynyl ligands (Fig. 2(b)).

2.1. Tweezer-like molecules, $\{[M](C{\equiv}CR^1)_2\}[M']$ ($M(C{\equiv}CR^1)_2$ and M′ coplanar)

2.1.1. Synthesis

In type **B** molecules, $\{[M](C{\equiv}CR^1)_2\}[M']$, the $[M](C{\equiv}CR^1)_2$ fragment acts as a host, with the [M′] unit as guest (Fig. 3) [2,11].

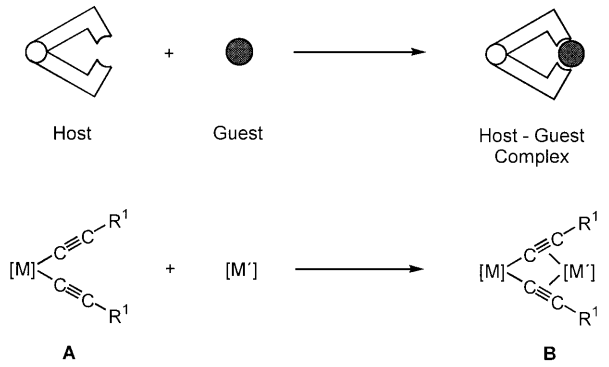


Fig. 3. Abstract representation of heterobinuclear type **B** compounds, {[M](C≡CR^1)$_2$}[M′], as host–guest complexes [2,11].

There are several methods used to synthesize the heterobimetallic compounds {[M](C≡CR^1)$_2$}[M′] **4**–**19** (Table 1) {[M], [M′] = transition metal entity}:

1. direct synthesis route from [M](C≡CR^1)$_2$ (type **A** molecule);
2. redox-reaction route;
3. metal acetylide route;
4. and modification of other tweezer complexes.

2.1.1.1. Direct synthesis route (method A). The bis(alkynyl) metallocenes R^{1}C≡C–[M]–C≡CR^2 {[M] = (η^5-C$_5$H$_5$)$_2$M, (η^5-C$_5$H$_4$SiMe$_3$)$_2$M, **1**: M = Ti, **2**: M = Zr, **3**: M = Hf; [M] = ([(η^5-C$_5$H$_3$R^3)(η^5-C$_5$H$_3$R^4)]SiMeR^{5}Ti); [M] = [(η^5-C$_5$H$_2$SiMe$_3$)SiMe$_2$]$_2$Ti; R^1-R^5 = singly bonded organic groups} [12,13] can be used as organometallic chelating species (organometallic π-tweezers) for the synthesis of the heterobimetallic complexes {[M](C≡CR^1)(C≡CR^2)}[M′] **4**–**8**, **11** and **13**–**18** (Table 1). Many of these heteronuclear complexes are best prepared using equimolar amounts of the organometallic chelating ligands R^{1}C≡C–[M]–C≡CR^2 and the appropriate [M′]$_x$L$_y$ starting materials (Table 1) at 25°C in *n*-pentane or toluene solutions (preparation of compounds **4**–**7**) or diethyl ether and tetrahydrofuran solutions (preparation of compounds **8**, **11** and **13**–**19**). This method has proven useful for a large number of low-valent transition metal salts (such as FeCl$_2$, NiCl$_2$, CuBr, AgCN, etc.) and organometallic complexes (Co$_2$(CO)$_8$, Ni(CO)$_4$, Pt(PPh$_3$)(CH$_2$=CH$_2$)$_2$, etc.). In the case of the organometallic complexes, auxiliary ligands are normally displaced by the tweezer molecule.

Although this method works best for low-valent metal centers, {[Ti](C≡CR^1)$_2$}MoO$_2$ (**4a**–**4c**), a high-valent metal center, is formed when [Ti](C≡CR^1)$_2$ ([Ti] = (η^5-C$_5$H$_5$)$_2$Ti; **1a**: R^1 = SiMe$_3$, **1b**: R^1 = ^{t}Bu; [Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti; **1c**: R^1 = SiMe$_3$) is allowed to react with Mo(CO)$_3$(N≡CCH$_3$)$_3$ in the presence of atmospheric oxygen. This was proposed to take place through the formation and subsequent oxidation of {[Ti](C≡CR^1)$_2$}Mo(CO)$_4$ [14]. Similar species were prepared for the tungsten analogues [15].

Table 1
Synthesis of type **B** compounds {[M](C≡CR^1)(C≡CR^2)}[M′] (**4**–**19**)

Compound	[M]	$[M']_xL_y$	[M′]	R^1, R^2	Method[a]	Refs.
4a	$(\eta^5\text{-}C_5H_5)_2Ti$	$Mo(N{\equiv}CMe)_3(CO)_3/O_2$	MoO_2	$SiMe_3$	**A**	[14]
4b	$(\eta^5\text{-}C_5H_5)_2Ti$	$Mo(N{\equiv}CMe)_3(CO)_3/O_2$	MoO_2	^{t}Bu	**A**	[14]
4c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Mo(N{\equiv}CMe)_3(CO)_3/O_2$	MoO_2	$SiMe_3$	**A**	[14]
4d	$(\eta^5\text{-}C_5H_5)_2Ti$	$W(N{\equiv}CMe)_3(CO)_3/O_2$	WO_2	$SiMe_3$	**A**	[15]
4e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$W(N{\equiv}CMe)_3(CO)_3/O_2$	WO_2	$SiMe_3$	**A**	[15]
5a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Co_2(CO)_8$	Co(CO)	Ph	**A**	[16]
5b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$Co_2(CO)_8$	Co(CO)	Ph	**A**	[17]
5c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$Co_2(CO)_8$	Co(CO)	$SiMe_3$	**A**	[17]
5d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$Co_2(CO)_8$	Co(CO)	^{t}Bu	**A**	[17]
6a	$(\eta^5\text{-}C_5H_5)_2Ti$	$Ni(CO)_4$	Ni(CO)	Ph	**A**	[18]
6b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	Ph	**A**	[19]
6c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	C_6H_4CN-4	**A**	[20]
6d	$(\eta^5\text{-}C_5H_5)_2Ti$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$	**A**	[21,22]
6e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$	**A**	[22]
6f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	^{t}Bu	**A**	[22]
6g	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	$C{\equiv}CC_2H_5$	**A**	[22]
6h	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	$C{\equiv}CSiMe_3$	**A**	[22]
6i	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	$SiMe_2C{\equiv}CSiMe_3$	**A**	[23]
6j	$[(\eta^5\text{-}C_5H_4)_2SiMe_2]Ti$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$	**A**	[24]
6k	$[(\eta^5\text{-}C_5H_3SiMe_3)_2SiMePh]Ti$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$	**A**	[24]
6l	$[(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3SiMe_3)SiMe_2]Ti$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$	**A**	[24]
6m	$[(\eta^5\text{-}C_5H_2SiMe_3)SiMe_2]_2Ti$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$	**A**	[24]
6n	$(\eta^5\text{-}C_5H_4SiMe_3)_2Zr$	$Ni(CO)_4$	Ni(CO)	Ph	**A**	[25]
6o	$(\eta^5\text{-}C_5H_4SiMe_3)_2Zr$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$	**A**	[25]
6p	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$Ni(CO)_4$	Ni(CO)	Ph	**A**	[17]
6q	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$	**A**	[25]
6r	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$Ni(CO)_4$	Ni(CO)	^{t}Bu	**A**	[25]
6s	$(\eta^5\text{-}C_5H_5)_2Ti$[b]	[b]	$Ni(PPh_3)$	Ph, $SiMe_3$	**D**,**E**	[26]
6t	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[c]	$Ni[PPh_2(C{\equiv}CPh)]$	Ph	**E**	[19]
6u	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[c]	$Ni[PPh(C{\equiv}CPh)_2]$	Ph	**E**	[19]

Table 1 (*Continued*)

Compound	[M]	$[M']_xL_y$	[M′]	R^1, R^2	Method[a]	Refs.
6v	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[c]	$Ni[P(OMe)_3]$	Ph	**E**	[19]
6w	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[c]	$Ni[P(OPh)_3]$	Ph	**E**	[22]
6x	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[c]	$Ni[P(OMe)_3]$	$SiMe_3$	**E**	[22,25]
6y	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[c]	$Ni[P(O^iC_3H_7)_3]$	$SiMe_3$	**E**	[22]
6z	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[c]	$Ni[P(OPh)_3]$	$SiMe_3$	**E**	[22]
6aa	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	$SiMe_3$[m]	**A**	[27]
6bb	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	^{t}Bu[m]	**A**	[27]
6cc	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Ni(CO)_4$	Ni(CO)	Ph[m]	**A**	[27]
7a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Pd(PPh_3)_4$	$Pd(PPh_3)$	Ph	**A**	[23,25]
7b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Pd(PPh_3)_4$	$Pd(PPh_3)$	$SiMe_3$	**A**	[28]
7c	$(\eta^5\text{-}C_5H_5)_2Ti$	$Pd(PPh_3)_4$	$Pd(PPh_3)$	$SiMe_3$	**A**	[25,29]
7d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Pd(PPh_3)_4$	$Pd(PPh_3)$	$C{\equiv}CC_2H_5$	**A**	[23]
7e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Pd(PPh_3)_4$	$Pd(PPh_3)$	Fc[d]	**A**	[29]
7f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$Pd(PPh_3)_4$	$Pd(PPh_3)$	Ph	**A**	[25]
8a	$(\eta^5\text{-}C_5H_5)_2Ti$	$Pt(C_2H_4)_2[P(^cC_6H_{11})_3]$	$Pt[P(^cC_6H_{11})_3]$	Ph	**A**	[30]
8b	$(\eta^5\text{-}C_5H_5)_2Ti$	$Pt(C_2H_4)_2[PMe_2Ph]$	$Pt(PMe_2Ph)$	Ph	**A**	[30]
8c	$(\eta^5\text{-}C_5H_5)_2Ti$	$Pt(C_2H_4)_2[PMePh_2]$	$Pt(PMePh_2)$	Ph	**A**	[30]
8d	$(\eta^5\text{-}C_5H_5)_2Ti$	$Pt(C_2H_4)_2[PPh_3]$	$Pt(PPh_3)$	Ph	**A**	[30]
8e	$(\eta^5\text{-}C_5H_5)_2Ti$	$Pt(C_2H_4)_2[PPh(^iC_3H_7)_2]$	$Pt[PPh(^iC_3H_7)_2]$	Ph	**A**	[30]
8f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Pt(C_2H_4)_2[PPh_3]$	$Pt(PPh_3)$	$SiMe_3$	**E**	[25]
9a	$(\eta^5\text{-}C_5HMe_4)_2Ti^-$		$Li(thf)_2^+$	$C{\equiv}CSiMe_3$	**C**	[31,32]
9b	$(\eta^5\text{-}C_5HMe_4)_2Ti^-$		Li^+	$SiMe_3$	**C**	[32]
9c	$(\eta^5\text{-}C_5HMe_4)_2Ti^-$		Na^+	$SiMe_3$	**C**	[32]
9d	$(\eta^5\text{-}C_5HMe_4)_2Ti^-$		K^+	$SiMe_3$	**C**	[32]
9e	$(\eta^5\text{-}C_5HMe_4)_2Ti^-$		Cs^+	$SiMe_3$	**C**	[32]
9f	$(\eta^5\text{-}C_5HMe_4)_2Zr^-$		K^+	$SiMe_3$	**C**	[33]
9g	$(\eta^5\text{-}C_5Me_5)_2Nd^-$		K^+	Ph	**C**	[34]
9h	$(\eta^5\text{-}C_5Me_5)_2Ce^-$		K^+	Ph	**C**	[34]
9i	$(\eta^5\text{-}C_5Me_5)_2Sm^-$		K^+	Ph	**C**	[34]
9j	$(\eta^5\text{-}C_5Me_5)_2Y^-$		$Li(thf)^+$	^{t}Bu	**C,G**	[157]
9k	$[PhC(NSiMe_3)_2]_2Y^-$		$Li(tmeda)^+$	^{t}Bu	**C,G**	[157]

Table 1 (*Continued*)

Compound	[M]	$[M']_xL_y$	[M′]	R^1, R^2	Method[a]	Refs.
10a	$(\eta^5\text{-}C_5HMe_4)_2Ti^-$		$MgCl(thf)^+$	$SiMe_3$	**B**	[35]
10b	$(\eta^5\text{-}C_5HMe_4)_2Ti^-$		$MgCl(thf)^+$	^{t}Bu	**B**	[36]
11a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl]_n$	CuCl	Ph	**A,B,C,F**	[37,38]
11b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl]_n$	CuCl	$SiMe_3$	**A,B,C,F**	[38]
11c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl]_n$	CuCl	^{t}Bu	**A**	[47]
11d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl]_n$	CuCl	Ph, $SiMe_3$	**A,B,C,F**	[42]
11e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl]_n$	CuCl	$SiMe_2C{\equiv}CSiMe_3$	**A,B,F**	[23]
11f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl]_n$	CuCl	Fc[d]	**A**	[39–41]
11g	$[(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_3SiMe_3)SiMe_2]Ti$	$[CuCl]_n$	CuCl	$SiMe_3$	**A,B,F**	[38]
11h	$[(\eta^5\text{-}C_5H_2SiMe_3)SiMe_2]_2Ti$	$[CuCl]_n$	CuCl	$SiMe_3$	**A,B,C,F**	[42,43]
11i	$(\eta^5\text{-}C_5H_5)_2Ti$	$[CuCl]_n$	CuCl	$C_6H_3(CH_2NMe_2)_2$-3,5	**A**	[44]
11j	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl]_n$	CuCl	C_6H_4CN-4	**A**	[45]
11k	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl]_n$	CuCl	$CMe{=}CH_2$	**A**	[45]
11l	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBr]_n$	CuBr	$SiMe_3$	**A,F**	[38]
11m	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBr]_n$	CuBr	^{t}Bu	**A**	[44]
11n	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBr]_n$	CuBr	Ph, $SiMe_3$	**A**	[42]
11o	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBr]_n$	CuBr	$C{\equiv}CC_2H_5$	**A**	[46]
11p	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBr]_n$	CuBr	$C{\equiv}CSiMe_3$	**A**	[46]
11q	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBr]_n$	CuBr	$C_6H_4C{\equiv}CSiMe_3$-4	**A**	[44]
11r	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBr]_n$	CuBr	$SiMe_2C{\equiv}CSiMe_3$	**A**	[23]
11s	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBr]_n$	CuBr	Fc [d]	**A**	[39]
11t	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuI]_n$	CuI	$SiMe_3$	**A**	[38]
11u	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuI]_n$	CuI	C_6H_4CN-4	**A**	[47]
11v	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuI]_n$	CuI	^{t}Bu	**A**	[47]
11w	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCN]_n$	CuCN	$SiMe_3$	**A,F**	[38]
11x	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCN]_n$	CuCN	^{t}Bu	**A,F**	[47]
11y	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSCN]_n$	CuSCN	$SiMe_3$	**A,F**	[38]
11z	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSeCN]_n$	CuNCSe	$SiMe_3$	**A**	[48]
11aa	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuOSO_2CF_3]_n$	$CuOSO_2CF_3$	$SiMe_3$	**A**	[49]
11bb	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$AgClO_4$	$CuClO_4$	$SiMe_3$	**G**	[50]
11cc	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuBF_4]$	$CuBF_4$	$SiMe_3$	**A**	[48]
11dd	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuPF_6]$	$CuPF_6$	$SiMe_3$	**A**	[48]

Table 1 (*Continued*)

Compound	[M]	$[M']_xL_y$	[M′]	R^1, R^2	Method[a]	Refs.
11ee	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[e]	CuF	$^tC_4H_9$	**G**	[2,55]
11ff	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuN_3]$	CuN_3	$SiMe_3$	**A,G**	[48]
11gg	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[Cu(N{\equiv}CMe)_4]NO_3$	$CuNO_3$	$SiMe_3$	**A**	[50]
11hh	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuPPh_2$	$SiMe_3$	**I**	[51]
11ii	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSCF_3]$	$CuSCF_3$	$SiMe_3$	**A**	[52]
11jj	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSC_2H_5]$	$CuSC_2H_5$	$SiMe_3$	**A**	[52]
11kk	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSC_6H_5]_n$	$CuSC_6H_5$	$SiMe_3$	**A,G**	[49]
11ll	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSC_6H_4NMe_2\text{-}2]_3$	$CuSC_6H_4NMe_2\text{-}2$	$SiMe_3$	**A,G**	[49]
11mm	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSC_6H_4CH_2NMe_2\text{-}2]_3$	$CuSC_6H_4CH_2NMe_2\text{-}2$	$SiMe_3$	**A,G**	[49]
11nn	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSC_6H_4CH_2NMe_2\text{-}2]_3$	$CuSC_6H_4CH_2NMe_2\text{-}2$	^tBu	**A,G**	[49]
11oo	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuSC_{10}H_6NMe_2\text{-}8]_9$	$CuSC_{10}H_6NMe_2\text{-}8$	$SiMe_3$	**A,G**	[49]
11pp	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$[CuBr]_n$	CuBr	$SiMe_3$	**A**	[25]
11qq	$(\eta^5\text{-}C_5H_4SiMe_3)_2Hf$	$[CuBr]_n$	CuBr	^tBu	**A**	[25]
11rr	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCl_2]$	$CuCl_2$	Fc[d]	**A**	[77]
12a	$(PPh_3)(CO)_3Re$	[g]	$CuPPh_3$	C_6F_5	**C**	[53]
12b	$(\eta^5\text{-}C_5H_5)Ru$	[g]	$CuPPh_3$	$C_6H_4Me\text{-}4$	**C**	[54]
12c	$(\eta^5\text{-}C_5H_5)Ru$	[g]	$CuPPh_3$	$C_6H_4F\text{-}4$	**C**	[54]
13a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuMe]_n$	$CuMe^n$	$SiMe_3$	**A,G,H**	[5]
13b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuMe]_n$	$CuMe^n$	^tBu	**A,G,H**	[52]
13c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	CuC_2H_5	$SiMe_3$	**G**	[5]
13d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	CuC_2H_5	^tBu	**G**	[55]
13e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$Cu^iC_3H_7$	$SiMe_3$	**G**	[56]
13f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$Cu^nC_4H_9$	$SiMe_3$	**G**	[5]
13g	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$Cu^cC_5H_9$	$SiMe_3$	**G**	[56]
13h	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCH_2SiMe_3]_4$	$CuCH_2SiMe_3$	$SiMe_3$	**A,G**	[5]
13i	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuCH{=}CH_2]_n$	$CuCH{=}CH_2$	$SiMe_3$	**G**	[5]
13j	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuPh]_n$	CuPh	$SiMe_3$	**A,G,H**	[5]
13k	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC_6H_4Me\text{-}4]_4$	$CuC_6H_4Me\text{-}4$	$SiMe_3$	**A,G**	[5]
13l	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC_6H_4OMe\text{-}4]_n$	$CuC_6H_4OMe\text{-}4$	$SiMe_3$	**A,G**	[5]
13m	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC_6H_4NMe_2\text{-}4]_n$	$CuC_6H_4NMe_2\text{-}4$	$SiMe_3$	**A,G**	[5]
13n	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC_6H_2Me_3\text{-}2,4,6]_5$	$CuC_6H_2Me_3\text{-}2,4,6$	$SiMe_3$	**A,G**	[5,57]

Table 1 (*Continued*)

Compound	[M]	$[M']_xL_y$	[M′]	R^1, R^2	Method[a]	Refs.
13o	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC_6H_4CH_2NMe_2\text{-}2]_4$	$CuC_6H_4CH_2NMe_2\text{-}2$	$SiMe_3$	**A,G**	[58]
13p	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC_6H_3(CH_2NMe_2)_2 2,6]$	$CuC_6H_3(CH_2NMe_2)_2\text{-}2,6$	$SiMe_3$	**G**	[2,58]
13q	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	CuC_6F_5	$SiMe_3$	**G**	[2]
13r	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$CuC_6H_2(CF_3)_3\text{-}2,4,6$	$SiMe_3$	**G**	[52]
13s	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$CuC_6H_2Ph_3\text{-}2,4,6$	$SiMe_3$	**G**	[52]
13t	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$CuC_6H_2Ph_3\text{-}2,4,6$	^{t}Bu	**G**	[52]
13u	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$CuC_{14}H_9$	$SiMe_3$	**G**	[56]
13v	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	CuC≡CH	^{t}Bu	**G**	[51,59]
13w	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC{\equiv}C'Bu]_8$	CuC≡C′Bu	$SiMe_3$	**A,G**	[51,59]
13x	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC{\equiv}C'Bu]_8$	CuC≡C′Bu	^{t}Bu	**A,G**	[51,59]
13y	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC{\equiv}CPh]_n$	CuC≡CPh	Ph	**A,G**	[51,59]
13z	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC{\equiv}CPh]_n$	CuC≡CPh	$SiMe_3$	**A,G**	[51,59]
13aa	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC{\equiv}CSiMe_3]_4$	$CuC{\equiv}CSiMe_3$	$SiMe_3$	**A,G**	[60]
13bb	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuC{\equiv}CC_6H_4CN\{Ru\}\text{-}4$[l]	^{t}Bu	**H**	[61]
13cc	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuC{\equiv}C\{C_6H_2(CH_2NMe_2)_2\text{-}2,6\}Pt\text{-}4\text{-}C{\equiv}CFc$[d]	^{t}Bu	**H**	[61]
13dd	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuC{\equiv}CSiMe_3]_4$[f,h]	$CuC{\equiv}CSiMe_3$	^{t}Bu	**A,G,I**	[45,51]
13ee	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f,h]	$CuC{\equiv}CCO_2Me$	$SiMe_3$	**A,G,I**	[45,51]
13ff	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f,h]	$CuC{\equiv}CCMe{=}CH_2$	^{t}Bu	**G,I**	[45,51]
13gg	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f,h]	$CuC{\equiv}CCMe{=}CH_2$	$SiMe_3$	**G,I**	[45,51]
13hh	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f,h]	$CuC{\equiv}CC_6H_4CN\text{-}4$	^{t}Bu	**G,I**	[45,51]
13ii	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f,h]	$CuC{\equiv}CCH_2CH_2CH_3$	^{t}Bu	**G,I**	[45,51]
13jj	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	CuC≡CC≡N	^{t}Bu	**G**	[48]
13kk	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$CuC{\equiv}CPPh_2$	^{t}Bu	**G**	[48]
13ll	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$CuC{\equiv}CC{\equiv}CC_2H_5$	^{t}Bu	**G**	[45]
13mm	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$CuC{\equiv}CFc$[d]	^{t}Bu	**G**	[48]
13nn	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuC{\equiv}CC_6H_4NO_2\text{-}4$	^{t}Bu	**I**	[51]
13oo	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f,h]	$CuC{\equiv}CC_6H_4CN\text{-}4$	$SiMe_3$	**G,I**	[45]
13pp	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$		$CuC{\equiv}NCr(CO)_5$	$SiMe_3$		[62]
14a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuO_2CPh]_4$	CuOC(O)Ph	$SiMe_3$	**A**	[38]
14b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CuO_2CMe]_4$	CuOC(O)Me	$SiMe_3$	**A**	[38]
14c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	CuOC(O)Me	^{t}Bu	**I**	[63]

Table 1 (*Continued*)

Compound	[M]	$[M']_xL_y$	[M′]	R^1, R^2	Method[a]	Refs.
14d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[i]	$CuO_2CCH{=}CHC(O)C{\equiv}C\text{–}SiMe_3$	^{t}Bu	**K**	[63]
14e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[i]	$CuO_2CCH{=}CHC(O)CH_3$	^{t}Bu	**K**	[63]
14f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[i]	$CuO_2CC_6H_4C(O)CH_3$	^{t}Bu	**K**	[63]
14g	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuO_2CCH{=}CMe_2$	^{t}Bu	**I**	[63]
14h	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuO_3CC_6H_4Cl\text{-}3$	$SiMe_3$	**I**	[63]
14i	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuO_2CCH_2C_6H_5$	$SiMe_3$	**I**	[63]
14j	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[i]	$CuO_2CC_6Cl_4C(O)\text{-}2\text{-}C{\equiv}CSiMe_3$	^{t}Bu	**K**	[63]
14k	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[i]	$CuO_2CC_6H_4C(O)\text{-}2\text{-}C{\equiv}CSiMe_3$	^{t}Bu	**K**	[63]
14l	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuO_2CC_6H_3(CO_2H)_2\text{-}3,5$	^{t}Bu	**I**	[63]
14m	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuO_2C(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4CO_2H)$	^{t}Bu	**I**	[63]
14n	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuO_2CCH_2C(CO_2H){=}CH_2$	^{t}Bu	**I**	[63]
14o	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	*trans*-$CuO_2CCH{=}CHCO_2H$	^{t}Bu	**I**	[63]
14p	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[f]	$CuO_2CC{\equiv}CH$	^{t}Bu	**I**	[63]
14q	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	Cu(acac)	$SiMe_3$	**A,G**	[64]
14r	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	Cu(trop)	$SiMe_3$	**G**	[48]
14s	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$Cu(O_2C_6H_5O)$	$SiMe_3$	**G**	[48]
14t	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[h]	$Cu(OC_9H_5N)$	$SiMe_3$	**G**	[48]
15a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgCl]_n$	AgCl	$SiMe_3$	**A,F**	[65]
15b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgCl]_n$	AgCl	$SiMe_2C{\equiv}CSiMe_3$	**A**	[23]
15c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgCl]_n$	AgCl	Fc[d]	**A**	[39]
15d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgBr]_n$	AgBr	$SiMe_3$	**A**	[65]
15e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgBr]_n$	AgBr	$SiMe_2C{\equiv}CSiMe_3$	**A**	[23]
15f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgI]_n$	AgI	$SiMe_3$	**A**	[65]
15g	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgCN]_n$	AgCN	$SiMe_3$	**A,F**	[65]
15h	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgSCN]_n$	AgSCN	$SiMe_3$	**A**	[65]
15i	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgSeCN]_n$	AgSeCN	$SiMe_3$	**A**	[48]
15j	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgNCO]_n$	AgNCO	$SiMe_3$	**A**	[48]
15k	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgOSO_2CF_3]_n$	$AgOSO_2CF_3$	$SiMe_3$	**A**	[49]
15l	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgBF_4]$	$AgBF_4$	$SiMe_3$	**A**	[50]
15m	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgBF_4]$	$AgBF_4$	Ph	**A**	[50]
15n	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgPF_6]$	$AgPF_6$	$SiMe_3$	**A**	[56]
15o	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgClO_4]$	$AgClO_4$	Ph	**A**	[50]
15p	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgBPh_4]$	$AgBPh_4$	$SiMe_3$	**A**	[56]

Table 1 (*Continued*)

Compound	[M]	$[M']_xL_y$	[M′]	R^1, R^2	Method[a]	Refs.
15q	$(\eta^5\text{-}C_5H_5)_2Ti$	$[AgBPh_4]$	$AgBPh_4$	$SiMe_3$	**A**	[66]
15r	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgN_3]$	AgN_3	$SiMe_3$	**A**	[48]
15s	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgNO_2]$	$AgNO_2$	$SiMe_3$	**A**	[65]
15t	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgNO_3]$	$AgNO_3$	$SiMe_3$	**A**	[52]
15u	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgNO_3]$	$AgNO_3$	^{t}Bu	**A**	[52]
15v	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgClO_4]$	$AgClO_4$	$SiMe_3$	**A**	[65]
15w	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgS_2CNEt_2]$	AgS_2CNEt_2	$SiMe_3$	**A**	[67]
16a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[j]	AgMe	$SiMe_3$	**G**	[52]
16b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[j]	AgMe	^{t}Bu	**G**	[52]
16c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[j]	$Ag^nC_4H_9$	$SiMe_3$	**G**	[48]
16d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgC_6H_2Me_3\text{-}2,4,6]_n$	$AgC_6H_2Me_3$-2,4,6	$SiMe_3$	**A,G**	[57]
16e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgC_6H_2Ph_3\text{-}2,4,6]_n$	$AgC_6H_2Ph_3$-2,4,6	$SiMe_3$	**A,G**	[52]
16f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$		$AgC_6H_2(CF_3)_3$-2,4,6	$SiMe_3$	**G**	[52]
16g	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	F[j]	$AgC{\equiv}CSiMe_3$	$SiMe_3$	**G**	[68]
16h	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[j]	$AgC{\equiv}CSiMe_3$	^{t}Bu	**G**	[68]
16i	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[j]	$AgC{\equiv}CPh$	$SiMe_3$	**G**	[68]
16j	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgO_2CPh]_n$	AgO_2CPh	$SiMe_3$	**A**	[52]
16k	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgO_2CMe]_n$	AgO_2CMe	$SiMe_3$	**A**	[52]
16l	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[AgO_2CMe]_n$	AgO_2CMe	^{t}Bu	**A**	[52]
16m	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[Agacac]_n$	Ag(acac)	$SiMe_3$	**A,G**	[48]
16n	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[j]	Ag(trop)	$SiMe_3$		[48]
16o	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[j]	$Ag(O_2C_6H_5O)$	$SiMe_3$		[48]
16p	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	[j]	$Ag(OC_9NH_5)$	$SiMe_3$		[48]
16q	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[Ag(CH(C(O)Ph)_2)]$	$Ag(CH(C(O)Ph)_2)$	$SiMe_3$	**A**	[50]
17a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Me_2SAuCH_3	$AuCH_3$	$SiMe_3$	**A**	[69]
17b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Me_2SAuC_6H_2(CF_3)_32,4,6$	$AuC_6H_2(CF_3)_3$-2,4,6	$SiMe_3$	**A**	[69]
17c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Me_2SAuC{\equiv}CSiMe_3$	$AuC{\equiv}CSiMe_3$	$SiMe_3$	**A**	[69]
17d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Me_2SAuC{\equiv}C^tBu$	$AuC{\equiv}C^tBu$	^{t}Bu	**A**	[69]
17e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$Me_2SAuCl/LiC{\equiv}C^tBu$	$AuC{\equiv}CSiMe_3$	$SiMe_3$, ^{t}Bu	**A**	[69]
18a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[FeCl_2]$	$FeCl_2$	$SiMe_3$	**A**	[37,70]
18b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[CoCl_2]$	$CoCl_2$	$SiMe_3$	**A**	[37,70]
18c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[NiCl_2]$	$NiCl_2$	$SiMe_3$	**A**	[37,70]

Table 1 (*Continued*)

Compound	[M]	$[M']_xL_y$	[M′]	R^1, R^2	Method[a]	Refs.
18d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[Hg(CF_3)(C_6H_5)]$	$Hg(CF_3)(C_6H_5)$	$SiMe_3$	**A**	[71]
18e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$[Hg(CN)_2]$	$Hg(CN)_2$	Ph	**A**	[71]
19a	$[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2]$	$[HgCl_2]$	$HgCl_2$	^{t}Bu	**A**	[72]
19b	$[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2]$	$[HgCl_2]$	$HgCl_2$	$SiMe_3$	**A**	[72]
19c	$[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2]$	$[HgBr_2]$	$HgBr_2$	^{t}Bu	**A**	[72]
19d	$[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2]$	$[HgBr_2]$	$HgBr_2$	$SiMe_3$	**A**	[72]
19e	$[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2]$	$[HgI_2]$	HgI_2	^{t}Bu	**A**	[72]
19f	$[NBu_4]_2[cis\text{-}Pt(C_6F_5)_2]$	$[HgI_2]$	HgI_2	$SiMe_3$	**A**	[72]
19g	$[NBu_4]_2[Pt(C{\equiv}CR)_2]^k$	$[HgCl_2]$	$HgCl_2$	^{t}Bu	**A**	[72]
19h	$[NBu_4]_2[Pt(C{\equiv}CR)_2]^k$	$[HgCl_2]$	$HgCl_2$	$SiMe_3$	**A**	[72]
19i	$[NBu_4]_2[Pt(C{\equiv}CR)_2]^k$	$[HgBr_2]$	$HgBr_2$	^{t}Bu	**A**	[72]
19j	$[NBu_4]_2[Pt(C{\equiv}CR)_2]^k$	$[HgBr_2]$	$HgBr_2$	$SiMe_3$	**A**	[72]
19k	$[NBu_4]_2[Pt(C{\equiv}CR)_2]^k$	$[HgI_2]$	HgI_2	^{t}Bu	**A**	[72]
19l	$[NBu_4]_2[Pt(C{\equiv}CR)_2]^k$	$[HgI_2]$	HgI_2	$SiMe_3$	**A**	[72]
19m	(bipy′)Pt	$[HgCl_2]$	$HgCl_2$	Ph	**A**	[73]
19n	(bipy′)Pt	$[HgI_2]$	HgI_2	Ph	**A**	[73]

[a] Methods: (**A**) direct synthesis route (Section 2.1.1.1); (**B**) redox reaction route (Section 2.1.1.2); (**C**) metal acetylide route (Section 2.1.1.3); (**D**) titanocene generator route (Section 2.1.1.2); (**E**) CO-substitution route (Section 2.1.2.1); (**F**) MCl_2-substitution route (M = Fe, Co, Ni) (Section 2.1.2.2); (**G**) metathesis reaction route (Section 2.1.2.3); (**H**) decarboxylation route (Section 2.1.2.3.2); (**I**) metathesis reaction of alkyl complexes with acidic substrates (Section 2.1.1.4); (**K**) insertion into Cu–R bonds (Section 2.1.2.3.2).

[b] Prepared by the reaction of $(PPh_3)Ni(\eta^2\text{-}PhC{\equiv}C\text{–}C{\equiv}CSiMe_3)$ (**23a**) with $[Ti](\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (**24a**).

[c] Reaction of $\{[Ti](C{\equiv}CR^1)_2\}Ni(CO)$ with phosphanes or phosphites.

[d] Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$.

[e] Synthesized by the reaction of $\{[Ti](C{\equiv}C'Bu)_2\}CuSC_6H_4CH_2NMe_2\text{-}2$ (**11nn**) with $[N^nBu_4]F$.

[f] Reaction of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CR^1)_2\}CuR$ with acidic substrates.

[g] Prepared by the reaction of [M]Cl with $[M'C{\equiv}CR^1]_n$ (M′ = Cu, Au).

[h] Prepared by the reaction of $\{[Ti](C{\equiv}CR^1)_2\}CuSC_6H_4CH_2NMe_2\text{-}2$ (**11mm**: $R^1 = SiMe_3$, **11nn:** R = ^{t}Bu) with LiR, BrMgR or ZnR_2.

[i] Reaction of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CR^1)_2\}CuR$ with cyclic anhydrides.

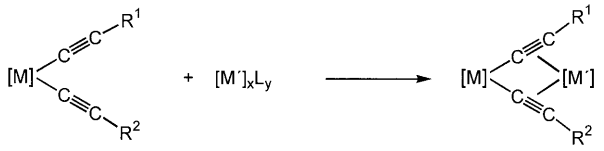
[j] Reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}AgNO_3$ with LiR.

[k] Composition $[NBu_4]_2\{Pt(C{\equiv}CR^1)_4\}[HgX_2]_2$.

[l] {Ru} = $RuCl_2(NN'N)$.

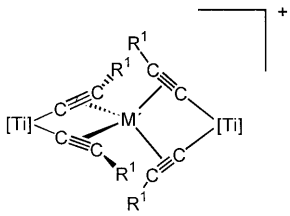
[m] $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CR^1)Cl\}[M']$.

[n] Extreme caution must be taken when preparing this compound through method **A**, due to the explosive nature of methylcopper.



1 - 3 **4 - 8, 11, 13 - 19**

Although reaction of the tweezer molecules $[M](C{\equiv}CR^1)_2$ with metal sources in a 1:1 ratio results in the formation of binuclear structural type **B** complexes, an interesting class of oligometallic species is produced when two equivalents of $[Ti](C{\equiv}CR^1)_2$ (R^1 = Ph, Fc, C≡CFc, etc.) are allowed to react with a copper(I) or silver(I) source, forming compounds of the type $[\{[Ti](C{\equiv}CR^1)_2\}_2M']X$ (**20a**–**20k**, Table 2) [44,50,74]. In these complexes, a single metal(I) center is tetrahedrally coordinated by two tweezer fragments, as shown below. In these compounds, the counterion X must be a poor ligand (such as tetrafluoroborate, perchlorate or hexafluorophosphate), to prevent the formation of $\{[Ti](C{\equiv}CR^1)_2\}M'X$ and free $[Ti](C{\equiv}CR^1)_2$. The preparation of these complexes is summarized in Table 2.



20

Similar compounds, derived from Pt-containing tweezers, are described in Section 2.2.

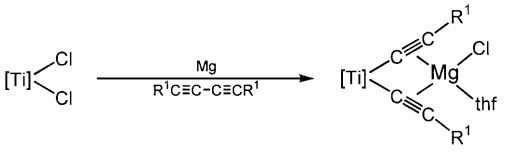
Table 2
Synthesis of complexes $[\{[Ti](C{\equiv}CR^1)_2\}_2M'][X]$ (**20**)

Compound	[Ti]	R^1	M′	X	Refs.
20a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Ph	Cu	BF_4	[50]
20b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Ph	Cu	PF_6	[50]
20c	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Fc[a]	Cu	BF_4	[44]
20d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Ph	Ag	BF_4	[50]
20e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Ph	Ag	PF_6	[50]
20f	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Ph	Ag	ClO_4	[50]
20g	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Fc[a]	Ag	PF_6	[74]
20h	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Fc[a]	Ag	ClO_4	[44]
20i	$(\eta^5\text{-}C_5H_5)_2Ti$	C≡CFc[a]	Ag	PF_6	[74]
20j	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	C≡CFc[a]	Ag	PF_6	[74]
20k	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Rc[b]	Ag	PF_6	[74]

[a] Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$.
[b] Rc = $(\eta^5\text{-}C_5H_4)Ru(\eta^5\text{-}C_5H_5)$.

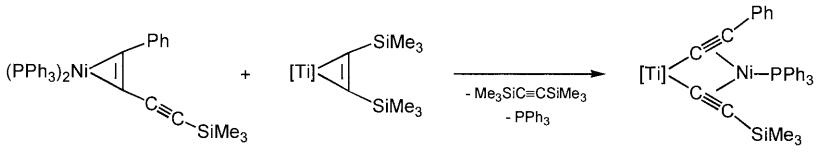
2.1.1.2. Redox-reaction route (*methods **B** and **D***). A second route to type **B** molecules is given by the reductive dehalogenation of [Ti]Cl_2 ([Ti] = (η^5-$C_5Me_4H)_2$Ti (**21a**)) by activated magnesium turnings in the presence of $R^1C{\equiv}C{-}C{\equiv}CR^1$ (**22a**: R = $SiMe_3$, **22b**: R = ^{t}Bu) in tetrahydrofuran. At 25°C the heterobimetallic Ti(III)–Mg(II) complex {[Ti]($C{\equiv}CR^1)_2$}Mg(thf)Cl (**10a**: R = $SiMe_3$, **10b**: R = ^{t}Bu) is formed [35,36].

Compound **10a** contains a titanium(III) center, as shown by EPR studies; solutions of **10a** exhibit a single EPR signal at $g = 1.9935$ and $\Delta H_{pp} = 2.5$ G with $\alpha(^{47/49}Ti) = 7.3$ G; frozen solutions gave the same rhombic g tensors [$g_1 = 2.0015$, $g_2 = 1.9938$, $g_3 = 1.9876$ ($g_{av} = 1.9943$)] [35]. Compound **10a** was also found to be a catalytic intermediate in the linear head-to-tail dimerization of terminal alkynes [36a,75]



21a **10**

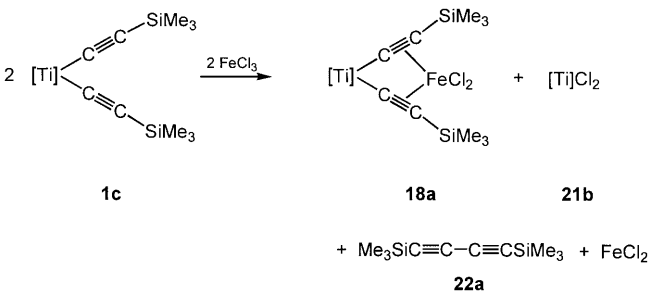
Another example in which a 1,3-butadiyne is reductively cleaved into two acetylide ligands is given by the reaction of $(PPh_3)_2$Ni(η^2-PhC≡C–C≡$CSiMe_3$) (**23**) with [Ti](η^2-$Me_3SiC{\equiv}CSiMe_3$) (**24**) ([Ti] = (η^5-$C_5H_5)_2$Ti) in toluene at 80°C [3,26].



23 **24** **6s**

The proposed mechanism for the formation of the titanium–nickel tweezer complex **6s** includes the cyclocumulene [Ti](η^4-PhC=C=C≡$CSiMe_3$) as an intermediate; intramolecular or intermolecular consecutive steps are discussed in Section 4.1.1.1 [3,26,76].

Electron transfer reactions are also involved when bis(alkynyl) titanocenes, e.g. [Ti]($C{\equiv}CSiMe_3)_2$ (**1c**: [Ti] = (η^5-$C_5H_4SiMe_3)_2$) are allowed to react with $FeCl_3$ in tetrahydrofuran at 25°C. The products formed by this redox reaction are **18a**, **21b**, **22a** and $FeCl_2$ [77].



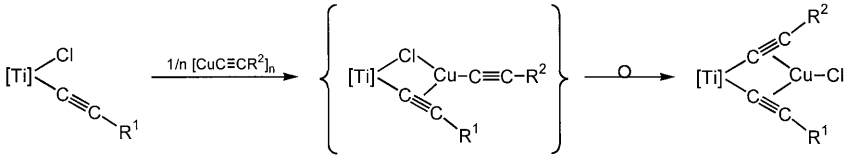
1c **18a** **21b** **22a**

As a key intermediate in this process, $\{[Ti](C{\equiv}CSiMe_3)_2\}FeCl_3$ is postulated, in which the iron center is in the trigonal-bipyramidal coordination mode [77].

In a similar manner, several bis(alkynyl)titanocenes react with copper(II) compounds CuX_2 (X = Cl, Br), yielding the bis(η^2-alkyne)-stabilized, monomeric copper(I) complexes $\{[Ti](C{\equiv}CSiMe_3)_2\}CuX$ (**11b**: X = Cl, **11l**: X = Br) (Table 1), along with $[CuX]_n$, $[Ti]X_2$ (**21**) and $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ (**22a**) [77]. This is an intramolecular reaction, since $[Ti](C{\equiv}CPh)(C{\equiv}CSiMe_3)$ (**1d**) reacts with $CuCl_2$ to give the products $\{[Ti](C{\equiv}CPh)(C{\equiv}CSiMe_3)\}CuCl$ (**11d**), $PhC{\equiv}C{-}C{\equiv}CSiMe_3$ (**22c**), $[Ti]Cl_2$ (**21b**) and $[CuCl]_n$ [77]. Similar results are observed in the reaction of $[Ti](C{\equiv}CR^1)_2$ with $PdCl_2$, $HgCl_2$, $CdCl_2$, $ZnCl_2$, $(C_5H_5N)AuCl_3$ or $RhCl_3$ [48,77]. In this light, the successful synthesis of the Cu(II) complex $\{[Ti](C{\equiv}CFc)_2\}CuCl_2$ (**11rr**) [77] and the M(IV) complexes $\{[Ti](C{\equiv}CR^1)_2\}MoO_2$ [14] and $\{[Ti](C{\equiv}CSiMe_3)_2\}$-$WO_2$ [15] (**4a**–**4e**) is somewhat surprising.

*2.1.1.3. Metal acetylide route (method **C**).* Method **C**, the reaction of a transition metal chloride [M]Cl with acetylides $M'C{\equiv}CR^1$ of lithium, copper or silver is also suitable for the preparation of type **B** molecules (Table 1).

An example of this synthetic approach to individual compounds is given by the reaction of σ-alkynyl titanocene chlorides, $[Ti](C{\equiv}CR^1)Cl$, ($[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2$-Ti, **25a**: R^1 = Ph, **25b**: $R^1 = SiMe_3$, **25c**: $R^1 = {}^t$Bu; $[Ti] = [(\eta^5\text{-}C_5H_2SiMe_3)SiMe_2]_2Ti$, **25d**: $R^1 = SiMe_3$) with one equivalent of $[CuC{\equiv}CR^2]_n$ (R^2 = Ph, $SiMe_3$, ^{t}Bu) to give compounds **11a–11d** and **11h** (Table 1) [2,37,38,42,43,49].

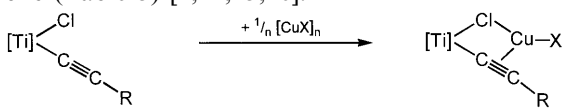


25 **11a - 11d, 11h**

In $\{[Ti](C{\equiv}CPh)(C{\equiv}CSiMe_3)\}CuCl$ (**11d**), a monomeric copper(I) halide moiety is complexed by two different alkynyl ligands, which provide the necessary conditions for enantioselective copper(I)-assisted organo-transfer reactions in organic and organometallic chemistry.

Complex **11d** can also be prepared in high yield by the stepwise reaction of $[Ti](C{\equiv}CR^1)Cl$ (R^1 = Ph, $SiMe_3$) with $LiC{\equiv}CR^2$ ($R^2 = SiMe_3$, Ph) and $[CuCl]_n$ [42]. In a similar manner, the corresponding CuBr complex **11n** (Table 1) is accessible.

Mono-alkynyl halo-bridged complexes $\{[Ti](C{\equiv}CR^1)(Cl)\}CuX$ (**26**, X = Cl, Br, I, O_2CMe; R^1 = Ph, $SiMe_3$, $C{\equiv}CC_2H_5$), similar to the postulated intermediate $\{[Ti](C{\equiv}CR^1)Cl\}CuC{\equiv}CR^2$, could be isolated when the mono-alkynyl halide complexes **25** are allowed to react with stoichiometric amounts of $[CuX]_n$ under similar reaction conditions (Table 3) [2,42,43,46].



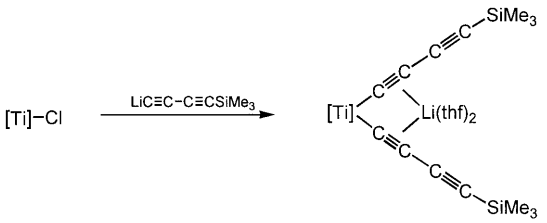
25 **26a - 26i**

Table 3
Synthesis of complexes {[Ti](C≡CR^1)X^1}CuX (**26**)[a]

Compound	[Ti]	R^1	X^1	X
26a	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Ph	Cl	Cl
26b	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$SiMe_3$	Cl	Cl
26c	$[(\eta^5\text{-}C_5H_2SiMe_3)SiMe_2]_2Ti$	$SiMe_3$	Cl	Cl
26d	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Ph	Cl	Br
26e	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$SiMe_3$	Cl	Br
26f	$[(\eta^5\text{-}C_5H_2SiMe_3)SiMe_2]_2Ti$	$SiMe_3$	Cl	Br
26g	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	Ph	Cl	I
26h	$[(\eta^5\text{-}C_5H_2SiMe_3)SiMe_2]_2Ti$	$SiMe_3$	Cl	OC(O)Me
26i	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$C{\equiv}CC_2H_5$	Cl	Br
26j	$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$	$SiMe_3$	Br	Br

[a] See Refs. [2,42,43,46].

A striking aspect about σ-1,3-butadiyn-1-yl functionalized titanocenes is their ability to coordinate $[Li(thf)_2]^+$ units, as shown by the reaction of [Ti]Cl ([Ti] = $(\eta^5\text{-}C_5Me_4H)_2Ti$) with $LiC{\equiv}C\text{–}C{\equiv}CSiMe_3$ in tetrahydrofuran [31,32].

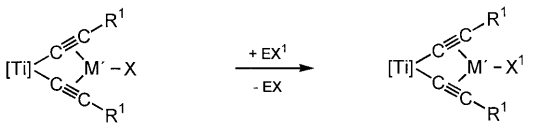


9a

In {[Ti](C≡C–C≡CSiMe$_3$)$_2$}Li(thf)$_2$ (**9a**) the lithium center is coordinated by the inner C≡C triple bonds of the 1,3-butadiyn-1-yl ligands C≡C–C≡CSiMe$_3$ and is thus isoelectronic with the previously described titanium–magnesium complex (Section 2.1.1.2) [35,36]. The analogous compounds {[M](C≡CR^1)$_2$}M′ ([M] = $(\eta^5\text{-}C_5Me_4H)_2Ti$, $(\eta^5\text{-}C_5Me_4H)_2Zr$, R^1 = SiMe$_3$, M′ = Li, Na, K, Cs; [M] = $(\eta^5\text{-}C_5Me_5)_2Ce$, $(\eta^5\text{-}C_5Me_5)_2Nd$, $(\eta^5\text{-}C_5Me_5)_2Sm$, R^1 = Ph, M′ = K) containing various alkali metal atoms within the tweezer could be synthesized in a similar way (Table 1) [31,34]. The structurally characterized potassium complexes **9f** [33] and **9i** [34] were found to be polymeric, with the potassium atom additionally coordinating to the C_5Me_4H or C_5Me_5 ring of an adjacent metallocene moiety.

Method **C** is not restricted to metallocene-containing systems, but can also be applied to the synthesis of binuclear tweezer compounds based on late transition metals. As an example, addition of CuC≡CR^1 to $[ReCl(CO)_3(PPh_3)_2]$ or $[(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2]$ yields the copper-containing tweezer complexes $[(PPh_3)(CO)_3\text{-}Re(\mu\text{-}C{\equiv}CC_6F_5)_2Cu(PPh_3)]$ (**12a**) or $[(\eta^5\text{-}C_5H_5)Ru(\mu\text{-}C{\equiv}CR^1)_2CuPPh_3]$ (R^1 = C_6H_4Me-4, **12b**; R^1 = C_6H_4F-4, **12c**) [53,54].

*2.1.1.4. Modification of other tweezer complexes (method **G**).* In addition to the synthetic routes mentioned above, many new complexes can be created through substitution reactions involving tweezer complexes bearing labile ligands. Compounds such as $\{[Ti](C{\equiv}CR^1)_2\}M'X$ ($M' = Cu$, Ag; $X = Cl$, Br, NO_3 and particularly $SC_6H_4CH_2NMe_2$-2), prepared by the direct route described above (Section 2.1.1.1), readily undergo metathesis reactions with organolithium, -magnesium and -zinc complexes EX^1 to give organocopper or organosilver complexes of the type $\{[Ti](C{\equiv}CR^1)_2\}M'X^1$ (Table 1). In these reactions, the insolubility of the resulting lithium, magnesium or zinc salts provides the driving force for the reaction and allows the products to be conveniently obtained in high purity [2,5,49,52].



11, 15 **13, 16**

The most significant advantage of this reaction is the availability of derivatives of alkylcopper and alkylsilver complexes for which the direct synthetic approach is difficult or impossible, due to the instability of the alkylmetal starting materials (such as methylsilver). Even in the case of complexes that can be made by the direct route, the metathesis reaction frequently gives higher yields.

The existence of alkylcopper and alkylsilver complexes allows for a second form of metathesis reaction. Addition of a compound containing an acidic hydrogen (such as carboxylic acids or terminal alkynes) to an alkyl complex such as $\{[Ti](C{\equiv}CR^1)_2\}CuCH_3$ leads to the loss of methane and the formation of $\{[Ti](C{\equiv}CR^1)_2\}CuX$ ($X = SR$, **11ii**–**11oo**; $X = PPh_2$, **11hh**; $X = C{\equiv}CR$, **13v**–**13oo**; $X = O_2CR$, **14a**–**14p**) (Table 1). Silver-containing complexes of the type $\{[Ti](C{\equiv}CR^1)_2\}AgX$ ($X = O_2CR$, **16j**–**16l**) can also be prepared through this route (Table 1).

In conclusion, organometallic 1,4-diynes $R^1C{\equiv}C$–[M]–$C{\equiv}CR^2$ {[M] = transition metal fragment; R^1, R^2 = singly bonded organic group) are suitable for the coordination of low-valent monomeric transition metal fragments M′L [M′ = Ni, Co, Pd, Pt; L = CO, PR_3, $P(OR)_3$, etc.], as well as $M'Cl_2$ (M′ = Fe, Co, Ni, Cu) or MgCl(thf) and alkali metal centers (Table 1). Another characteristic feature about compounds $R^1C{\equiv}C$–[M]–$C{\equiv}CR^2$ is their ability to act as organometallic π-tweezers for the breakdown of oligomeric or polymeric copper(I), silver(I) and gold(I) compounds to produce monomeric bis(η^2-alkyne)M′X species (M′ = Cu, Ag, Au; X = singly bonded organic or inorganic ligand) (Table 1).

In all heterobimetallic complexes $\{[M](C{\equiv}CR^1)(C{\equiv}CR^2)\}M'L/M'Cl_2/M'X$ (**4**–**19**) reported, the $[M](C{\equiv}CR^1)(C{\equiv}CR^2)$ fragments act as a host with the $M'L/M'X/M'Cl_2$ moieties representing the guests (Fig. 3).

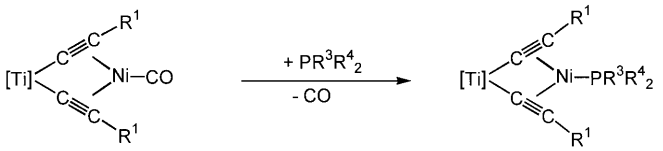
Table 4
Lewis base adducts of copper and silver tweezer complexes [{[M](C≡CR^1)$_2$}M′(L/L$_2$)][X] (**33**–**35**)

Compound	[M]	R^1	M′	L or L$_2$	X	Refs.
33a	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	N≡CCH$_3$	ClO$_4$	[50]
33b	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	N≡CCH$_3$	OTf	[48]
33c	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	N≡CCH$_3$	BF$_4$	[82]
33d	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	N≡CCH$_3$	PF$_6$	[56]
33e	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	N≡CCH$_3$	BPh$_4$	[56]
33f	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	N≡CPh	OTf	[82]
33g	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	N≡CAuPPh$_3$	BF$_4$	[62]
33h	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	PPh$_3$	OTf	[82]
33i	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	P(CH$_2$Ph)(C≡CPh)$_2$	OTf	[82]
33j	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	bipy	OTf	[48]
33k	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	bipy	BF$_4$	[50]
33l	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	bipy	PF$_6$	[50]
33m	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	bipy′	BF$_4$	[50]
33n	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Cu	phen	BF$_4$	[50]
34a	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	thf	BPh$_4$	[56]
34b	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	N≡CCH$_3$	BF$_4$	[50]
34c	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	N≡CCH$_3$	PF$_6$	[56]
34d	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	bipy	OTf	[48]
34e	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	phen	OTf	[48]
34f	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	bipyrimidine	OTf	[48]
35a	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	thf/OTf	–	[82]
35b	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	thf/BF$_4$	–	[82]
35c	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	N≡CCH$_3$/OTf	–	[82]
35d	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	N≡CPh/OTf	–	[82]
35e	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	P(OMe)$_3$/OTf	–	[82]
35f	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	P(CH$_2$Ph)(C≡CPh)$_2$/OTf	–	[82]
35g	(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti	SiMe$_3$	Ag	PPh$_3$/OTf	–	[82]

2.1.2. Chemical behavior

*2.1.2.1. Reaction chemistry of {[Ti](C≡CR^1)$_2$}NiL (**6**) (method **E**).* {[Ti](C≡CR^1)$_2$}-Ni(CO) (**6a**–**6m**) (Table 1) contains a low-valent nickel monocarbonyl building block in which the carbonyl ligand can be substituted by other ligands, such as phosphanes or phosphites [19,22,25,27,28].

X-ray structure analyses of these compounds (Table 7, Section 2.1.3) reveal a pronounced tendency of the alkynyl ligands C≡CR^1 to deform from linearity upon increasing steric demands of the organic groups R^1, R^3, R^4 used (Fig. 4) [22,25,28].



6a, 6b, 6d **6s - 6z**

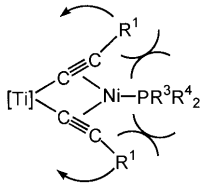
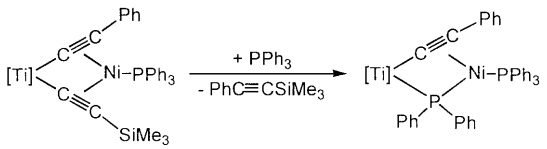


Fig. 4. Bending of the C≡C–R^1 groups in compounds **6s**–**6z** due to steric interaction between R^1 and the $PR^3R^4_2$ moieties.

If the groupings R^1, R^3 and R^4 are large enough, e.g. $R^1 = SiMe_3$, $R^3 = R^4 = Ph$, the steric congestion of the resulting molecule is relieved by migration of one of the two alkynyl groups from titanium to nickel, forming the type **D** molecule [Ti](μ-η^1:η^2-C≡CSiMe$_3$)(μ-η^2:η^1-C≡CSiMe$_3$)Ni(PPh$_3$) {[Ti] = (η^5-C_5H_5)$_2$Ti} [3,26]. This molecule contains two σ,π-bridging acetylide units in the solid state, while in solution at 25°C it is fluxional. The type **C** tweezer molecule {[Ti](μ-η^1:η^2-C≡CSiMe$_3$)$_2$}Ni(PPh$_3$) is in equilibrium with the type **D** isomer. This complex will be discussed in further detail in Section 4.1.1.1 [3,26].

Moreover, {[Ti](C≡CPh)(C≡CSiMe$_3$)}Ni(PPh$_3$) (**6s**) reacts in a 1:1 molar ratio with PPh$_3$ in boiling dioxane to give the phosphido-bridged heterobimetallic titanium–nickel compound **27** in 30% yield [78]. In this reaction, one phenyl group of the added PPh$_3$ is selectively coupled with the C≡CSiMe$_3$ ligand of **6s** to give rise to the formation of PhC≡CSiMe$_3$.

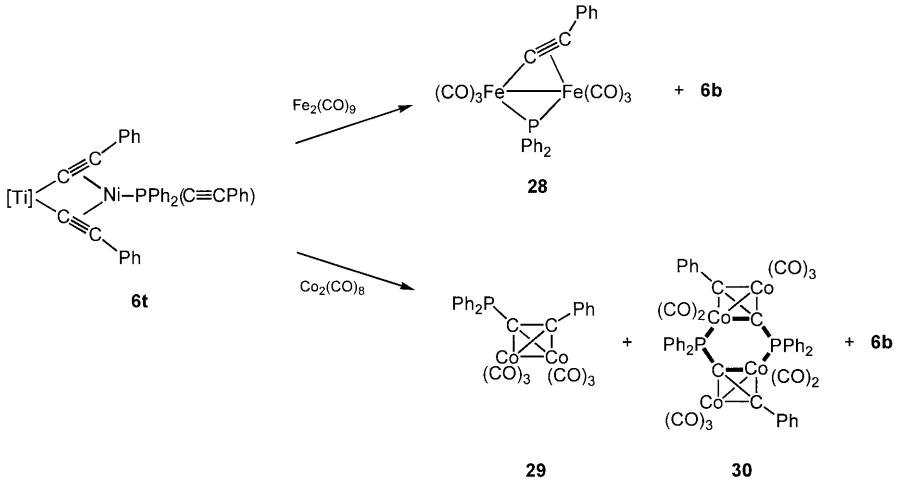


6s **27**

Compound **27** is the first example of a titanium–nickel phosphido-bridged acetylide complex [78].

The phosphane ligands of the (η^2-alkyne)$_2$Ni($PR^3R^4_2$) compounds are labile and can be displaced by a source of carbon monoxide. Addition of metal carbonyls, such as Fe$_2$(CO)$_9$ or Co$_2$(CO)$_8$ to {[Ti](C≡CPh)$_2$}Ni(PPh$_2$C≡CPh) (**6t**) results in the formation of the nickel carbonyl complex {[Ti](C≡CPh)$_2$}Ni(CO) (**6b**) [19]. The displaced phosphane reacts with the added metal centers, forming [Fe$_2$(CO)$_6$(μ-η^1:η^2-C≡CPh)(μ-PPh$_2$)] (**28**) or a mixture of [Co$_2$(CO)$_6$(μ-η^2:η^2-Ph$_2$PC≡CPh)] (**29**) and [Co$_2$(CO)$_5$(μ_3-η^1:η^2:η^2-Ph$_2$PC≡CPh)]$_2$ (**30**) (Scheme 1). These compounds are also formed by addition of the uncomplexed phosphane PhC≡CPPh$_2$ with Fe$_2$(CO)$_9$ or Co$_2$(CO)$_8$ [79,80]. A detailed discussion of the mechanism for the formation of molecules **28**–**30** is given in Ref. [19].

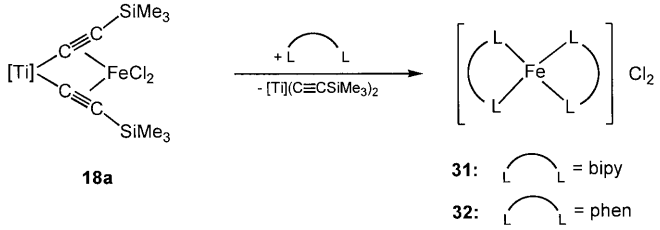
Several halo-bridged complexes of the type {[Ti](C≡CR^1)Cl}Ni(CO) (**6aa**: R^1 = SiMe$_3$, **6bb**: R^1 = ^{t}Bu, **6cc**: R^1 = Ph) were also prepared. Attempts to prepare phosphite derivatives through the reaction of **6aa** with P(OR)$_3$ resulted in decompo-



Scheme 1. Synthesis of **28**–**30** and **6b** upon reaction of **6t** with $Fe_2(CO)_9$ or $Co_2(CO)_8$ [19].

sition, yielding a mixture of $Ni(CO)_2(P(OR)_3)_2$, $[Ti](C{\equiv}CSiMe_3)_2$ (**1c**), $[Ti]Cl_2$ (**21b**), $\{[Ti](\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)\}_2$ (Section 4.1.1.1) and $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ (**22a**) [27].

*2.1.2.2. Reaction chemistry of {[Ti](C≡CSiMe$_3$)$_2$}FeCl$_2$ (**18a**) (method **F**).* $\{[Ti](C{\equiv}CSiMe_3)_2\}FeCl_2$ (**18a**) reacts smoothly with organic chelating ligands, such as 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen) in tetrahydrofuran at 25°C by replacement of the organometallic $[Ti](C{\equiv}CSiMe_3)_2$ fragment (**1c**), to yield the classical coordination complexes $[Fe(bipy)_2]Cl_2$ (**31**) or $[Fe(phen)_2]Cl_2$ (**32**) [70,81].



The $FeCl_2$ entity in **18a** can also be removed when **18a** is allowed to react with halides or pseudohalides of copper(I) or silver(I) [2]. Iron(II) chloride is eliminated and a titanium–copper or titanium–silver tweezer complex of structural type **B** is formed.

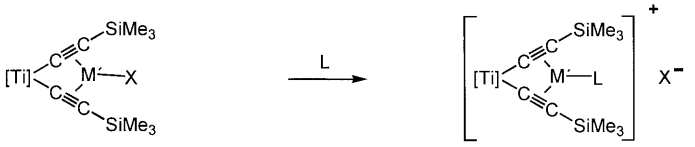
*2.1.2.3. Reaction chemistry of the bis(η^2-alkyne) copper(I) and silver(I) complexes **11**–**16** (methods **G** and **H**)*

Copper(I) and silver(I) triflate; Lewis base adducts. Like the isoelectronic nickel complexes **6a**–**6z**, the copper- or silver-containing tweezer complexes

{[Ti](C≡CR^1)$_2$}M′X (M′ = Cu: **11**, **13**, **14;** M′ = Ag: **15**, **16**) (Table 1) contain monomeric, 16-valence electron M′X entities, with the Group XI metal atom in a trigonal-planar environment (except for those compounds in which X represents a bidentate ligand). Compounds containing weakly coordinating (and thus easily replaced) anions, such as triflate, perchlorate or tetrafluoroborate, were seen as convenient starting materials for the preparation of a wide range of Lewis base adducts [2,49,50,56,82].

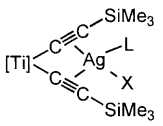
The reaction of a tweezer molecule such as {[Ti](C≡CSiMe$_3$)$_2$}M′X (M = Cu, X = OTf, BF_4, ClO_4, PF_6, BPh_4; M = Ag, X = BF_4, PF_6, BPh_4) with Lewis bases, such as nitriles or phosphanes, affords the corresponding cationic species [{[Ti](C≡CSiMe$_3$)$_2$}ML][X] (**33**, **34**; L = N≡CR, PR_3, etc.) (Table 4).

In the case of copper, coordination of a second equivalent of nitrile or phosphane (to give a tetrahedral copper(I) center) did not occur, even when an excess of ligand was used. However, the reaction of {[Ti](C≡CSiMe$_3$)$_2$}CuOTf (**11aa**) with a stronger Lewis base, such as P(OMe$_3$), resulted in the removal of the copper center as [Cu(P(OMe$_3$)$_n$][OTf] and formation of free [Ti](C≡CSiMe$_3$)$_2$ (**1c**) [49].



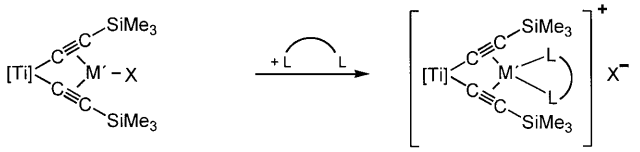
11, **15** **33a - 33i, 34a - 34c**

In the case of silver, the anion is more strongly coordinated to the metal center. Thus, addition of nitriles, phosphanes or phosphites to {[Ti](C≡CSiMe$_3$)$_2$}AgOTf (**15k**) does not result in the displacement of triflate, but in the formation of {[Ti](C≡CSiMe$_3$)$_2$}Ag(L)OTf (**35a**, **35c**–**35g**), in which the silver center achieves a pseudo-tetrahedral geometry (Table 4) [82]. A similar result is obtained when {[Ti](C≡CSiMe$_3$)$_2$}$AgBF_4$ (**15l**) is allowed to react with the weak Lewis base thf; the anion remains coordinated, forming {[Ti](C≡CSiMe$_3$)$_2$}Ag(thf)BF_4 (**35b**). Coordination of the anion to silver in these complexes is confirmed by IR spectroscopy and, in some cases, X-ray crystallography (Table 7).



35

When bidentate ligands such as bipy or phen (LL) are allowed to react with compounds **11** or **15**, cationic complexes containing pseudo-tetrahedrally coordinated copper(I) or silver(I) centers could be isolated. In the so-assembled heterobimetallic compounds [{[Ti](C≡CR^1)$_2$}M′(LL)][X] (**33j**–**33n**, **34d**–**34f**) (Table 4), the M′ centers attain, as do neutral {[Ti](C≡CSiMe$_3$)$_2$}Ag(L)(X) species (**35a**–**35g**), an 18-valence electron configuration [48,50,56,65].

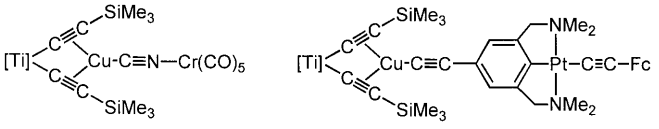


11aa - 11dd, 15k **33j - 33n, 34d - 34f**

In all of these compounds (**33j**–**33n, 34d**–**34f** and **35a**–**35g**) the coordination geometry around the metal centers M′ is pseudo-tetrahedral, as was shown by the X-ray structure analysis of a number of adducts, including {[Ti](C≡CSiMe$_3$)$_2$}-Ag(BF$_4$)(thf) (**35b**) and [{[Ti](C≡CSiMe$_3$)$_2$}Ag(bipy)][OTf] (**34d**) (selected bond lengths and bond angles of molecules **34d** and **35b** are given in Table 7) [48,82].

Another bidentate ligand which will displace a weakly coordinated anion from these complexes is the free tweezer molecule [Ti](C≡CR^1)$_2$, resulting in the formation of the oligonuclear complexes [{[Ti](C≡CR^1)$_2$}$_2$M′][X] (**20**, Table 2) [44,50,74]. In these cationic complexes, the M′ center is also in a pseudo-tetrahedral environment. It is interesting to note that the formation of these complexes is unsuccessful if R^1 or R^2 is very large, such as trimethylsilyl [44]. However, groups such as phenyl, ferrocenyl or ruthenocenyl appear to be sufficiently flexible to allow the formation of these trinuclear species [44,50,74].

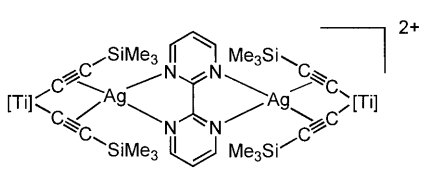
With the wide range of ligands that can be added to the M′ center through metathesis, it is not surprising that these strategies have been used to create multimetallic systems, linked together through di- and poly-functional ligands. Cyano or functionalized phenylethynyl ligands have been utilized to connect tweezer-chelated Cu(I) centers to other transition metals, such as chromium ({[Ti](C≡CSiMe$_3$)$_2$}CuCNCr(CO)$_5$ (**13pp**)) [62], ruthenium ({[Ti](C≡CSiMe$_3$)$_2$}-CuC≡CC$_6$H$_4$C≡N{Ru}-4 (**13bb**)) [61], iron–platinum ({[Ti](C≡CSiMe$_3$)$_2$}-CuC≡CC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Pt-4-C≡CFc (**13cc**)) [61] and gold ([{[Ti](C≡CSiMe$_3$)$_2$}CuN≡CAuPPh$_3$][BF$_4$] (**33g**)) [62].



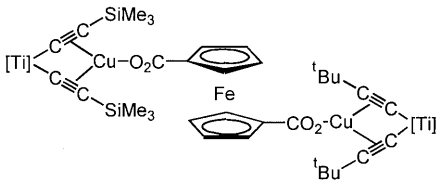
13pp **13cc**

These compounds are of interest in that such systems may display metal–metal communication, as the organic π-system connecting the metal centers may permit rapid intramolecular electron transfer [1,83–92].

Multiple tweezer systems have also been linked together by functionalized ligands, such as bipyrimidine or the salts of dicarboxylic acids. These compounds are summarized in Table 5.



37e



36d

*Group XI alkyls (methods **G** and **H**).* There are several methods which can be used for the preparation of monomeric bis(η^2-alkyne)-stabilized alkyl complexes of the Group XI metals (copper, silver and gold). The first route is the direct synthesis route (Section 2.1.1.1), which could only be used for a select few compounds, owing to the instability of most alkyl-copper or -silver species [102]. Of these species, only CuMe (generated in situ and used immediately, due to the extreme danger of isolating methylcopper) and $CuCH_2SiMe_3$ were sufficiently stable to be used in the direct synthesis of tweezer complexes [2,5,52].

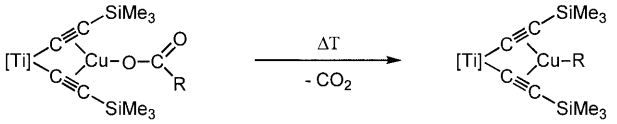
Table 5
Synthesis of complexes {[Ti](C≡CR^1)$_2$M^{1}L–LM^2(R^{2}C≡C)$_2$[Ti]} (**36**, **37**)

Compound	R^1	M^1	L–L	M^2	R^2	Method[a]	Refs.
36a	^{t}C$_4$H$_9$	Cu	(O$_2$C)$_2$C$_6$H$_3$-1,3-(CO$_2$H)-5	Cu	^{t}C$_4$H$_9$	**I**	[63]
36b	^{t}C$_4$H$_9$	Cu	{O$_2$C(η^5-C$_5$H$_4$)}$_2$Fe	Cu	^{t}C$_4$H$_9$	**I**	[63]
36c	^{t}C$_4$H$_9$	Cu	O$_2$CCH$_2$C(O)C(=CH$_2$)CO$_2$	Cu	SiMe$_3$	**I**	[63]
36d	^{t}C$_4$H$_9$	Cu	{O$_2$C(η^5-C$_5$H$_4$)}$_2$Fe	Cu	SiMe$_3$	**I**	[63]
36e	^{t}C$_4$H$_9$	Cu	O$_2$CC$_6$H$_4$CO$_2$-1,4	Cu	^{t}C$_4$H$_9$	**I**	[63]
36f	^{t}C$_4$H$_9$	Cu	*trans*-O$_2$CCH=CHCO$_2$	Cu	^{t}C$_4$H$_9$	**I**	[63]
36g	^{t}C$_4$H$_9$	Cu	*cis*-O$_2$CCH=CHCO$_2$	Cu	^{t}C$_4$H$_9$	**I**	[63]
36h	^{t}C$_4$H$_9$	Cu	O$_2$CCO$_2$	Cu	^{t}C$_4$H$_9$	**I**	[63]
36i	^{t}C$_4$H$_9$	Cu	*trans*-O$_2$CCH=CHCO$_2$	Cu	SiMe$_3$	**I**	[63]
36j	^{t}C$_4$H$_9$	Cu	O$_2$CC≡C	Cu	^{t}C$_4$H$_9$	**I**	[63]
36k	^{t}C$_4$H$_9$	Cu	O$_2$CC≡CCO$_2$	Cu	^{t}C$_4$H$_9$	**I**	[63]
36l	SiMe$_3$	Cu[b]	N≡CAuC≡N	Cu	SiMe$_3$	**G**	[62]
36m	SiMe$_3$	Cu	O$_4$C$_6$H$_2$[c]	Cu	SiMe$_3$	**G**	[48]
37a	SiMe$_3$	Ag	O$_2$CC$_6$H$_4$CO$_2$-1,4	Ag	SiMe$_3$	**A**	[50]
37b	SiMe$_3$	Ag	*trans*-O$_2$CCH=CHCO$_2$	Ag	SiMe$_3$	**A**	[50]
37c	Ph	Ag	O$_2$CCO$_2$	Ag	Ph	**A**	[50]
37d	SiMe$_3$	Ag	O$_4$C$_6$H$_2$[c]	Ag	SiMe$_3$	**A**	[48]
37e	SiMe$_3$	Ag[d]	C$_8$N$_4$H$_6$[e]	Ag	SiMe$_3$	**G**	[48]
37f	^{t}C$_4$H$_9$	Cu	C≡CC≡N	Ag(OTf)	SiMe$_3$	**G**	[48]

[a] Methods: (**A**) direct synthesis route (Section 2.1.1.1); (**I**) metathesis reaction of alkyl complexes with acidic substrates (Section 2.1.1.4); (**G**) metathesis raction route (Section 2.1.2.3).
[b] Contains one triflate (OTf) counterion.
[c] O$_4$C$_6$H$_2$ = dianion of 2,5- dihydroxybenzoquinone.
[d] Contains two triflate (OTf) counterions.
[e] C$_8$N$_4$H$_6$ = pyrimidine.

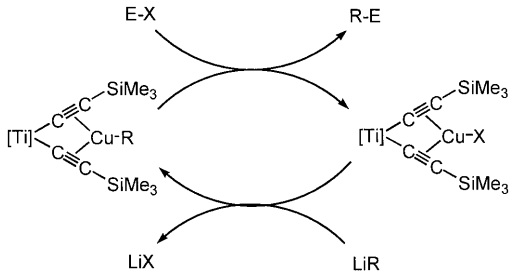
The second, and most important, synthetic route to Group XI alkyl complexes is the metathesis reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}M'X$ ($M' = Cu$, Ag; $X = Cl$, OTf, $SC_6H_4CH_2NMe_2$-2, NO_3) (Method **G**, Section 2.1.1.4) with the appropriate organometallic reagents EX^1 ($E = Li$, $BrMg$, X^1Zn; $X^1 = CH_3$, C_2H_5, ^{n}Bu, $CH{=}CH_2$) [2,5,52]. The advantage of the metathesis reaction is that it allows the high-yield synthesis of compounds $\{[Ti](C{\equiv}CR^1)_2\}MX^1$ ($M = Cu$, Ag; $R^1 = SiMe_3$, ^{t}Bu; $X^1 = CH_3$, C_2H_5, ^{n}Bu, $CH{=}CH_2$, etc.) (Table 1) of which the direct synthesis is difficult to achieve or even impossible.

A third synthetic method for the generation of bis(η^2-alkyne) organocopper(I) compounds makes use of the decarboxylation of alkyne-stabilized monomeric copper(I) carboxylates. Careful heating of the complexes $\{[Ti](C{\equiv}CSiMe_3)_2\}$-$CuOC(O)R$ (**14a**: $R = C_6H_5$, **14b**: $R = CH_3$) causes these molecules to smoothly eliminate CO_2, forming the corresponding organocopper species $\{[Ti](C{\equiv}CSiMe_3)_2\}CuR$ (**13j**: $R = C_6H_5$, **13a**: $R = CH_3$) [93,94].



14a, **14b** **13a**, **13j**

The alkyl complexes have been shown to undergo a number of interesting reactions. In addition to the metathesis reactions with acidic substrates (described in Section 2.1.1.4), the copper species $\{[Ti](C{\equiv}CSiMe_3)_2\}CuR$ ($R =$ alkyl, alkynyl) have been shown to act as a source of R^-, reacting with a number of electrophilic reagents EX to form $\{[Ti](C{\equiv}CSiMe_3)_2\}CuX$ and R–E ($EX = PhCH_2Cl$, $PhC(O)Cl$, CH_3I, $Me_3SiC{\equiv}CI$, $CH_3CO_2COCH_3$, Br_2, etc.) [2,20,51,93,94]. These reactions are summarized in Table 6. The ease with which the resulting halide or acetate complexes may be converted back to alkylcopper complexes would suggest that several catalytic cycles should be possible. However, no catalysis using these complexes has been reported [93].



With cyclic anhydrides, such as those of maleic and phthalic acids, the nucleophilic attack of the R group of $\{[Ti](C{\equiv}CR^1)_2\}CuR$ at one carbonyl of the anhydride results in an insertion reaction, forming a ketocarboxylate such as $\{[Ti](C{\equiv}C^tBu)_2\}CuO_2CCH{=}CHC(O)R$ (**14d**: $R = C{\equiv}CSiMe_3$, **14e**: $R = CH_3$; from

Table 6
Examples of electrophilic attack on organocopper tweezer complexes {[Ti](C≡CSiMe$_3$)$_2$}CuR[a]

Compound	R	EX	Copper product	Organic product
13a	CH_3	Br_2	[Ti](C≡CSiMe$_3$)$_2$CuBr	CH_3Br
13j	C_6H_5	Br_2	[Ti](C≡CSiMe$_3$)$_2$CuBr	C_6H_5Br
13aa	C≡CSiMe$_3$	I_2	[Ti](C≡CSiMe$_3$)$_2$CuI	IC≡CSiMe$_3$
13aa	C≡CSiMe$_3$	PhC(O)Cl	[Ti](C≡CSiMe$_3$)$_2$CuCl	PhC(O)C≡CSiMe$_3$
13a	CH_3	$PhCH_2Cl$	[Ti](C≡CSiMe$_3$)$_2$CuCl	$PhCH_2CH_3$
13aa	C≡CSiMe$_3$	IC≡CSiMe$_3$	[Ti](C≡CSiMe$_3$)$_2$CuI	Me$_3$SiC≡C–C≡CSiMe$_3$
13a	CH_3	$CH_3CO_2C(O)CH_3$	[Ti](C≡CSiMe$_3$)$_2$CuOC(O)CH$_3$	$CH_3C(O)CH_3$
13aa	C≡CSiMe$_3$	$CH_3CO_2C(O)CH_3$	[Ti](C≡CSiMe$_3$)$_2$CuOC(O)CH$_3$	$CH_3C(O)C{\equiv}CSiMe_3$
13a	CH_3	Me$_3$SiC≡N	[Ti](C≡CSiMe$_3$)$_2$CuC≡N	$SiMe_4$
13aa	C≡CSiMe$_3$	$C_6H_4(C_2O_3)$[b]	[Ti](C≡CSiMe$_3$)$_2$CuOC(O)-C_6H_4-2-C(O)C≡CSiMe$_3$	

[a] See Refs. [2,20,93,94].
[b] Phthalic anhydride.

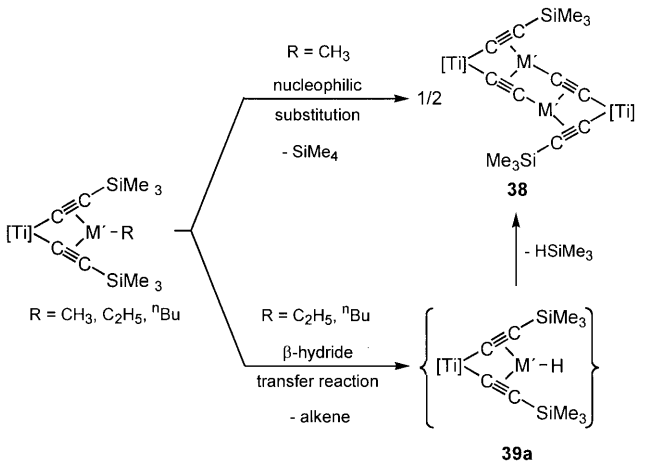
maleic anhydride) and {[Ti](C≡C^{t}Bu)$_2$}CuO$_2$CC$_6$H$_4$C(O)CH$_3$ (**14f**, from phthalic anhydride) (Table 1).

The alkyne-stabilized M′-alkyl complexes {[Ti](C≡CR^1)$_2$}M′R ([Ti] = (η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti; M′ = Cu, Ag, Au; R = CH_3, C_2H_5, ^{n}Bu, etc.) are remarkably stable, compared to the parent alkyl species such as methyl-, ethyl- or *n*-butylcopper. However, the highly nucleophilic nature of the alkyl ligands of these compounds cause them to slowly decompose in solution [2,5,52]. The decomposition of the silver and copper complexes results in the formation of the dimeric acetylide complex {[Ti](C≡CSiMe$_3$)(C≡CM′)}$_2$ (**38a**: M′ = Cu; **38b**: M′ = Ag) [2,51,52,56,60,94].

The structure of the copper compound **38a** has been determined crystallographically; cryoscopic molecular weight determination in benzene indicates that the dimeric structure is maintained in solution [60]. The titanium centers in **38a** are bound to two different kinds of alkynyl ligand — one trimethylsilylacetylide and one copper(I)acetylide. The copper atom forming the terminus of the one alkynyl ligand is further coordinated by the alkynyl ligands of the other titanium center. Thus, each copper atom possesses a somewhat distorted trigonal-planar environment set up by two η^2-coordinated and one σ-bonded alkynyl group. The arrangement of the central (C≡CCu)$_2$ core in **38a** can be regarded as the substructure of polynuclear copper(I) acetylides [CuC≡CR]$_n$ in which the C≡CR anions are η^1- as well as η^2-bonded to copper atoms, resulting in an infinite zigzag chain of polymeric [CuC≡CR]$_n$ [95,96].

The formation of these compounds from the alkyl species can proceed by two pathways: (1) nucleophilic attack of R at one of the two $SiMe_3$ groups of the

$Me_3SiC{\equiv}C$ entities ($R = CH_3$); or (2) β-hydride transfer reaction ($R = C_2H_5$, ^{n}Bu) [2,5,52,56,60,94]. The decomposition route of methyl complexes is the substitution reaction, which on elimination of $SiMe_4$ yields $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CM')\}_2$ (**38a**, **38b**). If β-hydride atoms are present, the main decomposition route is the β-hydrogen elimination pathway, as observed for $\{[Ti](C{\equiv}CSiMe_3)_2\}M'R$ ($R = C_2H_5$, ^{n}Bu). In the case of the copper(I) species, it was found that at first, the monomeric bis(η^2-alkyne)CuH complex **39a** is formed as an intermediate. This then continues decomposition via the nucleophilic substitution pathway outlined above [2,5,52,60,94].

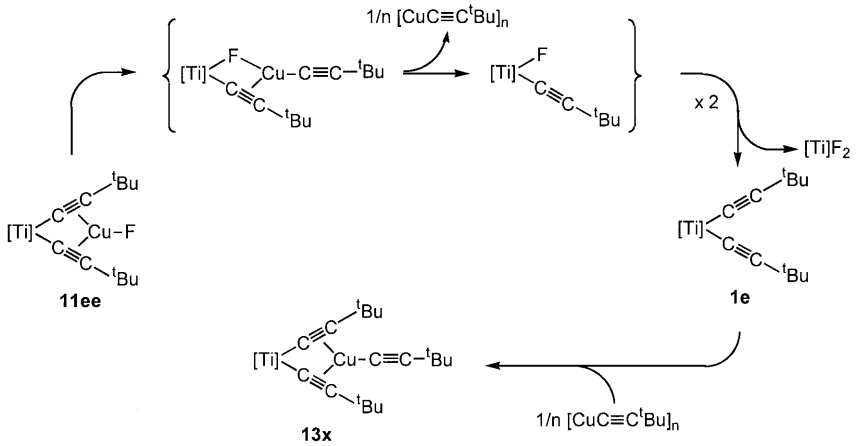


Compound **38a** was also generated in the attempted synthesis of compounds of the type $\{[Ti](C{\equiv}CSiMe_3)_2\}CuX$ (where X represents a hard nucleophile, such as O^{t}Bu, OPh or $N(SiMe_3)_2$) [48,51,60,94]. Reaction of **1c** with $[CuO^tBu]_4$ or treatment of the methylcopper complex **13a** with HX, led to the formation of **38a** and $XSiMe_3$. Although copper-containing tweezer complexes bearing monodentate alkoxide ligands could not be isolated, compounds containing bidentate enolate ligands (such as the deprotonated forms of acetylacetone and dibenzoylmethane) are quite stable and well-characterized (Table 1) [48,64]. It is uncertain if this added stability is due to the bidentate nature of these ligands or their lower nucleophilicity.

The replacement of the trimethylsilyl units by *t*-butyl groups in the alkynyl ligands of the alkyl complexes **13a**, **13c** and **13f** prevents the decomposition of these compounds through this mechanism, as the carbon–carbon bond is not susceptible to nucleophilic cleavage. However, many of these compounds also decompose slowly in solution. As an example, $\{[Ti](C{\equiv}C^tBu)_2\}CuC_2H_5$ (**13b**) decomposes in a fashion similar to that found for **13c** [2,5,48,55]. The first step is elimination of ethene, a β-hydride transfer reaction which produces the corresponding copper(I) hydride species $\{[Ti](C{\equiv}C^tBu)_2\}CuH$ (**39b**) as an intermediate. In contrast to $\{[Ti](C{\equiv}CSiMe_3)_2\}CuH$ (**39a**), which undergoes C–Si bond cleavage, **39b** decomposes through scission of the Ti–C(alkyne) σ-bond, yielding $\{[Ti](C{\equiv}C^tBu)_2\}$-$CuC{\equiv}C^tBu$ (**13x**), $\{[Ti]H_2\}$, and $[CuC{\equiv}C^tBu]_n$ [2,48,55].

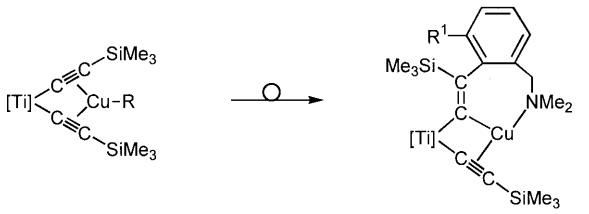
A similar product distribution is found in the decomposition of {[Ti](C≡C′Bu)$_2$}CuF (**11ee**, synthesized through the reaction of {[Ti](C≡C′Bu)$_2$}-CuSC$_6$H$_4$CH$_2$NMe$_2$-2 (**11nn**) with ^{n}Bu$_4$NF) [2,55]. Although **11ee** is sufficiently stable to be characterized by spectroscopic methods, it slowly rearranges in solution to produce a mixture of {[Ti](C≡C′Bu)$_2$}CuC≡C′Bu (**13x**), [Ti]F$_2$ and [CuC≡C′Bu]$_n$ [2,55]. A possible reaction sequence for this rearrangement is given in Scheme 2.

As an initial step, an alkynyl site exchange reaction in **11ee** occurs, yielding intermediate {[Ti](C≡C′Bu)F}CuC≡C′Bu at first (the synthesis of stable, chloro-bridged compounds isostructural to this complex is reported in Section 2.1.1.3). Elimination of [CuC≡C′Bu]$_n$ from the latter intermediate subsequently affords the σ-alkynyl substituted titanocene fluoride [Ti](C≡C′Bu)F (for related compounds see Section 2.1.1.3). This molecule slowly dismutates and, upon redistribution of its ligands F and C≡C′Bu, the complexes [Ti]F$_2$ and [Ti](C≡C′Bu)$_2$ (**1e**) are formed. This bis(alkynyl)titanocene **1e** takes up the previously-formed copper acetylide [CuC≡C′Bu]$_n$ to generate {[Ti](C≡C′Bu)$_2$}CuC≡C′Bu (**13x**) (Scheme 2) [2,55].



Scheme 2. Possible reaction sequence for the rearrangement of **11ee** to afford {[Ti](C≡C′Bu)$_2$}CuC≡C′Bu (**13x**), [Ti]F$_2$ and [CuC≡C′Bu]$_n$ [2,55].

Copper(I) aryls. While {[Ti](C≡CSiMe$_3$)$_2$}Cu(C$_6$H$_2$R$_3$-2,4,6) (**13n**: R = CH$_3$, **13r**: R = CF$_3$, **13s**: R = C$_6$H$_5$) is a stable compound, both in the solid state and in solution [2,5,52,57] it appeared that the bis(η^2-alkyne)CuR molecules **13j**–**13m**, **13o** and **13p** (Table 1) are less stable and slowly decompose in solution [2,5]. When the organometallic penta-1,4-diyne Me$_3$SiC≡C–[Ti]–C≡CSiMe$_3$ is allowed to react with the organocopper(I) species [CuC$_6$H$_4$CH$_2$NMe$_2$-2]$_3$ or [CuC$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]$_3$, a novel class of vinylidene-bridged species, {[Ti](C≡CSiMe$_3$)[μ-C=C(SiMe$_3$)R]Cu} (**40a**: R = C$_6$H$_4$CH$_2$NMe$_2$-2, **40b**: R = C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6), is obtained [2,58,97]. It is likely that {[Ti](C=CSiMe$_3$)$_2$}CuR [**13o**: R = C$_6$H$_4$CH$_2$NMe$_2$-2, **13p**: R = C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6] is formed at first [2,49,52,58].



13o: R = $C_6H_4CH_2NMe_2$-2
13p: R = $C_6H_3(CH_2NMe_2)_2$-2,6

40a: R^1 = H
40b: R^1 = CH_2NMe_2

Compounds **40a** and **40b** are produced by an intramolecular addition of the CuR moiety across the alkyne triple bond of one $Me_3SiC{\equiv}C$ unit of the $[Ti](C{\equiv}CSiMe_3)_2$ fragment. Migration of an organic group from a metal center to the β-carbon of an alkynyl ligand (rather than to the α-carbon) is not a common reaction, although it has been observed in other binuclear systems [98].

The molecular structure of **40b** in the solid state was determined by X-ray structure analysis (Fig. 5) [58]. In this structure, one can see that a vinylidene ligand, formed by the condensation of the trimethylsilylacetylide moiety with the bis(aminomethyl)phenyl ligand, is bridging the two metal centers. The copper atom in **40b** shows a slightly distorted trigonal-planar environment formed by the σ-bonded $C{\equiv}C(SiMe_3)[C_6H_3(CH_2NMe_2)_2$-2,6] bridge, the η^2-coordinated $Me_3SiC{\equiv}C$ fragment and the chelating CH_2NMe_2 group.

While the Cu(11)–C(11) bond was proposed to have an exclusively σ-character, the Ti(11)–C(11) bond was described as a bent bond in which the orbitals involved

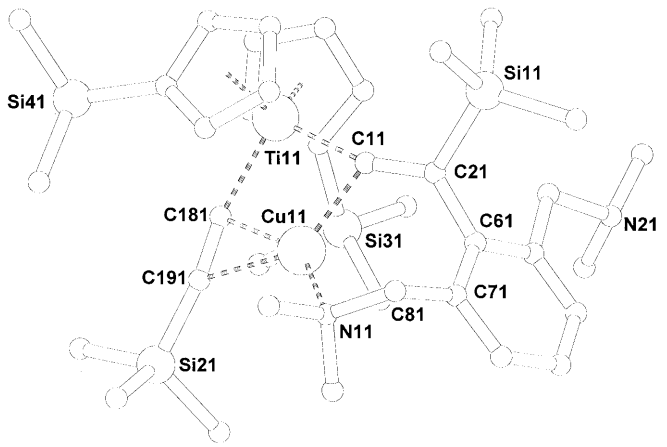


Fig. 5. Molecular geometry and atom numbering scheme for **40b**. Selected interatomic bond distances (Å) and angles (°) are as follows [58]: Ti(11)–Cu(11), 2.639(4); Cu(11)–C(11), 2.03(1); Cu(11)–C(181), 1.97(2); Cu(11)–C(191), 2.24(2); Cu(11)–N(11), 2.03(1); C(11)–C(21), 1.36(2); C(181)–C(191), 1.24(2); Ti(11)–C(11), 2.04(1); Ti(11)–C(181), 2.15(2); Cu(11)–C(11)–Ti(11), 80.7(5); Ti(11)–C(11)–C(21), 160(1); Cu(11)–C(11)–C(21), 118(1); Ti(11)–C(181)–C(191), 164(1); C(181)–C(191)–Si(21), 163(2); C(11)–Ti(11)–C(181), 95.8(6).

are positioned outside the Ti(11)–C(11)–Cu(11) triangle. Similar features were concluded from extended-Hückel calculations on μ-methylene transition metal compounds where the bonding is referred to be similar to the Walsh orbitals for cyclopropane [99].

Copper(I) acetylides. Many copper(I) acetylide complexes have been synthesized, normally through metathesis reactions (Section 2.1.1.4). The reaction behavior of copper(I) acetylides in the solid state differs significantly from that in solution. Thermolysis of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuC{\equiv}CSiMe_3$ (**13aa**) initially results in the formation of $[Ti](C{\equiv}CSiMe_3)_2$ (**1c**) and '$CuC{\equiv}CSiMe_3$'. The latter compound undergoes subsequent cleavage of the copper–carbon σ-bond, finally yielding $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ (**22a**) along with copper(0) [2,94]. This last elimination is equivalent to the well-known Glaser reaction in which two alkynes are oxidatively coupled by copper(I) ions to form symmetrical 1,3-diynes ($RC{\equiv}C{-}C{\equiv}CR$) [100].

However, when compound **13aa** is allowed to react with catalytic amounts of hard nucleophiles (such as F^- or $C_2H_5O^-$) in diethyl ether solution, the elimination of $Me_3SiC{\equiv}CSiMe_3$ is observed and the previously-described heterobimetallic acetylide complex $\{[Ti](C{\equiv}CSiMe_3)(C{\equiv}CCu)\}_2$ (**38a**) is formed [2,59,60].

Several alkynyl–silver(I) and alkynyl–gold(I) tweezer complexes have been synthesized (Table 1), which are very similar in structure to the copper(I) acetylide complexes (Table 1) [68,69]. Like the copper analogues, these species (**16g**–**16i**; **17c**–**17e**) also eliminate $RC{\equiv}C{-}C{\equiv}CR$ upon thermolysis, forming the free tweezer molecule $[Ti](C{\equiv}CR^1)_2$ along with metallic silver or gold.

*Copper(I) carboxylates (method **H**)*. Monomeric copper(I) carboxylates can be considered as model compounds for the Hunsdiecker reaction [101], a reaction used to decrease the length of a carbon chain by one unit, which formally corresponds on the replacement of a carboxyl group, e.g. in mercury or silver carboxylates, by one halogen atom. The copper(I) carboxylates $\{[Ti](C{\equiv}CSiMe_3)_2\}CuOC(O)R$ (**14a**: $R = C_6H_5$, **14b**: $R = CH_3$) (Scheme 3) eliminate CO_2 upon heating. The corresponding organocopper(I) species $\{[Ti](C{\equiv}CSiMe_3)_2\}CuR$ (**13a**: $R = CH_3$, **13j**: $R = C_6H_5$) are formed in high yields [Route (1), Scheme 3]. Treatment of **13a** or **13j** with one equivalent of bromine results in the formation of R–Br ($R = CH_3$, Ph) together with $\{[Ti](C{\equiv}CSiMe_3)_2\}CuBr$ (**11l**) [Route (2), Scheme 3]. The latter compound can be easily converted to the starting materials **14a** or **14b** by its reaction with $[AgO_2CR]_n$ ($R = CH_3$, Ph) [Route (3), Scheme 3] [2,47,94].

2.1.3. Structure, bonding and spectroscopy

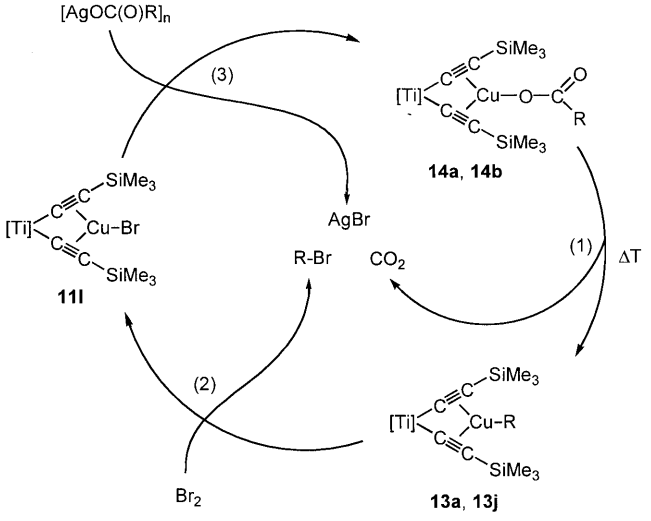
In all reported heterobinuclear tweezer compounds of structural type **B**, $\{[M](C{\equiv}CR^1)_2\}[M']$ {M = Ti, Zr, Hf, Re, Ru, Pt; [M′] = monomeric low-valent transition metal fragment; R^1 = singly bonded organic ligand} (Table 1) the 3-metallapenta-1,4-diynes $R^1C{\equiv}C{-}[M]{-}C{\equiv}CR^1$ act as organometallic bidentate chelating ligands (organometallic π-tweezers) to stabilize low-valent monomeric transition metal moieties (compounds **4**–**19**) (Table 1).

In these complexes, each η^2-coordinated alkynyl ligand of the $[M](C{\equiv}CR^1)_2$ fragment donates two electrons to the M′ transition metal center. Consequently, the $(\eta^2\text{-alkyne})_2[M']$ moieties have a formal electron count between 14 and 18. Important observations with respect to the alkyne-to-M′ interaction are: (1) a lengthening of the alkynyl C≡C bonds; and (2) bending of the M–C≡C–R^1 units by changing from the non-coordinated $[M](C{\equiv}CR^1)_2$ to the coordinated $\{[M](C{\equiv}CR^1)_2\}[M']$ complexes (**4**–**19**) (Table 7).

2.1.3.1. Structure and bonding. The solid-state structures of selected examples of compounds **4**–**19** (Table 1) have been determined by X-ray diffraction studies (Table 7, Figs. 6 and 7).

Figs. 6 and 7 clearly show the coordination of the metal centers M′ within the tweezer framework in all heterobimetallic complexes **4**–**19**. Considering the alkynyl ligands as occupying one coordination site each, the metal atoms M′ of the [M′] building blocks possess pseudo-tetrahedral (compounds **4**, **9a**, **10**, **14q**–**14t**, **15s**–**15w**, **16j**–**16q**, **18** and **19**) or pseudo-trigonal-planar environments (compounds **5**–**9** and **11**–**17**), comprising η^2-coordination of both alkynyl ligands of the $[M](C{\equiv}CR^1)_2$ fragment and η^1-bonding of the ligands X of the [M′] entities.

The tetrahedral environment around the iron(II) ion in compound **18a** is consistent with a d^6 high-spin electron configuration as confirmed by the experimentally observed paramagnetism of this compound ($\mu_{eff} = 4.6\ \mu_B$, indicating four unpaired electrons) [37,70]. Isostructural **18b**, which contains a $CoCl_2$ transition metal fragment, shows a magnetic moment of $\mu_{eff} = 3.9\ \mu_B$ with a total of three unpaired electrons, whereas the magnetic moment of the $NiCl_2$ derivative **18c** was determined to be 3.2 μ_B, indicating the presence of two unpaired electrons [37,70].



Scheme 3. Decarboxylative bromination of **14a** and **14b** [2,47,94].

Table 7
Selected X-ray data for compounds $[M](C{\equiv}CR^1)_2$ and $\{[M](C{\equiv}CR^1)_2\}[M']$

Compound	M···M′ (Å)	M–C_α (Å)	M′–C_α (Å)	M′–C_β (Å)	M′–X (Å)	C≡C (Å)	C_α–M–$C_{\alpha'}$ (°)	M–C≡C (°)	C≡C–R^1 (°)	Refs.
1b		211.7(3)				121.4(5)	104.1(2)	168.3(3)	175.6(4)	[56]
1c		2.124(5)				1.214(6)	102.8(2)	175.8(4)	174.8(4)	[56]
		2.103(5)				1.203(9)		178.2(5)	178.3(5)	
2a		2.249(3)				1.206(4)	103.6(1)	177.0(3)	179.4(4)	[10]
2b		2.227(4)				1.206(6)	102.7(2)	177.4(4)	175.9(4)	[33]
		2.223(5)				1.213(7)		177.0(4)	176.7(4)	
5a	2.819(1)	2.070(3)	1.982(3)	2.000(3)	1.753(5)	1.260(4)	89.2(1)	160.4(2)	152.1(3)	[16]
5b	2.933(2)	2.178(3)	2.004(3)	1.994(2)	1.768(6)	1.266(4)	86.2(2)	159.9(3)	149.7(3)	[17]
6l	2.785(4)	2.036(8)	2.01(1)	2.05(1)	1.70(1)	1.22(1)	91.8(4)	161.2(9)	157.4(9)	[24]
		2.04(1)	1.996(8)	2.038(9)		1.24(1)		161.2(9)	153.4(7)	
6p	2.968(1)	2.170(4)	2.043(4)	2.026(4)	1.736(7)	1.250(5)	87.0(2)	160.7(3)	153.0(4)	[17]
6s	2.840	2.040(4)	1.986(3)	2.065(3)	2.1659(9)	1.250(5)	89.3(1)	165.2(3)	134.1(3)	[26]
		2.058(4)	2.005(3)	2.038(3)		1.256(5)		160.4(3)	148.4(4)	
6x	2.8341(8)	2.059(4)	1.988(4)	2.046(4)	2.1038(11)	1.259(5)	89.05(14)	161.2(3)	143.9(3)	[25]
		2.061(4)	1.988(4)	2.042(4)		1.256(5)		161.5(3)	147.5(3)	
6z	2.863(2)	2.070(7)	2.015(7)	2.066(7)	2.086(2)	1.250(9)	89.1(3)	160.9(5)	139.9(6)	[22]
		2.079(6)	2.003(6)	2.063(7)		1.259(9)		162.0(5)	144.6(6)	
7a	2.957(1)	2.085(5)	2.176(4)	2.219(5)	2.312(1)	1.252(6)	94.8(2)	162.2(4)	155.2(5)	[25]
		2.085(5)	2.186(4)	2.251(5)		1.242(6)		163.6(4)	157.5(5)	
7d	2.900(4)	2.057(6)	2.165(8)	2.231(9)	2.276(4)	1.238(9)	95.6(3)	163.2(7)	159(1)	[23]
		2.052(8)	2.136(6)	2.201(7)		1.24(1)		163.4(5)	153.9(6)	
9a	3.215(4)	2.129(5)	2.277(7)	2.541(7)	1.969(8)	1.213(8)	89.9(2)	177.5(5)	178.8(6)	[31]
9d	4.033(1)	2.149(4)	2.946(4)	3.021(4)	3.186(5)[a]	1.228(5)	90.1(1)	174.9(3)	167.6(4)	[32b]
		2.142(4)	2.949(4)	2.961(4)		1.231(5)		177.8(3)	173.5(4)	
9f	3.818(1)	2.264(4)	2.868(4)	3.105(5)	2.871(5)[a]	1.225(6)	92.8(2)	175.3(4)	167.1(4)	[33]
		2.279(4)	2.896(4)	3.147(5)		1.226(6)		175.2(4)	165.4(4)	
10a	3.21	2.167(7)	2.269(8)	2.456(9)	2.042(6)[b]	1.22(1)	86.1(3)	178.0(7)	165.4(7)	[35a]
		2.164(7)	2.281(7)	2.469(9)	2.276(4)[c]	1.22(1)		178.6(7)	164.6(7)	

Table 7 (*Continued*)

Compound	M···M′ (Å)	M–C_α (Å)	M′–C_α (Å)	M′–C_β (Å)	M′–X (Å)	C≡C (Å)	C_α–M–$C_{\alpha'}$ (°)	M–C≡C (°)	C≡C–R^1 (°)	Refs.
11a	2.900(3)	2.09(1)	2.055(9)	2.18(1)	2.182(3)	1.23(2)	89.6(4)	167.8(9)	161(1)	[38]
		2.105(9)	2.04(1)	2.21(1)		1.24(2)		168.6(9)	163(1)	
11z	2.975(2)	2.114(6)	2.077(6)	2.135(6)	1.908(5)	1.234(8)	88.4(2)	165.1(5)	165.0(5)	[48]
		2.105(6)	2.072(5)	2.131(6)		1.234(8)		166.3(5)	164.2(5)	
11aa	2.998(1)	2.105(4)	2.066(4)	2.143(5)	1.969(2)	1.233(6)	87.4(2)	166.7(3)	156.8(4)	[49]
		2.110(4)	2.066(4)	2.158(5)		1.238(5)		166.9(3)	158.1(4)	
11ff	2.979(1)	2.103(6)	2.078(6)	2.130(6)	1.92	1.227(8)	88.8(2)	166.0(5)	163.8(5)	[48]
		2.108(7)	2.091(6)	2.161(6)		1.246(8)		166.2(5)	166.5(5)	
11ii	2.998(2)	2.109(5)	2.099(5)	2.201(5)	2.272(2)	1.236(8)	88.9(2)	168.3(5)	161.4(6)	[52]
		2.106(6)	2.105(5)	2.192(6)		1.251(9)		167.8(5)	164.2(6)	
11mm	2.963(2)	2.082(8)	2.072(8)	2.104(8)	2.237(3)	1.22(1)	88.7(9)	164.5(7)	161.2(7)	[49]
		2.083(8)	2.072(8)	2.120(9)		1.23(1)		165.0(7)	157.5(7)	
12a	3.078(3)	2.39(1)	1.98(2)	2.33(2)	2.01(1)					[53]
		2.26(2)	2.12(2)	2.34(2)						
13a	2.965(1)	2.075(2)	2.076(2)	2.080(2)	1.966(2)	1.247(3)	88.89(6)	163.7(1)	158.5(2)	[5]
13n	2.941(2)	2.079(2)	2.067(2)	2.083(2)	1.947(2)	1.250(3)	89.30(9)	163.6(2)	155.5(2)	[5]
13w	2.936(2)	2.075(5)	2.080(5)	2.126(5)	1.892(6)	1.240(7)	89.8(2)	164.3(5)	164.6(5)	[51]
		2.088(6)	2.068(5)	2.116(5)		1.235(8)		165.3(4)	164.5(5)	
13aa	2.9665(8)	2.081(4)	2.074(4)	2.112(4)	1.898(3)	1.236(5)	89.6(3)	165.0(3)	162.8(3)	[60]
		2.095(4)	2.069(4)	2.111(4)		1.240(5)		165.4(4)	162.9(4)	
14q	2.920(1)	2.081(4)	2.079(4)	2.171(4)	2.228(3)	1.235(5)	90.7(1)	164.7(3)	163.8(3)	[64]
		2.091(4)	2.088(3)	2.145(3)	1.949(3)	1.227(5)		165.8(3)	164.9(3)	
15a	3.125(1)	2.112(2)	2.287(3)	2.380(3)	2.372(1)	1.230(4)	94.1(1)	169.4(2)	170.4(3)	[48,65]
15i	3.193(1)	2.132(5)	2.311(5)	2.478(5)	2.547(1)	1.223(7)	93.0(2)	174.3(4)	170.1(4)	[48]
		2.139(5)	2.348(5)	2.499(5)		1.228(7)		172.5(4)	166.9(4)	
15k	3.157(2)	2.137(5)	2.287(5)	2.414(5)	2.252(5)	1.22(1)	93.3(2)	171.2(4)	163.8(5)	[49]
		2.141(6)	2.307(5)	2.477(5)		1.225(8)		173.2(4)	170.5(4)	
15s	3.162(5)	2.12(2)	2.29(2)	2.41(2)	2.45(1)	1.26(2)	93.8(7)	171(2)	170(2)	[65]
		2.10(2)	2.33(2)	2.43(2)	2.39(1)	1.27(3)		170(2)	171(2)	
16d	3.104(7)	2.090(8)	2.270(9)	2.305(9)	2.099(5)	1.24(1)	94.0(3)	166.6(6)	162.9(7)	[5]

Table 7 (*Continued*)

Compound	M···M′ (Å)	M–C_α (Å)	M′–C_α (Å)	M′–C_β (Å)	M′–X (Å)	C≡C (Å)	C_α–M–$C_{\alpha'}$ (°)	M–C=C (°)	C≡C–R^1 (°)	Refs.
16e	3.220(1)	2.116(4)	2.323(3)	2.392(3)	2.166(3)	1.252(5)	92.5(1)	167.5(3)	161.1(3)	[52]
		2.122(3)	2.335(3)	2.403(3)		1.252(5)		168.1(3)	161.2(3)	
16j	3.091(2)	2.118(7)	2.272(7)	2.381(7)	2.248(6)	1.23(1)	94.9(3)	168.2(6)	170.7(6)	[52]
		2.121(7)	2.284(7)	2.396(8)	2.623	1.24(1)		168.9(6)	170.3(7)	
17c	3.007(2)	2.12(1)	2.228(9)	2.255(9)	2.00(1)	1.26(1)	95.5(4)	162.4(8)	162.1(8)	[69]
		2.11(1)	2.23(1)	2.27(1)		1.23(1)		163.6(9)	162.1(9)	
18a	3.26	2.07(2)	2.23(2)	2.20(2)	2.225(6)	1.20(2)	85.4(9)	171(1)	163(1)	[37]
19j	3.267(2)	1.95(3)	2.64(2)	2.41(2)	2.572(2)	1.21(3)	88.0(9)	168(2)	156(2)	[72]
		1.98(3)	2.57(2)	2.46(2)	2.588(3)	1.19(3)		176(2)	160(2)	
20k	3.248(3)	2.13(2)	2.35(2)	2.81(2)		1.23(3)	93.8(6)	165.3(12)		[74]
	3.267(3)	2.13(2)	2.40(1)	2.77(1)		1.23(3)	93.7(6)	172.7(13)		
		2.12(2)	2.37(1)	2.78(1)		1.24(3)		162.9(12)		
		2.11(2)	2.41(2)	2.72(2)		1.22(2)		170.9(13)		
34d	3.125(2)	2.120(9)	2.286(9)	2.44(1)	2.322(7)	1.23(1)	94.4(3)	171.7(8)	169.4(9)	[48]
		2.13(1)	2.298(8)	2.44(1)	2.389(7)	1.22(1)		171.3(8)	166.5(8)	
35b	3.096(2)	2.114(7)	2.293(6)	2.447(7)	2.389(5)[a,c]	1.23(1)	95.6(3)	170.7(6)	168.8(6)	[82]
		2.128(7)	2.294(7)	2.472(8)	2.47(2)	1.222(9)		171.0(6)	166.8(7)	

[a] Distance between the potassium center and the centroid of the cyclopentadienyl ligand of an adjacent molecule.
[b] M′–O.
[c] M′–Cl.

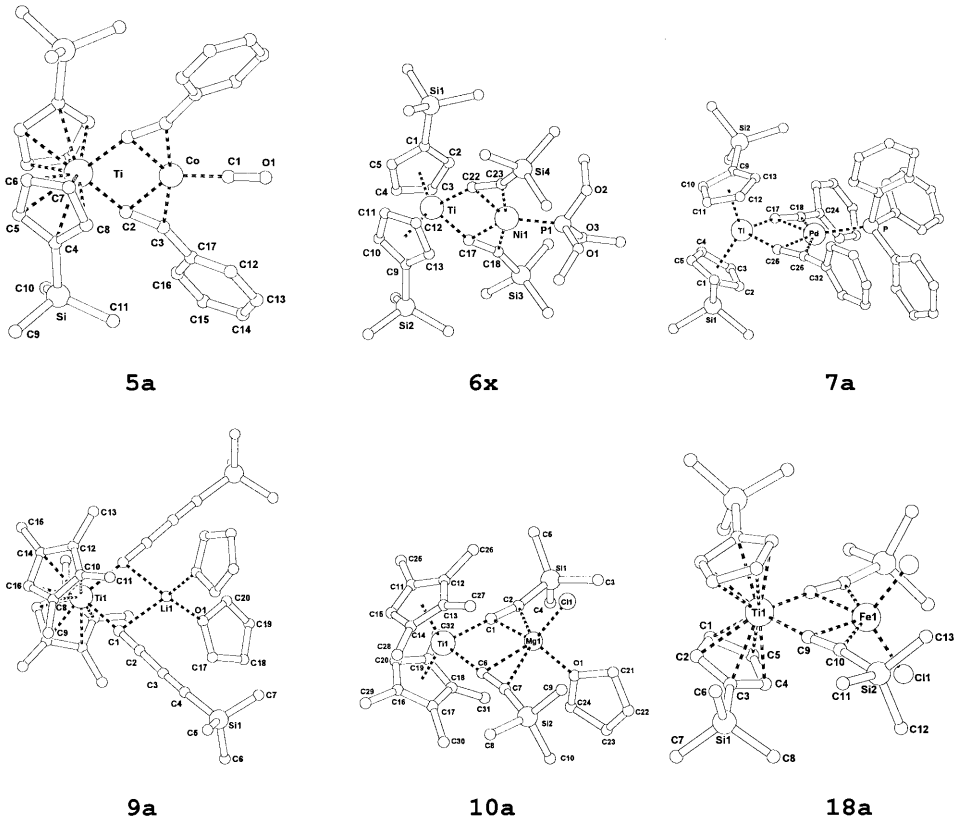


Fig. 6. Selected X-ray structures of compounds **4**–**19**. Top left, **5a**; top middle, **6x**; top right, **7a**; bottom left, **9a**; bottom middle, **10a**; bottom right, **18a** (Table 1). The interatomic bond lengths and angles are given in Table 7.

In $\{[Ti](C{\equiv}CSiMe_3)_2\}M'LL$ ($[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; $M' = Cu$, Ag), where LL is a bidentate ligand such as acac, trop etc., the metal(I) centers show a pseudo-tetrahedral environment in which the M′LL unit is almost perpendicularly oriented to the titanium–alkynyl–metal plane [48,50,64,65]. This is also true for the tweezer complexes containing MoO_2 (**4a**–**4c**), WO_2 (**4d**, **4e**), $Li(thf)_2$ (**9a**), MgCl(thf) (**10a**, **10b**) and mercury (**18d**, **18e**, **19**) (Table 1).

As a result of the η^2-coordination of each alkynyl ligand in complexes **4**–**19** to the M′ center, the bite angles C_α–Ti–$C_{\alpha'}$ decrease from, e.g. 96.1(3)° in **1a**, 102.8(2)° in **1c**, 103.6(1)° in $(\eta^5\text{-}C_5H_5)_2Zr(C{\equiv}CMe)_2$ (**2a**) [10,105], 100.6(2)° in $(\eta^5\text{-}C_5H_4SiMe_3)_2Zr(C{\equiv}CPh)_2$ (**2b**) [25] and 99.1(6)° in $(\eta^5\text{-}C_5H_4SiMe_3)_2Hf(C{\equiv}CPh)_2$ (**3**) [17] to 84–95° in compounds **4**–**18** (Table 7) (Figs. 6 and 7). This is accompanied by a deformation of the M–C≡C–R^1 entities (M = Ti, Zr, Hf), which are linear in the starting materials $[M](C{\equiv}CR^1)_2$. As consequence of this deformation, different M′–C bond lengths (M′–C_α, M′–C_β) are observed (Table 7) (Figs. 6–8). The

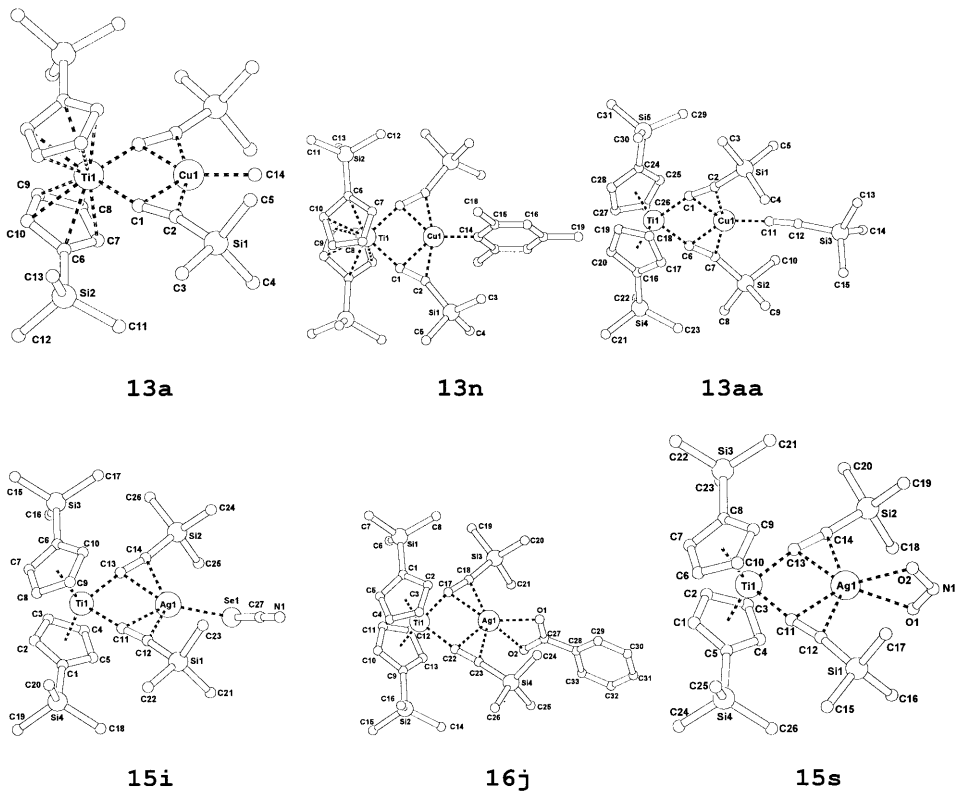


Fig. 7. Selected X-ray structures of compounds **4–19**. Top left, **13a**; top middle, **13n**; top right, **13aa**; bottom left, **15i**; bottom middle, **16j**; bottom right, **15s** (Table 1). The interatomic bond lengths and angles are given in Table 7.

D^1–Ti–D^2 angles (D^1, D^2 = centroids of the cyclopentadienyl ligands) are thereby not influenced.

Another interesting aspect about the deformation of the M–C≡C–R^1 segments in, for example, the titanium–nickel compounds {[Ti](C≡CR^1)$_2$}NiL (**6a–6z**: L = CO, PR_3, $P(OR)_3$) (Tables 1 and 7) is the fact that, depending on the steric demand of the organic groups R^1 at the C≡CR^1 units, as well as the steric constraints of the 2-electron donor ligands L at the nickel atom, a significant decrease of the C≡C–R^1

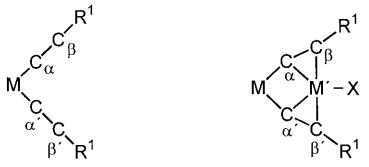


Fig. 8. Schematic representation of M(C≡CR^1)$_2$ (left) and {M(C≡CR^1)$_2$}M′X (right).

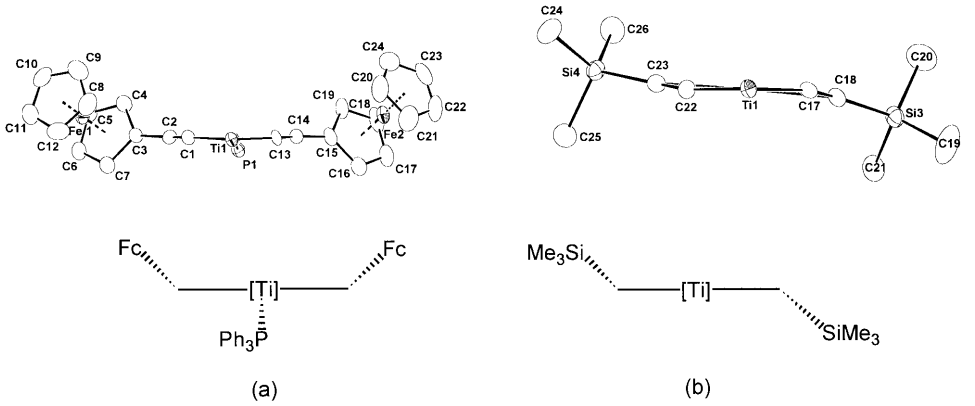


Fig. 9. View of compounds **7e** [29] (a) and **16e** [52] (b) along the Ti–M′ vector, showing displacement of alkynyl substituents from the titanium–alkynyl–M′ plane. (a) Ferrocenyl groups bent above the plane, palladium-bound phosphane ligand below the $M(C{\equiv}C)_2M'$ plane. (b) Trimethylsilyl groups above and below the $M(C{\equiv}C)_2M'$ plane.

angle is observed by changing from smaller to larger substituents (for additional comparison see Section 2.1.2.1) [19,22–27]. Owing to steric interactions with the bulky ligands, the substituents on the alkynyl ligands in these tweezer complexes are often pushed out of the plane of the $[Ti](C{\equiv}CR^1)_2[M']$ unit. This can be seen in $\{[Ti](C{\equiv}CFc)_2\}PdPPh_3$ (**7e**), in which the ferrocenyl groups are bent below the alkynyl–metal plane [29]. To reduce steric interactions, the triphenylphosphine ligand, in return, lies above this plane. This contrasts with $\{[Ti](C{\equiv}CR^1)_2\}$-$MC_6H_2Ph_3$-2,4,6 (M = Cu: **13s**, $R^1 = SiMe_3$; **13t**, $R^1 = {}^t$Bu; M = Ag, **16e**: $R^1 = SiMe_3$), in which the R^1 groups are bent in opposite directions, while the aryl group remains in the alkynyl–metal plane (Fig. 9) [48,52].

The η^2-coordination of the alkynyl ligands in **4**–**19** to the [M′] moieties is accompanied by a lengthening of the C≡C triple bonds from approximately 1.20/1.21 Å, e.g. in $[Ti](C{\equiv}CR^1)_2$ (**1**: R = Ph, $SiMe_3$, ^{t}Bu), $[Zr](C{\equiv}CCH_3)_2$ (**2a**) and $[Hf](C{\equiv}CPh)_2$ (**3**), to 1.24–1.27 Å in **4**–**18** (Table 4). This weakening of the C≡C triple bonds by going from **1**–**3** to heteronuclear **4**–**18** is additionally confirmed by IR spectroscopy (for a detailed discussion see Section 2.1.3.2).

As a consequence of the wealth of X-ray structure analyses carried out on single crystals of complexes **4**–**19**, especially of the monomeric copper(I), silver(I) and gold(I) species, a detailed discussion of tendencies is possible. With respect to the deformation of the Ti–C≡C and C≡C–R^1 angles, it must be noted that the whole series of $\{[Ti](C{\equiv}CR^1)_2\}M'X$ compounds (M′ = Cu, Ag, Au; X = singly bonded inorganic or organic ligand) show the following trend: an enhancement of the σ-donating properties of the ligand X (where X is either an inorganic or organic ligand) leads consistently to stronger distortions of the Ti–C≡C and C≡C–R^1 angles (Table 7).

Upon η^2-coordination of the alkynyl ligands C≡CR^1 of the $[Ti](C{\equiv}CR^1)_2$ fragment to a monomeric M′X entity in **11**–**17** (Table 1), a bond lengthening of the

C≡C triple bonds is observed (see above). However, the magnitude of the bond length increase is not significantly influenced by the ligands X at the M′ metal center (Table 7). However, IR and $^{13}C\{^1H\}$-NMR spectroscopic data show a clear correlation (for a detailed discussion see Section 2.1.3.2).

In $\{[Ti](C{\equiv}CR^1)_2\}M'X$ (M′ = Cu, Ag, Au; X = singly bonded inorganic or organic ligand; **11**–**17**) the Group XI metal center M′ has a formal 16-valence electron count [2,57,104]. The interatomic titanium–silver distances in **15** and **16** (Ti–Ag: 3.10–3.16 Å) are longer than either the corresponding titanium–copper distances found in **11**, **13** and **14** (Ti–Cu: 2.90–3.08 Å) or the titanium–gold distances found in **17** (Ti–Au: 2.98–3.01 Å) (Table 7).

Similar observations were made for the copper-to-alkyne (Cu–C_α, Cu–C_β; Fig. 8) and silver-to-alkyne distances (Ag–C_α, Ag–C_β; Fig. 8) in isostructural complexes $\{[Ti](C{\equiv}CSiMe_3)_2\}M'X$ (M′ = Cu, Ag; X = OTf, Cl, $C_6H_2Me_3$-2,4,6, $C_6H_2(CF_3)_3$-2,4,6, $C_6H_2Ph_3$-2,4,6, O_2CPh, etc.). In these compounds the copper-to-alkyne distances are approximately 0.25 Å shorter than those found in the corresponding silver complexes. Similarly, the Group XI metal-to-carbon distances of the M′X (X = $C_6H_2Me_3$-2,4,6, $C_6H_2(CF_3)_3$-2,4,6, $C_6H_2Ph_3$-2,4,6) entities are approximately 0.5 Å shorter for the analogous copper compounds (Table 7). The same trend is found in other isostructural titanium–copper(I) and titanium–silver(I) complexes.

In general, the M′–C_R bond lengths in $(\eta^2\text{-alkyne})_2M'R$ (M′ = Cu, Ag, Au) fit perfectly into the range of bond lengths observed for two-electron two-center (2e–2c) bonding of coordinated Group XI metal atoms (Table 7). For a detailed discussion of typical metal–carbon bond lengths, see Refs. [2,96,105–107].

In compounds $\{[Ti](C{\equiv}CR)_2\}M'X$ (**11**, **13**–**17**, Table 1) the alkyne-to-M′ bonding contains two components. The first component is σ-donation of electron density from a filled π-orbital of the alkyne to a suitable empty orbital of the Group XI metal M′. The second component involves the back-donation of electron density from a filled d-orbital of the Group XI metal on an empty π*-orbital on the alkyne [2,5,69b,108–111].

The result of extended-Hückel calculations, which have been carried out on $\{(\eta^5\text{-}C_5H_5)_2Ti(C{\equiv}CH)_2\}M'C{\equiv}CH$ (M′ = Cu, Ag, Au), is shown for the gold(I)-containing species in Figs. 10 and 11 [69b].

The calculations show that the complexation of the AuR moiety with the organometallic π-tweezer $[Ti](C{\equiv}CR^1)_2$ is best described by a four-center two-electron bond [69b]. The monomeric organogold(I) fragments AuR are stabilized by a synergetic in-plane donation and back-donation of electron density between the bis(alkynyl) titanocene and the corresponding M′R species (vide supra). In addition, a direct donor–acceptor Au–Ti interaction contributes to this stabilization [69b].

As a result, the M′X unit can be described as a nucleophile in which M′ represents a metal of low Lewis acidity (electrophilicity) (type **B** molecule). This is confirmed by DFT calculations, which show a significant decrease in electron density in the CuX fragment upon coordination of the tweezer molecule [69b].

Metals with a higher electrophilicity, such as R'_2Pt, tend to coordinate preferentially to the C_α-atom of the $[Ti](C{\equiv}CR^1)_2$ fragment, giving rise to a bonding

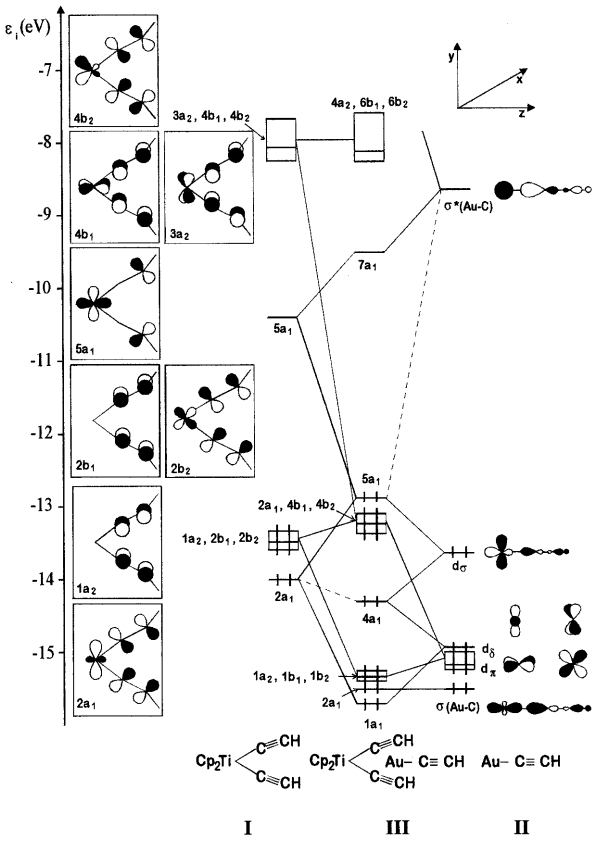


Fig. 10. Extended-Hückel interaction diagram between the valence molecular orbitals of **I** and **II** to give **III** [69b].

situation best described as μ-bridging of the C≡CR[1] fragments between two different metal centers such as titanium and platinum (type **C** molecules) (Fig. 12) (for a detailed discussion of type **C** molecules see Section 4) [6,7,112]. While electrophilic attack on a transition metal-bound alkynyl ligand normally takes place exclusively at the acetylide β-carbon, it must be noted that this is due to weak π-donation from the metal to the alkynyl ligand, which is not relevant in a d^0 Ti(IV) system.

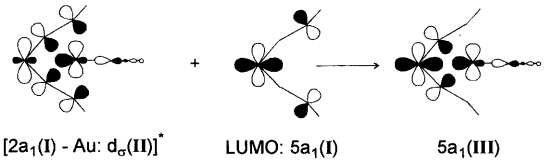


Fig. 11. Orbital mixing of [(2a_1(**I**)-Au: d_σ(**II**)]* and LUMO 5a_1(**I**) to give 5a_1(**III**) [69b].

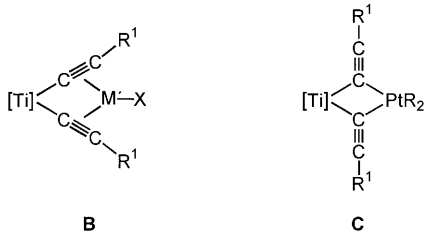


Fig. 12. Type **B** and **C** molecules, depending on the electrophilicity of the transition metal fragment M′X (M′ = Cu, Ag, Au; X = 2-electron anionic ligand; M′ = Ni, Co, Pd, Pt; X = CO, PR_3) or PtR_2 involved.

The influence of the σ-donating capacity of the ligands X in $\{[Ti](C{\equiv}CR^1)_2\}M'X$ (**11**–**17**) on the extend of back-donation becomes most obvious from the spectroscopic data of those molecules: stronger electron donating groups X result in lower C≡C stretching frequencies, higher C_α (Ti–C_α≡C) and lower C_β (Ti–C≡C_β) $^{13}C\{^1H\}$-NMR chemical shifts (Section 2.2) and greater distortion of the Ti–C≡C–R^1 entities from linearity. Moreover, the $\nu_{C\equiv C}$ frequencies correlate with the $^{13}C\{^1H\}$-NMR chemical shift of both the C_α and the C_β carbon nuclei of the C≡CR^1 ligands (Section 2.1.3.2).

The most striking feature about this set of data is the stronger influence on the $^{13}C\{^1H\}$-NMR chemical shift of the C_α than on that of the C_β atoms by replacement of an electron withdrawing group X by an electron donating ligand X or vice versa in heterobimetallic $\{[Ti](C{\equiv}CR^1)_2\}M'X$ (M′ = Cu, Ag) (for a detailed discussion, see Section 2.1.3.2).

2.1.3.2. Spectroscopy. As shown in Sections 2.1.1 and 2.1.2, $R^1C{\equiv}C{-}[M]{-}C{\equiv}CR^1$ (M = transition metal fragment, R^1 = singly bonded organic ligand) can be used as organometallic π-tweezers for the stabilization of monomeric low-valent transition metal moieties [M′]. In the so-assembled heterometallic compounds $\{[M](C{\equiv}CR^1)_2\}[M']$ (**4**–**19**, Table 1) the bis(alkynyl) transition metal fragments $M(C{\equiv}CR^1)_2$ are η^2-coordinated to the [M′] entities, as confirmed by manifold X-ray structure analyses (for a detailed discussion see Section 2.1.3.1). In addition, spectroscopic data (IR, ^{1}H-NMR and $^{13}C\{^1H\}$-NMR) give evidence for this bonding situation.

The NMR spectra of diamagnetic compounds **4**, **6**–**8**, **11**–**17**, **18d**, **18e** and **19** consist of well-resolved signals for each of the organic groupings present. The coupling patterns of several of these compounds (mainly the copper(I) and silver(I) species) were demonstrated to be essentially temperature independent within the range of 203–323 K. This finding is in agreement with monomeric structures of these compounds in solution, which is also confirmed by molecular weight determinations.

The $^{13}C\{^1H\}$-NMR spectra of the silver complexes provide direct information concerning the Ag–C bonding in $(\eta^2\text{-}C{\equiv}CR^1)_2AgX$ (X = singly bonded inorganic or organic ligand). Thus, the $^{13}C\{^1H\}$-NMR spectrum of compound

{[Ti](C≡CSiMe$_3$)$_2$}Ag(C$_6$H$_2$Me$_3$-2,4,6) (**16d**), a highly representative example of compounds **15** and **16** (Table 1), shows a typical splitting of the resonance signal for the Ag–C$_{ipso}$ atom: at 168.3 ppm two doublets due to coupling with ^{107}Ag and ^{109}Ag are found with $^1J(^{107}Ag, ^{13}C) = 142$ Hz and $^1J(^{109}Ag, ^{13}C) = 164$ Hz (Table 8) [5,60,113]. Similar observations were made for the C$_6$H$_2$Ph$_3$-2,4,6 and C$_6$H$_2$(CF$_3$)$_3$-2,4,6 analogues (compounds **16e** and **16f**) [52].

This observation indicates that the Ag–C$_{ipso}$ bond does not dissociate on the NMR time scale. These data are the first ^{107}Ag, ^{109}Ag coupling constant values for a two-electron two-center silver–carbon bond; ^3J(Ag, C) is also observed for the hydrogen-bearing carbon atoms of the aryl ligands. Examples of ^1J(Ag, C) values have been reported for two-electron three-center bonded aryl silver compounds and are significantly lower than those observed for **16d**–**16f** [96,114,115]. As further evidence for the π-coordination of the C≡CR^1 ligands to the silver centers in {[Ti](C≡CSiMe$_3$)$_2$}Ag(C$_6$H$_2$R$_3$-2,4,6) (**16d**–**16f**), the ^{13}C{^{1}H}-NMR signals for the alkynyl carbon nuclei show coupling to ^{107}Ag and ^{109}Ag nuclei. The C$_\alpha$ atoms show coupling to silver of between 5 and 10 Hz, while the C$_\beta$ atoms display a somewhat lower coupling ($^1J_{AgC} = 2$–5 Hz). Separate coupling constants to ^{107}Ag and ^{109}Ag nuclei could not be resolved [2,5,48,52,60].

A further remarkable feature about the ^{13}C{^{1}H}-NMR spectra of compounds **11** and **13**–**17** is the downfield shift for the C$_\alpha$ atoms and the upfield shift for the C$_\beta$ atoms upon η^2-coordination of the alkynyl ligands to the M′ atom in {[Ti](C≡CR^1)$_2$}[M′] (M′ = Cu, Ag, Au) (Table 8). As depicted in Fig. 13, the ^{13}C-NMR chemical shifts of the R^{1}C≡C ligands are almost linear with the ν(C≡C) frequencies.

Fig. 13 clearly shows that increasing the σ-donor strength of the ligand X in {[Ti](C≡CR^1)$_2$}M′X causes the resonance signals of the C$_\alpha$ atoms to shift downfield and the resonance signals of the C$_\beta$ atoms to shift to higher field (Fig. 13 and Table 8).

In the IR spectra of nearly all compounds listed in Table 1, a single C≡C stretching vibration is observed in the region of 1850–1980 cm^{-1}. This represents a distinct shift of the ν(C≡C) frequency from those of the parent compounds [M](C≡CR^1)$_2$ (**1**–**3**: 2010–2080 cm^{-1}) (Table 8) [2,10,12,13]. This shift resembles that generally observed for π-bonding of alkynes to transition metal fragments and reflects a weakening of the C≡C triple bonds [116–118].

Changing the monoanionic ligand X in compounds {[Ti](C≡CR^1)$_2$}M′X (**11**, **13**–**17**) from a weaker (e.g. X = OTf) to a stronger (e.g. X = C$_6$H$_2$Me$_3$-2,4,6) σ-donor, results in a distinct shift of the C≡C stretching vibration to lower frequencies (Table 8), which is ascribed to an increase in the back-donating component of the alkyne-to-copper interaction in the total bonding (Fig. 11). The deformation of the Ti–C≡C and C≡C–R^1 angles upon changing from the mononuclear bis(alkynyl) metallocene [Ti](C≡CR^1)$_2$ to the heterobinuclear species {[Ti](C≡CR^1)$_2$}M′X (Tables 1 and 7) also supports this conclusion, i.e. bending of the substituents of the C≡C unit becomes more significant with increasing σ-donation of the ligand X in {[Ti](C≡CR^1)$_2$}M′X (Table 7).

Table 8
Selected $^{13}C\{^1H\}$-NMR and IR data for compounds {[Ti](C≡CR^1)$_2$}[M′] (**1**, **11**–**17**)

Compound	M′	R^1	$^{13}C\{^1H\}$-NMR δ(C≡C) (ppm)	IR $\nu_{C\equiv C}$ (cm^{-1})	Refs.
1c		$SiMe_3$	C_α: 172.5; C_β: 135.4	2012	[12,65]
1e		^{t}Bu	C_α: 138.8; C_β: 139.7	2063	[12]
11w	Cu	$SiMe_3$	C_α: 173.6; C_β: 132.8	1901	[38]
11z	Cu	$SiMe_3$	C_α: 167.0; C_β: 135.0	1916	[48]
11aa	Cu	$SiMe_3$	C_α: 162.2; C_β: 140.2	1929	[49]
11bb	Cu	$SiMe_3$	C_α: 161.2; C_β: 139.4	1921	[50]
11ff	Cu	$SiMe_3$	C_α: 168.8; C_β: 134.1	1913	[48]
11ii	Cu	$SiMe_3$	C_α: 172.2; C_β: 136.3	1908	[52]
11jj	Cu	$SiMe_3$	C_α: 182.4; C_β: 129.3	1886	[52]
11mm	Cu	$SiMe_3$	C_α: 144.1; C_β: 150.2	1960	[49]
13a	Cu	$SiMe_3$	C_α: 203.6; C_β: 123.4	1867	[5]
13e	Cu	$SiMe_3$	C_α: 195.9; C_β: 128.3	1863	[56]
13i	Cu	$SiMe_3$	C_α: 199.3; C_β: 125.3	1868	[5]
13j	Cu	$SiMe_3$	C_α: 199.0; C_β: 126.0	1861	[5]
13k	Cu	$SiMe_3$	C_α: 199.3; C_β: 125.9	1862	[5]
13l	Cu	$SiMe_3$	C_α: 199.1; C_β: 126.0	1865	[5]
13m	Cu	$SiMe_3$	C_α: 200.1; C_β: 125.7	1863	[5]
13o	Cu	$SiMe_3$	C_α: 199.8; C_β: 148.0	1857	[58]
13q	Cu	$SiMe_3$	C_α: 184.2; C_β: 129.4	1887	[2]
13r	Cu	$SiMe_3$	C_α: 185.9; C_β: 130.2	1877	[52]
13s	Cu	$SiMe_3$	C_α: 195.8; C_β: 126.3	1858	[52]
13w	Cu	$SiMe_3$	C_α: 183.1; C_β: 128.6	1902/2095[a]	[51,59]
14b	Cu	$SiMe_3$	C_α: 170.9; C_β: 132.4	1901	[38]
14q	Cu	$SiMe_3$	C_α: 155.8; C_β: 137.5	1944	[64]
14r	Cu	$SiMe_3$	C_α: 174.1; C_β: 131.9	1911	[48]
14t	Cu	$SiMe_3$	C_α: 173.8; C_β: 131.2	1910	[48]
11c	Cu	^{t}Bu	C_α: 134.0; C_β: 150.5	1977	[47]
11m	Cu	^{t}Bu	C_α: 136.9; C_β: 150.7	1974	[44]
11nn	Cu	^{t}Bu	C_α: 141.1; C_β: 150.2	1960	[49]
13b	Cu	^{t}Bu	C_α: 169.1; C_β: 138.6	1909	[52]
13d	Cu	^{t}Bu	C_α: 172.1; C_β: 129.7	1907	[55]
13t	Cu	^{t}Bu	C_α: 159.4; C_β: 141.6	1926	[52]
13v	Cu	^{t}Bu	C_α: 149.6; C_β: 145.3	1944/2067[a]	[51,59]
13x	Cu	^{t}Bu	C_α: 151.7; C_β: 144.2	1941/2099[a]	[51,59]
13jj	Cu	^{t}Bu	C_α: 142.0; C_β: 148.7	1966/2039[a]	[48]
13kk	Cu	^{t}Bu	C_α: 147.2; C_β: 146.6	1954/2034[a]	[48]
13ll	Cu	^{t}Bu	C_α: 148.1; C_β: 145.9	1954/2052[a]	[45]
13mm	Cu	^{t}Bu	C_α: 150.3; C_β: 144.7	1946/2094[a]	[48]
15i	Ag	$SiMe_3$	C_α: 156.4; C_β: 140.8	1947	[48]
15k	Ag	$SiMe_3$	C_α: 150.3; C_β: 143.3	1956	[49]
15n	Ag	$SiMe_3$	C_α: 152.0; C_β: 134.6	1946	[50]
15p	Ag	$SiMe_3$	C_α: 170.6; C_β: 132.3	1945	[56]
15r	Ag	$SiMe_3$	C_α: 149.3; C_β: 127.2	1948	[48]
16a	Ag	$SiMe_3$	C_α: 185.7; C_β: 121.0	1905	[52]
16d	Ag	$SiMe_3$	C_α: 184.5; C_β: 125.6	1902	[57]
16e	Ag	$SiMe_3$	C_α: 177.5; C_β: 131.1	1914	[52]

Table 8 (*Continued*)

Compound	M′	R^1	$^{13}C\{^1H\}$-NMR δ(C≡C) (ppm)	IR $\nu_{C\equiv C}$ (cm^{-1})	Refs.
16f	Ag	$SiMe_3$	C_α: 166.7; C_β: 136.5	1930	[52]
16j	Ag	$SiMe_3$	C_α: 156.3; C_β: 137.4	1951	[52]
16k	Ag	$SiMe_3$	C_α: 155.8; C_β: 137.5	1944	[52]
16m	Ag	$SiMe_3$	C_α: 157.4; C_β: 134.1	1951	[48]
16n	Ag	$SiMe_3$	C_α: 155.3; C_β: 136.7	1948	[48]
16o	Ag	$SiMe_3$	C_α: 159.1; C_β: 135.0	1944	[48]
17a	Au	$SiMe_3$	C_α: 199.1; C_β: 122.6	1831	[69]
17b	Au	$SiMe_3$	C_α: 183.5; C_β: 123.5	1830	[69]
17c	Au	$SiMe_3$	C_α: 181.1; C_β: 122.0	1848/2054[a]	[69]
17d	Au	′Bu	C_α: 152.1; C_β: 138.5	1896/2069[a]	[69]

[a] Two C≡C bands appear in the IR spectrum due to the presence of an additional M′-bound alkynyl ligand.

2.2. *'Non-planar' molecules {[M](C≡CR¹)₂}[M′] (M and M′ non-coplanar)*

In contrast to planar tweezer complexes of structural type **B**, {[M](C≡CR^1)$_2$}[M′] (compounds **4**–**19**, Table 1) (Section 2.1) in which the M′ atom lies in the [M](C≡CR^1)$_2$ plane (Fig. 2(a)), in the heterobimetallic complexes {[M](C≡CR^1)$_2$}-[M′], where M represents heavier congeners of Group IX and X metals, the metal atom M′ lies out of the plane defined by the M(C≡CR^1)$_2$ fragment (Fig. 2(b)). These molecules are therefore referred to as 'non-planar' tweezer molecules.

2.2.1. *Synthesis*

Three main synthetic routes have been used for the preparation of non-planar heterobimetallic {[M](C≡CR^1)$_2$}[M′] compounds (M = Rh, Ir, Pd, Pt; M′ = Rh, Pd, Pt, Cu, Ag). The first method is the direct synthesis route, in which a source of M′ is added to the bis(alkynyl) complexes. The second method is the reaction of transition metal chlorides with copper(I) or silver(I) acetylides (indirect synthesis route). A third route, intermediate between the two, is the 'one-pot' reaction of a mixture of [M]Cl_2 and [M′]Cl with a basic solution of a terminal alkyne (R^1C≡CH).

2.2.1.1. Direct synthesis route. In accordance with the synthesis of the planar tweezer complexes {[M](C≡CR^1)$_2$}[M′] described in Section 2.1, alkynyl-substituted platinum compounds are suitable starting materials for the preparation of heterobimetallic compounds of type ({[Pt](C≡CR^1)$_2$}[M′])$^{m+m'}$ (**43**–**47**) in which the M′ atom lies out of the plane defined by the Pt(C≡CR^1)$_2$ core [112,119–126,128]. Thus, the reaction of {[Pt](C≡CR^1)$_2$}^{m} (**41a**: [Pt] = Pt(PPh_3)$_2$, **41b**: [Pt] = Pt(dppe), **41c**: [Pt] = Pt(cod), **41d**: [Pt] = Pt(bipy), **41e**: [Pt] = Pt(bipy′), **41f**: [Pt] = Pt(′Bu_2bipy), $m = 0$; **42**: [Pt] = Pt(C_6F_5)$_2$, $m = -2$) with transition metal fragments [M′]$^{m'}$ (such as [Pd(η^3-C_3H_5)Cl]$_2$, [CuBr], [AgSCN], [Pt(C_6F_5)$_2$(thf)$_2$] or [Rh(COD)Cl]$_2$) yield the binuclear neutral, cationic or anionic complexes ({[Pt](C≡CR^1)$_2$}[M′])$^{m+m'}$ (**43**–**47**) (Table 9).

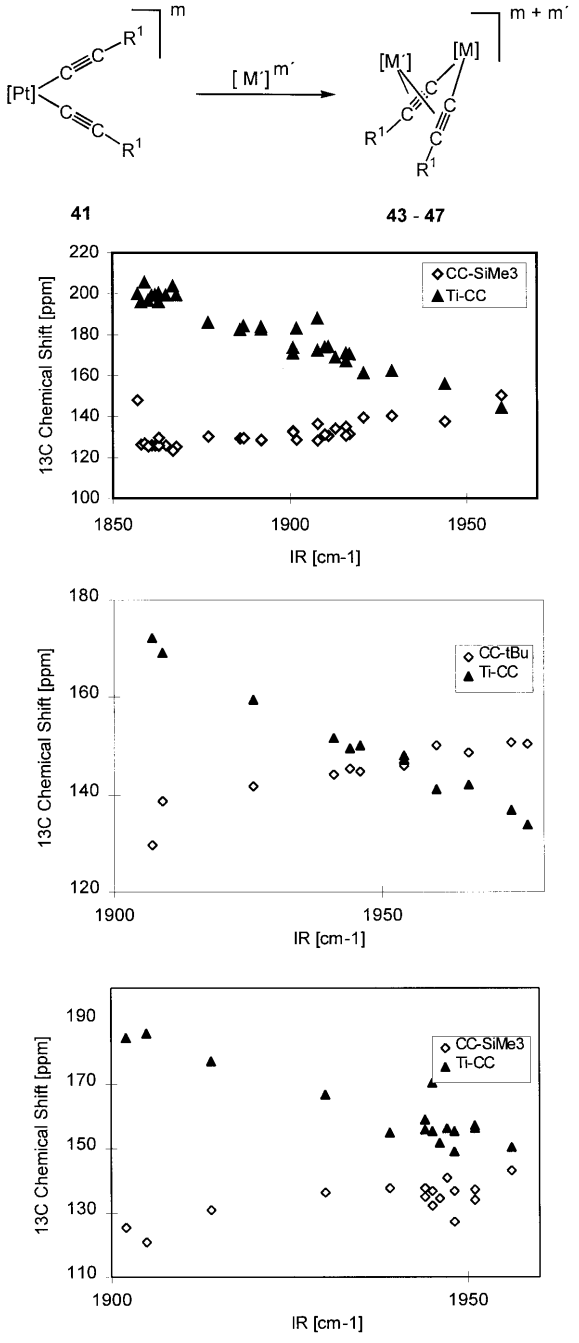


Fig. 13. Correlation between the $^{13}C\{^1H\}$-NMR chemical shifts of the C_α and C_β atoms with the C≡C stretching frequencies of selected compounds $\{[Ti](C{\equiv}CR^1)_2\}M'X$ (top, $M' = Cu$, $R^1 = SiMe_3$; center, $M' = Cu$, $R^1 = {}^tBu$; bottom, $M' = Ag$, $R^1 = SiMe_3$).

Table 9
Synthesis of non-planar compounds ({[Pt](C≡CR^1)$_2$}[M′])[X]$_n$

Compound	[M]	[M′]	R^1	[X]$_n$	Refs.
43a	$Pt(PPh_3)_2$	$Pd(\eta^3\text{-}C_3H_5)$	Ph	ClO_4	[112]
43b	$Pt(PPh_3)_2$	$Pd(\eta^3\text{-}C_3H_5)$	^{t}Bu	ClO_4	[112]
43c	$Pt(C_6F_5)_2$	$Pd(\eta^3\text{-}C_3H_5)$	Ph	$PMePh_3$	[112]
43d	$Pt(C_6F_5)_2$	$Pd(\eta^3\text{-}C_3H_5)$	^{t}Bu	NBu_4	[112]
43e	$Pt(C_6F_5)_2$	$Pd(\eta^3\text{-}C_3H_5)$	$SiMe_3$	NBu_4	[112]
43f	$Pt(C_6F_5)_2$	$Pt(\eta^3\text{-}C_3H_5)$	$SiMe_3$	NBu_4	[112]
43g	$Pt(C{\equiv}CR)_2$	$Pd(\eta^3\text{-}C_3H_5)$	Ph	NBu_4	[112]
43h	$Pt(C{\equiv}CR)_2$	$Pd(\eta^3\text{-}C_3H_5)$	^{t}Bu	NBu_4	[112]
43i	$Pt(C{\equiv}CR)_2$	$Pd(\eta^3\text{-}C_3H_5)$	$SiMe_3$	NBu_4	[112]
44a	$Pt(PPh_3)_2$	$Pt(C_6F_5)_2$	Ph		[119]
44b	$Pt(PPh_3)_2$	$Pt(C_6F_5)_2$	^{t}Bu		[119]
44c	Pt(dppe)	$Pt(C_6F_5)_2$	Ph		[119]
44d	Pt(dppe)	$Pt(C_6F_5)_2$	^{t}Bu		[119]
44e	Pt(cod)	$Pt(C_6F_5)_2$	Ph		[119]
44f	Pt(cod)	$Pt(C_6F_5)_2$	^{t}Bu		[119]
44g	$Pt(PPh_3)_2$	$Pd(C_6F_5)_2$	Ph		[119]
44h	$Pt(PPh_3)_2$	$Pd(C_6F_5)_2$	^{t}Bu		[119]
44i	$Pt(C_6F_5)_2$	$Pd(C_6F_5)_2$	^{t}Bu	$(NBu_4)_2$	[119]
45a	Pt(bipy)	CuCl	Ph		[73]
45b	Pt(bipy)	CuBr	Ph		[73]
45c	Pt(bipy)	CuI	Ph		[121]
45d	Pt(bipy)	$CuN{\equiv}CCH_3$	Ph	BF_4	[121]
45e	Pt(bipy)	$CuN{\equiv}CCH_3$	Ph	PF_6	[121]
45f	Pt(bipy′)	CuCl	Ph		[121]
45g	Pt(bipy′)	CuBr	Ph		[121]
45h	Pt(bipy′)	CuI	Ph		[121]
45i	Pt(bipy′)	CuOTf	Ph		[121]
45j	Pt(bipy′)	$CuNO_3$	Ph		[121]
45k	Pt(bipy′)	$CuN{\equiv}CCH_3$	Ph	ClO_4	[121]
45l	Pt(bipy′)	$CuN{\equiv}CCH_3$	Ph	BF_4	[121]
45m	Pt(^{t}Bu$_2$bipy)	CuSCN	$C_6H_4CH_3$-4		[122]
45n	Pt(^{t}Bu$_2$bipy)	CuSCN	$SiMe_3$		[122]
45o	$Pt(PPhMe_2)_2$	CuCl	^{t}Bu		[123]
45p	Pt(dppe)	CuCl	Ph		[123]
45q	Pt(dppe)	CuCl	^{t}Bu		[123]
45r	Pt(dppe)	$CuN{\equiv}CCH_3$	Ph	BF_4	[123]
46a	Pt(bipy)	AgO_2CCF_3	Ph		[121]
46b	Pt(bipy)	$AgNO_2$	Ph		[121]
46c	Pt(bipy)	$AgClO_4$	Ph		[121]
46d	Pt(bipy′)	$AgNO_2$	Ph		[121]
46e	Pt(bipy′)	$AgNO_3$	Ph		[121]
46f	Pt(bipy′)	$AgBF_4$	Ph		[121]
46g	Pt(bipy′)	AgO_2CCH_3	Ph		[121]
46h	Pt(bipy′)	$AgO_2C_7H_5$	Ph		[121]
46i	Pt(bipy′)	Ag(acac)	Ph		[121]
46j	Pt(bipy′)	$AgCH(C(O)Ph)_2$	Ph		[121]
46k	Pt(bipy′)	$AgCH(C(O)^tBu)_2$	Ph		[121]

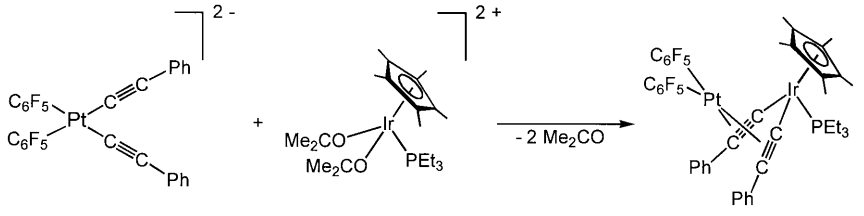
-

Table 9 (*Continued*)

Compound	[M]	[M′]	R^1	$[X]_n$	Refs.
46l	Pt(bipy′)	$AgCH(C(O)CF_3)_2$	Ph		[121]
46m	Pt(^{t}Bu$_2$bipy)	AgSCN	$C_6H_4CH_3$-4		[122]
46n	Pt(^{t}Bu$_2$bipy)	AgSCN	$SiMe_3$		[122]
47a	$Pt(C_6F_5)_2$	Rh(cod)	Ph	PPh_3Me	[128]
47b	$Pt(C_6F_5)_2$	Rh(cod)	^{t}Bu	NBu_4	[128]
47c	$Pt(C_6F_5)_2$	Rh(cod)	$SiMe_3$	NBu_4	[128]
48a	$(\eta^5\text{-}C_5Me_5)RhP(C_2H_5)_3$	$Pd(C_6F_5)_2$	Ph		[126]
48b	$(\eta^5\text{-}C_5Me_5)RhP(C_2H_5)_3$	$Pd(C_6F_5)_2$	$SiMe_3$		[126]
48c	$(\eta^5\text{-}C_5Me_5)IrP(C_2H_5)_3$	$Pd(C_6F_5)_2$	Ph		[126]
48d	$(\eta^5\text{-}C_5Me_5)IrP(C_2H_5)_3$	$Pd(C_6F_5)_2$	$SiMe_3$		[126]
48e	$(\eta^5\text{-}C_5Me_5)IrP(C_2H_5)_3$	$Pt(C_6F_5)_2$	Ph		[125,126]
48f	$(\eta^5\text{-}C_5Me_5)IrP(C_2H_5)_3$	$Pt(C_6F_5)_2$	$SiMe_3$		[126]
50a	$Ir(PPh_3)_2(C{\equiv}CC_6F_5)_2$	$CuPPh_3$	C_6F_5		[130]
50b	$Ir(PPh_3)_2(C{\equiv}CC_6F_5)_2$	$AgPPh_3$	C_6F_5		[130]
50c	$Rh(PPh_3)_2(C{\equiv}CC_6F_5)_2$	$AgPPh_3$	C_6F_5		[130]
61a	$Pt(C_6F_5)_2$	$AgPPh_3$	Ph	NBu_4	[124]
61b	$Pt(C_6F_5)_2$	$AgP(C_2H_5)_3$	Ph	NBu_4	[124]
61c	$Pt(C_6F_5)_2$	$AgPPh_3$	^{t}Bu	NBu_4	[124]
61d	$Pt(C_6F_5)_2$	$AgP(C_2H_5)_3$	^{t}Bu	NBu_4	[124]
61e	$Pt(C_6F_5)_2$	$1/2Ag_2$(dppe)	Ph	NBu_4	[124]
61f	$Pt(C_6F_5)_2$	$1/2Ag_2$(dppe)	^{t}Bu	NBu_4	[124]

In a similar fashion, bis(alkynyl)-rhodium or -iridium centers, such as $(\eta^5\text{-}C_5Me_5)M(PEt_3)(C{\equiv}CR^1)_2$ (M = Ir, Rh; R^1 = Ph, $SiMe_3$) will react with $M'(C_6F_5)_2(thf)_2$ (M′ = Pt, Pd) to give the complexes $\{(\eta^5\text{-}C_5Me_5)(Et_3P)M(C{\equiv}CR^1)_2\}M'(C_6F_5)_2$ (**48a**–**48f**) (Table 9) [125,126]. Attempts to make the analogous Rh–Pt complexes in this fashion, however, led to the transfer of one alkynyl ligand from rhodium to platinum and the formation of the type **D** complex $(\eta^5\text{-}C_5Me_5)(Et_3P)Rh(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^2{:}\eta^1\text{-}C{\equiv}CR^1)Pt(C_6F_5)_2$ (Section 4.3) [126].

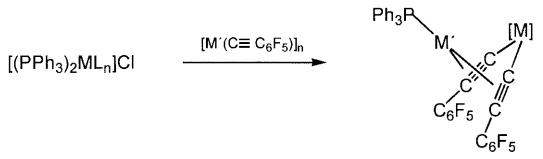
Alkynyl transfer between metal centers is also observed in the reaction of $(PMePh_3)_2[cis\text{-}(C_6F_5)_2Pt(C{\equiv}CPh)_2]$ with in situ generated $[(\eta^5\text{-}C_5Me_5)Ir(PEt_3)(Me_2CO)_2](ClO_4)_2$, which gives the neutral heterobinuclear species $[(\eta^5\text{-}C_5Me_5)(Et_3P)Ir(C{\equiv}CPh)_2Pt(C_6F_5)_2]$ (**48e**) in 60% yield [125,126]. In this reaction, both alkynyl ligands have been transferred to the iridium center from the $(C_6F_5)_2Pt(C{\equiv}CPh)_2$ moiety.



48e

Halide-bridged monoalkynyl complexes of the general formula $\{(\eta^5\text{-}C_5Me_5)(Et_3P)M(C{\equiv}CR^1)X\}M'(C_6F_5)_2$ (**48g**–**48l**) can be prepared by the reaction of $[(\eta^5\text{-}C_5Me_5)(Et_3P)M(C{\equiv}CPh)X]$ (M = Rh, Ir; X = Cl, I) with $M'(C_6F_5)_2(thf)_2$ (M′ = Pd, Pt) [126]. The heterobinuclear compounds $\{(\eta^5\text{-}C_5Me_5)(Et_3P)M\text{-}(C{\equiv}CPh)X\}M'(C_6F_5)_2$ (M = Rh: **48g**: X = Cl, M′ = Pt; **48h**: X = Cl, M′ = Pd; M = Ir: **48i**: X = Cl, M′ = Pt; **48j**: X = Cl, M′ = Pd; **48k**: X = I, M′ = Pt; **48l**: X = I, M′ = Pd) are structurally analogous to the titanocene–copper complexes **26a**–**26i**, described in Section 2.1.1.3. (Table 3) [2,42,43,46].

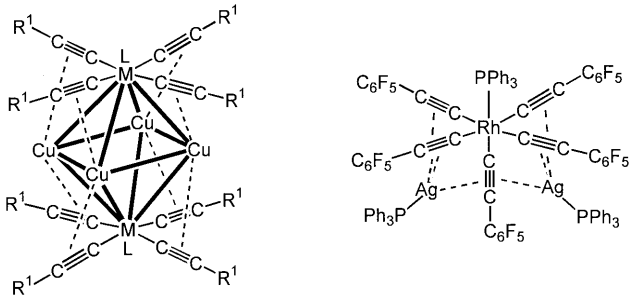
2.2.1.2. Indirect synthesis route. A further possibility for the synthesis of structural type **B** compounds in which the $\{M(C{\equiv}CR^1)_2\}M'$ core is distorted from planarity, is given by the reaction of transition metal chlorides with copper(I) or silver(I) acetylides. An early example of this synthetic method is the reaction of $[(PPh_3)_2ML_nCl]$ [**49a**: ML_n = Ir(CO), **49b**: ML_n = Rh(PPh$_3$)] with $[M'C{\equiv}CC_6F_5]_n$ (M′ = Cu, Ag) in refluxing acetone (Table 9) [130].



49 **50**

50a: [M] = Ir(PPh$_3$)$_2$(C≡CC$_6$F$_5$)$_2$, M′ = Cu
50b: [M] = Ir(PPh$_3$)$_2$(C≡CC$_6$F$_5$)$_2$, M′ = Ag
50c: [M] = Rh(PPh$_3$)$_2$(C≡CC$_6$F$_5$)$_2$, M′ = Ag

In addition to compounds **50a**–**50c**, two further products, the hexanuclear clusters $\{(PPh_3)M_2(C{\equiv}CC_6F_5)_8\}M'_4$ (M = Ir, Rh; M′ = Cu, Ag) (**51**) and the trinuclear compound $\{(PPh_3)Rh(C{\equiv}CC_6F_5)_5\}\{Ag(PPh_3)\}_2$ (**52**) are formed [2b,127,129,131].



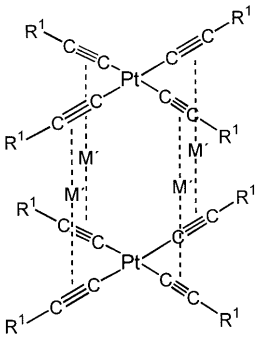
51 **52**

Clusters **51**, containing either iridium or rhodium as metal atoms M, are similar to $\{Pt_2(C{\equiv}CR^1)_8\}M'_4$ (M′ = Cu, Ag, Au; R^1 = Ph, ^{t}Bu) (**53a**–**53e**) (Table 10), which are accessible by the reaction of $PtCl_2(tht)_2$ with $[AgC{\equiv}CR^1]_n$ (**53a**, **53b**) or by the reaction of $[Pt(C{\equiv}CR^1)_4]^{2-}$ (**53c**–**53e**) with AuCl(tht) or $[CuCl]_n$ in dichloromethane or acetone [132].

Table 10
Synthesis of hexanuclear clusters $[\{Pt_2(C{\equiv}CR^1)_8\}M'_4]$ (**53**)[a1]

Compound	M′	R^1
53a	Cu	Ph
53b	Cu	ᵗBu
53c	Ag	Ph
53d	Ag	ᵗBu
53e	Au	ᵗBu

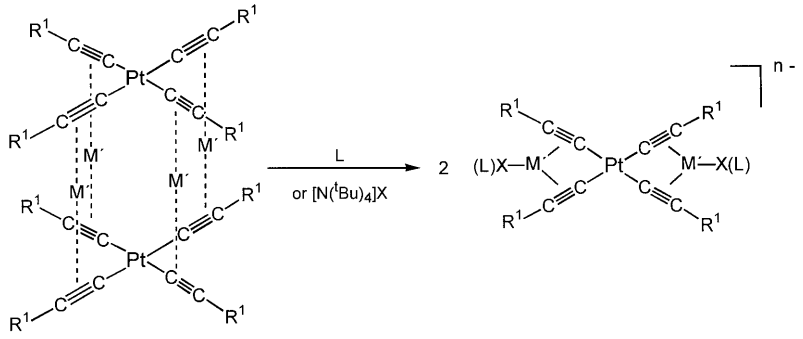
[a] See Ref. [132].



53

Moreover, clusters **53a**, **53b** and **53e** can be prepared by reacting hexanuclear **53c** or **53d** with $[AuCl]_n$ or $[CuCl]_n$ in acetone, resulting in displacement of silver [132]. As substructures, clusters **51** and **53** contain structural type **H** molecules (Fig. 14), which can be viewed as dimers of type **B** molecules.

A notable piece of work is the conversion of clusters **53a**–**53e** to heterobimetallic type **B** molecules, via structural type **H** systems [124,132–134]. Depending on the substrates and the organic groups R^1 present, different reaction products are formed. Whereas $\{Pt_2(C{\equiv}CPh)_8\}M'_4$ (M′ = Cu, Ag) (**53a**, **53c**) reacts with the Lewis bases L (L = C≡NᵗBu or C_5H_5N) in a 1:4 molar ratio to produce neutral $\{Pt(C{\equiv}CPh)_4\}(AgL)_2$ (**54a**: L = C≡NᵗBu, **54b**: L = C_5H_5N), with $[N^nBu_4]X$ (X = Cl, Br) ionic $[\{Pt(C{\equiv}CPh)_4\}(M'X)_2]^{2-}$ (**55a**–**55d**) is formed (Table 11) [124,132,134].



53a, **53c** **54**, **55**

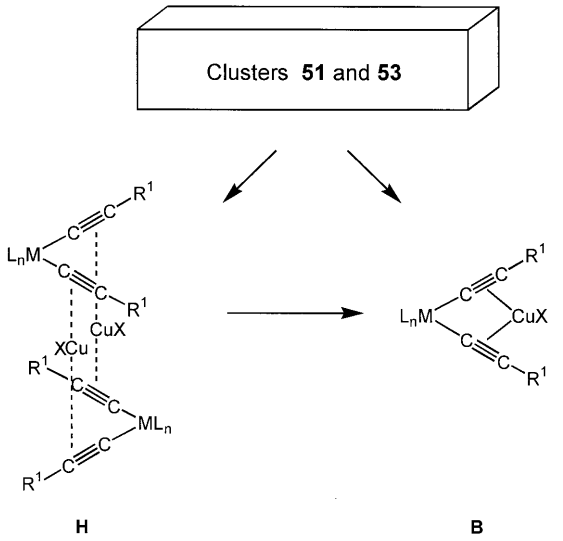


Fig. 14. Substructures of clusters **51** and **53** (top): Type **B** (bottom right) and type **H** molecules (bottom left).

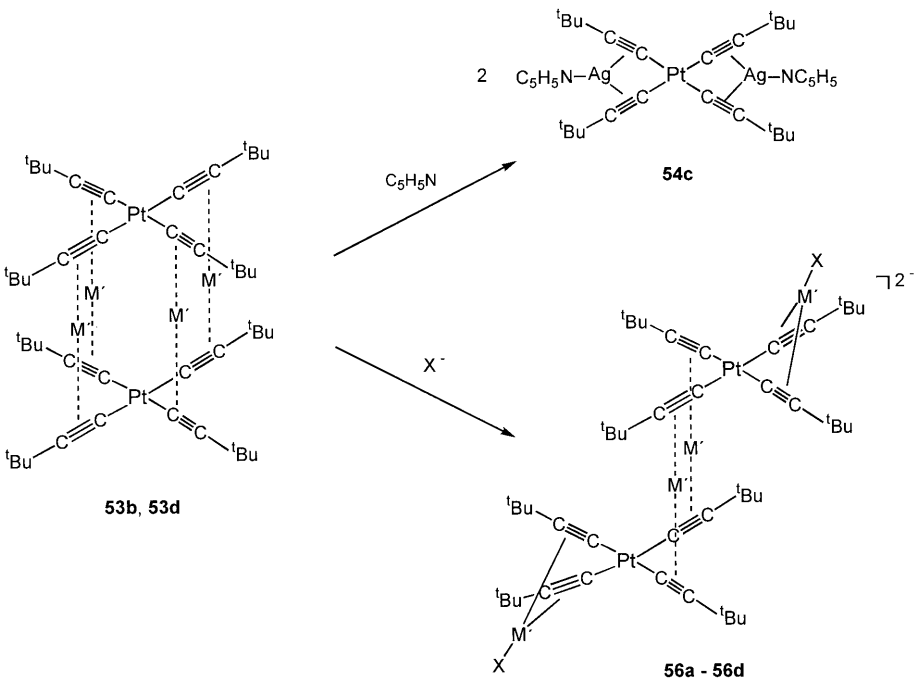
In contrast, the *t*-butyl substituted clusters $[Pt_2(C{\equiv}C^tBu)_8]M'_4$ (**53b**, **53d**) react with C_5H_5N or X^- (X = Cl, Br) to form the neutral compounds $\{Pt(C{\equiv}C^tBu)_4\}\{AgNC_5H_5\}_2$ (**54c**) (Table 11) or the hexanuclear dianionic complexes $[\{Pt_2(C{\equiv}C^tBu)_8\}M'_2\{M'X\}_2]^{2-}$ (**56a**: M′ = Cu, X = Cl; **56b**: M′ = Cu, X = Br; **56c**: M′ = Ag, X = Cl; **56d**: M′ = Ag, X = Br), respectively [134].

Table 11
Synthesis of $[\{Pt(C{\equiv}CR^1)_4\}(M'X)_2]^n$ (**54**, **55**)[a]

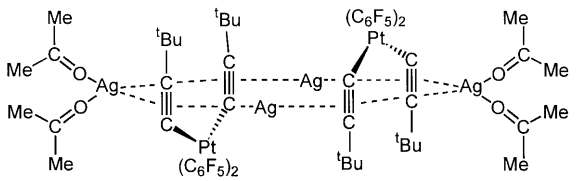
Compound	M′	X	R	*n*
54a	Ag	CN^tBu	Ph	0
54b	Ag	C_5H_5N	Ph	0
54c	Ag	C_5H_5N	^{t}Bu	0
54d	Pd	η^3-C_3H_5	Ph	0
54e	Pd	η^3-C_3H_5	$SiMe_3$	0
54f	Pd	η^3-C_3H_5	^{t}Bu	0
55a	Cu	Cl	Ph	−2
55b	Cu	Br	Ph	−2
55c	Ag	Cl	Ph	−2
55d	Ag	Br	Ph	−2

[a] See Refs. [124,132,134].

The neutral or dianionic trinuclear complexes **54** and **55** each contain a $Pt(C{\equiv}CR^1)_4$ fragment, chelating two M′X moieties with the resulting $\{Pt(C{\equiv}CR^1)_4\}(M'X)_2$ or $\{Pt(C{\equiv}CR^1)_4\}(M'L)_2$ species being distorted from planarity [132,134]. In **56a–56d** two dianionic $\{Pt(C{\equiv}C^tBu)_4\}M'X$ units are linked by two Group XI metal cations M'^+. These cations are π-bonded by two alkynyl groups of the $Pt(C{\equiv}C^tBu)_4$ fragments, retaining a linear coordination; the metal atoms M′ of the M′X units are η^2-coordinated by two alkynyl groups C≡C′Bu and η^1-bonded by a halide X (X = Cl, Br).



A similar geometrical environment around the metal centers M′ has been found in complexes such as the structurally characterized hexanuclear derivative $\{(C_6F_5)_4Pt_2(C{\equiv}C^tBu)_4\}Ag_2\{Ag(Me_2CO)_2\}_2$ (**57a**), which is formed by two identical $\{(C_6F_5)_2Pt(\mu\text{-}C{\equiv}C^tBu)_2\}Ag(Me_2CO)_2$ building blocks linked by two silver atoms [135,136].



57a

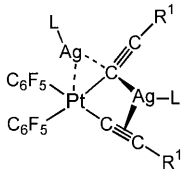
Table 12
Synthesis of $Q_2\{(C_6X_5)_2Pt(C{\equiv}CR^1)_2]M'\}_2$ (**59**)[a1]

Compound	M′	X	R^1	Q
59a	Ag	F	Ph	NBu_4
59b	Ag	F	^{t}Bu	NBu_4
59c	Ag	Cl	Ph	NBu_4
59d	Ag	Cl	^{t}Bu	NBu_4
59e	Ag	F	Ph	$PMePh_3$
59f	Cu	F	Ph	$PMePh_3$
59g	Cu	F	^{t}Bu	NBu_4

[a] See Ref. [133].

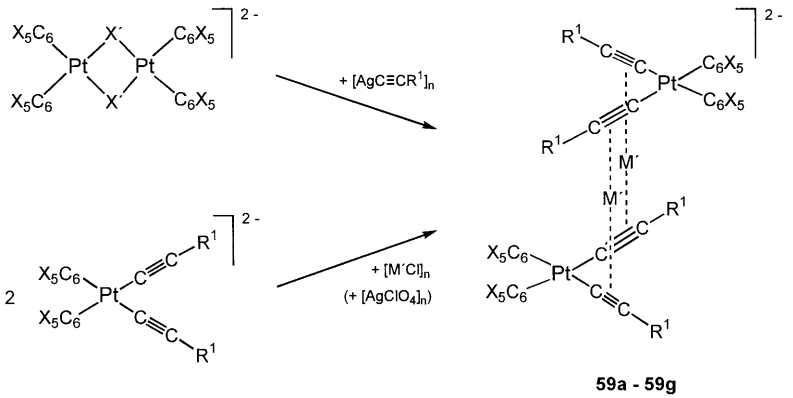
Molecule **57a** was produced by the reaction of acetone with polynuclear $[\{(C_6F_5)_2Pt(C{\equiv}C^tBu)_2\}Ag_2]_n$, which itself displays a polymeric structure thought to be based on square-planar *cis*-$(C_6F_5)_2Pt(C{\equiv}C^tBu)_2$ entities, connected by silver atoms η^2-bonded to the C≡C^{t}Bu ligands [135]. Moreover, it was found that on treatment of the polynuclear derivatives $[\{(C_6F_5)_2Pt(C{\equiv}CR^1)_2\}Ag_2]_n$ with neutral donor ligands L (L = PPh_3, $P(C_2H_5)_3$, C≡N^{t}Bu or C_5H_5N), two new types of platinum–silver complexes are formed, depending on the molar ratio of silver to ligand used. When one equivalent of ligand per silver atom is added, trinuclear $\{(C_6F_5)_2Pt(C{\equiv}CR^1)_2\}(AgL)_2$ [R^1 = Ph: **58a**: L = PPh_3, **58b**: L = $P(C_2H_5)_3$, **58c**: L = C≡N^{t}Bu, **58d**: L = C_5H_5N; R^1 = ^{t}Bu: **58e**: L = PPh_3, **58f**: L = $P(C_2H_5)_3$, **58g**: L = C≡N^{t}Bu, **58h**: L = C_5H_5N] is formed. However, when a 1:2 molar ratio is used, hexanuclear $\{(C_6F_5)_2Pt(C{\equiv}CR^1)_2\}Ag_2(AgL)_2$ (R^1 = Ph: **57b**: L = PPh_3, **57c**: L = $P(C_2H_5)_3$, **57d**: L = C≡N^{t}Bu, **57e**: L = C_5H_5N; R^1 = ^{t}Bu: **57f**: L = PPh_3, **57g**: L = $P(C_2H_5)_3$, **57h**: L = C≡N^{t}Bu, **54i**: L = C_5H_5N] results [135–137].

Trinuclear compounds **58a**–**58h** consist of one $(C_6F_5)_2Pt(C{\equiv}CR^1)_2$ moiety coordinating two AgL building blocks. The most remarkable feature of these complexes is that one of the AgL moieties is coordinated by both alkynyl ligands of the $(C_6F_5)_2Pt(C{\equiv}CR^1)_2$ entity, while the other silver center is bonded to the platinum atom and to one of the alkynyl ligands. As a consequence, one alkynyl ligand adopts a μ_3-σ-bridging mode, while the other is involved in a more common σ,π-coordination [137].



58a - 58h

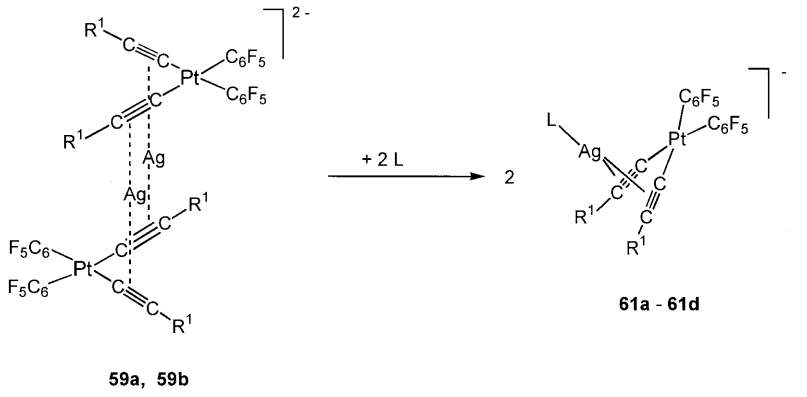
Compounds **59a**–**59g** (Table 12), which are related to **57a**–**57i**, are accessible either by the reaction of the square-planar d^8-platinum compounds $Q_2[Pt_2(\mu\text{-}X')_2(C_6X_5)_4]$ (X′ = Cl, Br; X = F, Cl) with $[AgC{\equiv}CR^1]_n$ or $Q_2[cis\text{-}(C_6X_5)_2Pt(C{\equiv}CR^1)_2]$ with $[M'Cl]_n$ (M′ = Cu, Ag) or $[AgClO_4]_n$ [133].



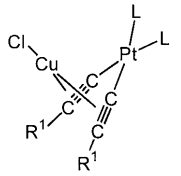
Cationic structural type **H** complexes containing platinum(II) and silver(I) ions can be prepared by reacting *cis*-$[Pt(C{\equiv}CR^1)_2]L_2$ with one equivalent of $AgClO_4$. Complexes $[Pt_2Ag_2(C{\equiv}CR^1)_4L_4](ClO_4)_2$ (**60a**: R^1 = Ph, L = PPh_3; **60b**: R^1 = Ph, L = PEt_3; **60c**: R^1 = Ph, L_2 = dppe; **60d**: R^1 = ^{t}Bu, L = PPh_3; **60e**: R^1 = ^{t}Bu, L_2 = dppe) are formed in yields between 50 and 85% (see also Section 2.2.1.4) [138].

Molecules of structural type **H** (compounds **59**, **60**) can formally be considered as dimers of type **B** molecules. In this respect, the dianionic tetranuclear platinum–silver compounds **59a** and **59b** were reacted with phosphanes PR_3 (R = C_6H_5, C_2H_5) in an attempt to break down these dimers [124,134,135]. When **59a** and **59b** are treated with PR_3 in a 1:2 or 1:4 molar ratio, the monoanionic non-planar tweezer complexes $\{(C_6F_5)_2Pt(C{\equiv}CR^1)_2\}AgL$ (**61a**: R^1 = Ph, L = PPh_3; **61b**: R^1 = Ph, L = PEt_3; **61c**: R^1 = ^{t}Bu, L = PPh_3; **61d**: R^1 = ^{t}Bu, L = PEt_3) are obtained, in which the alkynyl groups $C{\equiv}CR^1$ act as σ,π-bridges between the two transition metal atoms (Table 9) [124]

However, treatment of **59a** or **59b** with the bidentate phosphane dppe in a 1:1 molar ratio gives rise to the formation of the tetranuclear complex $[N^nBu_4]_2[\{(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR^1)_2Ag\}_2(\mu\text{-dppe})]$ (**61e**: R^1 = Ph, **61f**: R^1 = ^{t}Bu). In **61e** and **61f** two identical $(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR^1)_2Ag$ entities are linked by a dppe ligand; each silver atom possesses a trigonal coordination sphere, a consequence of the asymmetric η^2-coordination of each $C{\equiv}CR^1$ ligand and one phosphorus atom of the dppe ligand [124].



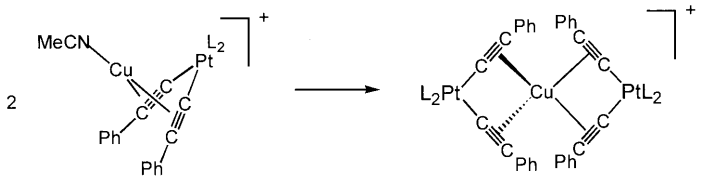
2.2.1.3. 'One-pot' synthesis route. Bis(alkynyl)-bridged platinum–copper complexes can also be obtained when [*cis*-L_2PtCl_2] is allowed to react with terminal alkynes and diethylamine in the presence of [CuCl], yielding $\{L_2Pt(C{\equiv}CR^1)_2\}CuCl$ (**45o**: $R^1 = {}^t$Bu, L = $PPhMe_2$; **45p**: R^1 = Ph, L_2 = dppe; **45q**: $R^1 = {}^t$Bu, L_2 = dppe) (Table 9) [123]. Presumably, this reaction proceeds through the in situ generation of $CuC{\equiv}CR^1$ and subsequent reaction of this species with the dichloroplatinum complex (as described in Section 2.2.1.2) [123].



45o - 45q

In the case of L = $PPhMe_2$, compound **45o** could only be obtained in low yield, using a threefold excess of the platinum complex. If a one-to-one stoichiometry is used, the resulting product is the polymeric [*trans*-$(PhMe_2P)_2Pt\{(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C'Bu)CuCl\}_2]_n$ [123b] In this compound, each alkynyl ligand of the $L_2Pt(C{\equiv}CR^1)_2$ moiety coordinates to a different copper atom, which is bound to the copper center on an adjacent moiety via two bridging chloride ligands [123b].

2.2.1.4. Synthesis of [{$L_2Pt(C{\equiv}CR^1)_2$}$_2$M′][X] complexes. When (dppe)$Pt(C{\equiv}CPh)_2$ is treated with $[Cu(MeCN)_4]BF_4$, the cationic complex $[\{L_2Pt(C{\equiv}CPh)_2\}$-$Cu(MeCN)]BF_4$ (**45r**) (L_2 = dppe) is obtained [123]. This species rearranges in an acetone–acetonitrile solution to give the trinuclear Pt_2Cu complex **62a** [123,138].



45r **62a**

Similar compounds could be prepared through direct reaction of bis(alkynyl) platinum complexes $[L_2Pt(C{\equiv}CR^1)_2]$ with a copper(I) or silver(I) salt M′X in a 2:1 mole ratio [121,123,138]. The resulting trinuclear species $[\{L_2Pt(C{\equiv}CR^1)_2\}_2M'][X]$ (**62b**: L_2 = bipy′, R^1 = Ph, M = Cu, X = BF_4; **62c**: L_2 = bipy, R^1 = Ph, M = Ag, X = BF_4; **62d**: L = PPh_3, R^1 = Ph, M = Ag, X = ClO_4; **62e**: L = PEt_3, R^1 = Ph, M = Ag, X = ClO_4; **62f**: L_2 = dppe, R^1 = Ph, M = Ag, X = ClO_4; **62g**: L = PPh_3,

$R^1 = {}^t$Bu, M = Ag, X = ClO_4; **62h**: L_2 = dppe, $R^1 = {}^t$Bu, M = Ag, X = ClO_4) are analogous to the dititanium complexes described in Section 2.1.2.3.1.

Unlike the binuclear platinum–silver and platinum–copper complexes described earlier, the M′ atom of the structurally-characterized trinuclear species **62a** lies only slightly out of the $Pt(C{\equiv}CR^1)_2$ plane, presumably to minimize steric interactions between the alkynyl R^1 groups and the phosphane ligands. Compound **62d**, which has also been structurally characterized, is asymmetric; the silver atom is significantly closer to one bis(alkynyl)platinum fragment than the other (Ag···Pt(1) = 3.384(1) Å, Ag···Pt(2) = 3.513(1) Å) and lies much closer to the platinum–alkynyl plane for Pt(2) (0.01 Å) than for Pt(1) (0.80 Å). The reasons for this asymmetry were not discussed [138].

2.2.2. Structure and bonding

In the non-planar heterometallic tweezer compounds of general type $\{[M](C{\equiv}CR^1)_2\}[M']$ (**43**–**48**, **50**, **54**, **55** and **61**) the bis(alkynyl) transition metal fragments $M(C{\equiv}CR^1)_2$ act as chelating ligands for the [M′] entities. However, the $M(C{\equiv}CR^1)_2M'$ segment of these compounds is distorted from planarity (for complexes $\{[M](C{\equiv}CR^1)_2\}[M']$, in which the M′ atom lies in the $M(C{\equiv}C)_2$ plane, see Section 2.1). Significant observations with respect to the alkyne-to-M′ interaction are:

1. bond weakening of the C≡C triple bond of the $R^1C{\equiv}C$ ligands;
2. bending of the M–C≡C–R^1 units upon η^2-coordination to the M′ center and;
3. diminution of the angle C_α–M–$C_{\alpha'}$.

Since these main aspects have already been discussed in detail in Section 2.1.3 for planar tweezer complexes of structural type **B**, $\{[M](C{\equiv}CR^1)_2\}[M']$, this section focuses only on general aspects of the non-planar tweezer species.

As already discussed for planar structural type **B** molecules (Section 2.1.3), the C≡C triple bond distances are lengthened upon η^2-coordination to the M′ centers. This is shown by numerous X-ray structure analyses and is supported by IR spectroscopy. In general, the IR spectra of the non-planar tweezer complexes $\{[M](C{\equiv}CR^1)_2\}M'X$ display a characteristic shift of the C≡C stretching vibration to lower wavenumbers, as compared to the non-coordinated starting materials. It is found that the $\nu_{C\equiv C}$ absorptions for the platinum–copper complexes are at lower frequencies than those of the analogous platinum–silver species, which indicates a weaker alkyne–metal interaction in the latter molecules. A similar trend has been observed for the tweezer molecules **11** and **13**–**16** listed in Tables 1 and 8 (Sections 2.1.1 and 2.1.3), as well as other analogous systems such as polymeric $[M'C{\equiv}CR^1]_n$ (M′ = Cu, Ag) aggregates and alkynyl-containing clusters of Group XI metals (Section 2.2.1.2, vide supra) [1,2,96,139,140].

With the exception of **48a**–**48f**, in which the alkynyl ligands are σ-coordinated to rhodium or iridium, X-ray structure analyses carried out on representative compounds (Table 13) (Fig. 15) affirm that the alkynyl ligands $C{\equiv}CR^1$ of the $Pt(C{\equiv}CR^1)_2$ fragments are each η^2-coordinated to a monomeric transition metal center M′. In all non-planar tweezer compounds reported, the metal atom M of the $L_2M(C{\equiv}CR^1)_2$ moieties are tetra-coordinate with a square-planar geometry, while the M′ centers are tri- or tetracoordinate.

Table 13
Selected X-ray data for non-planar tweezer complexes

Compound	M···M′ (Å)	M–C_α (Å)	M′–C_α (Å)	M′–C_β (Å)	M′–X (Å)	C≡C (Å)	C_α–M–$C_{\alpha'}$ (°)	M–C≡C (°)	C≡C–R^1 (°)	Refs.
43e	3.049(2)[a]	2.03(2) 1.99(2)	2.28(2) 2.29(2)	2.36(2) 2.35(2)	2.12(3) 2.10(3) 2.15(3)	1.20(3) 1.24(3)	81.8(7)	168(2) 168(2)	167(2) 166(2)	[112]
44c	3.27[b]	2.01(1) 1.98(1)	2.35(1) 2.28(1)	2.34(1) 2.27(1)	2.03(1) 2.03(1)	1.23(2) 1.23(2)	79.3(4)	167(1) 159(1)	165(1) 156(1)	[119]
45b	3.0343(6)[c]	1.966(5) 1.936(5)	2.193(5) 2.100(5)	2.328(5) 2.227(5)	2.3129(8)	1.207(6) 1.221(7)	84.8(2)	172.2(5) 173.1(4)	162.3(5) 166.1(5)	[73]
45m	3.148(2)[d]	1.971(12) 1.985(11)	2.156(11) 2.128(11)	2.254(11) 2.225(11)	1.908(9)	1.24(2) 1.20(1)	83.9(4)	175.5(9) 177(1)	162.8(11) 163.4(11)	[122]
45r	3.129(2)[e]	2.03(1) 2.022(9)	2.14(1) 2.18(1)	2.27(1) 2.29(1)	2.207(3)	1.22(2) 1.22(1)	84.6(4)	174(1) 174.0(9)	165(1) 166(1)	[123]
46n	4.779[f]	1.970(8) 1.960(8)	2.426(7) 2.458(8)	2.459(8) 2.536(7)	2.422(2)	1.224(11) 1.232(10)	87.0(3)	176.3(7) 178.9(7)	166.2(7) 170.7(7)	[122]
48e	3.51(1)	1.97(2) 1.99(2)	2.41(2) 2.46(2)	2.38(2) 2.30(2)	1.97(2) 2.00(2)	1.21(3) 1.21(3)		176.9(2) 160.9(2)	156.8(2) 154.2(2)	[125,126]
55b	2.945(2)[g]	2.020(8) 2.015(11)	2.157(11) 2.141(8)	2.338(10) 2.316(9)	2.298(2)	1.20(1) 1.21(2)	87.5(4)	172(1) 172.7(7)	168(1) 167.1(9)	[134]

Table 13 (*Continued*)

Compound	M···M′ (Å)	M–C_α (Å)	M′–C_α (Å)	M′–C_β (Å)	M′–X (Å)	C≡C (Å)	C_α–M–$C_{\alpha'}$ (°)	M–C≡C (°)	C≡C–R^1 (°)	Refs.
57a	2.950(1)	2.027(9)	2.221(9)	2.72(1)		1.20(1)	96.4(3)	168.5(8)	169(1)	[136]
	3.112(1)	2.044(9)	2.325(8)	2.69(1)		1.23(1)		173.8(7)	176(1)	
	3.106		2.437(8)	2.86(1)						
			2.224(9)	2.513(9)						
59a	3.106(1)	2.012(10)	2.257(9)	2.445(8)		1.22(1)	93.3(3)	176.6(8)	172.8(8)	[133]
		2.014(9)	2.225(7)	2.483(9)		1.21(1)				
61a	3.059(1)	2.012(7)	2.379(7)	2.679(7)	2.370(2)	1.240(9)	92.1(3)	170.9(6)	167.0(7)	[124]
			2.367(6)	2.545(7)		1.226(10)		177.8(6)	170.5(7)	
62a	3.133(5)[h]	2.01(3)	2.19(3)	2.41(3)		1.21(5)	90(1)			[123]
	3.088(5)	2.05(3)	2.24(3)	2.41(3)		1.22(4)	94(1)			
		2.00(3)	2.28(3)	2.49(3)		1.28(5)				
		2.02(3)	2.24(3)	2.39(4)		1.17(4)				
62d	3.384(1)	2.005(7)	2.367(7)	2.635(7)		1.212(10)	89.1(3)	169.4(7)	167.4(8)	[138]
	3.513(1)	2.007(7)	2.584(7)	2.709(7)		1.205(10)	88.5(3)	175.3(7)	171.6(8)	
		2.008(8)	2.498(7)	2.577(8)		1.196(19)		176.9(6)	166.1(8)	
		2.033(8)	2.506(8)	2.588(8)		1.189(11)		174.1(7)	166.9(9)	

[a] Dihedral angle: 123.4(2)°.
[b] Dihedral angle: 133.74°.
[c] Displacement of the copper atom out of the PtP_2 plane: 0.784(4) Å.
[d] Displacement of the copper atom out of the PtN_2 plane: 0.23 Å.
[e] Displacement of the copper atom out of the PtN_2 plane: 0.526 Å.
[f] Displacement of the silver atom out of the Pt_1N_2 plane: 0.44 Å.
[g] Displacement of the copper atoms out of the $Pt(CCR)_4$ plane: 0.905(2) Å (up and down).
[h] Displacement of the copper atom out of the PtP_2 plane: 0.120 Å, Pt_2P_2 plane: 0.086 Å.

The M···M′ distances are found in the range 2.9–3.5 Å, depending on the metal atoms M and M′ present, which indicates the absence of direct metal–metal interaction. The close proximity of M and M′ must be regarded simply as an effect due to the η^2-coordination of both C≡CR^1 ligands to the M′ center.

In addition to lengthening the alkynyl carbon–carbon triple bonds upon π-coordination to a metal center M′, a deformation of the ligand is also observed. The M–C_α–C_β angle is bent away from linearity, to allow the alkynyl β-carbon to approach the M′ center. The C_α–C_β–R^1 angle is more strongly affected, with the R^1 substituent bent away from the M′ center (Fig. 8) (Table 13). This is, however, not as pronounced as that found in planar tweezer complexes (Section 2.1). It must also be noted that in the non-planar tweezer complexes {[M](C≡CR^1)$_2$}M′X, the bite angle C_α–M–$C_{\alpha'}$ of the bis(alkynyl) transition metal fragments is also decreased as compared to the free [M](C≡CR^1)$_2$ starting materials. This is characteristic for organometallic tweezer complexes. In contrast, in compounds **57**, **59** and **62**, bite angles C_α–M–$C_{\alpha'}$ are found to be in the range 88–97° (Table 13).

In contrast to the planar tweezer complexes **4**–**19** (Table 1, Section 2.1) the non-planar molecules **43**–**47**, **54**–**59**, **61** and **62** possess an essentially square-planar platinum center, being part of the [Pt](C≡CR^1)$_n$ fragment ($n = 2, 4$). X-ray structure analyses confirm that the metal centers M′ in these complexes lie out of the plane defined by the platinum center and the α-carbons of the alkynyl ligands. Selected structures are shown in Fig. 15.

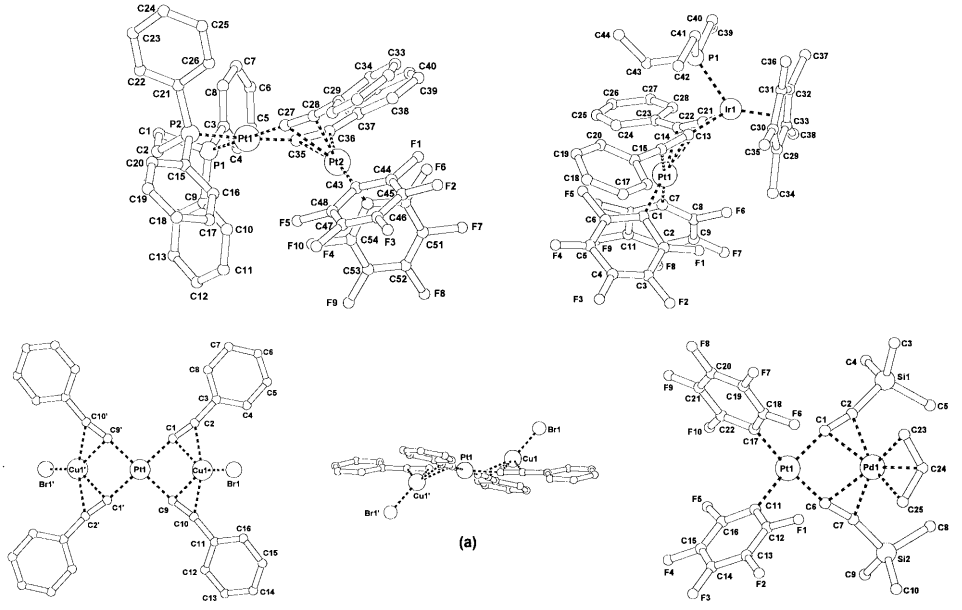
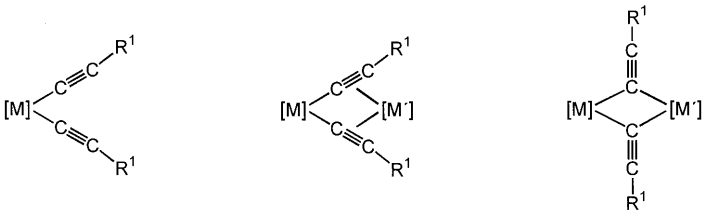


Fig. 15. Result of X-ray structure analyses of selected non-planar tweezer molecules [**44c** (top left), **48e** (top right), **55b** (bottom left; (a) perspective view showing the displacement of the CuBr unit out of the platinum coordination sphere), **43e** (bottom right)].

In contrast to the non-planar structures found in most platinum-based tweezer complexes, the mercury-containing compounds **19a**–**19n** were found to be nearly planar (the Hg atom lies only 0.076 Å out of the $Pt(C{\equiv}CR^1)_2$ plane) (Table 1, Section 2.1.1) [72].

3. Synthesis, structure and bonding of type C molecules, $[M](\mu,\eta^1\text{-}C{\equiv}CR^1)_2[M']$

Bis(alkynyl) transition metal complexes of structural type **A** can successfully be used as organometallic chelating ligands (organometallic π-tweezers) for the stabilization of monomeric low-valent [M′] moieties (Chapter 2). In the resulting heterobimetallic molecules of structural type **B** $\{[M](C{\equiv}CR^1)_2\}[M']$, the alkynyl ligands act as σ- and π-bridges between the transition metal centers M and M′.

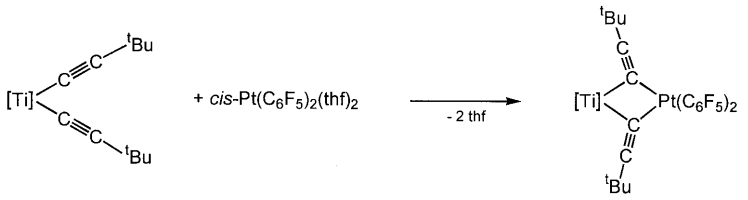


A **B** **C**

Depending on the nature of [M′], distinct coordination modes can be realized. When the transition metal M′ possesses nucleophilic character (i.e. is electron rich), coordination of polarized alkynyl ligands $C_\alpha{\equiv}C_\beta{-}R^1$ in type **A** molecules will occur via the C_β carbon atoms of the $C{\equiv}CR^1$ groups, thus forming structural type **B** molecules. In contrast, [M′] fragments containing M′ centers with a higher electrophilicity tend to bind more or less to the C_α atoms of the $[M](C{\equiv}CR^1)_2$ unit, giving rise to a bonding situation better described as an asymmetric μ,η-bridging of the $C{\equiv}CR^1$ groupings between M and M′ (type **C** molecule) [7,8]. Owing to their specific coordination characteristics, alkynyl ligands are additionally well-suited to link early transition metal centers and/or electropositive main group elements, thus forming stable $[M](\mu,\eta^1\text{-}C{\equiv}CR^1)_2[M']$ frameworks.

3.1. Synthesis

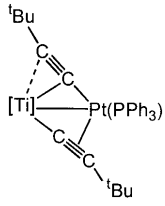
In the early work of Stone and co-workers, it was found that the reaction of $[Ti](C{\equiv}CPh)_2$ (**1f**) ($[Ti] = (\eta^5\text{-}C_5H_5)_2Ti$) with $Pt(PR_3)(H_2C{=}CH_2)_2$ affords the structural type **B** tweezer complexes $\{[Ti](C{\equiv}CPh)_2\}Pt(PR_3)$ (**8a**–**8e**) (Table 1) (Section 2.1) [30]. These molecules feature a platinum(0) atom as part of the heterobimetallic framework $\{Ti(C{\equiv}CPh)_2\}Pt$. However, when [*cis*-$Pt(C_6F_5)_2(thf)_2$] is used instead of $Pt(PR_3)(H_2C{=}CH_2)_2$, a structural type **C** molecule is obtained, due to the higher electrophilicity of the Pt^{2+} center [7]. In this respect, treatment of $[Ti](C{\equiv}C'Bu)_2$ (**1b**) $\{[Ti] = (\eta^5\text{-}C_5H_5)_2Ti\}$ with [*cis*-$Pt(C_6F_5)_2(thf)_2$] in a 1:1 molar ratio, produces the titanium–platinum compound $[Ti](\mu,\eta^1\text{-}C{\equiv}C'Bu)_2Pt(C_6F_5)_2$ (**63**).



1b **63**

IR spectroscopy and X-ray structure determinations show that **63** does not possess a structure typical for type **B** tweezer complexes (Sections 2.1.3.2 and 2.2.2) [7].

Besides electronic effects, the steric constraints of the organic groups R^1 of the alkynyl ligands $C{\equiv}CR^1$ and the ligands of the [M′] moieties have a certain influence on the structure of the products formed. They are normally either structural type **C**, **D** or **E** molecules (for a detailed discussion of the latter compounds see Section 4). However, in $\{[Ti](C{\equiv}C'Bu)_2\}Pt(PPh_3)$ (**64**), it is found that one C≡C′Bu group adopts a coordination mode which is intermediate between the σ,π-bridging and σ-bridging modes, while the other alkynyl ligand bridges the metal centers in a σ,π fashion [8].



64

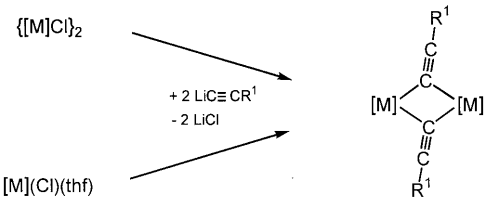
Compound **64** is obtained in the reaction of $[Ti](C{\equiv}C'Bu)_2$ (**1b**) $\{[Ti] = (\eta^5\text{-}C_5H_5)_2Ti\}$ with $[Pt(C_2H_4)(PPh_3)_2]$ in a titanium–platinum molar ratio of 1:1 [8]. This molecule is an impressive example of the steric effect of the organic groups R^1 of the alkynyl ligands, since the analogous phenylethynyl-substituted titanocene affords the tweezer complex $\{[Ti](C{\equiv}CPh)_2\}Pt(PPh_3)$ (**8d**) [30]. This is a structural type **B** molecule, in which both alkynyl ligands bridge the two metal centers in the σ,π-coordination mode (Section 2.1.1) (Table 1).

Complex **63** $([Ti](\mu,\eta^1\text{-}C{\equiv}C'Bu)_2Pt(C_6F_5)_2)$ is the first example of a dinuclear structural type **C** molecule in which both alkynyl ligands C≡C′Bu act as σ-bridges to two different transition metal centers, such as titanium(IV) and platinum(II) [7]. The only other examples of transition metal complexes that have been shown to adopt type C structure are dicopper complexes [141]. The first of these is $[(Cy_3P)Cu\text{-}(\mu,\eta^1\text{-}C{\equiv}C'Bu)_2Cu(PPh_3)_2]$ (**65a**) the structure of which has been confirmed by X-ray crystallography [141a]. In this species, the two alkynyl ligands are tilted somewhat towards the tetrahedral copper atom, presumably to avoid steric interac-

tions with the bulky tricyclohexylphosphine ligand, which (unlike the two triphenylphosphine ligands) is coplanar with the alkynyl ligands. In a second series of type **C** dicopper complexes $[Cu_2(\mu,\eta^1\text{-}C{\equiv}CR^1)_2L_4]$ (**65b**: L = PPh_2Me, R^1 = Ph; **65c**: L = 1/2 μ-dppf, R^1 = Ph; **65d**: L = 1/2 μ-dppf, $R^1 = C_6H_4CH_3$-4; **65e**: L = 1/2 μ-dppf, $R^1 = CH_2OCH_3$; **65f**: L = 1/2 μ-dppf, $R^1 = {}^n$Pr; **65g**: L = 1/2 μ-dppf, R^1 = Fc), both copper centers are in tetrahedral environments [141b,c]

All other crystallographically-characterized examples of such complexes involve either main group elements (compounds **66**) or f-orbital centers (compounds **67**) (Table 14) [142–153,157]. These compounds can mainly be synthesized by two general methods, depending on the nature of the metal atoms involved:

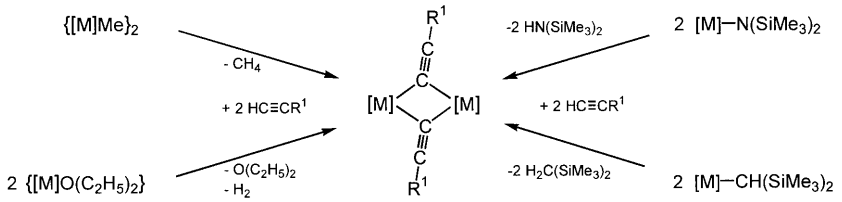
(1) by a metathesis reaction of dimeric $\{[M]Cl\}_2$ or monomeric [M](Cl)(thf) with $LiC{\equiv}CR^1$



66, 67

and

(2) by the reaction of $\{[M]Me\}_2$, $[M]CH(SiMe_3)_2$ or $[M]O(C_2H_5)_2$ with terminal alkynes $HC{\equiv}CR^1$.



66, 67

All compounds $[M](\mu,\eta^1\text{-}C{\equiv}CR^1)_2[M]$ (**66**: M = main group element; **67**: M = lanthanide metal atom) reported so far are summarized in Table 14. It is interesting to note that, whereas $[(\eta^5\text{-}C_5H_4Me)_2Sm(C{\equiv}C'Bu)]_2$ (**67a**) contains two σ-bridging alkynyl ligands, the permethyl complex $[(\eta^5\text{-}C_5Me_5)_2Sm(C{\equiv}C'Bu)]_2$ is bridged by agostic interactions with the hydrogen atoms of the C_5Me_5 methyl groups and contains terminal alkynyl ligands [151]. In contrast, the phenylethynyl complex $[(\eta^5\text{-}C_5Me_5)_2Sm(C{\equiv}CPh)]_2$ undergoes carbon–carbon bond formation and adopts a structure similar to those found in type **E** complexes (Section 4) [151a].

A polymeric complex of composition $[YbH(C{\equiv}C^nBu)_3]_n$ (**67z**) can be obtained through cocondensation of ytterbium vapor with 1-hexyne. This compound is thought to contain both hydride and $\eta^1{:}\eta^1$-alkynyl bridges [152b].

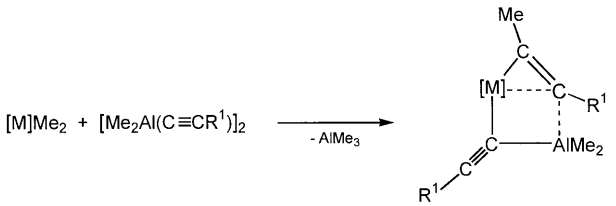
Table 14
Synthesis of selected main group and lanthanide compounds [M](μ-C≡CR[1])$_2$[M] (**66**, **67**)

Compound	[M]	R[1]	Type	Refs.
66a	(tmpda)Li	Ph	**C**	[142]
66b	$Me_2Al[N(^iC_3H_7)_2]_2Mg$	Ph	**C**	[143a]
66c	$Me_2Al[N(^iC_3H_7)_2]_2Mg$	$C_6H_4CH_3$-4	**C**	[143a]
66d	$Me_2Al[N(^iC_3H_7)_2]_2Mg$	^{t}Bu	**C**	[143a]
66e	$Me_2Al[N(^iC_3H_7)_2]_2Mg$	$SiMe_3$	**C**	[143a]
66f	$Me_2Al[N(C_2H_5)_2]_2Mg$	Ph	**C**	[143a]
66g	$Me_2Al[N(C_2H_5)_2]_2Mg$	$C_6H_4CH_3$-4	**C**	[143a]
66h	$\{\eta^5$-$C_5H(^iC_3H_7)_4\}$(thf)Ca	Ph	**C**	[144]
66i	$(Me_3N)(Me)Be$	Me	**C**	[145]
66j	$(Me_3N)(MeC{\equiv}C)Be$	Me	**C**, **D**	[145]
66k	Me_2Al	Me	**D**	[143c]
66l	Me_2Al	$^cC_6H_{11}$	**D**	[146]
66m	Me_2Al	^{t}Bu	**D**	[146]
66n	Me_2Al	$SiMe_3$	**D**	[146]
66o	Me_2Al	Ph	**D**	[146]
66p	Ph_2Al	Ph	**D**	[143b,d]
66q	Ph_2Al	^{n}Bu	**D**	[143d]
66r	Me_2Ga	Me	**D**	[149]
66s	Me_2Ga	Ph	**D**	[147,150]
66t	Me_2In	Me	**D**	[149]
66u	Me_2In	Ph	**D**	[150]
66v	$(\eta^5$-$C_5H_5)_2Sc$	Ph	[a]	[148]
67a	$(\eta^5$-$C_5H_4Me)_2Sm$	^{t}Bu	**C**	[151]
67b	$(\eta^5$-$C_5Me_5)Eu(thf)_2$	Ph	**C**	[152a]
67c	$(\eta^5$-$C_5H_5)_2Gd$	Ph	[a]	[153]
67d	$(\eta^5$-$C_5H_4^tBu)_2Gd$	Ph	**C**	[153d]
67e	$(\eta^5$-$C_7H_{11})_2Gd$[b]	Ph	**C**	[164]
67f	$(\eta^5$-$C_5H_5)_2Er$	^{t}Bu	[a]	[154a,156]
67g	$(\eta^5$-$C_5H_5)_2Er$	Ph	[a]	[153c]
67h	$(\eta^5$-$C_7H_{11})_2Er$[b]	Ph	**C**	[164]
67i	$(\eta^5$-$C_5H_4Me)_2Yb$	^{t}Bu	[a]	[151,154a]
67j	$(\eta^5$-$C_5H_5)_2Yb$	Ph	[a]	[153,155]
67k	$(\eta^5$-$C_5H_5)_2Yb$	^{n}Bu	[a]	[155]
67l	$(\eta^5$-$C_5H_5)_2Yb$	$^nC_6H_{13}$	[a]	[155]
67m	$(\eta^5$-$C_5H_5)_2Yb$	C_5H_{11}	[a]	[155]
67n	$(\eta^5$-$C_5H_5)_2Yb$	Fc[c]	[a]	[155]
67o	$[PhC(NSiMe_3)_2]_2Y$	H	**C**	[157]
67p	$[PhC(NSiMe_3)_2]_2Y$	CH_3	**C**	[157]
67q	$[PhC(NSiMe_3)_2]_2Y$	$^nC_3H_9$	**C**	[157]
67r	$[PhC(NSiMe_3)_2]_2Y$	$SiMe_3$	**C**	[157]
67s	$[PhC(NSiMe_3)_2]_2Y$	^{t}Bu	**C**	[157]
67t	$[PhC(NSiMe_3)_2]_2Y$	Ph	**C**	[157]
67u	$(\eta^5$-$C_5H_5)_2Ho$	Ph	[a]	[153,154]
67v	$(\eta^5$-$C_5H_5)_2Nd$	^{n}Bu	[a]	[155]
67w	$(\eta^5$-$C_5H_5)_2Nd$	$^nC_6H_{13}$	[a]	[155]
67x	$(\eta^5$-$C_5H_5)_2Nd$	Fc[c]	[a]	[155]
67y	$(\eta^5$-$C_5H_4^tBu)_2Nd$	Ph	**C**	[153d]

[a] The structures of these compounds are not known with certainty, however, their spectral characteristics are consistent with a type **C** structure.
[b] C_7H_{11} = 2,4-dimethylpentadienyl.
[c] Fc = Ferrocenyl.

A well-defined trinuclear complex, $[\{(\eta^5\text{-}C_5Me_5)_2Yb(C{\equiv}CPh)_2\}_2Yb]$ (**67aa**), is obtained in the reaction of $(\eta^5\text{-}C_5Me_5)_2Yb(OEt_2)$ with phenylacetylene. This species is structurally related to the previously described trinuclear species **20** (Section 2.1.1.1) and **62** (Section 2.2.1.4) and can be viewed as a Yb(II) cation coordinated by two anionic Yb(III) tweezer molecules [152].

In the broader sense of the application of acetylides as bridging groups in binuclear complexes, the work of Erker and co-workers, concerning the synthesis and structural characterization of the aluminum–zirconium and aluminum–hafnium compounds **68a**–**68h**, must be mentioned. They have extensively made use of the suitability of bridging σ-acetylides to link electropositive main group elements and/or transition metal atoms to construct stable heterobimetallic molecules [103,146,158]. These complexes can best be prepared by treatment of $[M]Me_2$ {$[M] = (\eta^5\text{-}C_5H_5)_2Zr$, Hf} with $[Me_2Al(C{\equiv}CR^1)]_2$ (R^1 = singly bonded organic ligand) (Table 15).



68a - 68h

In the aluminum-containing complexes **68a**–**68h**, a square-planar coordination geometry of carbon atoms that involve sp^2-hybridized carbon centers is found, which form a three-center two-electron bond to the appropriate metal atoms in the σ-plane. Three ligands at the planar tetra-coordinate carbon atom (Al, R^1, CMe) thereby serve as σ-donors, while the zirconocene or hafnocene unit [M] acts as a strong σ-acceptor by using its empty valence orbital in the central σ-ligand plane for bonding. Moreover, a small additional contribution resulting from a conjugative interaction between the metallocene building blocks and the neighboring C=C double bond, which aids stabilization of this extraordinary coordination geometry around the carbon atom, is discussed [158].

Table 15
Synthesis of compounds $[M](\mu\text{-}\eta^1{:}\eta^2\text{-}MeC{\equiv}CR^1)(\mu\text{-}C{\equiv}CR^1)AlMe_2$[a]

Compound	[M]	R^1
68a	$(\eta^5\text{-}C_5H_5)_2Zr$	Ph
68b	$(\eta^5\text{-}C_5H_4Me)_2Zr$	Ph
68c	$(\eta^5\text{-}C_5H_5)_2Zr$	$^cC_6H_{11}$
68d	$(\eta^5\text{-}C_5H_5)_2Zr$	^{t}Bu
68e	$(\eta^5\text{-}C_5H_5)_2Zr$	$SiMe_3$
68f	$(\eta^5\text{-}C_5H_5)_2Hf$	Ph
68g	$(\eta^5\text{-}C_5H_5)_2Hf$	$^cC_6H_{11}$
68h	$(\eta^5\text{-}C_5H_5)_2Hf$	$SiMe_3$

[a] See Refs. [146,158].

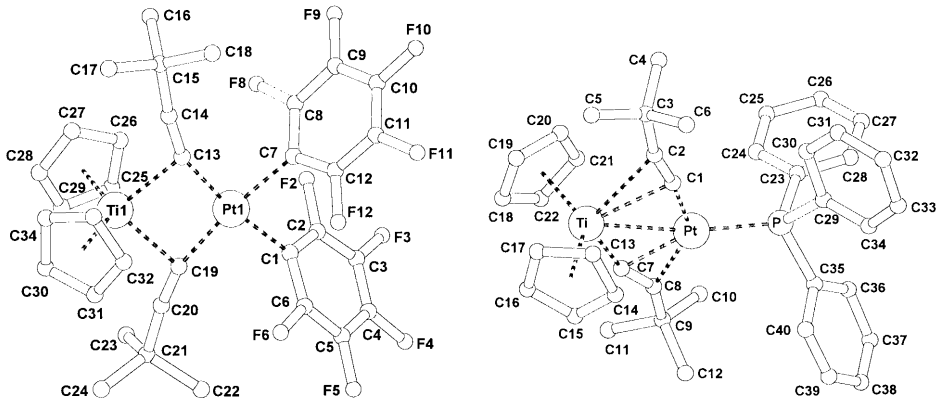


Fig. 16. Molecular geometry and atom numbering scheme for compounds **63** [7] (left) and **64** [8] (right). Selected bond distances (Å) and angles (°) are as follows. **63**: Ti–C(13), 2.26(1); Ti–C(19), 2.24(1); Pt–C(13), 2.01(1); Pt–C(19), 2.02(1); Pt–C(1), 2.043(9); Pt–C(7), 2.059(9); C(13)–C(14), 1.23(3); C(19)–C(20), 1.20(2); Ti–Pt, 2.831(2); Ti–C(13)–Pt, 82.8(4); Ti–C(19)–Pt ,83.2(4); C(13)–Ti–C(19), 89.8(4); C(13)–Pt–C(19), 103.8(4); C(1)–Pt–C(7), 85.7(4); Pt–C(13)–C(14), 158.1(8); Ti–C(13)–C(14), 118.8(7); Pt–C(19)–C(20), 161.5(9); Ti–C(19)–C(20), 115.1(8); C(13)–C(14)–C(15), 172(1); C(19)–C(20)–C(21), 173(1). **64**: Ti–Pt, 2.789(3); Ti–C(1), 2.435(14); Ti–C(2), 2.795(14); Ti–C(7), 2.102(14); Pt–C(1), 1.990(13); Pt–C(7), 2.054(13); Pt–C(8), 2.191(15); C(1)–C(2), 1.197(19), C(7)–C(8), 1.236(19); Pt–P, 2.247(3); Ti–C(7)–C(8), 163.8(12); C(1)–C(2)–C(3), 165.7(16); C(7)–C(8)–C(9), 147.8(15).

*3.2. Structure and bonding of compounds **63–67***

In complexes **63–67** acetylide ligands C≡CR[1] link two transition metal and/or main group centers in a μ,η^1-fashion [7,8,142–147,147,149–157]. IR studies as well as X-ray structure determinations were used to confirm this coordination mode.

The infrared spectra of transition metal complexes containing σ,π-bridging alkynyl ligands (such as type **B** molecules) display $\nu_{C\equiv C}$ stretching frequencies in the range 1830–1960 cm^{-1} (Table 8, Section 2.1.3.2). In complexes where an alkynyl ligand bridges two transition metals in the σ,η^1 mode, the shift to lower frequency is not nearly so pronounced. The heterobimetallic type **C** compound **63**, for example, gives rise to a $\nu_{C\equiv C}$ absorption band at 2042 cm^{-1}, which is only 20 cm^{-1} lower than the corresponding $\nu_{C\equiv C}$ absorption in the mononuclear bis(alkynyl)titanocene [Ti](C≡C′Bu)$_2$ (**1b**) [7]. This significant difference in behavior allows the two binding modes to be distinguished through IR spectroscopy [7].

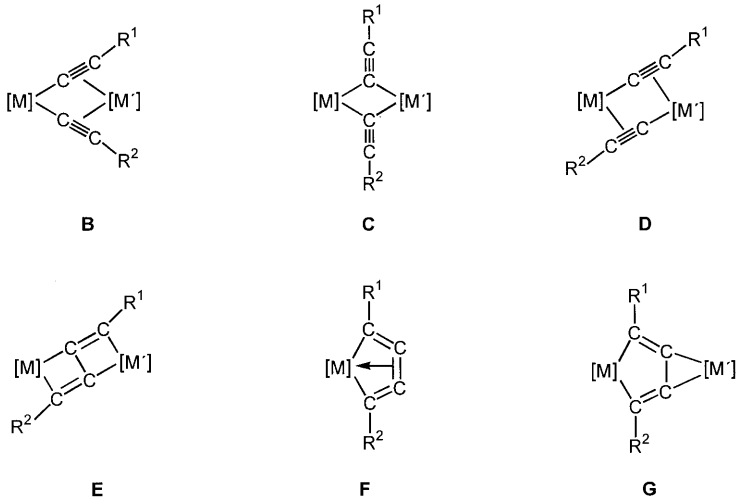
The result of the X-ray structure analysis on single crystals shows that compound **64** [8] represents a structural configuration intermediate between type **B** and **C** molecules. Both C≡C′Bu groups are π-bonded to a platinum and a titanium atom, differing in the strength of bonding: the platinum–carbon distances of 2.054(13) and 2.191(15) Å are relatively short and thus indicate a strong alkyne-to-platinum interaction (Fig. 16, right), whereas the alkyne-to-titanium distances at 2.435(14) and 2.795(14) Å imply a weaker bond providing mainly σ-character. Moreover, in complex **64**, the titanium–platinum distance (2.789(3) Å) is shorter than those typically found in type **B** molecules and is attributed to a dative platinum–titanium interaction.

A single-crystal X-ray diffraction study of heterobimetallic **63** showed that the two C≡C′Bu ligands are asymmetrically σ-bonded (μ,η^1) to a titanium(IV) and platinum(II) center (Fig. 16, left) [7]. The metal–carbon interatomic bond distances clearly show that σ-bonding dominates in the interaction of the bridging C≡C′Bu ligands and the appropriate metal atoms (Ti–C(13): 2.26(1), Ti–C(19): 2.24(1), Pt–C(13): 2.01(1), Pt–C(19): 2.02(1) Å) (Fig. 16, left). The metal–carbon distances show that the platinum–carbon σ-bonds are stronger than the corresponding titanium–carbon σ-bonds.

4. Synthesis, structure and bonding of type D, [M](μ-η^1:η^2-C≡CR^1)(μ-η^2:η^1-C≡CR^2)[M′]; E, [M](μ-η$^{(1-3)}$: η$^{(2-4)}$-R^{1}C=C–C=CR^2)[M′]; F, [M](η^4-R^{1}C=C=C=CR^2) and G Molecules, [M](μ-η$^{(1-4)}$: η$^{(2-3)}$-R^{1}C=C–C=CR^2)[M′]]

The bonding arrangements of type **B** and **C** molecules are documented in Sections 2 and 3, respectively. A third coordination mode involving two bridging alkynyl ligands has been observed in molecules of structural type **D**. In this bridging mode, two alkynyl groups, C≡CR^1 and C≡CR^2 (R^1 = R^2, R^1 ≠ R^2) are each σ-bonded to a different metal atom (M and M′), as well as η^2-coordinated to the other metal atom (M′ and M, respectively).

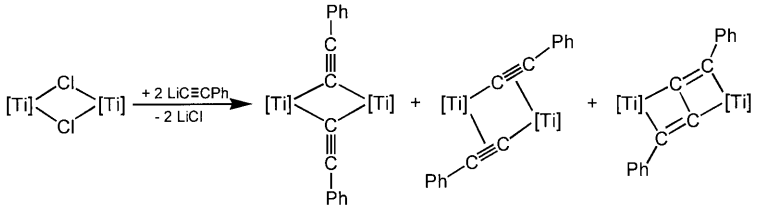
In compounds of structural type **E**–**G**, both alkynyl groups undergo a further transformation and couple in a 'head-to-head' fashion to form a butadiyne molecule, which bridges the two metal centers M and M′ (M = M′, M ≠ M′) (**E**, **G**). In type **E** molecules, the butadiyne bridges in a 'zigzag' fashion and is generally considered as a tetradehydro-μ-(1-3-η):(2-4-η)-*trans*,*trans*-butadiene ligand. In contrast, in type **F** molecules the butadiyne molecule binds to one metal center with the two outer carbon atoms, resulting in the formation of a five-membered metallacyclocumulene ring. The inner carbon–carbon double bond additionally coordinates to the metal atom M. Type **G** molecules have a similar framework, however, the inner carbon–carbon double bond is η^2-coordinated to a second metal center (M′), thus acting as a bridge between the two metals M and M′.



4.1. Structural type *D*–*G* molecules

4.1.1. Synthesis

4.1.1.1. Synthesis of titanium compounds. An interesting reaction, which enables the synthesis of structural type **C**, **D** and **E** molecules by starting out from $([Ti]Cl)_2$ (**69a**: $[Ti] = [(\eta^5\text{-}C_5H_4)_2SiMe_2]Ti$) was outlined by Royo and co-workers [9]. The products formed depend strongly on conditions such as solvent, temperature, time of reaction and presence of light.

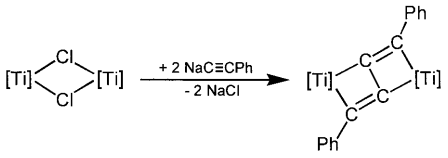


69a **70a** **71a** **72a**

When the reaction is carried out in a 1:1 molar titanium–lithium ratio in tetrahydrofuran at -40°C in the dark, the binuclear compound **70a** can be isolated; prolongation of reaction time selectively yields complex **71a**. When the reaction mixture is allowed to warm to 25°C, the initial red solution (containing complexes **70a** and **71a**) changes to dark green, the color of the tetradehydro-*trans*,*trans*-butadiene compound **72a**. A further possibility to regulate the product distribution is given by the choice of the solvent utilized. In acetone solution **71a** can be smoothly transformed into green **72a** [9].

Though all three complexes possess the same analytical composition, they strongly differ in their structures, as clearly shown by their spectroscopic data [9]. The kinetic product, complex **70a**, is paramagnetic and displays IR stretching frequencies characteristic for a σ-alkynyl ligand (2068 cm^{-1}). It was therefore proposed to have a type **C** structure, although a mononuclear structure {[Ti](C≡CPh)} could not be ruled out [9]. The titanium(III) centers in **70a** (whether mononuclear or binuclear) have a formal electron count of 15 valence electrons. To alleviate the resulting electron deficiency, this compound readily converts to the more thermodynamically stable complex **71a** even at low temperature [9]. The diamagnetic character of this species will be discussed in detail in Section 4.1.2. Intramolecular rearrangement of **71a** by means of an oxidative carbon–carbon coupling results in the formation of **72a**, a type **E** molecule with a central 'zigzag' butadiene entity [9].

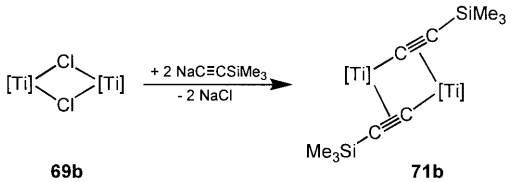
In a similar fashion, treatment of $[(\eta^5\text{-}C_5H_4R)_2TiCl]_2$ (**69b**: R = H, **69c**: R = CH_3) with NaC≡CPh in benzene or tetrahydrofuran at 25°C affords compounds **72b** and **72c**, respectively (Table 16) [159–161]. Unlike the reaction with **69a**, no alkynyl-bridged intermediates were observed in the preparation of these compounds.



69b, 69c **72b**: [Ti] = $(\eta^5\text{-}C_5H_5)_2Ti$

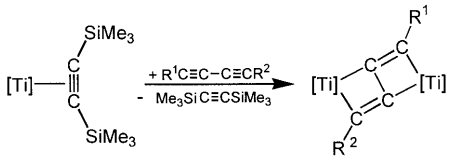
72c: [Ti] = $(\eta^5\text{-}C_5H_4CH_3)_2Ti$

In contrast, the titanium(III) chloride $\{[Ti]Cl\}_2$ $\{[Ti] = (\eta^5\text{-}C_5H_5)_2Ti\}$ (**69b**) reacts with a stoichiometric amount of $NaC{\equiv}CSiMe_3$ in diethyl ether at 0°C to produce the type **D** complex $\{[Ti](\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)\}_2$ (**71b**) [13f].



69b **71b**

Type **E** molecules can also be prepared by the reaction of $R^1C{\equiv}C{-}C{\equiv}CR^2$ (**22b:** $R^1 = R^2 = {}^t\text{Bu}$; **22c**: $R^1 = SiMe_3$, $R^2 = Ph$; **22d**: $R^1 = R^2 = Ph$; **22e**: $R^1 = SiMe_3$, $R^2 = {}^t\text{Bu}$; **22f**: $R^1 = R^2 = C{\equiv}CSiMe_3$) with $[Ti](\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ (**24a**) $\{[Ti] = (\eta^5\text{-}C_5H_5)_2Ti\}$ (Table 16) [3,26,76,161–163,165].



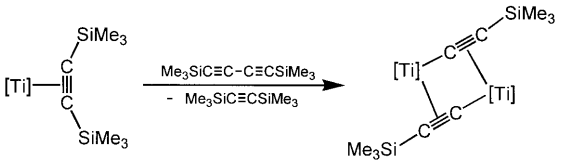
24a **72b, 72d - 72g**

It was found that the reaction mode of disubstituted 1,3-butadiynes $R^1C{\equiv}C{-}C{\equiv}CR^2$ with the in situ generated titanocene species [Ti] [166] strongly depends on the nature of the substituents R^1 and R^2 applied. With $R^1C{\equiv}C{-}C{\equiv}CR^2$ ($R^1 = R^2 = {}^t\text{Bu}$, Ph; $R^1 = SiMe_3$, $R^2 = Ph$; $R^1 = SiMe_3$, $R^2 = {}^t\text{Bu}$; and $R^1 = R^2 =$

Table 16
Synthesis of type **E** compounds $[Ti]_2(\mu\text{-}\eta^{(1-3)}{:}\eta^{(2-4)}\text{-}R^1C{=}C{-}C{=}CR^2)$ (**72a**–**72h**)

Compound	[Ti]	R^1	R^2	Refs.
72a	$[(\eta^5\text{-}C_5H_4)_2SiMe_2]Ti$	Ph	Ph	[9]
72b	$(\eta^5\text{-}C_5H_5)_2Ti$	Ph	Ph	[159,160,162]
72c	$(\eta^5\text{-}C_5H_4Me)_2Ti$	Ph	Ph	[160]
72d	$(\eta^5\text{-}C_5H_5)_2Ti$	^{t}Bu	^{t}Bu	[3,76,162,163]
72e	$(\eta^5\text{-}C_5H_5)_2Ti$	$SiMe_3$	Ph	[2,162]
72f	$(\eta^5\text{-}C_5H_5)_2Ti$	$SiMe_3$	^{t}Bu	[76,162]
72g	$(\eta^5\text{-}C_5H_5)_2Ti$	$SiMe_3$	$SiMe_3$	[162]
72h	$(\eta^5\text{-}C_5H_5)_2Ti$	$C{\equiv}CSiMe_3$	$C{\equiv}CSiMe_3$	[165]

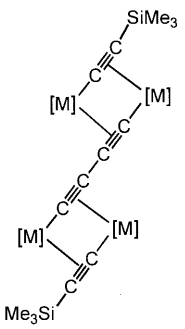
$C{\equiv}CSiMe_3$), the reaction products are binuclear with an intact 'zigzag' butadiene unit between the two titanium centers. However, in the case of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ (**22a**), cleavage of the carbon–carbon σ-bond of the 1,3-butadiyne occurs, resulting in the formation of the type **D** dimer $\{[Ti](\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)\}_2$ (**71b**) $\{[Ti] = (\eta^5\text{-}C_5H_5)_2Ti\}$ [3,162]. This reaction represents an oxidative addition of $Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3$ to the titanocene fragment [Ti] via cleavage of the central C–C bond. It must be noted that the formation of structural type **D** and/or **E** complexes in these reactions is independent of the oxidation state of the starting materials; the same products are obtained when [Ti] is allowed to react with $R^1C{\equiv}C{-}C{\equiv}CR^1$ as when [Ti]Cl is allowed to react with $NaC{\equiv}CR^1$. Thus, it is clear that these products are the thermodynamic products, rather than kinetic ones.

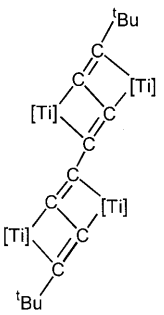


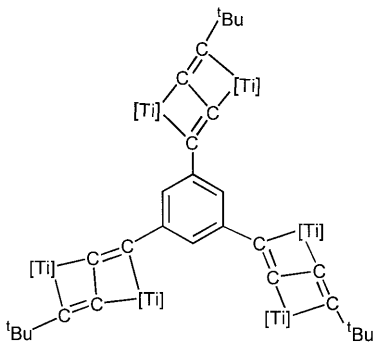
24a **71b**

Although a particular system may favor the formation of structure **E** over **D**, there is evidence to suggest that the internal carbon–carbon bond of the butadiene ligand of a type **E** molecule may be broken through photolysis, with the complex $[Ti]_2(\mu\text{-}\eta^{(1\text{-}3)}{:}\eta^{(2\text{-}4)}\text{-}R^1C_4R^1)$ reversibly dissociating into unstable $[Ti]C{\equiv}CR^1$ monomers. Photolysis of a mixture of $\{[Ti](\mu\text{-}C{\equiv}CSiMe_3)\}_2$ (**71b**) and $[Ti]_2(\mu\text{-}\eta^{(1\text{-}3)}{:}\eta^{(2\text{-}4)}\text{-}{}^t\!BuC_4'Bu)$ (**72d**) leads to the formation of the asymmetric type **E** molecule $[Ti]_2(\mu\text{-}{}^t\!BuC_4SiMe_3)$ (**72f**), in addition to starting materials.

The octatetrayne $Me_3SiC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}CSiMe_3$ (**22f**), as mentioned above, reacts with two molecules of the titanocene generator **24a** to form the type **E** complex **72h** (Table 16). If two more equivalents of titanocene are added, however, carbon–carbon bond cleavage occurs, giving the tetranuclear type **D** complex **74** (shown below) [165]. The analogous reaction with ${}^t\!Bu{-}(C{\equiv}C)_4{-}{}^t\!Bu$, which contains *t*-butyl rather than trimethylsilyl groups, proceeds differently, giving the tetranuclear 'double zigzag' **75** [165]. Similarly interconnected type **E** complexes **76** can be formed by the reaction of titanocene sources with poly(butadiynyl) molecules such as $C_6H_3(C{\equiv}CC{\equiv}C{}^t\!Bu)_3$-1,3,5 [167].







74: M = Ti
73: M = Zr

75 **76**

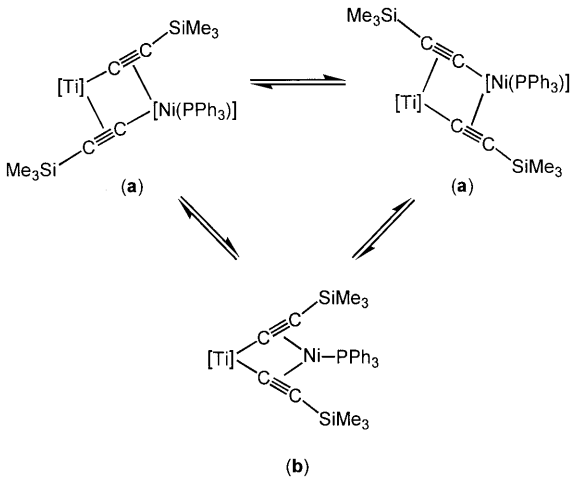
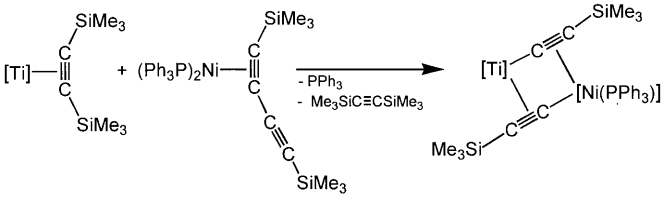


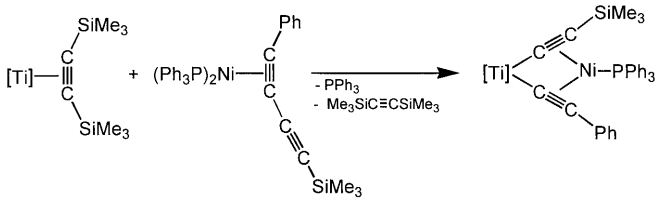
Fig. 17. Exchange of ligands, C≡CSiMe$_3$, between unsymmetrical [top, (**a**)] and symmetrical [bottom, (**b**)] structures of **78** [26].

In the same manner, heterobimetallic doubly alkynyl bridged complexes of type **D**, [Ti](μ-η^1:η^2-C≡CR^1)(μ-η^2:η^1-C≡CR^2)[M′], are accessible. A representative example is given by the reaction of [Ti](η^2-Me$_3$SiC≡CSiMe$_3$) (**24a**) with the butadiyne complex (PPh$_3$)$_2$Ni(η^2-Me$_3$SiC≡C–C≡CSiMe$_3$) (**23b**) in toluene at 50°C [3,26]. The titanium–nickel complex [Ti](μ-η^1:η^2-C≡CSiMe$_3$)(μ-η^2:η^1-C≡CSiMe$_3$)Ni(PPh$_3$) (**78**) is formed in 70% yield [26].

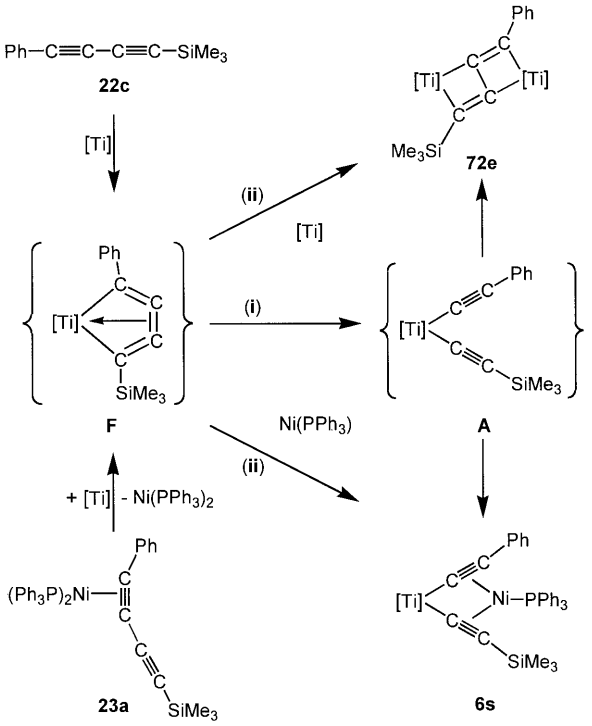


Both ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy indicates that **78** exists as a mixture of two isomers in solution; the alkynyl ligands are rapidly exchanged between the two metal centers, titanium and nickel, giving rise to the unsymmetrical type **D** (**a**) and symmetrical type **B** structure (**b**) (ratio **D**:**B** = 5:1) (Fig. 17) [26].

However, when compound **24a** is allowed to react with the nickel(0) complex (PPh$_3$)$_2$Ni(η^2-PhC≡C–C≡CSiMe$_3$) (**23a**), which contains an asymmetric butadiyne, the formation of the symmetrical compound **6s** (Table 1), a type **B** tweezer complex, is favored, presumably due to the reduced steric interactions resulting from replacement of a bulky trimethylsilyl group with a smaller phenyl substituent [26].



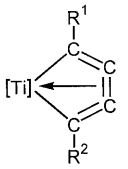
The different reaction pathways of [Ti](η^2-$Me_3SiC{\equiv}CSiMe_3$) with $PhC{\equiv}C–C{\equiv}CSiMe_3$ (formation of **72e**, Table 16) or with $(PPh_3)_2Ni(\eta^2$-$PhC{\equiv}C–C{\equiv}CSiMe_3)$ (formation of **6s**) are shown in Scheme 4. The key molecule in the formation of **6s** and **72e** was proposed to be a titanocene cyclocumulene of type **F**, for which the bis(*t*-butyl) analogue [Ti](η^4-^{t}BuC=C=C=C^{t}Bu) has been structurally characterized [3,26,76,168]. Intermediate **F** can react directly with a second titanium center to afford **72e** (Scheme 4, reaction pathway (ii)). Additionally, intermediate **F** may rearrange intramolecularly to give a tweezer molecule of structural type **A**, which can also react with a second titanium center to afford **72e** (Scheme 4, reaction pathway (i)). However, in presence of the transition metal fragment $Ni(PPh_3)$ (from the original complex $(PPh_3)_2Ni(\eta^2$-$PhC{\equiv}C–C{\equiv}CSiMe_3)$ (**23a)**), the bis(alkynyl) titanocene [Ti]($C{\equiv}CSiMe_3$)-



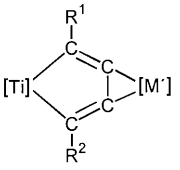
Scheme 4. Reaction behavior of [Ti] with $PhC{\equiv}C–C{\equiv}CSiMe_3$ or $(PPh_3)_2Ni(\eta^2$-$PhC{\equiv}C–C{\equiv}CSiMe_3)$ {[Ti] = $(\eta^5$-$C_5H_5)_2Ti$}; formation of heterobinuclear molecules **72e** and **6s** [26].

(C≡CPh) produces the titanium–nickel tweezer complex {[Ti](C≡CSiMe$_3$)(C≡CPh)}-Ni(PPh$_3$) (**6s**) [3,26]. It is likely that the nickel fragment Ni(PPh$_3$) acts as a trapping agent for an intermediate of the cleavage reaction.

Evidence for the intermediate formation of a structural type **G** molecule in the reaction of compound **24** with $R^1C{\equiv}C{-}C{\equiv}CR^2$ or $(PPh_3)_2Ni(\eta^2\text{-}R^1C{\equiv}C{-}C{\equiv}CR^2)$ is given by the isolation and characterization of type **F** molecules [Ti](η^4-$R^1C_4R^1$) (by reaction of [Ti](η^2-Me$_3$SiC≡CSiMe$_3$) with PhC≡C–C≡CPh or ^{t}BuC≡C–C≡C^{t}Bu) and type **G** molecules [Ti](μ-$\eta^{(1\text{-}4)}$:$\eta^{(2\text{-}3)}$-$R^1C_4R^2$)Ni(PPh$_3$)$_2$ (by reaction of [Ti](η^2-Me$_3$SiC≡CSiMe$_3$) with (PPh$_3$)$_2$Ni(η^2-PhC≡C–C≡CPh) [168].



F

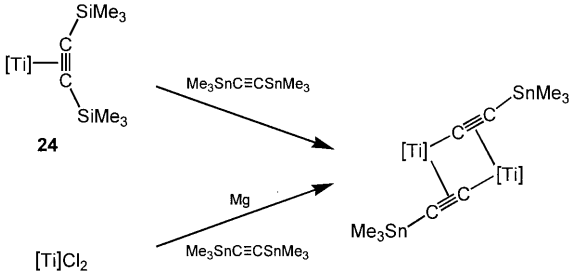


G

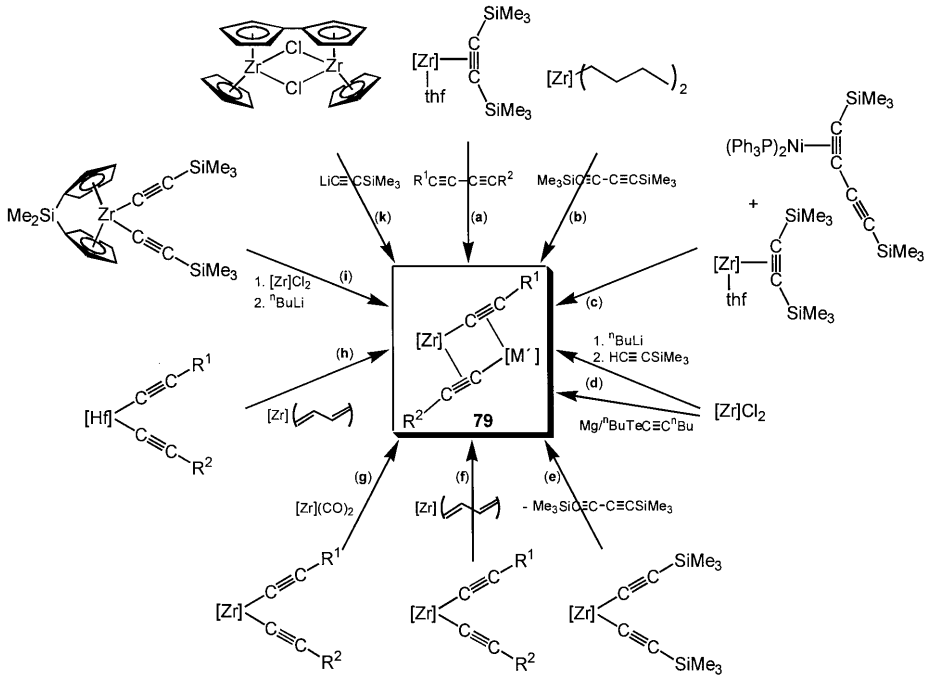
Rearrangement of the latter intermediate produces, depending on the [M′] building blocks present, type **B**, **D** or **E** complexes (Scheme 4).

Another heterobinuclear complex of structural type **G** can be synthesized through the reaction of the tweezer molecule [Ti](C≡CPh)$_2$ with vanadocene ((η^5-C$_5$H$_5$)$_2$V), resulting in the formation of [Ti](μ-$\eta^{(1\text{-}4)}$:$\eta^{(2\text{-}3)}$-PhC$_4$Ph)V(η^5-C$_5$H$_5$)$_2$ [169]. The structure of this complex was proposed on the basis of its similarity to the structurally-characterized zirconium analogue, which is described in detail in Section 4.1.1.2 [169].

A further example for the synthesis of a bimetallic titanium compound of structural type **D**, {[Ti](μ-η^1:η^2-C≡CSnMe$_3$)}$_2$ (**71c**: [Ti] = (η^5-C$_5$H$_5$)$_2$Ti, **71d**: [Ti] = (η^5-C$_5$H$_3$Me$_2$)$_2$Ti, **71e**: [Ti] = (η^5-C$_5$Me$_5$)$_2$Ti) arises from the oxidative addition of Me$_3$SnC≡CSnMe$_3$ to a titanocene, generated in situ, either by loss of alkyne from [Ti](η^2-Me$_3$SiC≡CSiMe$_3$) (**24a**: [Ti] = (η^5-C$_5$H$_5$)$_2$Ti, **24b**: [Ti] = (η^5-C$_5$H$_3$Me$_2$)$_2$Ti, **24c**: (η^5-C$_5$Me$_5$)$_2$Ti) or by magnesium reduction of the appropriate titanocene dichloride [Ti]Cl$_2$ (**21c**: [Ti] = (η^5-C$_5$H$_5$)$_2$Ti, **21d**: [Ti] = (η^5-C$_5$H$_3$Me$_2$)$_2$Ti, **21e**: (η^5-C$_5$Me$_5$)$_2$Ti) [170].

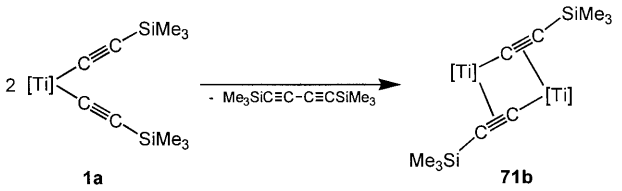


In this reaction the formation of the [Ti](C≡CSnMe$_3$)(SnMe$_3$) intermediate is followed by thermal elimination of a Me$_3$Sn radical, yielding Sn$_2$Me$_6$ and a [Ti](C≡CSnMe$_3$) entity, which then dimerizes to form **71** [170].



Scheme 5. Synthesis of structural type **D** molecules, containing transition metal centers zirconium and M′ (M′ = Ti, Zr, Hf, Ni) (Table 17).

Besides the above-described oxidative reaction, the reverse process, reductive elimination, is also a suitable method for the synthesis of structural type **D** molecules, as described below [13f,22,27,162].



4.1.1.2. Synthesis of zirconium and hafnium compounds. Different procedures for the preparation of type **D** molecules containing zirconium and a second transition metal atom M′ (**79a**–**79q**: M′ = Ti, Zr, Hf, Ni) are summarized in Scheme 5. All reported compounds so far are listed in Table 17.

While routes (**a**)–(**d**) represent oxidative addition reactions of 1,3-butadiynes ($R^1C{\equiv}C{-}C{\equiv}CR^2$) or alkynes ($HC{\equiv}CSiMe_3$ and ^{n}BuTeC≡C^{n}Bu) to zirconocene moieties [Zr], the opposite reaction, reductive elimination, is utilized in route (**e**).

A more general route to bimetallic or heterobimetallic compounds of the type [Zr](μ-η^1:η^2-C≡CR^1)(μ-η^2:η^1-C≡CR^2)[M′] is given by comproportionation [routes (**f**)–(**i**)].

Reaction route (**k**) describes the treatment of the zirconium(III) species [{(η^5-C_5H_5)Zr}$_2$(μ-Cl)$_2$(μ-η^5-C_5H_4-η^5-C_5H_4)] with LiC≡CSiMe$_3$ (Scheme 5).

As previously discussed in Section 4.1.1.1, the in situ generated titanocene entity [Ti] only cleaves the butadiyne Me$_3$SiC≡C–C≡CSiMe$_3$ to afford binuclear {[Ti](μ-η^1:η^2-C≡CSiMe$_3$)}$_2$ (**71b**), whereas other disubstituted diynes R^{1}C≡C–C≡CR^2 (R^1 = R^2 = ^{t}Bu; R^1 = R^2 = Ph; R^1 = SiMe$_3$, R^2 = Ph; R^1 = SiMe$_3$, R^2 = ^{t}Bu; R^1 = R^2 = C≡CSiMe$_3$) remain intact. However, the zirconocene source [Zr](η^2-Me$_3$SiC≡CSiMe$_3$)(thf) (**77**) favors the oxidative addition of the appropriate R^{1}C≡C–C≡CR^2 1,3-diyne, with the exception of ^{t}BuC≡C–C≡C^{t}Bu [route (**a**); Scheme 5]. Similar results are obtained by treatment of [Zr](^{n}Bu)$_2$ with Me$_3$SiC≡C–C≡CSiMe$_3$ [route (**b**); Scheme 5].

A zirconium analogue of the titanium–nickel compound **78** is accessible by reacting the zirconocene generator [Zr](η^2-Me$_3$SiC≡CSiMe$_3$)(thf) {[Zr] = (η^5-C_5H_5)$_2$Zr} (**77**) with (PPh$_3$)$_2$Ni(η^2-Me$_3$SiC≡C–C≡CSiMe$_3$) (**23b**) [route (**c**); Scheme 2]. The structure of the heterobimetallic complex [Zr](μ-C≡CSiMe$_3$)$_2$[Ni(PPh$_3$)] (**79a**) is unsymmetrical and displays two Me$_3$SiC≡C groups, σ-bonded to different metal atoms, zirconium or nickel, as well as η^2-bonded to the other transition metal center.

As reported by Rosenthal and co-workers, [Zr](C≡CSiMe$_3$)$_2$ (**2**) {[Zr] = (η^5-C_5H_5)$_2$Zr} reductively eliminates Me$_3$SiC≡C–C≡CSiMe$_3$ to yield {[Zr](μ-η^1:η^2-C≡CSiMe$_3$)}$_2$ (**79a**) [route (**e**); Scheme 5].

Table 17
Synthesis of complexes **79a**–**79r**

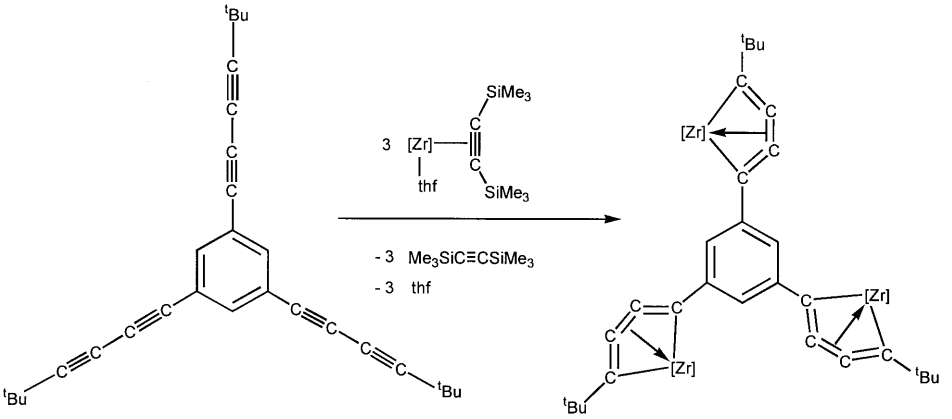
Compound	[Zr]	[M′]	R^1	R^2	Route	Refs.
79a	(η^5-C_5H_5)$_2$Zr	Ni(PPh$_3$)	SiMe$_3$	SiMe$_3$	c	[3,26,76]
79b	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_5)$_2$Zr	SiMe$_3$	SiMe$_3$	a, b, d, e	[10,171,172]
79c	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_5)$_2$Zr	Ph	SiMe$_3$	a	[173]
79d	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_5)$_2$Zr	^{t}Bu	SiMe$_3$	a	[173]
79e	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_5)$_2$Zr	^{t}Bu	^{t}Bu		[3,76]
79f	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_5)$_2$Zr	Me	Me	f, g	[10]
79g	(η^5-C_5H_4Me)$_2$Zr	(η^5-C_5H_4Me)$_2$Zr	Me	Me	f	[10]
79h	(η^5-C_5H_4Me)$_2$Zr	(η^5-C_5H_4Me)$_2$Zr	Ph	Ph	f	[10]
79i	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_4Me)$_2$Zr	Me	Me	f	[10]
79j	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_4Me)$_2$Zr	Ph	Ph	f	[10]
79k	(η^5-C_5H_5)$_2$Zr	(η^5-$C_5H_4^t$Bu)$_2$Zr	Me	Me	f, g	[10]
79l	(η^5-C_5H_5)$_2$Zr	(η^5-$C_5H_4^t$Bu)$_2$Zr	Ph	Ph	f	[10]
79m	(η^5-C_5H_5)$_2$Hf	(η^5-C_5H_5)$_2$Zr	Me	Me	h	[10]
79n	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_5)$_2$Zr	^{n}Bu	^{n}Bu	d	[174]
79o	[a]	[a]	SiMe$_3$	SiMe$_3$	i	[4]
79p	[b]	[b]	SiMe$_3$	SiMe$_3$		[9,175]
79q	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_5)$_2$Ti	^{t}Bu	^{t}Bu	c	[3,76]
79r	(η^5-C_5H_5)$_2$Zr	(η^5-C_5H_5)$_2$Zr	^{t}Bu	[c]	a	[167]

[a] [(η^5-C_5H_4)$_2$SiMe$_2$]Zr.
[b] [Zr((η^5-C_5H_5)$_2$]$_2$[μ-(η^5-C_5H_4-η^5-C_5H_4)].
[c] 1/3C$_6$H$_3$(C≡C)$_3$-2,4,6.

A further method including redox processes is presented in Scheme 5 [route (**d**)] and involves the treatment of $[Zr]Cl_2$ ($[Zr] = (\eta^5\text{-}C_5H_5)_2Zr$) with ^{n}BuLi or magnesium followed by addition of $HC{\equiv}CSiMe_3$ or ^{n}BuTe$C{\equiv}C^n$Bu [174].

A wide variety of homo- and heterobinuclear structural type **D** molecules (**79f**–**79m**) (Table 17) can be formed, when bis(σ-alkynyl)metallocenes containing zirconium or hafnium centers, are treated either with $[Zr](CH_2{=}CH{-}CH{=}CH_2)$ [routes (**f**) and (**h**); Scheme 5] or with $[Zr](CO)_2$ [route (**g**); Scheme 5]. In a similar manner, the *ansa*-bis(alkynyl) zirconocene $\{(\eta^5\text{-}C_5H_4)_2SiMe_2\}Zr(C{\equiv}CSiMe_3)_2$ reacts with [Zr] (generated in situ from $[Zr]Cl_2$ and ^{n}BuLi) [176] $\{[Zr] = [(\eta^5\text{-}C_5H_4)_2SiMe_2]Zr\}$ to produce **79o** [route (**i**), Scheme 5] (Table 17) [4].

Although the zirconium complexes normally adopt bis(alkynyl) structures, such as in type **D** molecules, there are a few reported complexes that contain intact C_4 ligands. Reaction of $[Zr](thf)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$ ($[Zr] = (\eta^5\text{-}C_5H_5)_2Zr$) with one equivalent of a substituted butadiyne such as ^{t}BuC≡C–C≡C^{t}Bu or $C_6H_3(C{\equiv}C{-}C{\equiv}C^t\text{Bu})_3$-2,4,6 results in the formation of the type **F** five-membered metallacyclocumulene complexes $[Zr](\eta^4\text{-}R^1C_4R^2)$ (**80a**: $R^1 = R^2 = {}^t$Bu; **80b**: $R^1 = {}^t$Bu, $R^2 = 1/3\ C_6H_3$) [167,177].



80b

A binuclear zirconium–vanadium complex $[Zr](\mu\text{-}\eta^{(1\text{-}4)}{:}\eta^{(2\text{-}3)}\text{-}PhC_4Ph)V(\eta^5\text{-}C_5H_5)_2$ (**81**), which contains a type **G** butadiyne bridge, can be obtained through the reaction of $[Zr](C{\equiv}CPh)_2$ with $(\eta^5\text{-}C_5H_5)_2V$ [169]. Unlike the titanium–nickel complexes described in Section 4.1.1.1 (Scheme 4), compound **81** was proposed to form through the intermediacy of '[Zr]' and $Cp_2V(C{\equiv}CPh)_2$, rather than a mononuclear cyclocumulene complex [169].

The formation of all compounds listed in Table 17 can simply be explained in terms of a migration of one σ-bonded alkynyl ligand $C{\equiv}CR^1$ between the two transition metal centers zirconium and M′ (M′ = Ti, Zr, Hf, Ni). Formally, two [Zr] and [M′] building blocks can combine to form homodinuclear organometallic frameworks (formation of complexes **79b**–**79l**, **79n**–**79p** and **79r**) or heterobimetallic complexes (formation of **79a, 79m** and **79q**). The core of these molecules is set up by the two metal centers Zr and M′, as well as four acetylide carbon atoms.

4.1.2. Spectroscopy, structure and bonding

The structure of compounds **71**, **78** and **79** can be regarded as being intermediate between the bonding situations of type **C** (Sections 4 and 4.1.1.1) and **E** molecules (Section 4.1.1.1) obtained by carbon–carbon bond formation between the alkynyl ligands. These diamagnetic complexes can be interpreted as dimers of two formally d^1 mono-alkynyl zirconocene fragments or of mono-alkynyl zirconium(III) and either mono-alkynyl hafnium(III), titanium(III) or nickel(I) entities. The single d-electrons in the metal centers (zirconium and M′) in structural type **D** molecules are coupled to each other solely through the planar alkynyl ligand system. A carbon–carbon bond between the two alkynyl ligands, on the other hand, has been verified, thus constituting a 1,3-butadiene unit as a characteristic feature of type **E** molecules.

4.1.2.1. Spectroscopy. Complexes of structural type **D** and **E** exhibit very characteristic spectroscopic features, reflecting the alkynyl bonding situation. A representative $^{13}C\{^1H\}$-NMR spectrum shows a distinct low-field shift and resonance signal separation of the four alkynyl carbon atoms (Table 18). The parent bis(alkynyl) metallocenes $[M](C{\equiv}CR^1)_2$ (M = Ti, Zr, Hf; R^1 = singly bonded organic ligand), in comparison, show resonance signals for the acetylide carbon atoms at much higher field (Table 8, Section 2.1.3.2). Typical $^{13}C\{^1H\}$-NMR chemical shifts for the alkynyl carbon atoms of structural type **D** and **E** molecules are 110–160 ($C{\equiv}\boldsymbol{C}R^1$) and 200–245 ppm ($\boldsymbol{C}{\equiv}CR^1$) (Table 18). A striking feature about the trimethylsilyl-substituted alkynyl ligands is the more extended low-field shift of the sp-hybridized carbon atoms, as compared with C≡CR (R = Ph, ^{t}Bu, ^{n}Bu). One explanation is given by the β-Si effect of the $SiMe_3$ group, which causes a partial positive charge to form on the early transition metal bonded carbon atom [26].

Type **D** molecules tend to be fluctional in solution. This behavior is due to rapid intramolecular alkynyl migrations between the two early transition metals Zr and M′ and has been studied by dynamic NMR (^1H-, $^{13}C\{^1H\}$-NMR) spectroscopy [10,175]. Kinetic parameters for this σ-,π-conversion of the alkynyl ligands have been determined. These studies indicate that the process is an intramolecular transformation through a transition state characterized by C_s symmetry, instead of the C_{2v} symmetry, corresponding to the ground state. Moreover, the almost zero values of $\Delta S^{\neq}$ indicate that no bond breaking is required to reach the transition state [10,175]. Therefore, the dynamic process is related only to the coordination mode of the alkynyl, changing from a σ-π-bonded group (type **D** molecule) in the ground state to a σ-σ-bonded group (type **C** molecule) in the transition state, as depicted in Scheme 6 [10].

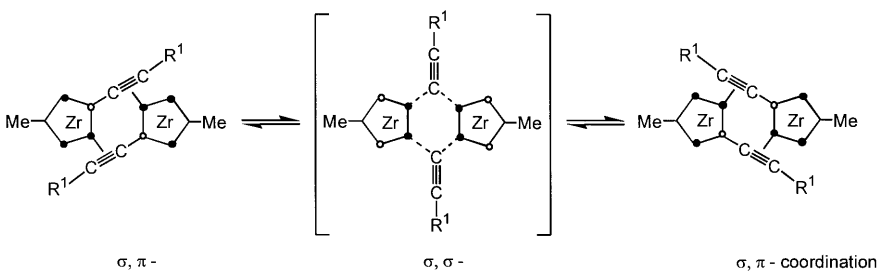
It must be noted that the trimethylsilyl- and methyl-substituted derivatives require higher $\Delta G^{\neq}$ values than the phenyl-substituted compounds. This observation is based on the lower total energy required by the phenyl complexes to reach the transition state, which is stabilized by the phenyl π-electrons [10].

Another spectroscopic method which is useful in determining the alkynyl coordination mode of structural type **C**, **D** and **E** molecules is IR spectroscopy, since it is sensitive to even small changes in the geometric and/or chemical environment of the

Table 18
Selected $^{13}C\{^1H\}$-NMR and IR data of compounds **71**, **72**, **78** and **79**

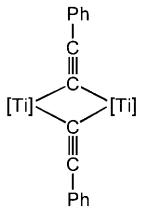
Compound	$^{13}C\{^1H\}$-NMR δ (ppm)		IR (cm^{-1})	Refs.
	C≡***C***R[1]	***C***≡CR[1]		
71a			1769[a]	[9]
71b	142.9	236.8	1798[b]	[13f,162]
71c	139.7	236.0	1768[b]	[35a,170]
71d	140.8	242.0	1740[b]	[35a,170]
72d	125.3	234.4		[76,162,163]
72e	135.4, 164.4	221.9, 227.4		[26,162]
72f	129.1, 149.1	219.0, 237.7		[76,162]
78			1780, 1911[a]	[26]
79a	109.8, 112.1	214.6, 233.9	1771, 1876[a]	[26,76,167]
79b			1751[a]	[10,171,172]
79c	147.7($SiMe_3$), 158.5(Ph)	232.5(Ph), 238.6($SiMe_3$)	1749, 1820[a]	[173]
79d	148.6($SiMe_3$), 170.7(^{t}Bu)	224.4(^{t}Bu), 241.2($SiMe_3$)	1770, 1820[a]	[173]
79e			1778[b]	[76]
79f	147.9	204.2	1820[b]	[10]
79g	148.7	207.7	1817, 1870[b]	[10]
79h	154.7	228.9	1780[b]	[10]
79i	147.5, 148.3	204.6, 207.5	1815[b]	[10]
79j	153.9	224.2, 227.7	1783[b]	[10]
79k	142.1	178.1	1815, 1870[b]	[10]
79l	148.1, 154.5	211.5, 225.8	1717, 1870[b]	[10]
79m	146.8, 148.9	201.8, 206.6	1810	[10]
79n	154	206	1820	[174]
79o			1741[b]	[4]
79p			1773[a]	[9,175]

[a] Nujol.
[b] KBr.



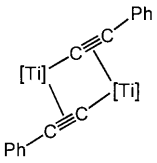
Scheme 6. Dynamic process of structural type **D** molecules [10,175].

C≡C units. The influence of the coordination mode of C≡C units on the IR spectroscopic data is clearly visible in a series of *ansa*-titanocenes (compounds **70a**, **71a** and **72a**) reported by Royo and co-workers (Section 4.1.1.1) [9].



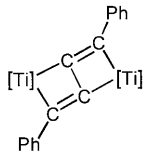
70a

(Type **C** molecule)



71a

(Type **D** molecule)



72a

(Type **E** molecule)

Complex **70a** exhibits a $\nu_{C\equiv C}$ absorption band at 2068 cm^{-1}, as expected for alkynyl groups σ-bonded to transition metal atoms. In **71a** the $\nu_{C\equiv C}$ absorption is shifted to 1769 cm^{-1}, which is a typical value for an alkynyl ligand that is π-coordinated to a second transition metal center. The π-interaction results in a weakening of the C≡C bond, which causes a shift of the C≡C vibration to lower wavenumbers. In general, structural type **D** molecules again show that the C≡C-coordination mode is better identified through IR and NMR spectroscopic data (Table 18) than by structural parameters obtained from X-ray structure analysis (for details see Section 4.1.2.2 and Table 19); no $\nu_{C\equiv C}$ vibration is found in the IR spectrum of the 'zigzag' butadiene-bridged **72a** [9].

These IR data are representative for these structural type **C** (Section 3), **D** and **E** molecules (Sections 4.1.1.1 and 4.1.1.2) (Table 18).

A remarkable aspect of the IR spectra of type **D** compounds is that the replacement of titanium in $\{[Ti](C\equiv CR^1)\}_2$ by zirconium results in a shift of the C≡C stretching vibration to lower wavenumbers. This fact is consistent with the more electron deficient [Zr] building block.

Molecules of type **D** formally contain titanium(III), zirconium(III) or hafnium(III) centers and, therefore, are expected to exhibit paramagnetism. However, these molecules are diamagnetic at 25°C. The observed diamagnetism can be explained by an antiferromagnetic coupling, since a similar phenomenon is observed in other species, e.g. titanium(III) species at ambient temperature [178]. For example, in dimeric $\{[Ti]X\}_2$ $\{[Ti] = (\eta^5\text{-}C_5H_5)_2Ti;\ X = Cl, Br\}$ it is found that, as the titanium–titanium distances decrease, the antiferromagnetic coupling increases [178]. Moreover, the electronic coupling between the Group IV transition metal centers in structural type **D** molecules can take place via the unsaturated bridging alkynyl ligands. As shown by X-ray structure determinations, the titanium–titanium and zirconium–zirconium distances (Ti···Ti: 3.5–3.7 Å, Zr···Zr: 3.4–3.5 Å) (Table 19) (Section 4.1.2.2) are too long to allow direct metal–metal bonding, thus pointing more towards an alkynyl-mediated electronic communication.

4.1.2.2. Structure and bonding. The described type **D** molecules feature a metallacyclic organometallic core, consisting of two early transition metal centers or of one Group IV metal in combination with a nickel atom bridged by the four alkynyl carbon atoms.

Table 19
Selected X-ray data of structural type **D** and **E** molecules

Compound	M···M′ (Å)	M–C_α [M′–$C_{\alpha'}$] (Å)	M–$C_{\alpha'}$ [M–C_β] (Å)	M′–C_α [M′–C_β] (Å)	C≡C (Å)	C_α–$C_{\alpha'}$ (Å)	C_α–M′–$C_{\alpha'}$ [C_α–M′–$C_{\alpha''}$] (°)	M–C≡C (°)	C≡C–R^1 (°)	Refs.
71b	3.550(3)	2.056(11)	2.395(7) [2.312(8)]	2.393(1) [2.318(2)]	1.253(15)	2.71(2)	74.5(3)	176.1(7)	140.3(8)	[13f]
		2.069(1)			1.244(3)	2.726(2)		176.4(1)	141.5(2)	[162]
71d	3.631(1)	2.089(11)	2.424(11) [2.287(12)]		1.252(16)		73.0(4)	175.0(10)	135.0(10)	[170]
72c	4.227(1)	2.153(2)	2.325(2) [2.083(2)]		1.325(3)	1.485(4)		155.8(2)	128.1(2)	[160]
72d		2.142(3)	2.310(3) [2.093(4)]		1.325(5)	1.494(6)			132.0(3)	[162]
72e		2.164(7) [2.114(7)]	2.337(7) [2.083(7)]	2.302(7) [2.115(7)]	1.327(9)	1.511(9)		154.9(6)	130.8(7)	[26]
					1.317(9)			156.4(6)	135.0(6)	
72f		2.146(3)	2.312(3) [2.094(3)]		1.313(4)				131.9(2)	[162]
78	2.7277(10)	2.067(4) [1.828(5)]	2.331(4) [2.628(.)]	1.909(5) [2.061(5)]	1.261(7)			164.5(4)	1.458(4)	[26]
					1.233(7)			170.4(4)	1.644(4)	
79a	2.830(1)	2.178(9) [1.835(8)]	2.385(7) [2.557(.)]	1.961(8) [2.035(9)]	1.284(13)			160.4(7)	141.7(7)	[26]
					1.236(12)			166.4(7)	159.2(7)	

Table 19 (*Continued*)

Compound	M···M′ (Å)	M–C_α [M′–$C_{\alpha'}$] (Å)	M–$C_{\alpha'}$ [M–$C_{\beta'}$] (Å)	M′–C_α [M′–C_β] (Å)	C≡C (Å)	C_α–$C_{\alpha'}$ (Å)	C_α–M′–$C_{\alpha'}$ [C_α–M′–$C_{\alpha''}$] (°)	M–C≡C (°)	C≡C–R^1 (°)	Refs.
79b	3.522(2)	2.191(5) 2.191(5)]	2.420(5) [2.399(5)]		1.249(7)			172.7(4)	142.5(4)	[172]
			2.426(5) [2.407(5)]		1.260(7)					
79c	3.528(2)	2.216(3) 2.157(3)]	2.416(3) [2.354(3)]	2.448(3) [2.442(3)]	1.267(4)	2.986(6)	80.3(1) [85.0(2)]	173.3(3)	141.2(3)	[173]
					1.246(5)			171.5(3)	144.6(3)	
79j		2.188(2)	2.431(2) [2.407(2)]		1.261(2)		81.4(1)			[10]
79n	3.469	2.206(6)	2.437(5) [2.413(6)]		1.210(7)		83.4(2)	171.0(4)	153.5(6)	[174]
79o	3.489	2.177(6) [2.187(6)]	2.394(5) [2.394(6)]	2.394(5) [2.397(6)]	1.254(8)		80.9(2) [80.7(2)]	168.7(5)	143.7(5)	[4]
					1.270(8)			167.5(5)	145.2(5)	
79p	3.405(1)	2.181(9) [2.18(1)]	2.417(8) [2.433(9)]	2.411(8) [2.421(8)]	1.25(1)		82.4(3) [82.6(3)]	169.3(7)	146.8(8)	[175]
					1.25(1)			169.1(7)		
86b	3.339(1)	1.98(2) [2.01(1)]	2.24(2) [2.18(1)]	2.23(2) [2.18(2)]	1.21(2)		68.7(5)	176(1)	146(1)	[181]
					1.23(2)		68.3(6)	175(1)	146(1)	

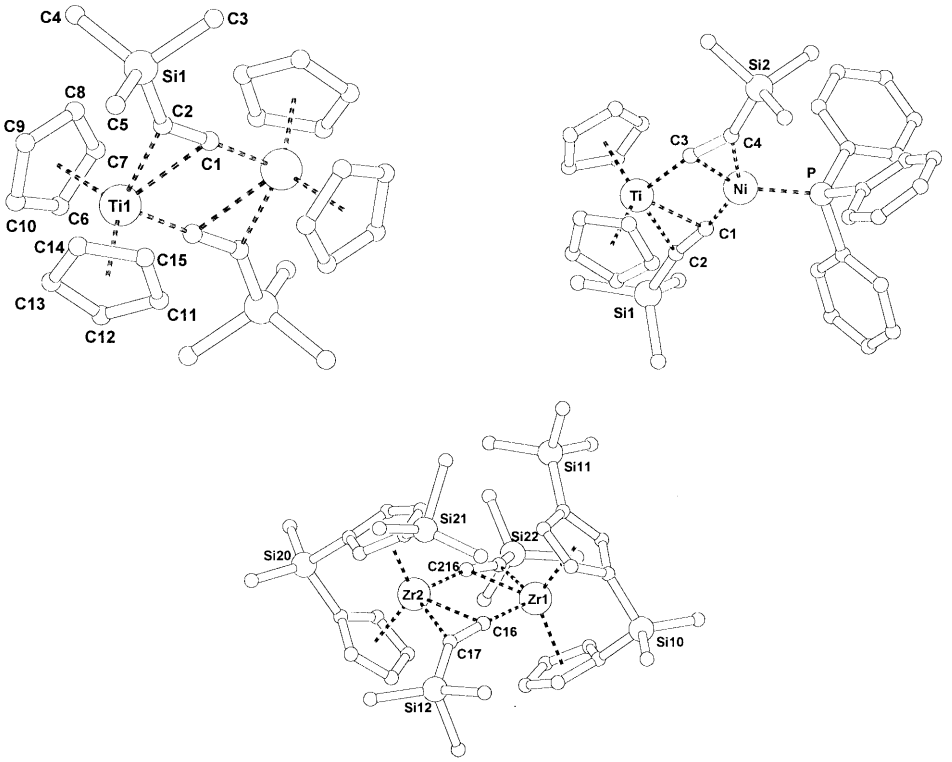


Fig. 18. Molecular geometry and atom numbering scheme for **71b** (top left), **78** (top right) and **79o** (bottom); the interatomic bond lengths and angles are given in Table 19.

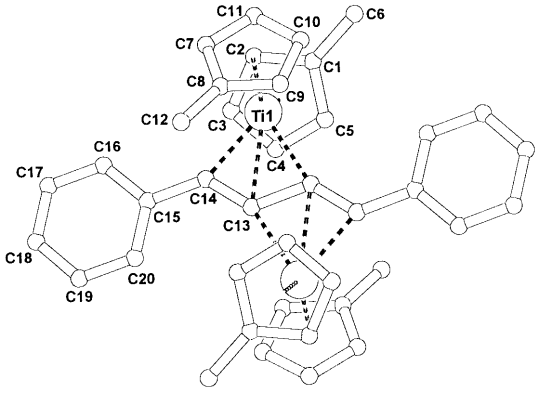
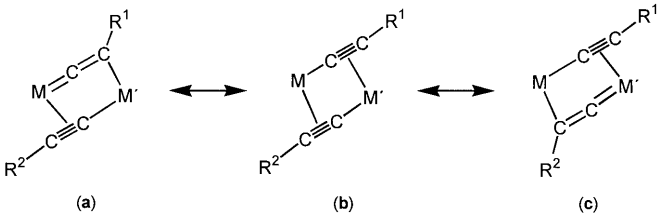


Fig. 19. Molecular geometry of **72c**. Interatomic bond lengths and angles are given in Table 19 [160].



Scheme 7. Resonance formulae (**a**), (**b**) and (**c**) for type **D** molecules.

The solid-state structures of selected type **D** and **E** molecules have been determined by X-ray diffraction studies [Fig. 18 (type **D** molecules), Fig. 19 (type **E** molecules)] (Table 19).

The central MC_4M' core of the $M(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^2{:}\eta^1\text{-}C{\equiv}CR^2)M'$ entities is almost planar. However, in **79o** and **79p** dihedral angles of 13.6 and 15.9°, respectively, are found between the planes formed by the zirconium and π-associated carbon atoms (Table 19) [4,175]. This observation can be explained by the coordinated fulvalene (the fulvalene itself has become non-planar in **79p**) or the steric constraints owing to the Me_2Si-bridged cyclopentadienyl ligands in **79o**. Generally, no direct M···M′ interaction between M and M′ is observed; the M···M′ (M = M′, M ≠ M′) distances are significantly larger than the sum of the M and M′ van der Waals radii (Table 19).

Despite the η^2-coordination of the alkynyl ligands to a second metal center, the M/M′–C≡C units remain almost linear, whereas the C≡C–R^1 angles are significantly reduced (Table 19). The short metal–carbon bond distances (Table 19) justify a description of compounds $[M](\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^2{:}\eta^1\text{-}C{\equiv}CR^2)[M']$ by the resonance formulae (**a**), (**b**) and (**c**) (Scheme 7), with a considerable π-interaction between the metal centers M and M′ and the adjacent organic π-system $C{\equiv}CR^1$/$C{\equiv}CR^2$ across the connecting σ-bond.

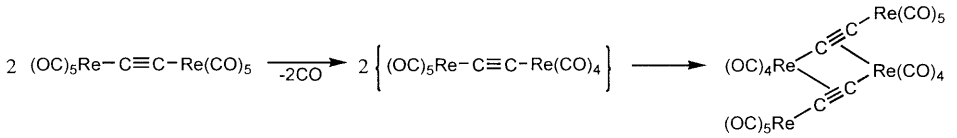
Moreover, it is found that the C≡C bond length is consequently longer than in the parent compound $[M](C{\equiv}CR^1)_2$ (Table 19).

The alkynyl ligands in type **D** complexes can undergo an oxidative coupling reaction to produce molecules of type **E**, which feature a tetradehydro-μ-[($\eta^{(1\text{-}3)}$:$\eta^{(2\text{-}4)}$-*trans*,*trans*-butadiene] unit ('zigzag' butadiene) as elucidated by X-ray structure analyses (Table 20). As an example, the result of the X-ray structure analysis of compound **72c** is depicted in Fig. 19 [160].

In the unit cell, **72c** is located on a crystallographic center of inversion [160]. The two titanium and all carbon atoms of the C_4Ph_2 entity are approximately coplanar. The configuration around the titanium center represents a four-membered metallacyclic geometry, involving three carbon atoms of the 1,4-diphenyl-butadiene unit. The titanium–carbon as well as the carbon–carbon bond lengths are consistent with the proposed configuration.

4.2. Structural type **D** molecules with a Re_4C_4 core

Tetranuclear complexes of the type M_4C_4 are readily accessible by the decarbonylation of $(CO)_5Re–C\equiv C–Re(CO)_5$ (**82**), as shown by Beck and co-workers [179]. The σ,π-bridged complex $[(CO)_5Re–C\equiv C–Re(CO)_4]_2$ (**83**) is formed in good yield. The binuclear species $[Re(CO)_4C\equiv CSiMe_3]_2$ (**84**) could be prepared in a similar manner [179].



82 **83**

Both compounds were characterized by X-ray structure analysis. Fig. 20 shows the molecular geometry of $[(CO)_4Re–C\equiv C–Re(CO)_5]_2$ (**83**).

The most noticeable feature of **83** is that it contains four rhenium carbonyl fragments and that the alkynyl ligands are coplanar with the four rhenium atoms (max. deviation: ± 2 pm) [179]. A further conspicuous characteristic is the relatively short C≡C bond distances of 1.16(2) Å, which are significantly shorter than those found in other alkyne or alkynyl ligands. This phenomenon is accompanied by an elongation of the $Re–C_{C\equiv C}$ bond lengths (for comparison: $(CO)_5Re–C\equiv C–Re(CO)_5$, 2.141(16) Å; $[(CO)_4Re–C\equiv C–Re(CO)_5]_2$, 2.177(13), 2.181(13) Å) [179,180]. As is typical for other type **D** molecules, the $(CO)_4Re–C\equiv C$ units are almost linear (171(1) or 170(1)°), whereas the $C\equiv C–Re(CO)_5$ entities are significantly deformed from linearity (150(1)°) [179].

Table 20
Synthesis of compounds $Q_n\{[M](\mu\text{-}\eta^1\text{:}\eta^2\text{-}C\equiv CR^1)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}C\equiv CR^1)[M']\}$ (**86**, **89** and **90**)[a]

Compound	[M]	[M′]	R^1	Q_n
86a	Rh(cod)	Rh(cod)	$SiMe_3$	
86b	Ir(cod)	Ir(cod)	$SiMe_3$	
89a	$(\eta^5\text{-}C_5Me_5)(Et_3P)Rh$	$Pt(C_6F_5)_2$	Ph	
89b	$(\eta^5\text{-}C_5Me_5)(Et_3P)Rh$	$Pt(C_6F_5)_2$	$SiMe_3$	
89c	Ir(cod)	$Pt(C_6F_5)_2$	$SiMe_3$	NBu_4
90a	$Pt(C_6F_5)_2$	$Pt(C_6F_5)_2$	Ph	$(PMePh_3)_2$
90b	$Pt(C_6F_5)_2$	$Pt(C_6F_5)_2$	^{t}Bu	$(NBu_4)_2$
90c	$Pt(C_6F_5)_2$	$Pd(C_6F_5)_2$	Ph	$(PMePh_3)_2$
90d	$Pt(C_6F_5)_2$	$Pd(C_6F_5)_2$	^{t}Bu	$(NBu_4)_2$
90e	$Pt(C_6F_5)(C\equiv CPh)$	$Pt(C_6F_5)_2$	Ph	$(PMePh_3)_2$
90f	$Pt(C_6F_5)(C\equiv C'Bu)$	$Pt(C_6F_5)_2$	^{t}Bu	$(NBu_4)_2$

[a] See Refs. [119,126,182].

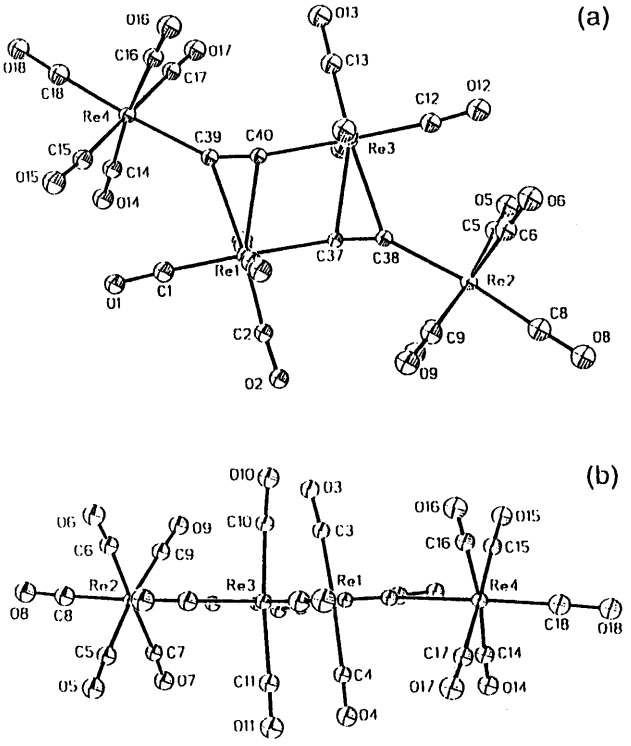


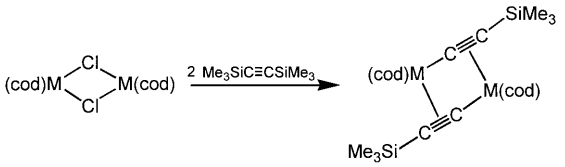
Fig. 20. Molecular geometry and atom numbering scheme for **83** [179]; (a) view from above the Re_4 plane; (b) view along the Re_4 core. Selected interatomic distances (Å) and angles (°) are as follows: Re(1)–C(37), 2.177(13); Re(1)–C(39), 2.49(2); Re(3)–C(40), 2.181(13); Re(3)–C(38), 2.494(14); Re(1)–C(40), 2.408(14); Re(2)–C(37), 2.424(12); Re(4)–C(39), 2.211(14); C(37)–C(38), 1.16(2); C(39)–C(40), 1.16(2); Re(1)–C(37)–C(38), 171.5(11); Re(2)–C(38)–C(37), 150.1(12).

*4.3. Type **D** molecules [M](μ-η¹:η²-C≡CR¹)(μ-η²:η¹-C≡CR²)[M′] containing platinum metals*

In comparison to planar type **D** molecules, discussed in Sections 4.1 and 4.2, which are characterized by a planar $M(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^2\text{:}\eta^1\text{-}C{\equiv}CR^2)M'$ core ($R^1 = R^2$, $R^1 \neq R^2$) containing titanocene, zirconocene and/or hafnocene entities, the content of this part describes their non-planar analogues, containing rhodium, iridium, platinum and/or palladium metal atoms in which the $MC{\equiv}CR^1$ units are folded along the M–M/M–M′ axis.

4.3.1. Synthesis

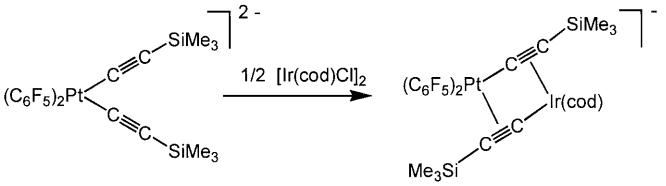
The bimetallic rhodium or iridium containing molecules $[(cod)M(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CSiMe_3)]_2$ (**86a**: M = Rh, **86b**: M = Ir) can be synthesized by the reaction of $[(cod)MCl]_2$ (**85a**: M = Rh, **85b**: M = Ir) with $Me_3SiC{\equiv}CSiMe_3$, as shown by Müller and co-workers [181].



86a: M = Rh
86b: M = Ir

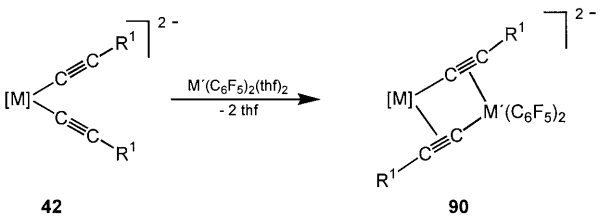
While the formation of **86b** runs unassisted, the synthesis of **86a** requires the addition of MeLi. Presumably, $[(cod)Rh(\mu\text{-}Me)]_2$ is formed first, which then reacts with $Me_3SiC{\equiv}CSiMe_3$ by elimination of $SiMe_4$ to afford bimetallic **86a**. Addition of PMe_3 as a Lewis base to **86a** or **86b** breaks down the dimeric structures to form the mononuclear species $[(cod)(PMe_3)_2M(C{\equiv}CSiMe_3)]$ (**87a**: M = Rh, **87b**: M = Ir) [181].

A common method to prepare heterobimetallic compounds of type **D** with a non-planar MC_4M' core (M, M′ = Rh, Ir, Pd, Pt) is the reaction of a bis(alkynyl)platinum complex with a metal source, which contains a metal center with similar electronic properties to the platinum center. Thus, reaction of $[(C_6F_5)_2Pt(C{\equiv}CR^1)_2]^{2-}$ (**42a**: R^1 = Ph, **42b**: $R^1 = SiMe_3$) with $[(\eta^5\text{-}C_5Me_5)(Et_3P)Rh(O{=}CMe_2)_2][ClO_4]_2$ (**88**) results in the formation of $(\eta^5\text{-}C_5Me_5)(Et_3P)Rh(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^2{:}\eta^1\text{-}C{\equiv}CR^1)Pt'(C_6F_5)_2$ (**89a**: R^1 = Ph, **89b**: $R^1 = SiMe_3$) [125,126,182]. Similarly, reaction of **42b** with $[Ir(cod)Cl]_2$ yields the platinum–iridium complex $[NBu_4][(C_6F_5)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)(\mu\text{-}\eta^2{:}\eta^1\text{-}C{\equiv}CSiMe_3)Ir(cod)]$ (**89c**) [125,126,182].



42b **89c**

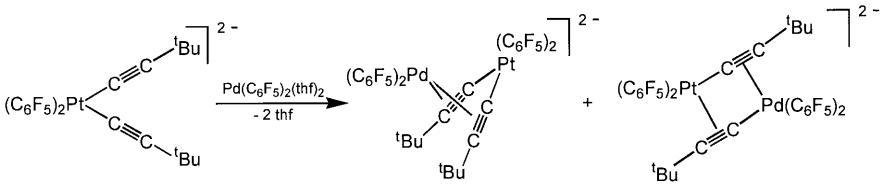
Similarly, structural type **D**, diplatinum or platinum–palladium molecules could be synthesized by treatment of $Q_2[cis\text{-}[M](C{\equiv}CR^1)_2]$ (**42**) with $cis\text{-}M'(C_6F_5)_2(thf)_2$ (M′ = Pd, Pt), yielding the anionic derivatives $Q_2[[M](\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^2{:}\eta^1\text{-}C{\equiv}CR^1)M'(C_6F_5)_2]$ (**90a**–**90f**) (Table 20) [119].



42 **90**

The synthesis of heterobinuclear **90c** and **90d**, which feature platinum and palladium centers, requires the use of lower temperatures. However, binuclear **90a**, **90b**, **90e** and **90f**, featuring two platinum atoms, can be synthesized at 25°C.

When $[N^nBu_4]_2[(C_6F_5)_2Pt(C{\equiv}C'Bu)_2]$ (**42c**) is treated with $Pd(C_6F_5)_2(thf)_2$ in diethyl ether at -10°C, two products are initially formed: a tweezer compound of structural type **B** with a non-planar $Pt(C{\equiv}C'Bu)_2Pd$ core (**44i**, Section 2.2.1.1) (Table 9); and a structural type **D** molecule (**90d**) (Table 20) [119]. Upon standing in solution, the tweezer complex **44i** isomerizes to the type **D** complex **90d**, as shown below.



42c **44i** **90d**

This observation shows that molecules **89** and **90** (Table 20) are formed in two steps: (i) the initial formation of tweezer complexes (type **B** molecules); and (ii) the transfer of one alkynyl ligand from one metal center to the other, affording bimetallic doubly alkynyl-bridged anionic compounds of structural type **D**. This can be explained in terms of the two metal fragments [M] and [M′] having similar affinities for the anionic alkynyl ligands. If one metal center has significantly greater affinity for the anionic ligand than the other (e.g. $[M] = Pt(PPh_3)_2$, $[M'] = [Pt(C_6F_5)_2]^{2-}$ or $[M] = [(\eta^5\text{-}C_5Me_5)(Et_3P)Ir]^{2+}$, $[M'] = [Pt(C_6F_5)_2]^{2-}$), then both alkynyls are found to σ-coordinate to [M], forming a tweezer complex of structural type **B** (Section 2.2.1.1). It must be noted that the charge on the metal centers is not the only factor determining the affinity of a metal center for the alkynyl ligand — the platinum–rhodium complex $(\eta^5\text{-}C_5Me_5)(Et_3P)Rh(C{\equiv}CR^1)_2Pt(C_6F_5)_2$ (**89a**, **89b**) adopts a type **D** structure, in spite of the higher formal charge on the Rh(III) center. In contrast, the palladium–rhodium, platinum–iridium and palladium–iridium analogues (**48a**–**48f**) all adopt type **B** structures, with both alkynyl ligands σ-coordinated to the Rh(III) or Ir(III) center. Similarly, $[NBu_4][(C_6F_5)_2Pt(C{\equiv}CR^1)_2Ir(cod)]$ (**89c**) adopts a type **D** structure, with the Pt(II) and Ir(I) centers competing effectively for the alkynyl ligands. In the platinum–rhodium analogue, however, both alkynyl ligands are σ-bonded to the platinum center, resulting in a type **B** tweezer structure (Section 2.2.1.1). This is consistent with the known tendency for third-row metal centers to form stronger metal–ligand bonds than their second-row counterparts.

4.3.2. Spectroscopy, structure and bonding

4.3.2.1. Spectroscopy. As previously discussed for structural type **D** molecules which feature a planar $M(C{\equiv}CR^1)_2M'$ core (M, M′ = early transition metal atoms,

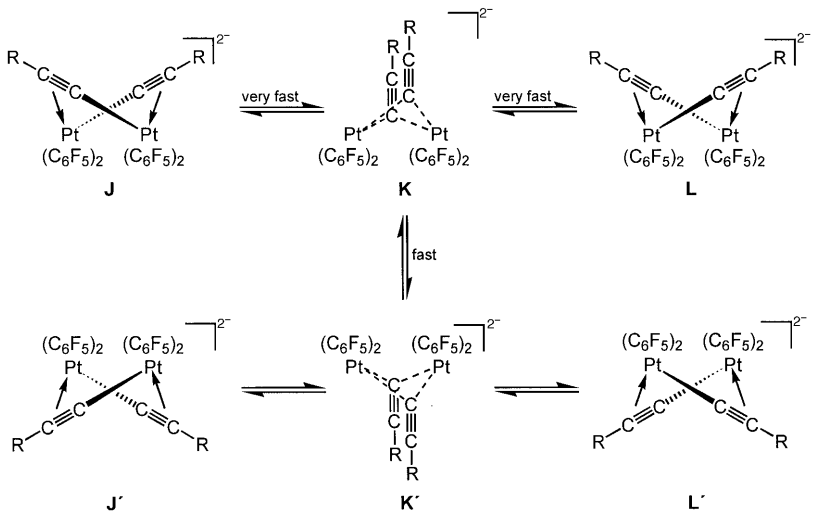
such as titanium, zirconium or hafnium) (Section 4.1), structural type **D** molecules with rhodium, iridium or platinum and palladium centers (which possess a non-planar $M(C{\equiv}CR^1)_2M'$ core) also show diagnostic IR and NMR spectroscopic features.

In all cases, the IR spectra of compounds **86**, **89** and **90** exhibit strong absorption bands between 1930 and 2040 cm^{-1}, which can be assigned to the $\nu_{C\equiv C}$ stretching vibration of the $M(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR^1)(\mu\text{-}\eta^2{:}\eta^1\text{-}C{\equiv}CR^1)M'$ building blocks (M, M′ = Rh, Ir, Pt, Pd).

Compounds **90a**–**90f** are fluxional in solution, as could be shown by temperature dependent ^{19}F-NMR studies [119]. It was found that two processes take place: (i) an intramolecular $C{\equiv}CR^1$ migration occurs between the platinum atoms (transformation of type **J** into type **L** molecules or vice-versa) via an intermediate of type **K** with symmetrical alkynyl bridges; and (ii) since the molecules **90a**–**90f** posses a bent arrangement, an inversion of the diplatinacycle is required to produce a time-averaged plane of symmetry. A plausible mechanism for the inversion process is shown in Scheme 8. Finally, the ^{19}F-NMR spectrum of $[(C_6F_5)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}\eta^2{:}\eta^1\text{-}C{\equiv}CPh)Pt(C_6F_5)_2]^{2-}$ seems to indicate that in this case the energy barrier between **J** and **L** (or **J′** and **L′**) is smaller than that of the inversion process involving **K** and **K′** [119].

The dynamic behavior of the alkynyl ligands in **90** is also observed in the ^{1}H- as well as in the ^{13}C-NMR spectra [119].

4.3.2.2. Structure and bonding. As representative examples for all binuclear compounds described in Section 4.3.1, the results of the X-ray structure analysis of compounds $\{[(C_6F_5)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)]_2\}^{2-}$ (**90a**) [119] and $[(cod)Ir(C{\equiv}CSiMe_3)]_2$ (**86b**) [181] are described (Fig. 21).



Scheme 8. Possible inversion process for compounds **90a**–**90f** [119].

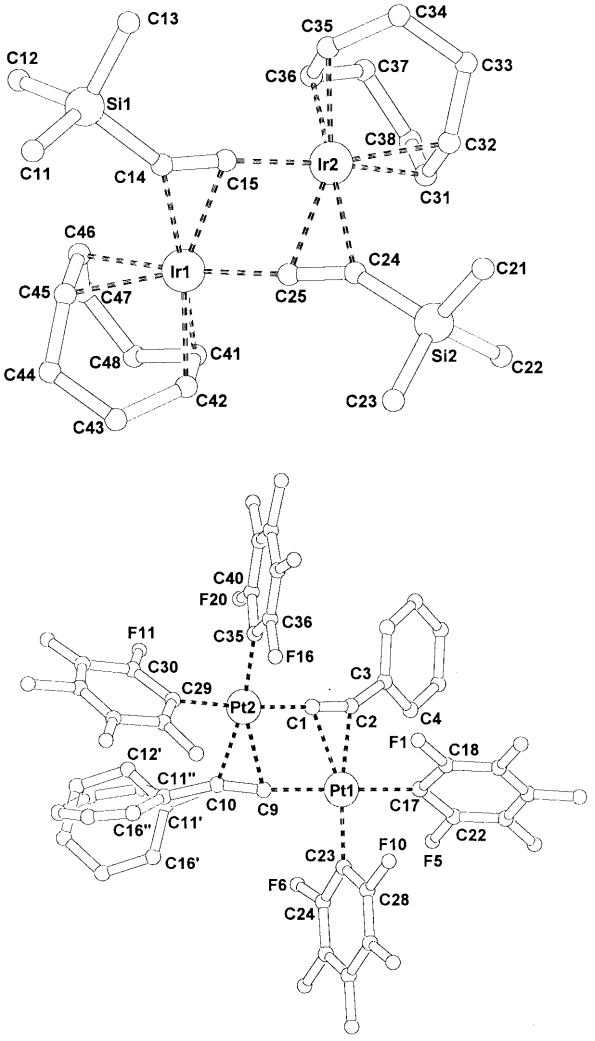


Fig. 21. Molecular geometry and atom labeling scheme for **86b** [181] (top) and **90a** [119] (bottom). Selected bond distances (Å) and angles (°) are as follows. **86b**: Ir(1)–Ir(2), 3.339(1); Ir(1)–C(14), 2.18(1); Ir(1)–C(15), 2.24(2); Ir(1)–C(25), 1.98(2); Ir(2)–C(15), 2.01(1); Ir(2)–C(24), 2.18(2); Ir(2)–C(25), 2.23(2); C(14)–C(15), 1.21(2); C(24)–C(25), 1.23(2); Ir(1)–C(25)–C(24), 176(1); Ir(2)–C(15)–C(14), 175(1); C(15)–C(14)–Si(1), 146(1); C(25)–C(24)–Si(2), 146(1). **90a**: Pt(1)–Pt(2), 3.49, Pt(1)–C(1), 2.263(12); Pt(1)–C(2), 2.267(12); Pt(1)–C(9), 2.023(13); Pt(2)–C(1), 1.978(14); Pt(2)–C(9), 2.369(15); Pt(2)–C(10), 2.304(15); C(1)–C(2), 1.230(19); C(9)–C(10), 1.219(17); Pt(1)–C(9)–C(10), 173.2(1.1); Pt(2)–C(1)–C(2), 170.4(1.0); C(1)–C(2)–C(3), 152.6(1.2); C(9)–C(10)–C(11), 160.5(1.7).

Both compounds **86b** and **90a** are alkynyl-bridged dimers of two identical (cod)Ir(C≡CSiMe$_3$) or (C$_6$F$_5$)$_2$Pt(C≡CPh) moieties.

The platinum atom in **90a** is thereby σ-bonded to two mutually *cis*-oriented C$_6$F$_5$ ligands, σ-bonded to one C≡CPh unit and η^2-coordinated by the second alkynyl ligand (Fig. 21) [119].

The most notable feature of molecules **86b** and **90a** is that, unlike the early transition metal-containing structural type **D** molecules described in Section 4.1.1, the MC$_4$M′ core (M = M′ = Ir, Pt) is not planar [dihedral angle for molecule **90a**: Pt(1), Pt(2), C(1), C(2)/Pt(1), Pt(2), C(9), C(10) = 136°] (Fig. 21) [119]. A similar non-planar structure has been found in [(cod)Ir(C≡CSiMe$_3$)]$_2$ (**86b**) [181]. Furthermore, it should be mentioned that the metal–alkyne π-linkages are nearly symmetric (Fig. 20). The M–C$_\alpha$–C$_\beta$ units remain almost linear [**86b**: Ir–C$_\alpha$–C$_\beta$ 175(1), 176(1)°; **90a**: Pt-C$_\alpha$-C$_\beta$ 170.4(1.0), 173.2(1.1)°]. However, in both molecules, the deviations from linearity are more pronounced at the β-carbon atoms [**86b**: C$_\alpha$–C$_\beta$–Si, 146(1)°; **90a**: C$_\alpha$–C$_\beta$–C$_{Ph}$, 152.6(1.2), 160.5(1.7)°]. The Pt(1)···Pt(2) distance is 3.49 Å and the Ir(1)···Ir(2) distance 3.339(1) Å, indicating that direct metal–metal bonding is absent in both compounds.

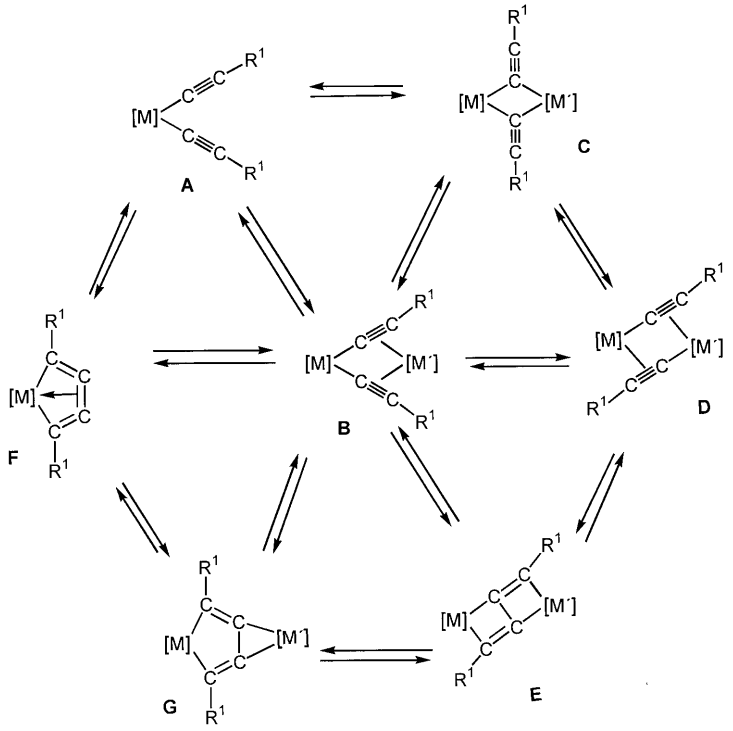
5. Conclusions

Bis(alkynyl)-bridged binuclear species (type **B**–**E** and **G** molecules) and their mononuclear precursors (type **A** and **F** molecules), can adopt a number of different structures, depending upon the steric and electronic properties of the metal centers and ligands involved. The possible structures of these complexes and their derivatives, as well as their potential interconversions, are shown below (Scheme 9).

The structure adopted by a bis(alkynyl) binuclear complex is strongly influenced by the relative affinity of the metal centers for electron density. If one metal center (e.g. M) is significantly more electrophilic than the other (M′), then the alkynyl ligands R^{1}C$_\beta$≡C$_\alpha$ will preferentially coordinate to the electrophilic metal M through the α-carbons. This results in structural type **B** complexes, in which both of the alkynyl ligands are σ-bound to one metal (M) and π-coordinated to the second metal center (M′). This is the preferred structure type for many early–late heterobinuclear complexes such as the titanium–copper species.

If the two metal centers are competitive in their affinity towards the alkynyl ligands, or if steric factors prevent the formation of a type **B** tweezer complex, then type **C** or **D** molecules are formed. In these molecules, the alkynyl ligands are more evenly shared, either with both metal centers σ-coordinated by both alkynyl ligands (type **C**) or with each metal center σ-bonded by one alkynyl ligand and π-coordinated to the other.

Because the two alkynyl ligands are held in close proximity, coupling reactions between the two ligands are also possible, forming molecules of type **E** or **G**. 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 R^1 substituents or in the ancillary ligands of the M/M′ centers can induce or prevent these reactions.



Scheme 9. Interconversions of alkynyl coordination modes in binuclear systems.

Despite the large quantity of work done in this field, the exact factors which control the interconversion of these structures in these systems is still an open question and will continue to stimulate fruitful work in this field.

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Appendix A. Nomenclature

acac	acetylacetonate
bipy	2,2′-bipyridyl
bipy′	4,4′-dimethyl-2,2′-bipyridyl
cod	1,5-cyclooctadiene
dppe	1,2-bis(diphenylphosphino)ethane
dppf	1,1′-bis(diphenylphosphino)ferrocene
Et	ethyl
Fc	ferrocenyl, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$
Me	methyl
nbd	norbornadiene
NN′N	$C_5H_3N(CH_2NMe_2)_2$-2,6
phen	1,10-phenanthroline
Ph	phenyl
py	pyridine
R	univalent organic group
Rc	ruthenocenyl, $(\eta^5\text{-}C_5H_4)Ru(\eta^5\text{-}C_5H_5)$
{Ru}	$(\eta^3\text{-}C_5H_3N(CH_2NMe_2)_2)RuCl_2$
thf	tetrahydrofuran
tht	tetrahydrothiophene
tmda	*N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane
tmpda	*N*,*N*,*N*′,*N*′-tetramethyl-1,3-diaminopropane
trop	troponolato
η^n	ligand is coordinated through *n* carbons
$\eta^{(n\text{-}m)}$	ligand is coordinated through carbons *n* and *m*

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