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Bis-*ortho*-chelated Diaminoaryl Platinum Compounds with σ-Acetylene Substituents. Investigations into Their Stability and Subsequent Construction of Multimetallic Systems. The Crystal Structure of $[(\mu^2\text{-}[(\eta^2\text{-NCN})Pt(\eta^1\text{-CO})C{\equiv}CSiMe_3])Co_2(CO)_6]$ (NCN = 2,6-Bis[(dimethylamino)methyl]phenyl)

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A series of related platinum σ-acetylide complexes {Pt}C≡CR ({Pt} = $[Pt(C_6H_3\{Me_2NCH_2\}_2\text{-}2,6)]^+$) were prepared by reacting lithium acetylides with {Pt}Cl (**1**) in order to investigate the stability of the Pt−acetylide σ-bond and their possible application in the assembly of multimetallic compounds containing the {Pt} "pincer" unit. This may be achieved by η^2-coordination of the acetylide or by incorporating a second ligating site in the acetylide anion. Both of these approaches are demonstrated herein. {Pt}C≡CSiMe$_3$ (**2**) was reacted with [M][BF$_4$] ([M] = [Cu(NCMe)$_4$], Ag) and different forms of Cu(I) halides. Only with the former was the formation of stable π-coordinated M(I) compounds observed. [(η^2-[{Pt}C≡CSiMe$_3$]$_2$)-Cu][BF$_4$] exhibits η^2-coordination of both acetylenic units to a formal Cu(I) metal center, thus forming a heterotrimetallic compound. In the presence of halide ions, **2** undergoes cleavage of the Pt−C≡C σ-bond with concomitant formation of {Pt}X (X = Cl or I). The reaction of **2** with Co$_2$(CO)$_8$ leads via π-coordination to the formation of a trimetallic dicobaltatetrahedrane. The structure of [(μ^2-[(η^2-NCN)Pt(η^1-CO)C≡CSiMe$_3$])Co$_2$(CO)$_6$] in the solid state shows that one *ortho*-CH$_2$NMe$_2$ substituent of the NCN ligand is no longer coordinated to the Pt metal center. Instead, a CO ligand coordinates *trans* to the Pt−N bond, yielding a metal center with four different ligand donor atoms. Attempts to obtain related Pt(IV) acetylides by reaction of **2** with CuCl$_2$ resulted in the formation of {Pt}Cl$_3$, [CuX]$_n$, and [CuC≡CSiMe$_3$]$_n$. The reaction with I$_2$ gave neither a Pt(IV) diiodide nor a Pt(II) η^1−I$_2$ complex, but instead led to Pt−C(acetylide) bond cleavage and formation of {Pt}I and IC≡CSiMe$_3$. The reaction of {Pt}C≡CC$_6$H$_4$CN-4 with [{Pt}H$_2$O][BF$_4$] and {Ru}N≡N{Ru} ({Ru} = [RuCl$_2$(C$_5$H$_3$N{CH$_2$NMe$_2$}$_2$-2,6)]) gives air-stable well-defined bimetallic compounds. In contrast, the reaction of {Pt}C≡CC$_6$H$_4$CN-4 with [AuCl$_3$]$_2$ or Au(CO)Cl leads to the formation of a gold mirror, NCC$_6$H$_4$(C≡C)$_2$C$_6$H$_4$CN, and {Pt}Cl$_3$ or {Pt}Cl, respectively. Cyclic voltammetry studies with representative Pt−acetylides show irreversible oxidative processes which are shifted to a more negative potential upon substitution of Cl by acetylide.

Introduction

The organometallic chemistry of the potentially η^3-chelating, monoanionic diaminoaryl ligand NCN {NCN = $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$},[1] in addition to the related diphosphino-[2] and disulfido-aryl anions,[2] has been extensively investigated due to the stability of the resulting complexes and catalytic properties of these "pincer" metal compounds.[3] Recently, we reported that the Pt−carbon bond in the pincer halide complex **1** (cf. Chart 1) possesses a surprising stability and remains inert to protonation by water or diluted acids under certain conditions.[4] This opened the possibility to prepare *para*-functionalized NCN Pt−X complexes, e.g., **A** or **B**, which can be used as building blocks for the

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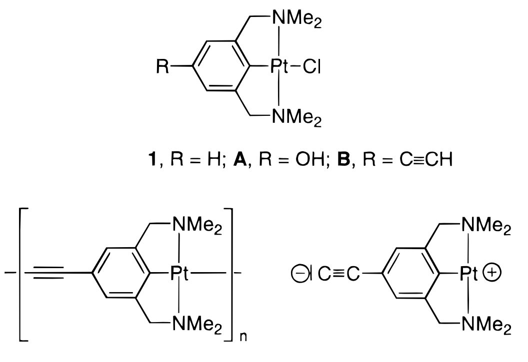
Chart 1



1, R = H; **A**, R = OH; **B**, R = C≡CH

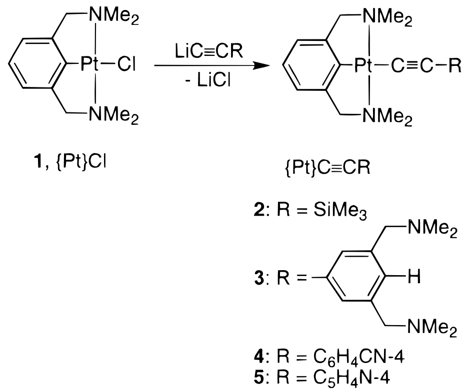
C **D**

assembly of larger molecules[3,5] or H-bonded networks which offer a high degree of directionality.[6] These can serve as model compounds for molecules that exhibit qualities that are necessary for application (i) in liquid crystalline materials (due to their rigid-rod-like structure),[7] (ii) as compounds with high hyperpolarizabilities,[8] and (iii) as models for electronic conduction along conjugated organometallic chains.[9]

One of these possible molecules is represented as **C**, which is built up by repeating units of zwitterionic-type **D**. We choose a stepwise approach, since a direct route to obtain compounds such as **C** is unknown. Also, an important factor for the construction of polymeric compounds such as **C** is the stability of the Pt−C σ-bonds. Therefore, we focused this work on the synthesis of model complexes based on **1**, which contain solely one Pt σ-acetylide. Here, the formation, stability, and electrochemical behavior of Pt σ-acetylides can be studied. Furthermore, these Pt acetylides can be functionalized to incorporate a second reactive site. This allows the assembly of bimetallic molecules in which the {Pt} ({Pt} = $[Pt(C_6H_3\{Me_2NCH_2\}_2\text{-}2,6)]^+$) unit can be connected to a second transition metal (TM) complex fragment via a conjugated system. Another possibility to form multimetallic assemblies is given by the C≡C unit itself. Here, transition metals (TMs) such as Cu(I) or Ag(I) can be attached via η^2-coordination. Examples of such complexes are known.[10,11] These multimetallic systems will allow for the investigation of possible metal−metal interactions along the organic fragments and hence evaluate these complexes as "nano-conducting" materials.

Results and Discussion

Preparation and Characterization of Monoplatinum Acetylides. Reaction of {Pt}Cl (**1**)[4] with in situ prepared lithium acetylides (eq 1) at −78 °C leads to



1, {Pt}Cl

{Pt}C≡CR

2: R = $SiMe_3$

3: R =

4: R = C_6H_4CN-4

5: R = C_5H_4N-4

(1)

the formation of platinum acetylides **2**−**5**. These complexes can be isolated as pure materials in 20−80% yield.

The most representative spectroscopic data (IR, ^1H, and $^{13}C\{^1H\}$ NMR) of these compounds are given in Table 1.

In comparison with the $\nu_{C\equiv C}$ values of free acetylenes,[12] the IR spectra of compounds **3**−**5** all exhibit ca. 35 cm^{-1} lower values (Table 1). For complex **2** this $\nu_{C\equiv C}$ band is observed at 2018 cm^{-1}. In the sharp and well-resolved ^1H NMR spectra of the acetylides **2**−**5**, singlet resonances of the CH_2NMe_2 methyl and CH_2 protons are generally shifted (in comparison with **1**) by about 0.1 ppm to lower field with coupling constants ($^3J_{PtH}$) between 38 and 44 Hz (Table 1). In the $^{13}C\{^1H\}$ NMR spectra, the ^{13}C resonances of the NCN ligand are shifted by 15−20 ppm (C_{ipso}) and ca. 3 ppm for the *ortho*-carbon atoms, respectively. The δ $^{13}C(C\equiv C)$ of the two acetylenic carbon atoms are found in regions that are typical for Pt acetylides. Due to the low intensity of the C_{ipso} of the aryl [C(1)] and acetylide ligands, ^{195}Pt−C satellite resonances could not be detected.

Reactions of {Pt}C≡CSiMe₃ (2). Knowledge of the stability of the metal−carbon bonds in compounds such as **2** in the presence of various TM complexes such as Cu reagents is necessary for two reasons: (i) when the C≡C unit is used for the construction of multimetallic systems containing, for example, a Cu(I) metal center [13] and (ii) when larger Pt acetylides are created based on **1**.[14] We were concerned that the use of functionalized acetylenes in organolithium reactions might lead to

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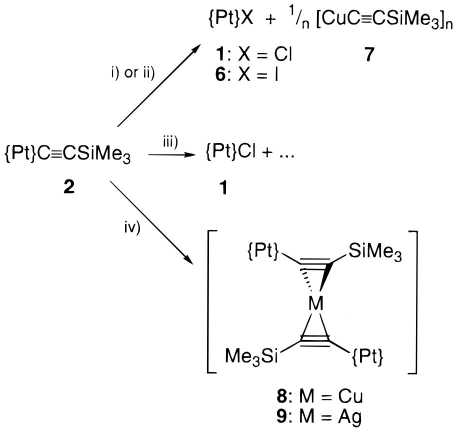
(14) Cu(I)-catalyzed reactions to form stable metal acetylides are well known and have recently been applied to the preparation of acetylene TM complexes such as (η^5-C_5H_5)Ni(PPh_3)C≡CC≡CH[15] or (bipy)Pt(C≡CR)$_2$.[16]

Table 1. Representative IR and ^{1}H and ^{13}C{^{1}H} NMR Spectroscopic Data of the Platinum Acetylides 3−5 as Well as of {Pt}Cl (1) for Comparison

		^{1}H ($^3J_{PtH}$ [Hz])		^{13}C {^{1}H} (J_{PtC} [Hz])			
compound	IR [cm^{-1}]	NMe$_2$	CH$_2$	C$_{ipso}$(Pt)	C$_{ipso}$(CH$_2$)	PtC≡***C***	Pt***C***≡C
1		3.08 (38.0)	4.01 (45.9)	145.2	143.3 (76.4)		
2	2018	3.15 (43.3)	4.08 (43.4)	159.6	146.2 (56.4)	110.6	138.9
3	2071	3.21 (41.3)	4.14 (42.6)	165.5	146.0	107.5	133.8
4	2076	3.21 (41.1)	4.11 (43.0)	166.6	146.1	103.3	138.2
5	2079	3.19 (41.8)	4.12 (41.3)	166.1	146.0 (58.3)	106.0	136.5

Scheme 1



i) $^1/_n$ [CuCl]$_n$, CH$_2$Cl$_2$, 25°C;
ii) $^1/_n$ [CuI], CH$_2$Cl$_2$, 25°C;
iii) [*n*-Bu$_4$N]Cl ,CH$_2$Cl$_2$, 25°C;
iv) [Cu(NCMe)$_4$][BF$_4$] or Ag[BF$_4$], CH$_2$Cl$_2$, 25°C.

reactions at sites other than the acetylenic unit (i.e., poor chemoselectivity).

Thus, we carried out a series of experiments to address the stability and reactivity of the Pt−acetylide bond (Scheme 1). As model compound, the prototypical Pt−acetylide {Pt}C≡CSiMe$_3$ (**2**) was used.

First the stability of **2** toward [CuX]$_n$ (X = Cl, I) was tested, since these salts are likely intermediates in Cu(I)-mediated reactions at the acetylene fragment. As can be deduced from Scheme 1, treatment of **2** with equimolar amounts of [CuX]$_n$ leads to virtually quantitative formation of {Pt}Cl (**1**) or {Pt}I (**6**, identified by ^{1}H NMR)[4] and of a yellow precipitate, which was subsequently identified as [CuC≡CSiMe$_3$]$_n$ (**7**).[16] Formation of **1** was also observed when [n-Bu$_4$N]Cl was added to a solution of **2**. Interestingly, this result points toward a crucial role of the halide ions in these reactions. Thus, it can be concluded that the bonding of {Pt} to Cl (or I) is favored over a {Pt} σ-acetylide bond (as in **2**), cf. ref 4b. Furthermore, this implies that the applied Cu(I) halides are likely solubilized in the course of the reaction. Examples of Cu(I) complexes containing metal-bound acetylides are well known and usually incorporate a Cu$_2$Cl$_2$ unit with each of the Cu(I) centers η^2-coordinated to an alkyne.[10] Various reactions were carried out to test this hypothesis. No reaction was observed when equimolar amounts of {Pt}C≡CSiMe$_3$ (**2**) were reacted with [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]CuCl (**10**) in THF (25 °C, 12 h).[18] Obviously, the monomeric CuCl entity in **10** is shielded against a possible η^2-coordination of **2** by the bis-η^2-chelation of the titanocene bis(acetylide) unit. Thus, in the case of **10** the chloride ion is not available for subsequent formation of **1**. To see if the Pt−acetylide **2** is stable under similar conditions in the absence of free halide sources, it has been reacted with [Cu(NCMe)$_4$][BF$_4$] or Ag[BF$_4$], respectively. In these cases (Scheme 1), all spectroscopic data point toward retention of the Pt−acetylide bond and a reaction of the alkyne bond resulting in the formation of the heterotrimetallic complexes **8** (M = Cu) or **9** (M = Ag). Most informative data are derived from the IR spectra (KBr) and involve a shift of the $\nu_{C\equiv C}$ vibration from 2018 cm^{-1} (**2**) to 1918 cm^{-1} (**8**) or 1947 cm^{-1} (**9**). This indicates a bond weakening of the C≡C entity upon η^2-coordination of the triple bond to the M(I) center. [19] Also, in the case of complex **8**, absorption bands typical for η^1-coordinated acetonitriles (ca. 2200−2300 cm^{-1}) are absent.[20] Compared to **2**, the ^{1}H NMR spectra of **8** or **9** do not exhibit significant changes upon η^2-coordination of the respective M(I) center. However, in the ^{13}C{^{1}H} NMR spectrum of **9** two doublets are observed for the η^2-coordinated Pt−C$_\alpha$≡C$_\beta$ unit at 113.8 ppm (C$_\beta$, $^1J_{AgC}$ = 17 Hz) and 151.3 ppm (C$_\alpha$,$^1J_{AgC}$ = 19 Hz).

At −30 °C, crystals of **8** were grown from a THF/Et$_2$O solution. Preliminary X-ray crystallographic results suggest a tetrahedral environment around the Cu(I) center with two {Pt}C≡CSiMe$_3$ entities coordinated via their C≡C triple bonds. Similar complexes containing this structural motif have been prepared earlier.[21] The crystal packing of **8** displays large channel-like cavities in which the [BF$_4$] ions and solvent molecules are disordered. This restricts a more detailed crystallographic analysis.

In conclusion these results suggest that the reaction of **2** with Cu(I) halides is likely to proceed via intermediates in which the Cu(I) halide in some stage of the process becomes η^2-bonded to the acetylide unit. This situation leads to ligand exchange and hence the formation of compounds **1** and **7**, respectively. However, it must be recalled that the cleavage experiment of **2** with [*n*-Bu$_4$N]Cl points to a crucial role of the nucleophilic halide ion in the Pt−C bond cleavage process. It moreover underlines the strong *trans*-influence of the central C(sp^2) anion of the NCN ligand. As a direct consequence of this observation, Cu(I) halide-catalyzed reactions cannot be used with **1** to form other Pt(II) monoacetylides.

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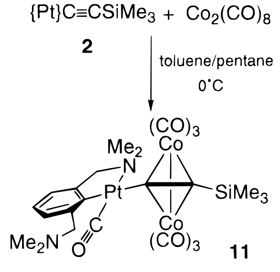
The successful formation of multimetallic complex **8** and **9**, using non-halide-containing transition metal complexes, prompted us to react **2** with other halogenless complexes which are known to coordinate acetylene derivatives. A classical example of this is $Co_2(CO)_8$, which upon reaction with alkynes leads to the formation of dicobaltatetrahedranes.[22] The result of the reaction of **2** with $Co_2(CO)_8$ is presented in eq 2. After workup, complex **11** is obtained as a dark-brown solid, which is stable at ambient temperature under a nitrogen atmosphere.



(2)

The ^1H NMR spectrum of **11** is consistent with the presence of one coordinated and one noncoordinated CH_2NMe_2 unit. The former shows J_{PtH} couplings on both the CH_2 and NMe_2 protons, due to Pt−N coordination. The resonance signals of the free CH_2NMe_2 group appear in the region typical for the free [NCN]H ligand [2.21 ppm (NMe_2), 3.44 ppm (CH_2)]. The IR spectrum of **11** displays the expected bands of the CO ligands (1980−2075 cm^{-1}).[22] The band at 2075 cm^{-1} is assigned to the $\nu_{C\equiv O}$ vibration of CO coordinated to Pt, although this value is slightly lower than that reported for, for example, $[(\eta^2\text{-}C_6H_4\{CH_2NMe_2\}\text{-}2)Pt(CO)I]$.[23] The related complex $[\{Pt\}CO]^+$, in which the CO ligand is η^1-coordinated *trans* to C(1) of the aryl, has a CO mode at 2086 cm^{-1}.[4] Hence, the *trans*-influence of NMe_2 is stronger than that of the aryl carbanion of the NCN ligand. The vibration mode of the C≡C unit was detected at 1558 cm^{-1}, a region that is typical for dicobalt-bound acetylenes and strongly indicates a weakening of the C≡C bond due to coordination.[22] Taking into account the spectroscopic evidence, compound **11** is the first example of a Pt−NCN complex where a Pt−N coordination has been replaced by an incoming monodentate ligand, in this case CO.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been used to study the liberation of the Pt-centered CO molecule from compound **11**. In the TGA plot, a weight loss of 3.5% is observed at 105 °C. This loss corresponds with the liberation of one molecule CO per formula unit of **11**. Further heating causes slow degradation. The DSC experiment reveals that the liberation of CO is exothermic (105 °C, $\Delta H = 65 \pm 5$ kJ mol^{-1}). Thus, these data indicate that **11** is the kinetic reaction product.

From a pentane solution of **11** (−40 °C), crystals suitable for an X-ray crystal diffraction study have been obtained. The molecular structure of **11** in the solid state is shown in Figure 1. It fully corroborates the interpretation of the spectroscopic data for the compound in solution (vide supra). Selected bond lengths and angles are presented in Table 2.

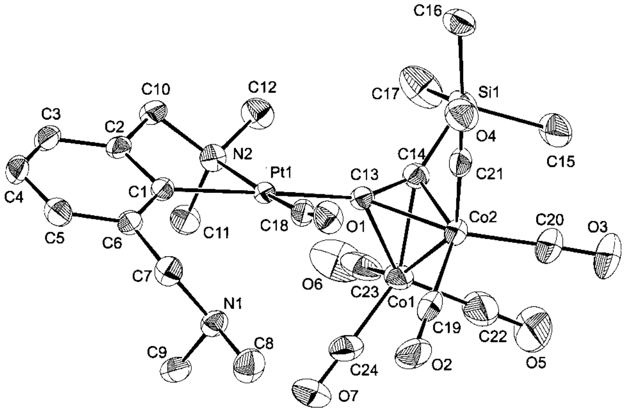


Figure 1. Displacement ellipsoid drawing (50% probability level) of **11** with molecular geometry and atom-numbering scheme.

The coordination environment around the Pt center reveals a slightly distorted square-planar geometry. The distance Pt(1)−C(1) [2.062(4) Å] is in the range of other known Pt−aryl bonds, e.g., that reported by Brune et al. (ca. 2.06 Å)[24] or in $[\textit{cis}\text{-}(PPh_3)_2Pt(CO_2H)(C_6H_5)]$ [2.071(8) Å].[25] This bond is longer, however, than that in η^3-coordinated NCN compounds such as $[PtCl\{C_6H_2(Me_2NCH_2)_2\text{-}2,6\text{-}(C\equiv CH)\text{-}4\}]$ [1.911(12) Å].[6] This mirrors the change in the coordination mode of the NCN ligand from η^3-*N,C,N* to η^2-*N,C*. The distance of the noncoordinating nitrogen N1 to the carbonyl group is small [N1−C18 2.726(4) Å; N1−O1 2.990(4) Å], but the nitrogen lone pair does not point in the direction of this group, so there is no direct binding interaction. The bond length of Pt to the carbonyl carbon atom [Pt(1)−C(18) 1.844(4) Å] resembles other previously reported Pt−carbonyl distances [ref 23, 1.842(16) Å; ref 26, 1.82(2) Å]. The other bond lengths of the tetrahedrane framework [Co(1)−Co(2) 2.4896(9) Å; Co(1)−C(13) 2.069(4); Co(1)−C(14) 2.008(4) Å] and the C−O distances of the carbonyl ligands attached to Co are in accordance with earlier published values.[22] Interestingly, the bond distance of Pt to the tetrahedrane unit [Pt(1)−C(13) 2.084(4) Å] does not have the value expected for a Pt bound to sp-hybridized carbon atoms (around 1.9 Å).[27] In fact, it features separations detected for bonds between Pt and sp^2-hybridized[28] or even sp^3-hybridized carbon centers.[29] Also, the bond length C(13)−C(14) [1.325(5) Å] of the former C≡C unit of **4** is in agreement with the expected change in hybridization of these carbon atoms upon binding to the Co_2 carbonyl unit. Actually, this distance resembles that of C=C double bonds,[22] which is supported by the aforementioned shift of the C−C stretching mode. The Si(1)−C(14) [1.858(4) Å] bond

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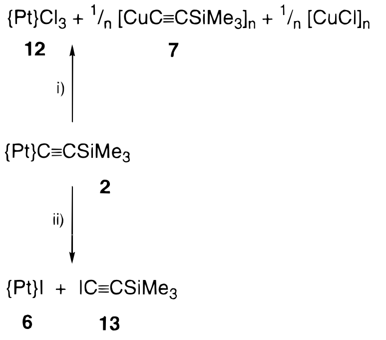
Table 2. Selected Bond Lengths [Å] and Angles [deg] for 11[a]

bond lengths				angles	
Pt1−C1	2.062(4)	O1−C18	1.126(4)	N2−Pt1−C18	171.68(14)
Pt1−N2	2.112(3)	O2−C19	1.139(5)	C1−Pt1−C13	173.76(14)
Pt1−C13	2.084(4)	N2−C10	1.494(5)	C13−Co1−C14	37.89(14)
Pt1−C18	1.844(4)	N1−C7	1.450(5)	C7−N1−C8	109.3(3)
Co1−Co2	2.4896(9)	C13−C14	1.325(5)	N1−C7−C6	114.2(3)
Co1−C13	2.069(4)	Si1−C14	1.858(4)	N2−C10−C2	109.7(3)
Co1−C14	2.008(4)	N1−C18	2.726(4)	Pt1−C13−C14	157.1(3)
Co1−C22	1.775(5)	N1−O1	2.990(4)	Si1−C14−C13	150.9(3)
Pt1−N1	3.416(3)			Pt1−C18−O1	172.4(3)
Si1−C15	1.863(4)			Pt1−C1−C4	169.1(2)

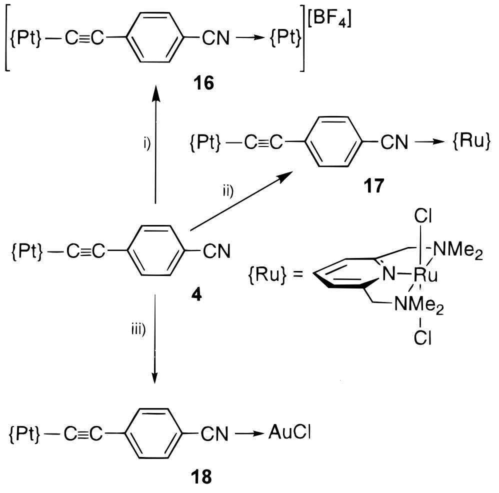
[a] Standard deviation in units of the last significant figure in parentheses.

Scheme 2



i) 2 CuCl$_2$, MeOH, 25°C;
ii) I$_2$, THF, 25°C.

Scheme 3



i) [{Pt}·H$_2$O]BF$_4$ (**14**), CH$_2$Cl$_2$, 25°C;
ii) $^1/_2$ {Ru}N≡N{Ru} (**15**), THF, 25°C;
iii) Au(CO)Cl, CH$_2$Cl$_2$, - 78°C to - 40°C .

length lies in the range expected for Si−C(sp) or Si−C(sp^2) distances.[30] The angles N(2)−Pt(1)−C(18) [171.68(14)°] and C(1)−Pt(1)−C(13) [173.76(14)°] are those of a distorted square-planar coordination. The Pt(1)−C(1)−C(4) angle of 169.1(2)° reflects also the η^2-*N,C* coordination mode of the NCN framework, which leads to a tilt of the Pt−C bond away from the bulky (i.e., noncoordinating) *ortho*-CH$_2$NMe$_2$ substituent.[5e]

Previously, the reaction of {Pt}Cl (**1**) with either 2 equiv of CuCl$_2$ or an excess of Cl$_2$(g) has been investigated, which results in the clean formation of Pt(IV)−NCN pincer complex {Pt}Cl$_3$.[31] To investigate if related Pt(IV) monoacetylides could be synthesized, {Pt}C≡CSiMe$_3$, **2,** was reacted with a 2-fold excess of CuCl$_2$ (Scheme 2).

During the course of this reaction an orange precipitate was formed while the supernatant solution turned intensely yellow. By IR spectroscopy, the precipitate was identified as the Cu(I) acetylide **7**. Evaporation of the solution to dryness yielded a yellow compound, which was identified as the previously characterized Pt(IV) complex {Pt}Cl$_3$ (**12**). Traces of the butadiyne Me$_3$Si-(C≡C)$_2$SiMe$_3$ could not be detected. This result indicates that initially oxidation of the Pt(II) center to Pt(IV) takes place followed by a ligand exchange between the resulting Cu(I) chloride and an intermediate Pt(IV) acetylide.

Furthermore, **2** was reacted with 1 equiv of I$_2$ to see if the oxidation product {Pt(IV)}(C≡CSiMe$_3$)I$_2$ could be obtained. A similar reaction in the case of {Pt}C$_6$H$_4$Me-4 successfully gave *cis*-{Pt}(C$_6$H$_4$Me-4)I$_2$.[32] However, the only products formed in this reaction of **2** with I$_2$ were {Pt}I (**6**) and IC≡CSiMe$_3$ (**13**).[33] Both were identified by their respective IR and ^{1}H NMR spectra. Thus, the preparation of Pt(IV) acetylides via this route is not a viable option. It is likely that also in these reactions the halide effect (reaction with [CuCl]$_n$) plays a dominant role and leads to cleavage of the Pt−acetylide bond.

Coordination Chemistry of {Pt}C≡CC$_6$H$_4$CN (4). The replacement of the SiMe$_3$ substituent by a functionalized arene, e.g., a 4-benzonitrile substituent as in compound **4**, permits the construction of heterobimetallic systems in which the two metals are connected in a linear, one-dimensional fashion to each other. The capability of nitriles to form linear complexes is already well established.[20] Typically, the CN unit has the potential for η^1-*N*-coordination, which leads to the formation of linear bridges between two metal atoms. Accordingly, **4** was reacted with equimolar amounts of [{Pt}·H$_2$O][BF$_4$] (**14**)[4] or 0.5 equiv of [Ru]N≡N[Ru] (**15**) ({Ru} = [η^3-*mer*-(2,6-{Me$_2$NCH$_2$}$_2$C$_5$H$_3$N}RuCl$_2$])[34] (Scheme 3). In another approach, **4** was also reacted with Au(CO)Cl or [Au$_2$Cl$_6$], which are known for their ability to form linear molecular aggregates (Scheme 3).

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The reaction of **4** in CH_2Cl_2 solution with equimolar amounts of ionic **14** leads to the formation of the monocationic bis-Pt complex **16** in virtually quantitative yield. Here, both Pt-containing units are orientated in a head-to-head fashion. With the neutral dinitrogen-bridged bis-Ru compound **15**, formation of neutral bimetallic **17** occurs following liberation of N_2. Here, the reaction can be followed visually by the change of the reaction mixture from brown to an intense red color and can be monitored by following the ν_{CN}, which changes from 2220 cm^{-1} (**4**) to 2248 cm^{-1} (**16**). For neutral heterobimetallic **17** the ν_{CN} is found at lower frequency (2198 cm^{-1}), which is an unusual result for η^1-bound nitriles.[20] This shift to lower wavenumbers can be explained by the different back-bonding properties of the neutral {Ru} fragment in **17** and the cationic $\{Pt\}^+$ fragment in **16**. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **16** and **17** show well-resolved signals for the organic groups present. The ^1H NMR spectrum of **17** shows singlets for the CH_2 and NMe_2 protons of the {Ru} fragment, which indicates that the Pt−cyanide ligand **4** is coordinated *trans* to the pyridine-N of the {Ru} fragment with the Cl ligands in *trans*-position. This interpretation is corroborated by X-ray crystal data obtained for {Ru}NCPh, which can be considered as a model for **17**.[35] In contrast to the results of the reactions of {Pt}−acetylide fragments with Cu(I) and Cu(II) halides, the presence of halides in {Ru} fragments does not result in Pt−C≡ bond cleavage. Therefore, other TM complexes known to form linear assemblies were investigated, e.g., of Au(I), since a number of linear Au(I)−nitrile or isonitrile complexes are known.[36] The reaction of Au(CO)Cl (CH_2Cl_2) with equimolar amounts of **4** in the temperature range −78 to −40 °C leads to the immediate formation and precipitation of an intermediate, which was surmised to be the η^1-adduct of **4** to AuCl, i.e., **18**, through substitution of CO by the nitrile group (Scheme 3). The formation of this intermediate can be followed by IR spectroscopy. The CO vibration (2158 cm^{-1})[37] loses intensity, and the stretching band of the nitrile is shifted to higher wavenumbers, i.e., from 2220 to 2248 cm^{-1}. This is fully consistent with η^1-coordination of CN to Au.[20] Unfortunately, intermediate **18** could not be isolated. With the reaction still incomplete, upon raising the temperature above −40 °C, a gold mirror begins to appear on the walls of the reaction vessel. This observation can be explained by a group-exchange reaction between **18**, which leads again to {Pt}Cl (**1**) and the corresponding Au(I)−acetylide (cf. the reactions with $[CuCl]_n$ above). Oxidative coupling of two acetylide units then leads to the formation of the 1,4-butadiyne derivative **19** (which can be isolated as an off-white solid) and formation of Au(0). Compound **19** was identified by IR and ^1H NMR spectroscopy.[38] In addition, ^1H NMR investigation of the reaction mixture shows the presence of **1**.[4]

Table 3. Comparison of Electrochemical Data of Compounds 1, 2, 4, 17, and {Ru}NCPh[a]

		oxidation		
		Pt	Ru	
compound		E_{ox} [V]	$E_{1/2}$	ΔE [mV]
{Pt}Cl	**1**	0.76		
{Pt}C≡XSiMe$_3$	**2**	0.55		
{Pt}C≡CC$_6$H$_4$CN-4	**4**	0.50		
{Pt}C≡CC$_6$H$_4$CN{Ru}	**17**	0.48	0.31	50
{Ru}NCPh			0.32	70

[a] Cyclic voltammograms have been recorded in the presence of $[n\text{-}Bu_4N]\ [PF_6]$ ($c = 0.1$ mol dm^{-3}) at 25 °C under N_2; scan rate 100 mV s^{-1}; potentials are referenced to FcH/FcH$^+$ ($E_{1/2} = 0.00$ V).

The reaction of $[Au_2Cl_6]$ with nitriles typically yields air-stable Au(III) nitrile adducts.[42] However, reaction of this Au(III) species with equimolar amounts of compound **4** (−78 °C, CH_2Cl_2) leads again, after immediate formation of a brown precipitate, to the buildup of a gold mirror on the walls of the reaction flask after ca. 2 min. Workup of the reaction mixture yields the Pt(IV) compound **12**[31] and the butadiyne **19**.[41]

Electrochemical Behavior of Mononuclear Platinum Acetylides. The preparation of the Pt acetylides **2**−**5** and the study of their reactivity have revealed that the Pt σ-acetylide bond is not stable to halogen-containing oxidants such as $CuCl_2$, I_2, or Au_2Cl_6. As the monoanionic NCN ligand stabilizes transition metals in high oxidation states,[31,32] it is of interest to study if Pt(IV) acetylides can be detected electrochemically. Also, partial oxidation of oligometallic compounds offers the opportunity to form stable mixed-valence compounds. This has been observed in, for example, the bis-Ru complex $\{(terpy)Ru[2,6\text{-}(Me_2NCH_2)_2C_6H_2]\}_2^{4+}$ [5c] or the bis-Pt compound $\{(MeCN)Pt[2,6\text{-}(Me_2NCH_2)_2C_6H_2]\}_2^{4+}$.[5b] There, oxidation of the metal centers did not affect the ligand framework. Therefore, representative examples of the Pt acetylides presented above were subjected to cyclovoltammetric investigation, and the results were compared to the values obtained for **1** (Table 3).

All oxidative processes are irreversible in THF solution and are shifted from +0.76 V (**1**) by ca. 200 mV to more negative potentials. This mirrors the substitution of the Cl ligand by an acetylide (Table 3). An interpretation is that the electron density on the Pt center has increased and thus it is easier to oxidize. The measurement of the total current of the cathodic process for compound **2** suggests that during the oxidation two electrons are removed irreversibly from the Pt center, thus forming a Pt(IV) species. However, reductive processes could not be observed in this system. The electrochemical study of the mixed-metal complex **17** clearly shows that attachment of the {Ru} fragment to the Pt system does not alter the electrochemical properties of the latter metal. Also, comparison with the aforementioned benzonitrile complex {Ru}NCPh ($E_{1/2} = 0.32$V, $\Delta E = 70$ mV) [35] reveals that the oxidation potential Ru(II)/Ru(III) is not influenced by the remote

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{Pt} unit. This contrasts with recent findings obtained for a related Ti–Ru system.[43]

Conclusions

A series of Pt monoacetylides of the form {Pt}$C\equiv CR$ ({Pt} = $[Pt(C_6H_3\{Me_2NCH_2\}_2\text{-}2,6)]^+$) have been synthesized and fully characterized. The crystal structure determination of {Pt}$C\equiv CC_6H_2I\text{-}1\text{-}(CH_2NMe_2)_2\text{-}3,5$ (**6**) exhibits a rigid-rod-like arrangement. The acetylenic unit is designed to carry different functionalities which enable the construction of oligometallic complexes. Stability studies have been carried out on the prototypical complex {Pt}$C\equiv CSiMe_3$ (**2**). This has revealed that the $C\equiv CSiMe_3$ unit is easily substituted by halide ions. In the case of reactions with Cu(I) halides, this likely proceeds via the formation of an η^2-coordinated intermediate. The accessibility of this has been shown by the assembly of M(I)-bridged dimeric structures $[\{\eta^2\text{-}[\{Pt\}C\equiv CSiMe_3]\}_2M][BF_4]$ (**8**, M = Cu; **9**, M = Ag). The structure of this compound has been confirmed by an X-ray crystal structure analysis. The coordination ability of the $C\equiv C$ unit was used for the synthesis of heterotrimetallic $[(\mu^2\text{-}[(\eta^2\text{-}NCN)Pt(\eta^1\text{-}CO)C\equiv CSiMe_3])\text{-}Co_2(CO)_6]$ (**11**). Here, an unprecedented lowering of the hapticity of an η^3-coordinated NCN ligand was observed upon coordination of an incoming monodentate CO. TGA and DSC studies revealed that **11** is the kinetic product of the reaction. The construction of Pt(IV) monoacetylides using $CuCl_2$ or I_2 could not be achieved. Instead, cleavage of the Pt–acetylide σ-bond was observed and, in the case of $CuCl_2$, the formation of {Pt}Cl_3. The attachment of the functionalized Pt acetylide {Pt}$C\equiv CC_6H_4CN\text{-}4$ (**4**) to {Ru}, {Pt}, AuCl, or $AuCl_3$ has been carried out successfully via the η^1-coordination of the $-C\equiv N$ functionality. However, both of the gold adducts decompose at low temperatures, and this leads to the formation of the butadiyne $NCC_6H_4(C\equiv C)_2C_6H_4CN$ (**19**) via oxidative coupling and {Pt}Cl or {Pt}Cl_3, respectively. Cyclic voltammetric studies of representative examples reveal that the irreversible two-electron Pt(II)/Pt(IV) oxidation is shifted to a more negative potential relative to {Pt}Cl (**1**). This is indicative of an increase in electron density on the Pt-core upon substitution of Cl by an acetylide. The coordination of a Ru-containing complex fragment does not alter the electrochemical properties of the Pt core. Also, no influence of the Pt center on the electrochemical behavior of this Ru complex fragment has been observed. This indicates that the Pt–acetylides presented here can be used for the construction of multimetallic compounds but they are of limited scope.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified by distillation from sodium/benzophenone ketyl; pentane was purified by distillation from calcium hydride. Infrared spectra were obtained with a Mattson Galaxy Series FTIR 5000. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC 300 spectrometer. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the internal reference signal. FAB mass spectra were recorded at the Department of Mass Spectrometry, Bijvoet Center, Utrecht University, on a JEOL JMS SX/SX 102A four-sector mass spectrometer operating at 10 kV accelerating voltage. Melting points were determined on a Büchi melting point apparatus. Microanalyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr, Germany. Electrochemical measurements were carried out by cyclic voltammetry in a solution of NBu_4PF_6 (0.1 mol dm^{-3}) in THF at 25 °C, using a standard three-electrode cell on a Princeton Applied Research EG&G 263A analyzer. All potentials were referenced to the ferrocene/ferrocenium couple, which was defined to have $E_{1/2} = 0.00$ V.

General Remarks. {Pt}Cl (**1**),[4] $C_6H_3(CH_2NMe_2)_2\text{-}2,6\text{-}(C\equiv CH)\text{-}4$,[6] $HC\equiv CC_6H_4CN\text{-}4$,[44] $HC\equiv CC_5H_4N\text{-}4$,[45] $[Cu(NCMe)_4][BF_4]$,[46] $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2]CuCl$ (**10**),[18] $[\{Pt\}\cdot H_2O][BF_4]$ (**14**),[4] {Ru}$N\equiv N${Ru} (**15**),[34] Au(CO)Cl,[37] and $[Au_2Cl_6]$[37] were prepared following literature procedures. All other materials were commercially available and used as received.

Synthesis of {Pt}$C\equiv CSiMe_3$ (2). To a solution of $LiC\equiv CSiMe_3$ (320 mg, 3.1 mmol) in Et_2O (200 mL) was added {Pt}Cl (**1**) (1.28 g, 3.1 mmol) at − 78 °C. The cooling bath was then removed, and after stirring (24 h, 25 °C), all volatiles were evaporated in vacuo. The residue was extracted with pentane (2 × 40 mL) and then with benzene (3 × 40 mL). Concentration of the combined benzene extracts to ca. 5 mL was followed by addition of pentane (150 mL). This lead to the precipitation of **4** as an off-white solid (960 mg, 65% yield based on **1**). Mp: [°C] > 200. IR (KBr): [cm^{-1}] 2018 (s) [$\nu_{C\equiv C}$]. ^1H NMR (300 MHz) ($CDCl_3$): [δ] 0.13 (s, 9 H, Si*Me*$_3$), 3.15 (s, $^3J_{HPt} = 44$ Hz, 12 H, N*Me*$_2$), 4.07 (s, $^3J_{HPt} = 41$ Hz, 4 H, C*H*$_2$), 6.7−7.1 (m, 3 H, C$_6$*H*$_3$). $^{13}C\{^1H\}$ NMR (75 MHz) ($CDCl_3$): [d] 1.4 (Si*Me*$_3$), 55.8 (N*Me*$_2$), 80.0 (s, $^2J_{CPt} = 42$ Hz, *C*H$_2$), 110.6 (PtC≡*C*), 118.5 (s, $^3J_{CPt} = 18$ Hz, *CH*/C$_6$H$_3$), 128.3 (*CH*/C$_6$H$_3$), 138.9 (Pt*C*≡C), 146.2 (s, $^2J_{CPt} = 56$ Hz, ^{i}*C*/C$_6$H$_3$), 159.6 (^{i}*C*/C$_6$H$_3$). Electrospray-MS [*m/z* (rel int)]: 851 (20) $\{M^+ + [C_{12}H_{19}N_2Pt]\}$, 483 (10) M^+, 386 (100) $\{M^+ - [C_5H_9Si]\}$. Anal. Calcd for $C_{17}H_{28}N_2PtSi$ (483.60): C, 42.22; H, 5.84; N, 5.79. Found: C, 42.14; H, 5.94; N, 5.72.

Synthesis of {Pt}$C\equiv CC_6H_3(CH_2NMe_2)_2\text{-}3,5$ (3). $HC\equiv CC_6H_3(CH_2NMe_2)_2\text{-}3,5$ (250 mg, 1.2 mmol) was dissolved in Et_2O (150 mL), and the solution was cooled to − 78 °C. Then *n*-BuLi (0.8 mL, 1.6 M) was added, and the solution was stirred for 3 h. Then **1** (510 mg, 1.2 mmol) was added, and the reaction mixture was allowed to warm to 25 °C. After 24 h, all volatile materials were removed in vacuo. The residue was extracted with pentane (4 × 30 mL) and with Et_2O (3 × 40 mL). Separation from undissolved material was effected by centrifugation. Evaporation to dryness of the collected Et_2O extracts yielded **5** (300 mg, 40% yield based on **1**) as an off-white solid. Mp: [°C] 150 (dec). IR (KBr): [cm^{-1}] 2076 (s) [$\nu_{C\equiv C}$]. ^1H NMR (300 MHz) ($CDCl_3$): [δ] 2.22 (s, 12 H, N*Me*$_2$), 3.23 (s, $^3J_{HPt} = 46$ Hz,12 H, N*Me*$_2$), 3.38 (s, 4 H, C*H*$_2$), 4.11 (s, $^3J_{HPt} = 48$ Hz, 4 H, C*H*$_2$), 6.8−7.1 (m, 3 H, C$_6$*H*$_3$), 7.23 (s, 2 H, C$_6$*H*$_2$). $^{13}C\{^1H\}$ NMR (75 MHz) ($CDCl_3$): [δ] 45.4 (N*Me*$_2$), 56.0 (N*Me*$_2$), 64.3 (*C*H$_2$), 80.0 (*C*H$_2$), 107.7 (PtC≡*C*), 118.5 (*CH*/C$_6$H$_3$), 125.3 (^{i}*C*/C$_6$H$_3$), 127.6 (*CH*/C$_6$H$_3$), 131.2 (*CH*/C$_6$H$_2$), 136.8 (Pt*C*≡C), 138.1 (^{i}*C*/C$_6$H$_2$), 146.1 (^{i}*C*/C$_6$H$_3$), 166.5 (^{i}*C*/C$_6$H$_3$). FAB-MS [*m/z* (rel int)]: 601 (50) M^+, 385 (100) $\{[C_{12}H_{19}N_2Pt]^+\}$, 217 (10) $\{[C_{14}H_{17}N_2]^+\}$, 215 (10) $\{[C_{14}H_{15}N_2]^+\}$. Anal. Calcd for $C_{26}H_{38}N_4Pt$ (601.70): C, 51.90; H, 6.37; N, 9.31. Found: C, 52.11; H, 6.32; N, 9.22.

Synthesis of {Pt}$C\equiv CC_6H_4C\equiv N\text{-}4$ (4). To a Et_2O solution (100 mL) of $LiC\equiv CC_6H_4CN\text{-}4$ (110 mg, 0.8 mmol) was added **1** (340 mg, 0.8 mmol) at − 78 °C. After gradual warming to 25

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°C and stirring for 24 h, all volatile material was removed in vacuo. The brown residue was extracted with CH_2Cl_2 (3 × 50 mL) and then separated from undissolved material by centrifugation. After evaporation of the CH_2Cl_2 solution, the resulting solid was washed with ethyl acetate (3 × 10 mL) to yield **7** (250 mg, 60% yield based on **1**) as an off-white solid. Mp: [°C] > 200. IR (KBr): [cm^{-1}] 2220 (s) [ν_{CN}], 2071 (s) [$\nu_{C\equiv C}$]. ^{1}H NMR (300 MHz) ($CDCl_3$): [δ] 3.21 (s, $^3J_{HPt}$ = 41 Hz, 12 H, N*Me*$_2$), 4.14 (s, $^3J_{HPt}$ = 43 Hz, 4 H, C*H*$_2$), 6.7–7.1 (m, 3 H, C_6*H*$_3$), 7.4–7.5 (m, 4 H, C_6*H*$_4$). ^{13}C{^{1}H} NMR (75 MHz) ($CDCl_3$): [δ] 56.0 (N*Me*$_2$), 80.0 (***C***H$_2$), 107.2 (*C*N), 107.5 (PtC≡*C*), 118.7 (*CH*/C_6H_3), 119.7 (*^{i}C*/C_6H_4), 125.3 (*CH*/C_6H_3), 129 (*^{i}C*/C_6H_4), 131.6 (*CH*/C_6H_4), 131.9 (*CH*/C_6H_4), 133.8 (Pt*C*≡C), 146.0 (*^{i}C*/C_6H_3), 165.5 (*^{i}C*/C_6H_3). FAB-MS [*m*/*z* (rel int)]: 512 (30) {[M + H]$^+$}, 511 (10) M$^+$, 389 (100) {[$C_{12}H_{19}N_2Pt$]$^+$}, 58 (50) {[C_3H_8N]$^+$}. Anal. Calcd for $C_{21}H_{23}N_3Pt$ (512.53): C, 49.21; H, 4.52; N, 8.20. Found: C, 49.08; H, 4.60; N, 8.23.

Synthesis of {Pt}C≡CC$_5$H$_4$N-4 (5). Experimental conditions and workup were the same as for the preparation of compound **7**. Specific experimental details: 4-LiC≡CC$_5$H$_4$N (190 mg, 1.8 mmol), {Pt}Cl (**1**) (750 mg, 1.8 mmol). Yield: 600 mg, 68% yield based on **1**. Mp: [°C] > 200. IR (KBr): [cm^{-1}] 2079 (s) [$\nu_{C\equiv C}$]. ^{1}H NMR (300 MHz) ($CDCl_3$): [δ] 3.19 (s, $^3J_{HPt}$ = 42 Hz, 12 H, N*Me*$_2$), 4.12 (s, $^3J_{HPt}$ = 39 Hz, 4 H, C*H*$_2$), 6.8–7.1 (m, 3 H, C_6*H*$_3$), 7.1–7.2 (m, 2 H, C_5*H*$_4$N), 8.3–8.4 (m, 2 H, C_5*H*$_4$N). ^{13}C{^{1}H} NMR (75 MHz) ($CDCl_3$): [δ] 56.0 (N*Me*$_2$), 79.9 (*C*H$_2$), 106.0 (PtC≡*C*), 118.7 (*CH*/C_6H_3), 123.7 (*CH*/C_6H_3), 125.0 (*^{i}C*/C_6H_3), 126.2 (*CH*/C_5H_4N), 136.5 (Pt*C*≡C), 146.3 (*^{i}C*/C_6H_3), 149.1 (*CH*/C_5H_4N), 166.1 (*^{i}C*/C_6H_3). Anal. Calcd for $C_{19}H_{23}N_3Pt$ (488.50): C, 46.72; H, 4.75; N, 8.60. Found: C, 46.58; H, 4.86; N, 8.66.

Reaction of {Pt}C≡CSiMe$_3$ (2) with [CuCl]$_n$. To a suspension of [CuCl]$_n$ (20 mg, 0.2 mmol) in CH_2Cl_2 (30 mL) was added {Pt}C≡CSiMe$_3$ (**2**) (100 mg, 0.2 mmol). After 1 h stirring at 25 °C, the orange suspension was separated by centrifugation. Subsequently, the supernatant liquid was concentrated to 5 mL. Addition of 30 mL of pentane gave an off-white precipitate. By ^{1}H NMR spectroscopy, this was identified as **1**.[4] The precipitate was identified as **7** by IR spectroscopy.

Reaction of {Pt}C≡CSiMe$_3$ (2) with [CuI]$_n$. Experimental conditions and workup were the same as for the reaction of {Pt}C≡CSiMe$_3$ (**2**) with [CuCl]$_n$. Specific experimental details: **2** (80 mg, 0.2 mmol), [CuI]$_n$ (30 mg, 0.2 mmol), 30 mL of CH_2Cl_2. By ^{1}H NMR spectroscopy, the precipitate formed after addition of pentane was identified as **6**.[4]

Reaction of {Pt}C≡CSiMe$_3$ (2) with {[Ti](C≡CSiMe$_3$)$_2$}CuCl (10). To a THF solution (30 mL) of **10** (60 mg, 0.1 mmol) was added **2** (40 mg, 0.1 mmol). After stirring (12 h, 25 °C) all volatile material was evaporated. IR and ^{1}H NMR spectra reveal solely the presence of the starting materials.

Synthesis of ({η^2-{Pt}C≡CSiMe$_3$}$_2$Cu)[BF$_4$] (8). [Cu(MeCN)$_4$][BF$_4$] (20 mg, 0.06 mmol) and **2** (60 mg, 0.12 mmol) were brought together in a reaction flask. After addition of CH_2Cl_2 (30 mL), the reaction mixture was stirred for 2 h. Concentration to ca. 5 mL and cooling to − 40 °C (48 h) resulted in the precipitation of **8** (55 mg, 80% yield based on **2**) as an off-white solid. Mp: [°C] 155 (dec). IR (KBr): [cm^{-1}] 1918 (s) [$\nu_{C\equiv C}$]. ^{1}H NMR (300 MHz) ($CDCl_3$): [δ] 0.28 (s, 18 H, SiMe$_3$), 3.16 (s, $^3J_{HPt}$ = 37.7 Hz, 24 H, N*Me*$_2$), 4.12 (s, $^3J_{HPt}$ = 39 Hz, 4 H, C*H*$_2$), 6.8–7.1 (m, 3 H, C_6*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz) ($CDCl_3$): [δ] 1.0 (Si*Me*$_3$), 56.1 (N*Me*$_2$), 79.3 (*C*H$_2$), 118.8 (PtC≡*C*), 119.5 (*CH*/C_6H_3), 125.4 (*CH*/C_6H_3), 145.8 (*^{i}C*/C_6H_3), 162.6 (Pt*C*≡), 163.3 (*^{i}C*/C_6H_3). Anal. Calcd for $C_{34}H_{56}BCuF_4N_4Pt_2Si_2$ (1117.55): C, 36.54; H, 5.05; N, 5.01. Found: C, 36.64; H, 5.02; N, 5.08.

Synthesis of ({η^2-{Pt}C≡CSiMe$_3$}$_2$Ag)[BF$_4$] (9). All handlings were carried out under the exclusion of light; all other experimental procedures were as described for the preparation of **8**. Specific experimental details: Ag[BF$_4$] (20 mg, 0.1 mmol), **2** (90 mg, 0.2 mmol), CH_2Cl_2 (10 mL). Yield: 100 mg, 90% based on **2**. Mp: [°C] 115 (dec). IR (KBr): [cm^{-1}] 1947 (s) [$\nu_{C\equiv C}$], 1257 (s) [$\nu_{C\equiv Si}$]. ^{1}H NMR (300 MHz) ($CDCl_3$): [δ] 0.27 (s, 18 H, SiMe$_3$), 3.15 (s, $^3J_{HPt}$ = 41.6 Hz, 24 H, N*Me*$_2$), 4.09 (s, $^3J_{HPt}$ = 48.2 Hz, 4 H, C*H*$_2$), 6.8–7.1 (m, 3 H, C_6*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz) ($CDCl_3$): [δ] 1.60 (Si*Me*$_3$), 56.3 (N*Me*$_2$), 79.4 (*C*H$_2$), 113.8 (d, ^1J = 17 Hz, PtC≡*C*), 119.3 (*CH*/C_6H_3), 125.2 (*CH*/C_6H_3), 145.4 (*^{i}C*/C_6H_3), 151.3 (d, $^1J_{AgC}$ = 19 Hz, Pt*C*≡), 163.3 (*^{i}C*/C_6H_3). Anal. Calcd for $C_{34}H_{56}AgBF_4N_4Pt_2Si_2$ (1163.90): C, 35.09; H, 5.02; N, 4.81; Si, 4.83. Found: C, 34.86; H, 5.10; N, 4.89; Si, 4.91.

Synthesis of {μ^2-[(η^1-NCN)Pt(η^1-CO)C≡CSiMe$_3$][Co$_2$(CO)$_6$]} (11). A toluene/pentane solution (40 mL, 1:1) of $Co_2(CO)_8$ (85 mg, 0.2 mmol) and **2** (100 mg, 0.2 mmol) was stirred at 0 °C (2 h). All volatiles were then evaporated, and the residue was extracted with pentane (3 × 20 mL). The pentane extracts were filtered through Celite. Concentration to ca. 10 mL and crystallization (−20 °C) yielded **11** as dark crystals (50 mg, 30% yield based on **2**). Mp: [°C] 125 (dec). IR (KBr): [cm^{-1}] 2075, 2026, 1990 (s) [ν_{CO}]. ^{1}H NMR (300 MHz) ($CDCl_3$): [δ] 0.36 (s, 9 H, Si*Me*$_3$), 2.21 (s, 6 H, N*Me*$_2$), 2.86 (s, $^3J_{HPt}$ = 38 Hz, 6 H, N*Me*$_2$), 3.44 (s, 2 H, C*H*$_2$), 4.19 (s, $^3J_{HPt}$ = 34 Hz, 2 H, C*H*$_2$), 6.9–7.2 (m, 3 H, C_6*H*$_3$). Anal. Calcd for $C_{24}H_{28}Co_2N_2O_7PtSi$ (769.53): C, 36.14; H, 3.54; N, 3.51; Si, 3.52. Found: C, 36.02; H, 3.60; N, 3.38; Si, 3.61.

Crystal Structure Determination of 11. $C_{24}H_{28}Co_2N_2O_7PtSi$, fw = 797.52, black plate, 0.63 × 0.45 × 0.25 mm^3, monoclinic, $P2_1/c$, a = 10.0863(13) Å, b = 17.4645(15) Å, c = 16.437(2) Å, β = 96.188(10)°, V = 2878.5(6) Å^3, Z = 4, ρ = 1.840 g cm $^{-3}$, 13 921 measured reflections, 6597 unique reflections (R_{int} = 0.0538). Absorption correction based on ψ-scans (PLATON, μ = 6.071 mm^{-1}, 0.58–0.99 transmission), 341 refined parameters, no restraints. R ($I > 2\sigma(I)$): R1 = 0.0268, wR2 = 0.0489. R (all data): R1 = 0.0398, wR2 = 0.0520. S = 1.054. Intensities were measured on an Enraf-Nonius CAD4T diffractometer with rotating anode (Mo Kα, λ = 0.71037 Å) at a temperature of 100 K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The structure was solved with direct methods (SIR97[38]) and refined with the program SHELXL97[39] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups. The drawing, structure calculations, and checking for higher symmetry were performed with the program PLATON.[40]

Reaction of {Pt}C≡CSiMe$_3$ (2) with CuCl$_2$. {Pt}C≡CSiMe$_3$ (**4**) (50 mg, 0.1 mmol) and $CuCl_2$ (30 mg, 0.2 mmol) were dissolved in methanol (30 mL). After 3 h (25 °C), the initially green solution had turned into a yellow suspension. After evaporation of all volatile material, the residue was extracted with CH_2Cl_2 (3 × 20 mL) and separated by centrifugation. Concentration of the CH_2Cl_2 extracts to ca. 5 mL and addition of 30 mL of pentane resulted in the precipitation of **12** as a yellow solid, which was identified by ^{1}H NMR spectroscopy.[31]

Reaction of {Pt}C≡CSiMe$_3$ (2) with I$_2$. A THF solution (20 mL) of I_2 (50 mg, 0.2 mmol) and **2** (95 mg, 0.2 mmol) was stirred for 2 h (0 °C). The THF was then removed under reduced pressure, and the resulting dark brown residue was extracted with pentane (3 × 10 mL) and CH_2Cl_2 (2 × 10 mL). After concentration of the combined pentane extracts, the resulting residue was identified (IR, ^{1}H NMR) as IC≡CSiMe$_3$ (**13**). Concentration of the combined CH_2Cl_2 extracts yielded a dark solid, which was subsequently identified (^{1}H NMR, FAB MS) as **6**.

Synthesis of [({Pt}C≡CC$_6$H$_4$C≡N-4){Pt}][BF$_4$] (16). Compound **4** (90 mg, 0.2 mmol) and {{Pt}H$_2$O}BF$_4$ (**14**) (115 mg, 0.2 mmol) were dissolved in CH_2Cl_2 (50 mL). After 24 h (25 °C), the solution was concentrated to 5 mL, and 50 mL of pentane was added. Complex **16** (190 mg, 95% yield based on **4**) precipitated as an off-white solid. Mp: [°C] > 200. IR (KBr): [cm^{-1}] 2248 (s) [ν_{CN}], 2071 (s) [$\nu_{C\equiv C}$]. ^{1}H NMR (300 MHz) ($CDCl_3$): [δ] 3.21 (s, $^3J_{HPt}$ = 40.1 Hz, 12 H, N*Me*$_2$), 3.26 (s,

${}^3J_{\mathrm{HPt}} = 39.8$ Hz, 12 H, $\mathrm{N}Me_2$), 4.25 (s, ${}^3J_{\mathrm{HPt}} = 41.2$ Hz, 4 H, $\mathrm{C}H_2$), 4.32 (s, ${}^3J_{\mathrm{HPt}} = 40.8$ Hz, 4 H, $\mathrm{C}H_2$), 6.8−7.2 (m, 6 H, $\mathrm{C_6}H_3$), 7.7−8.0 (m, 4 H, $\mathrm{C_6}H_4$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75 MHz) ($\mathrm{CDCl_3}$): [δ] 55.0 ($\mathrm{N}Me_2$), 57.0 ($\mathrm{N}Me_2$), 77.9 ($C\mathrm{H_2}$), 80.0 ($C\mathrm{H_2}$), 108.5 ($\mathrm{PtC{\equiv}}C$), 111.5 ($C\mathrm{N}$), 120.0 ($CH/\mathrm{C_6H_3}$), 120.4 ($CH/\mathrm{C_6H_3}$), 121.8 ($^{i}C/\mathrm{C_6H_4}$), 126.0 ($^{i}C/\mathrm{C_6H_3}$), 126.3 ($CH/\mathrm{C_6H_3}$), 132.8 ($CH/\mathrm{C_6H_4}$), 133.1 ($^{i}C/\mathrm{C_6H_4}$), 135.0 ($CH/\mathrm{C_6H_4}$), 146.3 ($^{i}C/\mathrm{C_6H_3}$), 147.4 ($^{i}C/\mathrm{C_6H_3}$), 163.9 ($^{i}C/\mathrm{C_6H_3}$)$^{a)}$. FAB-MS [m/z (rel int)]: 898 (40) $[\mathrm{M} - \mathrm{BF_4}]^+$, 798 (60) $[\mathrm{C_{25}H_{38}N_3Pt_2}]^+$, 386 (100) $[\mathrm{C_{12}H_{19}N_2Pt}]^+$. Anal. Calcd for **16**: C, 40.21; H, 4.29; N, 7.10. Found: C, 40.39; H, 4.36; N, 6.97.

Synthesis of ({Pt}C≡CC$_6$H$_4$C≡N-4){Ru} (17). In $\mathrm{CH_2Cl_2}$ (20 mL), **4** (50 mg, 0.1 mmol) and {Ru}N≡N{Ru} (**15**) (37 mg, 0.05 mmol) were dissolved. After stirring (3 h, 25 °C), all volatile materials were evaporated and the residue was extracted with $\mathrm{Et_2O}$ (6 × 20 mL). Evaporation of the combined $\mathrm{Et_2O}$ extracts gave **17** (40 mg, 60% yield based on **4**) as a red solid. Mp: [°C]. IR (KBr): [cm^{-1}] 2198 (s) [ν_{CN}], (s) [$\nu_{\mathrm{C{\equiv}C}}$]. ^{1}H NMR (300 MHz) ($\mathrm{CDCl_3}$): [$\delta$] (s, ${}^3J_{\mathrm{HPt}} = 40.1$ Hz, 12 H, $\mathrm{N}Me_2$), (s, ${}^3J_{\mathrm{HPt}} = 41.2$ Hz, 4 H, $\mathrm{C}H_2$), (m, 6 H, $\mathrm{C_6}H_3$), (m, 4 H, $\mathrm{C_6}H_4$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75 MHz) ($\mathrm{CDCl_3}$): [δ] ($\mathrm{N}Me_2$), ($\mathrm{N}Me_2$), ($C\mathrm{H_2}$), ($C\mathrm{H_2}$), ($\mathrm{PtC{\equiv}}C$), ($C\mathrm{N}$), ($CH/\mathrm{C_6H_3}$), ($CH/\mathrm{C_6H_3}$), ($^{i}C/\mathrm{C_6H_4}$), ($^{i}C/\mathrm{C_6H_3}$), ($CH/\mathrm{C_6H_3}$), ($CH/\mathrm{C_6H_4}$), ($^{i}C/\mathrm{C_6H_4}$), ($CH/\mathrm{C_6H_4}$), ($^{i}C/\mathrm{C_6H_3}$), ($^{i}C/\mathrm{C_6H_3}$), ($^{i}C/\mathrm{C_6H_3}$). Anal. Calcd for **17**: C, 43.78; H, 4.82; N, 9.57. Found: C, 43.69; H, 4.95; N, 9.38.

Reaction of {Pt}C≡CC$_6$H$_4$C≡N-4 (4) with Au(CO)Cl. To a solution of **4** (155 mg,0.3 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added Au(CO)Cl (80 mg, 0.3 mmol) (−78 °C). The reaction mixture was then gradually warmed to −40 °C, during which time it turned into a yellowish suspension. Monitoring via IR spectroscopy reveals the development of a band at 2248 cm^{-1}, indicating the formation of **18**. When the temperature rose to over −40 °C, a gold mirror started to appear on the walls of the reaction flask. After 20 min of stirring, the reaction solution was evaporated to dryness and the resulting residue was extracted with pentane (2 × 10 mL) and $\mathrm{CH_2Cl_2}$ (3 × 5 mL). After concentration of the combined pentane extracts, the remaining solid was identified as $\mathrm{N{\equiv}CC_6H_4(C{\equiv}C)_2C_6H_4C{\equiv}N}$ (**19**).[41] The remaining residue after concentration of the combined $\mathrm{CH_2Cl_2}$ extracts was identified as **1**.

Reaction of {Pt}C≡CC$_6$H$_4$C≡N-4 (4) with [Au$_2$Cl$_6$]. At −78 °C, [$\mathrm{Au_2Cl_6}$] (40 mg, 0.13 mmol) was brought into a $\mathrm{CH_2Cl_2}$ solution (20 mL) of **4** (65 mg, 0.13 mmol). Immediately, a yellow precipitate formed. After 2 min stirring, the yellow suspension turned brown (green in transparent light) and a gold mirror appeared on the walls of the reaction vessel. After 20 min, the solvent was removed under reduced pressure and the residue was then extracted with pentane (2 × 10 mL) and with $\mathrm{CH_2Cl_2}$ (2 × 10 mL). The combined pentane extracts were concentrated, and the residue was identified (IR, ^{1}H NMR) as $\mathrm{N{\equiv}CC_6H_4(C{\equiv}C)_2C_6H_4C{\equiv}N}$ (**19**).[41] After concentration of the combined $\mathrm{CH_2Cl_2}$ extracts, the remaining residue was identified (^{1}H NMR) as **12**.[31]

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Supporting Information Available: Tables of crystal data collection and refinement details, positional and thermal parameters, and bond distances and angles for **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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