Mixed Metal Acetylides: The Pt^{II} Aryl Acetylide “$[PtC_6H_2(CH_2NMe_2)_2$-2,6-($C{\equiv}C$)-4]” as a Connective Fragment

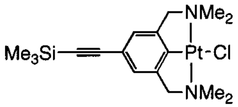
Stephan Back,[a] Robert A. Gossage,[b] Heinrich Lang,*[a] and Gerard van Koten*[b]

Keywords: Alkynes / Cyclic voltammetry / Metal-metal interactions / Conjugation / Platinum

Using $Me_3SiC{\equiv}C\{Pt\}Cl$ (**1**; $Me_3SiC{\equiv}C\{Pt\}$ = $[Pt(C_6H_2\text{-}\{CH_2NMe_2\}_2\text{-}2,6\text{-}\{C{\equiv}CSiMe_3\}\text{-}4]^+$) a series of platinum monoacetylides of the type $XC{\equiv}C\{Pt\}C{\equiv}CR$ [X = $SiMe_3$: **2**, R = Ph; **3**, R = (η^5-C_5H_4)Fe(η^5-C_5H_5) (abbreviated as Fc); **4**, R = C_6H_4CN-4; **5**, R = $C_6H_4(C{\equiv}CSnMe_3)$-4; X = H: **7**, R = Ph; **8**, R = Fc; **9**, R = C_6H_4CN-4] have been prepared. Studies directed towards the coordinative properties of the C_2 unit of **1** have been carried out and heterotrimetallic [μ-($Me_3SiC{\equiv}C\{Pt\}Cl$)][$Co_2(CO)_6$] (**10**) could be synthesised. The successful attachment of **1** to a Ph_3PAu unit leads to linear $Ph_3PAuC{\equiv}C\{Pt\}Cl$ (**11**). Treatment of **11** with $FcC{\equiv}CSnMe_3$ produces the heterotrimetallic rigid-rod shaped complex $Ph_3PAuC{\equiv}C\{Pt\}C{\equiv}CFc$ (**13**). Cyclic voltammetric studies carried out on these Ph_3PAu-capped molecules show that the attachment of an organometallic entity on either side of the $C{\equiv}C\{Pt\}$ fragment leads to a facilitation of the Pt^{II}/Pt^{IV} oxidation.

Introduction

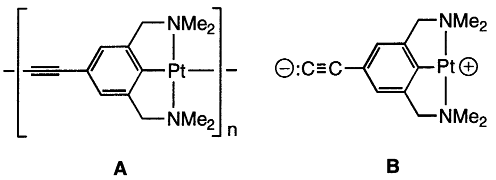
The growing interest in the application of organometallic compounds as building blocks for new materials has led to a large number of publications on their synthesis,[1] and the evaluation of theoretical aspects.[2] In particular, the assembly, chemistry, and the physical properties of a number of homo- and heterometallic acetylenic compounds have been investigated containing metals such as Re,[3] Pt,[4] Pd,[5] Ru,[6] Os,[7] Fe,[8] Rh,[9] or Ti,[10] and Au.[11] Also, a variety of tungsten carbonyl containing complexes have been studied, e.g. by McCleverty et al.[12] and other groups.[13] Many of these mixed-metal σ-acetylide compounds contain a Fc group [Fc = (η^5-C_5H_4)Fe(η^5-C_5H_5)] as electron “reservoir”. The main features of these molecules include: (i) high and readily modified electron density at the metal centres, which should lead to (ii) facile hyperpolarisability due to interaction(s) along the π-conjugated backbone, which connects the different metals.[14] In this context, the application of ethynyl functionalised molecules such as $Me_3SiC{\equiv}C\{Pt\}Cl$ (**1**, $Me_3SiC{\equiv}C\{Pt\}$ = $[Pt(C_6H_2\text{-}\{CH_2NMe_2\}_2\text{-}2,6\text{-}\{C{\equiv}CSiMe_3\}\text{-}4]^+$) seems attractive, since in this platinum containing molecule a metal centre is directly attached to a conjugated π-system, and is further stabilised by the N-donor units of the ligand framework.[15] The Pt-monochloride **1** (Scheme 1) was therefore chosen as a precursor of such heterometallic compounds.



1

Scheme 1. Precursor complex **1**

A useful property of **1** is that it possesses two chemically unique reactive sites. These can be used for building-up bi- or trimetallic systems in sequential steps. Therefore, the $C{\equiv}C$ unit of **1** can be attached to a transition metal (TM) complex fragment in two different binding modes: (i) either *via* σ-bonding or (ii) through η^2-coordination. Both approaches are presented herein. Furthermore, the Cl ligand of **1** can be substituted by, for example, σ-acetylides. This leads to the formation of linear heterometallic monoacetylides. This structural motif can be found in long-chain molecules, such as the hypothetical molecule **A** (Scheme 2), which offers a high degree of directionality along the acetylene-arene-metal vector.



Scheme 2. Model of a long-chain molecule showing high directionality (**A**) and its repeating unit (**B**)

Molecule **A** can be considered as being built-up from repeating units of the di-ionic substructure **B**. Thus, the attachment of the C_2 unit present in **1** to a TM complex fragment, and the substitution of Cl by a σ-acetylide group leads to the transformation of **1** into the structural type **B** molecule. Such molecules can be envisioned as model compounds of **A**. With the synthesis of these complexes, the

---

[a] Lehrstuhl Anorganische Chemie der Technischen Universität,
Straße der Nationen 62, D-09111 Chemnitz, Germany
E-mail: heinrich.lang@chemie.tu-chemnitz.de
[b] Debye Institute, Department of Metal-Mediated Synthesis,
Utrecht University,
Padualaan 8, NL-3584 CH Utrecht, The Netherlands
E-mail: g.vankoten@chem.uu.nl

1434−1948/00/0707−1457 $ 17.50+.50/0

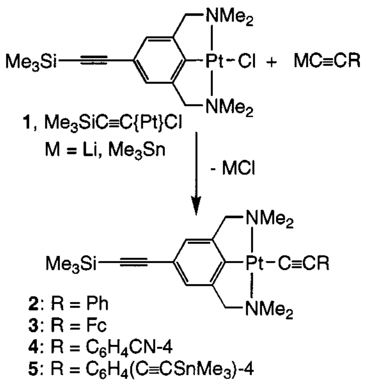
behaviour of the subunit **B** can be studied and evaluated towards its application in materials science.

Since Au is known to form very stable linear σ-acetylide complexes,[11] we choose to investigate the Ph_3PAu moiety as the terminating fragment on the 4-ethynyl unit. The formation of Pt monoacetylides containing the anionic potentially tridentate NCN "pincer" ligand (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) has been previously reported.[16]

Results and Discussion

Preparation of Platinum Acetylides

Reaction of the platinum monochloride $Me_3SiC\equiv C\{Pt\}Cl$ (**1**; $Me_3SiC\equiv C\{Pt\}$ = $[Pt(C_6H_2\text{-}\{CH_2NMe_2\}_2\text{-}2,6\text{-}\{C\equiv CSiMe_3\}\text{-}4]^+$)[15] with an equimolar amount of $LiC\equiv CR$ {R = Ph, Fc [Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$], C_6H_4CN-4, $C_6H_4(C\equiv CSnMe_3)$-4} leads to the formation of the platinum acetylides **2−4** as air-stable, off-white solids (Equation 1). The rigid-rod like molecule **5** has been obtained by a procedure that uses a Me_3Sn-substituted acetylene.[17] Heterobimetallic **3** was synthesised alternatively by both routes. We tested this different approach because Cu^I catalysed reactions for the formation of Pt monoacetylides of this type have failed.[16]



(1)

The deprotection of the acetylenic unit of compounds **1−4** yields the mono-substituted acetylenes **7−9** (Equation 2).[15] The compound $HC\equiv C\{Pt\}Cl$ (**6**) has been described elsewhere.[15]

Analytic and spectroscopic data of compounds **1−9** are listed in Table 1. For comparison, the data of the previously reported Pt monochlorides **1** and **6** are included.[15]

$$Me_3SiC\equiv C\{Pt\}C\equiv CR \xrightarrow{[n\text{-}Bu_4N]F(H_2O)_3} HC\equiv C\{Pt\}C\equiv CR \qquad (2)$$

2: R = Ph
3: R = Fc
4: R = C_6H_4CN-4

7: R = Ph
8: R = Fc
9: R = C_6H_4CN-4

Compounds **1−9** display the $\nu_{C\equiv C}$ frequencies of the acetylene units attached to the NCN system at the expected wavenumbers between 2090 and 2150 cm^{-1} in their IR spectra.[15,18] For the Pt σ-bound acetylenic units, the C≡C stretching band appears between 2070 and 2090 cm^{-1}, respectively (Table 1). These values lie in the range reported for this type of vibration.[4,16] In the ^1H NMR spectra of compounds **2−5** and **7−9**, a common general feature can be observed with respect to the chemical shift of the signals of the CH_2NMe_2 units. A comparison with the chloride-substituted Pt compounds **1** and **6** reveals that upon substitution of Cl by an acetylide, the singlet of the NMe_2 unit experiences a slight but diagnostic low-field shift, as does the resonance signal of the benzylic protons (Table 1). Both singlets appear with a set of satellites, due to the presence of spin active ^{195}Pt (I = 1/2, 33% abundance) with coupling constants ($^3J_{PtH}$) between 40 and 46 Hz (Table 1). Of particular interest in the $^{13}C\{^1H\}$ NMR spectra is the signal of the Pt-substituted carbon atom of the NCN system. Compared to its position in compound **1** (δ = 147.4) and **6** (δ = 147.6) this signal appears strongly shifted to lower field in the spectra of **2−5** and **7−9** (Table 1). The C_{ortho} resonance signal is also shifted to lower field (by around 3 ppm), when compared to **1** or **6**, respectively. This mirrors results obtained with the Pt monochloride $[PtCl(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$.[16] The carbon atoms of the

Table 1. Most representative IR, ^1H and ^{13}C {^1H} NMR spectroscopic data of **1−9**

Compound $Me_3SiC\equiv C\{Pt\}X$ X =		IR[a]		^1H NMR ($^3J_{HH}$ [Hz])[b]		$^{13}C\{^1H\}$ NMR[b]			
		$\nu_{C\equiv C}$	$\nu_{C\equiv CPt}$	CH_3	CH_2	C_{ipso}(Pt)	$C_{ipso}(CH_2)$	***C***≡CPt	C≡***C***Pt
Cl	**1**	2145	–	3.04(37)	3.96(46)	147.4	143.3	–	–
C≡CPh	**2**	2148	2077	3.18(42)	4.05(44)	169.0	145.9	108.2	135.8
C≡CFc	**3**	2144	2089	3.19(42)	4.04(40)	166.2	145.9	103.7	130.6
$C\equiv CC_6H_4CN$-4	**4**	2145	2071	3.19(41)	4.08(42)	168.3	145.9	107.4	133.6
$C\equiv CC_6H_4(C\equiv CSnMe_3)$-4	**5**	2148	2081	3.19(37)	4.07(39)	168.8	145.9	108.2	139.3
$HC\equiv C\{Pt\}X$									
Cl	**6**	2099	–	3.06(38)	3.98(45)	147.6	143.4	–	–
C≡CPh	**7**	2126	2083	3.21(43)	4.08(44)	169.1	146.0	108.2	131.1
C≡CFc	**8**	2090	2078	3.20(41)	4.07(40)	169.2	146.0	103.7	130.7
$C\equiv CC_6H_4CN$-4	**9**	2102	2083	3.20(40)	4.11(42)	168.4	146.0	107.7	133.6

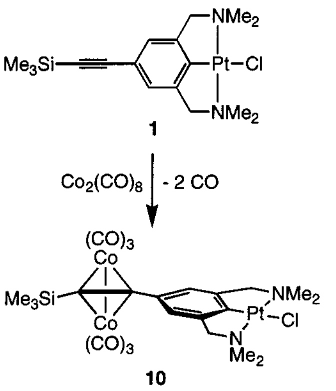
[a] Recorded in KBr [cm^{-1}]. – [b] All spectra were recorded in $CDCl_3$, with the solvent signal [rel. to $SiMe_4$ (0.00 ppm)] as internal standard.

Pt-bound acetylenic unit exhibit signals at chemical shifts that are comparable to those of other known Pt-acetylides.[4] Due to the low intensity of the C_{ipso} atom signals of the NCN unit [C(1)] and the platinum bonded acetylide ligands, ^{195}Pt-C satellites could not be detected.

The FAB mass spectra show the peak of the respective molecular ion M^+ at the expected m/z values as well as a typical fragmentation pattern such as m/z 481 $[C_{17}H_{28}N_2PtSi]^+$ or m/z 409 for $[C_{14}H_{19}N_2Pt]^+$.

Reactions of [4-$Me_3SiC{\equiv}CC_6H_2(CH_2NMe_2)_2$-2,6]PtCl (1) with Cobalt Carbonyl and Copper(I) Salts

The replacement of two CO ligands of $[Co_2(CO)_8]$ by the C_2 unit of acetylene derivatives leads to the formation of dicobaltatetrahedranes.[19] Hence, organometallic acetylides can readily yield mixed metal compounds. In order to study whether the same reactivity could be achieved with a {Pt}-substituted acetylene (i.e., with retention of the Pt−C and Pt−Cl bonds), **1** was reacted with equimolar amounts of $[Co_2(CO)_8]$ in toluene at 0 °C. This leads to the formation of the green trimetallic complex **10** in 50% isolated yield (Equation 3).



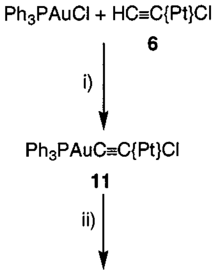
(3)

Compound **10** features a dicobaltatetrahedrane unit with the Pt-containing entity directly connected to this polyhedron. The values and pattern of the ν_{CO} frequencies resemble typical values found for $Co_2(CO)_6$ fragments.[19] The resonance signals in the ^{1}H NMR spectrum are generally slightly shifted to higher field, compared to **1**.[15] The $^{13}C\{^1H\}$ NMR spectrum displays virtually the same signal pattern as for **1**. However, the chemical shifts of the μ-C_2 unit with $\delta = 79.3$ (C≡*C*Si) and $\delta = 107.6$ (*C*≡CSi) experience a high-field shift of approximately 13 ppm for ≡*C*Si and a slight shift to lower field by ca. 1 ppm for *C*≡CSi. The signals assigned to the carbonyl ligands are found as a broad singlet at $\delta = 196.7$. The FAB mass spectrum exhibits a peak for the molecular ion $[M]^+$ at m/z = 796. Also, the sequential loss of all six CO ligands can be observed.

The reaction of copper(I) halides with acetylene derivatives is well-known and generally yields dimeric η^2-acetylene copper(I) halides.[20] In order to investigate if the C≡C unit present in **1** can be used for the design of other bimetallic compounds, **1** has been reacted with $[CuCl]_n$ or $[Cu(NCMe)_4][BF_4]$. However, even after prolonged stirring (48 h) at low (−20 °C, CH_2Cl_2) or elevated temperatures (40−50 °C, C_6H_6), **1** did not react with $[CuCl]_n$. All spectroscopic evidence (IR, ^{1}H NMR, $^{13}C\{^1H\}$ NMR) indicated the presence of starting materials only. This mirrors results obtained earlier in a $Cu^I-(Me_3SiC{\equiv}CPh)$ system.[21] This result contrasts with reports on the formation of complexes of the type $[Cu_2X_2(R'C{\equiv}CR')_2]$ [e.g. R′ = $SiMe_3$,[20] $Re(CO)_5$[22]]. In contrast to this lack of reactivity, the reaction of **1** with $[Cu(NCMe)_4][BF_4]$ led to a mixture of products that could not be separated. Moreover, the IR spectrum of the crude reaction mixture gave no indication for the occurrence of Cu^I-alkyne coordination.

Preparation of Linear Mixed Metal Compounds

Due to their stability and easy accessibility, Au^I acetylides have attracted a great deal of interest. Also, the preferred geometry and the electron-rich character of the Au^I centre makes this class of compounds attractive candidates for materials science.[11] In principle, the preparation of Au^I acetylides can be achieved by two routes: i) first a silyl-protected Pt acetylide is prepared, followed by deprotection of the C≡C functionality, and subsequent reaction of the monosubstituted acetylene with Ph_3PAuCl, or ii) treatment of HC≡C{Pt}Cl (**4**) with Ph_3PAuCl and then substitution of Cl by acetylide anions. The first route seemed to us being of little advantage because the platinum monoacetylides of this type have been reported to be sensitive to halide sources, i.e., giving rise to cleavage of the Pt-acetylide bond.[16] Therefore, the Au σ-acetylide complex **11** was synthesised first, according to well-established literature procedures (Scheme 3).[23] For comparative purposes, the gold-ferrocenyl acetylide complex $Ph_3PAuC{\equiv}CFc$ (**12**) was also prepared.



Scheme 3. Preparation of linear mixed metal (Au, Fe) complexes. i. $[CuCl]_n$, $HNEt_2$, 25 °C; ii. $FcC{\equiv}CSnMe_3$, THF, 50 °C.

Subsequently, complex **11** was reacted with $FcC{\equiv}CSnMe_3$ to form linear trimetallic **13** in virtually quantitative yield (Scheme 3). This reaction variation has been previously used in the synthesis of compound **5** (vide supra).

Experimental data with respect to the spectroscopic characterisation of complexes **11**−**13** are listed in Table 2.

The IR spectra of compounds **11**−**13** exhibit the C≡C stretching modes for the Au-bonded acetylide at typical values (Table 2).[23] The corresponding band for the Pt-bonded acetylide appears at much lower frequency than ob-

Table 2. Most diagnostic spectroscopic data (IR, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR) of **11−13**

Compound Ph_3PAuX		IR[a]		$^{31}P\{^1H\}$NMR[b]	$^{13}C\{^1H\}$ NMR[b]
X =		C≡CAu	C≡CPt	PPh_3	C≡CAu
Cl		–	–	33.8	–
C≡C{Pt}Cl	**11**	2102	–	43.1	105.4, 105.7
C≡CFc	**12**	2109	–	42.9	102.5[c]
C≡C{Pt}C≡CFc	**13**	2098	1971	43.1	–[d]

[a] Recorded in KBr ($\tilde{\nu}$ [cm^{-1}]). − [b] All spectra were recorded in $CDCl_3$ with the solvent signal [rel. to $SiMe_4$ (0.00 ppm)] as internal standard. − [c] Only one signal could be detected. − [d] Due to the low solubility of **13** in any organic solvent, a $^{13}C\{^1H\}$ NMR spectrum could not be recorded.

served in compounds **2−5** (around 2070 cm^{-1}, Table 1). This points to a bond weakening of the Pt-centred C≡C unit, which is obviously caused by the remote presence of the Ph_3PAu fragment. The ^1H NMR spectra exhibit no change in the chemical shifts of the C≡C{Pt} fragment compared to **1** (Table 1). In the ^1H NMR spectrum of **13**, however, the resonance signals of the {Pt} unit only appear as very broad singlets. In the $^{13}C\{^1H\}$ NMR spectra of compounds **11** and **12**, the acetylenic carbon resonance signals are found at chemical shifts that are typical for gold acetylides.[11,23] Due to the low solubility of **13** in all common organic solvents, a $^{13}C\{^1H\}$ NMR spectrum could not be obtained. Compared with Ph_3PAuCl (δ = 33.8), the signal for the phosphorus atom datively bonded to Au has shifted by about 10 ppm to lower field when Cl is substituted by an acetylide anion (**11−13**, Table 2). This shift is characteristic for Au^I acetylides carrying organic groups and indicates that the presence of a remote Pt atom does not influence the behaviour of the $AuPPh_3$ unit in a spectroscopically noticeable manner. The FAB mass spectrum reveals the peak for the molecular ion $[M]^+$ at the expected *m*/*z* values, together with an expected fragmentation pattern. Most characteristic fragments are found at *m*/*z* = 459 $[C_{18}H_{15}AuP]^+$, *m*/*z* = 409 $[C_{14}H_{18}N_2Pt]^+$ and *m*/*z* = 210 $[C_{12}H_9Fe]^+$.

At −30 °C, crystals of the bimetallic complex **11** could be grown from a CH_2Cl_2/pentane solution. Unfortunately, these crystals were not of sufficient quality to obtain a full X-ray structural analysis (*R* = 0.1544). Nevertheless, the representation given in Figure 1 serves to corroborate the predicted linear arrangement of the metal centres in the heterobimetallic complex **11**.

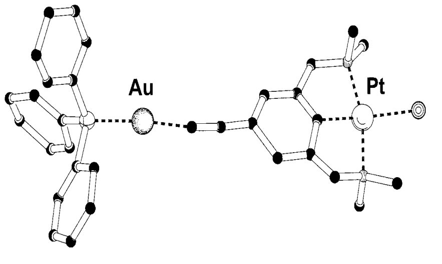


Figure 1. Structural representation of the heterobimetallic complex **11**

Electrochemical Behaviour

The mononuclear complex Me_3SiC≡C{Pt}Cl (**1**), the heterobinuclear molecules **3**, **11**, and **12**, as well as the heterotrinuclear compound **13** have been investigated by cyclic voltammetry. The results of the electrochemical measurements are listed in Table 3. For comparative purposes, the electrochemical data of Ph_3PAuCl have been measured and these are also presented.

It appears that the reductive irreversible one-electron process for the system Au^I/Au^0 is generally shifted to a more negative potential upon substitution of the Cl ligand by acetylide (Table 3). However, the strength of the shift depends on the nature of the organometallic fragment. While for the NCN−Pt substituted acetylide a shift by approximately 0.2 V is found, the same effect for C≡CFc is larger (ca. 0.4 V). This indicates that the reduction of Au^I to Au^0 is more hampered by the presence of a Fc fragment than by the NCN−Pt unit. However, in the cyclic voltammetric experiment with the heterotrimetallic complex **13**, the Au-centred reductive process could not be detected due to the low solubility of **13** and the proximity of the edge of the electrochemical window in this system. This may also be explained by a shift of the Au^I/Au^0 reduction potential beyond this electrochemical edge. The cyclic voltammogram of **1** exhibits a concerted irreversible two-electron oxidative process that can be assigned to the system Pt^{II}/Pt^{IV}. This process is typical for Pt monochlorides of this type.[16] Upon substitution of the Cl by acetylide, as demonstrated in Me_3SiC≡C{Pt}C≡CFc (**3**), a similar effect can be observed as in the Au^I-centred reductive process: a shift to a more negative value of the Pt^{II}/Pt^{IV} oxidation potential by ca. 0.4 V. A similar observation has been reported earlier for $PtCl[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$.[16] In this case, a shift of the Pt^{II}/Pt^{IV} oxidation to a more negative potential by ca. 0.2 V was reported when Cl was replaced by, e.g. $C{\equiv}CSiMe_3$. Surprisingly, the Pt-containing unit of the complexes described in the present study shows no reduction process at all. The attachment of the C≡C{Pt}Cl fragment to Ph_3PAu also leads to a shift of the Pt^{II}/Pt^{IV} oxidation to a more negative potential. As in the case of the Pt−Fc complex **3**, this indicates a facilitation of the oxidative process (Table 3). In the heterotrimetallic complex **13**, this process is shifted to a more negative value than in the bimetallic compound **11** (Table 3) but less than in complex

Table 3. Cyclic voltammetric data of compounds **11**−**13**, Ph_3PAuCl and **1** are presented for comparison; the cyclic voltammograms have been recorded in THF solutions in the presence of $[nBu_4N][PF_6]$ (c = 0.1 mol dm^{-3}) at 25 °C under N_2; scan-rate 100 mV s^{-1}; potentials are referenced to FcH/FcH^+ couple ($E_{1/2}$ = 0.00 V)

Compound		Oxidation			Reduction	
		$E_{1/2}$(Fc) [V]	ΔE [mV]	E_{ox}(Pt) [V]	E_{red}(Au) [V]	E_{red}(Pt) [V]
Ph_3PAuCl		–	–	–	−2.70	–
$Me_3SiC\equiv C\{Pt\}Cl$	**1**	–	–	0.76	–	–
$Me_3SiC\equiv C\{Pt\}C\equiv CFc$	**3**	−0.13	75	0.38	–	–
$Ph_3PAuC\equiv C\{Pt\}Cl$	**11**	–	–	0.53	−2.91	–
$Ph_3PAuC\equiv CFc$	**12**	−0.15	80	–	−3.12	–
$Ph_3PAuC\equiv C\{Pt\}C\equiv CFc$	**13**	−0.02	90	0.41	–[a]	–

[a] Due to low solubility of **13** and the proximity of the reductive process Au^I/Au^0 to the edge of the electrochemical window, a reductive process could not be observed.

3. Looking at the reversible one-electron redox process of the Fc entity, the attachment of $C\equiv CFc$ to Ph_3PAu or $Me_3SiC\equiv C\{Pt\}$ also results in a shift to a more negative potential, with about equal magnitude. Still, the assembly of these three fragments to form complex **13** does not result in changes to the redox potential of the Fc unit with respect to the reference potential FcH/FcH^+.

It can be concluded that the stepwise increase of size and composition of the organometallic systems in the described complexes **3**−**12** induces a facilitation of the oxidative processes in each of the metal-containing subunits. This indicates that the linking of further organometallic fragments to the 4-ethynyl-substituted Pt−NCN system induces a change in the electronic system of the Pt^{II} centre. The fact that this is also induced by the remote Ph_3PAu unit suggests that the extended π-system of the $-C\equiv CC_6H_2(CH_2NMe_2)_2$-2,6-$Pt^+$ fragment, which also includes the coplanar coordination plane of the Pt^{II} centre, is able to conduct electronic information.

Conclusions

A series of Pt monoacetylides containing the 4-ethynyl-substituted NCN−Pt unit has been synthesised and characterised. Their use as the basis for the preparation of multimetallic systems has been shown by the assembly of $Ph_3PAuC\equiv C\{Pt\}C\equiv CFc$, **13**. Apart from the use of Li-acetylides, Me_3Sn-substituted acetylenes have been applied to the high-yield synthesis of Pt monoacetylides. The $C\equiv C$ unit of $Me_3SiC\equiv C\{Pt\}Cl$ (**1**) can act as an η^2-coordinating ligand, as was shown by the formation of a characteristically green-coloured dicobaltatetrahedrane complex by reaction of **1** with $Co_2(CO)_8$. Electrochemical studies of these heterometallic systems revealed that the reversible oxidation of the Fc units in complexes $Me_3SiC\equiv C\{Pt\}C\equiv CFc$ (**3**) and $PPh_3AuC\equiv C\{Pt\}C\equiv CFc$ (**13**), and the irreversible Pt^{II}/Pt^{IV} oxidation are both facilitated. On the basis of these results we conclude, that the 4-ethynyl NCN unit supports electronic communication between two metal atoms through the conjugated π-system. Further work will be directed towards the construction of longer chains of repeating $C\equiv C\{Pt\}$ units with high directionality approximating an organometallic polymer as suggested in type **A** complexes (vide supra) in a stepwise approach.

Experimental Section

General: 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 CaH_2. − IR: Mattison Galaxy Series FTIR 5000. − NMR: Bruker AC 300 (^1H, ^{31}P, and ^{13}C); chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the internal reference signal. − FAB-MS: JEOL JMS SX/SX 102A four sector mass spectrometer (10 kV accelerating voltage) at the Department of Mass Spectrometry, Bijvoet Center, Utrecht University. − MP: Büchi melting point apparatus. − Elemental analyses: H. Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr, Germany. − CV: Princeton Applied Research EG& G 263A analyser in a solution of $[nBu_4N][PF_6]$ (c = 0.1 mol dm^{-3}) in THF at 25 °C; all potentials were referenced to the ferrocene/ferrocenium couple as internal reference ($E_{1/2}$ = 0.00 V).

Remarks: The starting materials $Me_3SiC\equiv C\{Pt\}Cl$ (**1**),[15] $HC\equiv C\{Pt\}Cl$ (**6**),[15] $HC\equiv CC_6H_4CN$-4,[24] 1,4-$(Me_3SnC\equiv C)_2$-C_6H_4,[25] $HC\equiv CFc$,[26] Ph_3PAuCl,[23] and $Me_3SnC\equiv CFc$[25] were prepared following published procedures. Other reagents were purchased from commercial suppliers.

Synthesis of $Me_3SiC\equiv C\{Pt\}C\equiv CPh$ (2): To a Et_2O solution (150 mL, −78 °C) of $LiC\equiv CPh$ (190 mg, 1.80 mmol) was added **1** (880 mg, 1.70 mmol). The mixture was allowed to warm up (25 °C) and stirred (16 h, 25 °C). All volatile material was then evaporated in vacuo and the residue was extracted with Et_2O (3 × 50 mL) and CH_2Cl_2 (3 × 40 mL). Separation from the solid residue was effected by centrifugation. The combined CH_2Cl_2 fractions were then concentrated to ca. 5 mL and addition of pentane (50 mL) yielded **2** (580 mg, 60% yield based on **1**) as off-white solid; m.p. > 200 °C. − IR (KBr): $\tilde{\nu}$ = 2148 [$\nu_{C\equiv C}$], 2077 [$\nu_{C\equiv C}$] cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.21 (s, 9 H, $SiMe_3$), 3.18 s, $^3J_{HPt}$ = 42 Hz, NMe_2), 4.05 (s, $^3J_{HPt}$ = 44 Hz, 4 H, CH_2), 7.01 (s, 2 H, C_6H_2), 7.1−7.5 (m, 5 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.1 ($SiMe_3$), 55.9 (NMe_2), 79.5 (CH_2), 91.8 ($SiC\equiv C$), 107.2 ($SiC\equiv C$), 108.2 ($PtC\equiv C$), 117.4 (iC/C_6H_2), 122.4 (CH/C_6H_2), 124.8 (CH/C_6H_5), 127.8 (CH/C_6H_5), 128.5 (iC/C_6H_5), 131.6 (CH/C_6H_5), 135.8 ($PtC\equiv C$), 145.9 (iC/C_6H_2), 169.0 (iC/C_6H_2). − FAB-MS; m/z (rel. int.): 583 (30) [M^+], 482 (100) [$M^+ - C_8H_5$]. − $C_{25}H_{32}N_2PtSi$ (583.73): calcd. C 51.44, H 5.53, N 4.80; found C 51.32, H 5.55, N 4.73.

Synthesis of $Me_3SiC\equiv C\{Pt\}C\equiv CFc$ (3): Experimental conditions and workup were identical to those for the preparation of **2**. Experimental details: $LiC\equiv CFc$ (170 mg, 0.80 mmol), **1** (400 mg, 0.77 mmol), Et_2O (100 mL). Yield: 330 mg, 60% based on **1**. − Mp:

$>$ 200 °C. − IR (KBr): ṽ = 2144 [$\nu_{C\equiv C}$], 2089 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.22 (s, 9 H, Si*Me*$_3$), 3.19 (s, $^3J_{HPt}$ = 42 Hz, 12 H, N*Me*$_2$), 4.04 (br s, 2 H, C_5H_4), 4.04 (s, $^3J_{HPt}$ = 40 Hz, 4 H, CH_2), 4.15 (s, 5 H, C_5H_5), 4.36 (br s, 2 H, C_5H_4), 7.01 (s, 2 H, C_6H_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.1 (Si*Me*$_3$), 55.9 (N*Me*$_2$), 66.9 (*CH*/C_5H_4), 69.4 (C_5H_5), 70.0 (*iC*/C_5H_4), 70.9 (*CH*/C_5H_4), 79.5 (CH_2), 90.9 (Si*C*≡C), 103.7 (PtC≡*C*), 107.2 (SiC≡*C*), 117.3 (*iC*/C_6H_2), 122.4 (*CH*/C_6H_2), 130.6 (Pt*C*≡C), 145.9 (*iC*/C_6H_2), 166.2 (*iC*/C_6H_2). − FAB-MS; *m*/*z* (rel. int.): 692 (20) [M$^+$], 481 (100) [M$^+$ − $C_{12}H_9Fe$]. − $C_{29}H_{36}FeN_2PtSi$ (691.95): calcd. C 50.36, H 5.25, N 3.71; found C 50.48, H 5.23, N 3.97.

Synthesis of $Me_3SiC\equiv C\{Pt\}C\equiv CC_6H_4CN$-4 (4): Experimental conditions and workup were identical to those for the preparation of **2**. Experimental details: $LiC\equiv CC_6H_4CN$-4 (100 mg, 0.80 mmol), **1** (390 mg, 0.76 mmol), Et_2O (100 mL). Yield: 200 mg, 40% based on **1**. − Mp: $>$ 200 °C. − IR (KBr): ṽ = 2220 [ν_{CN}], 2144 [$\nu_{C\equiv C}$], 2089 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.22 (s, 9 H, Si*Me*$_3$), 3.19 (s, $^3J_{HPt}$ = 41 Hz, 12 H, N*Me*$_2$), 4.08 (s, $^3J_{HPt}$ = 42 Hz, 4 H, CH_2), 7.03 (s, 2 H, C_6H_2), 7.3−7.5 (m, 4 H, C_6H_4). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.1 (Si*Me*$_3$), 55.9 (N*Me*$_2$), 79.5 (CH_2), 92.1 (Si*C*≡C), 106.9 (SiC≡*C*), 107.4 (PtC≡*C*), 107.7 (*C*N), 117.9 (*iC*/C_6H_2), 119.7 (*iC*/C_6H_4), 122.5 (*CH*/C_6H_2), 131.5 (*iC*/C_6H_4), 131.6 (*CH*/C_6H_4), 131.9 (*CH*/C_6H_4), 133.6 (Pt*C*≡C), 145.9 (*iC*/C_6H_2), 168.3 (*iC*/C_6H_2). − FAB-MS: *m*/*z* (rel. int.): 608 (10) [M$^+$], 481 (100) [$C_{17}H_{27}N_2PtSi$]$^+$. − $C_{26}H_{31}N_3PtSi$ (608.74): calcd. C 51.30, H 5.13, N 6.90. A satisfactory elemental analysis could not be obtained.

Synthesis of $Me_3SiC\equiv C\{Pt\}C\equiv CC_6H_4(C\equiv CSnMe_3)$-4 (5): Compound **1** (50 mg, 0.10 mmol) and 1,4-$(Me_3SnC\equiv C)_2C_6H_4$ (90 mg, 0.20 mmol) were dissolved in THF (40 mL). The solution was stirred (10 h, 25 °C) and then concentrated to ca. 5 mL. Addition of pentane (50 mL) formed a precipitate that was separated from the supernatant solution. The residue was then dried (5 h, *vacuo*). **Note: Me_3SnCl is volatile and very toxic. An extra cooling trap has to be installed right after the reaction vessel.** Complex **5** (60 mg, 80% based on **1**) was obtained as off-white solid. − Mp: $>$ 200 °C. − IR (KBr): ṽ = 2148 [$\nu_{C\equiv C}$], 2132 [$\nu_{C\equiv C}$], 2089 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.22 (s, 9 H, Si*Me*$_3$), 0.34 (s, $^3J_{HSn}$ = 59.8 Hz, 9 H, $SnMe_3$), 3.19 (s, $^3J_{HPt}$ = 37 Hz, 12 H, N*Me*$_2$), 4.07 (s, $^3J_{HPt}$ = 40 Hz, 4 H, CH_2), 7.02 (s, 2 H, C_6H_2), 7.29 (s, 4 H, C_6H_4). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = −7.7 ($SnMe_3$), 0.1 (Si*Me*$_3$), 55.9 (N*Me*$_2$), 79.5 (CH_2), 91.8 (Si*C*≡C), 93.2 (Sn*C*≡C), 107.3 (SiC≡*C*), 108.2 (PtC≡*C*), 109.7 (SnC≡*C*), 117.5 (*iC*/C_6H_2), 122.4 (*CH*/C_6H_2), 131.1 (*iC*/C_6H_4), 131.4 (*CH*/C_6H_4), 131.5 (*CH*/C_6H_4), 131.7 (*iC*/C_6H_4), 139.3 (Pt*C*≡C), 145.9 (*iC*/C_6H_2), 168.8 (*iC*/C_6H_2). − FAB-MS; *m*/*z* (rel. int.): 770 (10) [M$^+$], 607 (20) [M − $SnMe_3$]$^+$, 481 (100) [$C_{17}H_{27}N_2PtSi$]$^+$, 73 [C_3H_9Si]$^+$. − $C_{30}H_{40}N_2PtSiSn$ (770.53): calcd. C 46.76, H 5.23, N 3.64; found C 47.01, H 5.01, N 3.32.

Synthesis of $HC\equiv C\{Pt\}C\equiv CPh$ (7): To a solution of **2** (400 mg, 0.76 mmol) in CH_2Cl_2 (100 mL), was added [*n*Bu_4N]F·$3H_2O$ (240 mg, 0.76 mmol). After stirring (2 h, 25 °C), all volatile material was evaporated and the residue was extracted with acetone (2 × 10 mL). Separation by centrifugation and drying (*vacuo*) yielded **5** (190 mg, 50%) as a brown solid. − Mp: $>$ 200 °C. − IR (KBr): ṽ = 3302 [$\nu_{\equiv CH}$], 2126 [$\nu_{C\equiv C}$], 2083 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.01 (s, 1 H, ≡C*H*), 3.21 (s, $^3J_{HPt}$ = 43.4 Hz, N*Me*$_2$), 4.08 (s, $^3J_{HPt}$ = 44 Hz, 4 H, CH_2), 7.04 (s, 2 H, C_6H_2), 7.2−7.5 (m, 5 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 55.9 (N*Me*$_2$), 75.0 (≡*C*H), 79.6 (CH_2), 85.6 (*C*≡CH), 108.2 (PtC≡*C*)[a] , 116.4 (*iC*/C_6H_2), 122.5 (*CH*/C_6H_2), 124.6 (*CH*/C_6H_5), 127.8 (*CH*/C_6H_5), 128.5 (*iC*/C_6H_5), 131.6 (*CH*/C_6H_5), 131.1 (Pt*C*≡C), 146.0 (*iC*/C_6H_2), 169.1 (*iC*/C_6H_2). − FAB-MS; *m*/*z* (rel. int.): 512 (20) [M$^+$], 409 (100) [M$^+$ − C_8H_5]. − $C_{22}H_{24}N_2Pt$ (511.54): calcd. C 51.66, H 4.73, N 5.48; found C 51.78, H 4.72, N 5.36.

Synthesis of $HC\equiv C\{Pt\}C\equiv CFc$ (8): Experimental conditions and workup were identical to those for the preparation of **5**. Experimental details: **3** (760 mg, 1.08 mmol), [*n*Bu_4N]F·$3H_2O$ (340 mg, 1.08 mmol), CH_2Cl_2 (30 mL). Yield: 330 mg, 60% based on **3**. − Mp: $>$ 200 °C. − IR (KBr): ṽ = 3272 [$\nu_{\equiv CH}$], 2090 [$\nu_{C\equiv C}$], 2078 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.01 (s, 1 H, ≡C*H*), 3.20 (s, $^3J_{HPt}$ = 41 Hz, 12 H, N*Me*$_2$), 4.04 (t, $^3J_{HH}$ = 1.4 Hz, 2 H, C_5H_4), 4.07 (s, $^3J_{HPt}$ = 40 Hz, 4 H, CH_2), 4.15 (s, 5 H, C_5H_5), 4.36 (t, $^3J_{HH}$ = 1.4 Hz, C_5H_4), 7.02 (s, 2 H, C_6H_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 55.9 (N*Me*$_2$), 66.9 (*CH*/C_5H_4), 69.4 (C_5H_5), 70.1 (*iC*/C_5H_4), 75.0 (*C*≡CH), 77.2 (C≡*C*H), 79.2 (CH_2), 103.7 (PtC≡*C*), 116.2 (*iC*/C_6H_2), 122.5 (*CH*/C_6H_2), 130.7 (Pt*C*≡C), 146.0 (*iC*/C_6H_2), 169.2 (*iC*/C_6H_2). − FAB-MS; *m*/*z* (rel. int.): 619 (10) [M$^+$], 409 (60) [M$^+$ − $C_{12}H_9Fe$], 210 (10) [$C_{12}H_9Fe$]$^+$. − $C_{26}H_{28}FeN_2Pt$ (619.46): calcd. C 50.41, H 4.56, N 4.52; found C 50.28, H 4.51, N 4.46.

Synthesis of $HC\equiv C\{Pt\}C\equiv CC_6H_4CN$-4 (9): Experimental conditions and workup were identical to those for compound **7**. Experimental details: **4** (260 mg, 0.51 mmol), [*n*Bu_4N]F·$3H_2O$ (160 mg, 0.51 mmol), CH_2Cl_2 (30 mL). Yield: 100 mg, 40% based on **4**. − Mp: $>$ 200 °C. − IR (KBr): ṽ = 3302 [$\nu_{\equiv CH}$], 2220 [ν_{CN}], 2102 [$\nu_{C\equiv C}$], 2083 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.01 (s, 1 H, ≡C*H*), 3.20 (s, $^3J_{HPt}$ = 39 Hz, 12 H, N*Me*$_2$), 4.11 (s, $^3J_{HPt}$ = 40 Hz, 4 H, CH_2), 7.05 (s, 2 H, C_6H_2), 7.3−7.5 (m, 4 H, C_6H_4). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 55.9 (N*Me*$_2$), 75.3 (≡*C*H), 79.5 (s, $^3J_{CPt}$ = 38 Hz, CH_2), 85.4 (*C*≡CH), 107.4 (*C*N), 107.7 (PtC≡*C*), 116.8 (*iC*/C_6H_2), 119.7 (*iC*/C_6H_4), 122.6 (*CH*/C_6H_2), 131.7 (*CH*/C_6H_4), 132.2 (*CH*/C_6H_4), 133.6 (Pt*C*≡C), 146.0 (s, $^3J_{CPt}$ = 35.9 Hz, *iC*/C_6H_2), 168.4 (*iC*/C_6H_2). − FAB-MS; *m*/*z* (rel. int.): 536 (10) [M$^+$], 409 (60) [$C_{14}H_{19}N_2Pt$]$^+$. − $C_{23}H_{23}N_3Pt$ (536.55): calcd. C 51.49, H 4.32, N 7.83; found C 51.32, H 4.40, N 7.69.

Synthesis of [μ-($Me_3SiC\equiv C\{Pt\}Cl$)][$Co_2(CO)_6$] (10): To a toluene solution (100 mL) of **1** (200 mg, 0.39 mmol), was added $Co_2(CO)_8$ (140 mg, 0.43 mmol) in one portion. After stirring (3 h, 25 °C), the solvent was reduced to ca. 10 mL and pentane (100 mL) was added. The supernatant solution was carefully decanted and the green precipitate redissolved in toluene (5 mL). Crystallisation at − 20 °C yielded **10** (140 mg, 50% based on **1**) as a green solid. − Mp: 140 °C (dec). − IR (KBr): ṽ = 2087, 2035, 2015, 1990 [ν_{CO}] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 0.40 (s, 9 H, Si*Me*$_3$), 3.11 (s, $^3J_{HPt}$ = 32 Hz, 12 H, N*Me*$_2$), 4.06 (s, $^3J_{HPt}$ = 42 Hz, 4 H, CH_2), 6.96 (s, 2 H, C_6H_2). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.9 (Si*Me*$_3$), 54.5 (N*Me*$_2$), 79.3 (C≡*C*Si), 107.6 (*C*≡CSi), 121.0 (*CH*/C_6H_2), 132.7 (*iC*/C_6H_2), 143.2 (*iC*/C_6H_2), 147.0 (*iC*/C_6H_2), 201−204 (CO). − FAB-MS; *m*/*z* (rel. int.): 796 (20) [M$^+$], 768 (25) [M$^+$ − CO], 740 (30) [M$^+$ − 2 CO], 712 (20) [M$^+$ − 3 CO], 684 (10) [M$^+$ − 4 CO], 656 (20) [M$^+$ − 5 CO], 628 (20) [M$^+$ − 6 CO], 481 (100) [$C_{16}H_{27}N_2PtSi$]$^+$. − $C_{22}H_{27}ClCo_2N_2O_6PtSi$ (791.96): calcd. C 33.37, H 3.44, N 3.54; Si 3.55; found C 33.45, H 3.36, N 3.46; Si 3.59.

Reaction of 1 with [CuCl]$_n$. − Method A: [CuCl]$_n$ (20 mg, 0.20 mmol) and **1** (50 mg, 0.10 mmol) are stirred in C_6H_6 (30 mL, 48 h, 50 °C). − **Method B:** [CuCl]$_n$ (10 mg, 0.10 mmol) and **1** (30 mg, 0.6 mmol) are stirred in CH_2Cl_2 (30 mL, 24 h, − 20 °C).

In both cases, after removal of the solvent (in vacuo), the spectroscopic investigation (IR, ^{1}H NMR, $^{13}C\{^1H\}$ NMR) of the crude residue revealed the presence solely of **1**.

Reaction of 1 with [$Cu(NCMe)_4$][BF_4]: Compound **1** (100 mg, 0.19 mmol) and [$Cu(NCMe)_4$][BF_4] (30 mg, 0.10 mmol) are dissolved in CH_2Cl_2 (30 mL]. During the course of the reaction, the solution gradually turns brown. After stirring (24 h, 25 °C),the solvent is removed (in vacuo). Spectroscopic investigation (IR, ^{1}H NMR, ^{13}C {^{1}H} NMR) of the residue showed that a complicated mixture of compounds had been formed.

Synthesis of $Ph_3PAuC{\equiv}C\{Pt\}Cl$ (11): Compound **6** (127 mg, 0.30 mmol), Ph_3PAuCl (140 mg, 0.30 mmol) and $[CuCl]_n$ (8 mg, 0.08 mmol) were dissolved in degassed $HNEt_2$ (30 mL). After stirring (12 h, 25 °C) and evaporation (in vacuo), the residue was extracted with water (3 × 10 mL) and then with C_6H_6 (3 × 20 mL). The combined C_6H_6 extracts were evaporated and redissolved in CH_2Cl_2. The CH_2Cl_2 solution was dried over $MgSO_4$, filtered and evaporated (in vacuo). Complex **11** (170 mg, 60% based on **6**) was obtained as an off-white solid. − Mp: > 200 °C. − IR (KBr): $\tilde{\nu}$ = 2102 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.05 (s, $^3J_{HPt}$ = 37.8 Hz, 12 H, N*Me*$_2$), 4.09 (s, $^3J_{HPt}$ = 44 Hz, 4 H, C*H*$_2$), 6.92 (s, 2 H, C_6*H*$_2$), 7.3−7.6 (m, 15 H, C_6*H*$_5$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 54.4 (N*Me*$_2$) 77.6 (*C*H_2), 105.4 (C≡C), 105.7 (C≡C), 119.4 (*iC*/C_6H_2), 123.2 (s, $^3J_{PtC}$ = 33 Hz, *CH*/C_6H_2), 129.1 (d, $^3J_{PH}$ = 11 Hz, *CH*/C_6H_5), 129.8 (d, $^1J_{PH}$ = 63 Hz, *iC*/C_6H_5), 131.5 (*CH*/C_6H_5), 134.3 (d, $^2J_{PH}$ = 14 Hz, *CH*/C_6H_5) 142.9 (s, $^2J_{PtC}$ = 76 Hz, *iC*/C_6H_2), 144.8 (*iC*/C_6H_2). − ^{31}P {^{1}H} NMR ($CDCl_3$): δ =43.1 (PPh_3). − FAB-MS; *m*/*z* (rel. int.): 904 (10) $[M]^+$, 868 (60) $[M - Cl]^+$, 459 (100) $[C_{18}H_{15}AuP]^+$, 401 (20) $[C_{14}H_{18}N_2Pt]^+$. − $C_{34}H_{33}AuClFeN_2PPt$ (928.17): calcd. C 42.51, H 3.68, N 3.10; found C 42.45, H 3.74, N 3.12.

Synthesis of $Ph_3PAuC{\equiv}CFc$ (12): Ph_3PAuCl (100 mg, 0.21 mmol), FcC≡CH (50 mg, 0.24 mmol) and K_2CO_3 (100 mg) were dissolved in MeOH (40 mL). After stirring (12 h, 25 °C), the reaction mixture was evaporated (in vacuo). The orange residue was extracted with Et_2O (2 × 20 mL) and CH_2Cl_2 (2 × 10 mL). The combined CH_2Cl_2 extracts were concentrated to ca. 5 mL and pentane (30 mL) was added. The supernatant solution was decanted. After drying (in vacuo), **12** (120 mg, 90% based on Ph_3PAuCl) was obtained as an orange solid. − Mp: 141 °C. − IR (KBr): $\tilde{\nu}$ = 2109 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 4.11 (t, $^3J_{HH}$ = 3.6 Hz, 2 H, C_5*H*$_4$), 4.22 (s, 5 H, C_5*H*$_5$), 4.44 (t, $^3J_{HH}$ = 1.4 Hz, C_5*H*$_4$), 7.4−7.6 (m, 15 H, C_6*H*$_5$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 67.8 (*CH*/C_5H_4), 68.7 (*iC*/C_5H_4), 70.0 (C_5H_5), 102.5 (C≡C), 129.1 (d, $^3J_{PH}$ = 11 Hz, *CH*/C_6H_5), 129.9 (d, $^1J_{PH}$ = 63 Hz, *iC*/C_6H_5), 131.5 (*CH*/C_6H_5), 134.3 (d, $^2J_{PH}$ = 14 Hz, *CH*/C_6H_5). − ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 42.9 (PPh_3). − FAB-MS; *m*/*z* (rel. int.): 668 (90) $[M]^+$, 459 (100) $[C_{18}H_{15}AuP]^+$, 210 (10) $[C_{12}H_9Fe]^+$. − $C_{30}H_{24}AuFeP$ (668.35): calcd. C 53.91, H 3.62; found C 53.82, H 3.51.

Synthesis of $Ph_3PAuC{\equiv}C\{Pt\}C{\equiv}CFc$ (13): Compound **11** (120 mg, 0.13 mmol) and $FcC{\equiv}CSnMe_3$ (75 mg, 0.20 mmol) were dissolved in THF (20 mL). After stirring (6 h, 50 °C), the solution was concentrated to ca. 5 mL and Et_2O (40 mL) was added. The supernatant solution was decanted from the precipitate that had formed. Subsequently, this was extracted with Et_2O (2 × 10 mL) and then dried (in vacuo). Complex **13** (100 mg, 80% based on **11**) was obtained as an amber solid. − Mp: > 200 °C. − IR (KBr): $\tilde{\nu}$ = 2098 [$\nu_{C\equiv C}$], 1971 [$\nu_{C\equiv C}$] cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 3.19 (s, 12 H, N*Me*$_2$), 4.04 (br s, 2 H, C_5*H*$_4$), 4.04 (s, 4 H, C*H*$_2$), 4.15 (s, 5 H, C_5*H*$_5$), 4.36 (br s, 2 H, C_5*H*$_4$), 7.01 (s, 2 H, C_6*H*$_2$), 7.4−7.6 (m, 15 H, C_6*H*$_5$). − ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 43.1. − FAB-MS; *m*/*z* (rel. int.): 1078 (20) $[M^+]$, 867 (50) $[M - Fc]^+$, 668 (10) $[C_{30}H_{24}AuFeP]^+$, 459 (100) $[C_{18}H_{15}AuP]^+$, 409 $[C_{14}H_{18}N_2Pt]^+$, 210 (10) $[C_{12}H_9Fe]^+$. − $C_{44}H_{43}AuFeN_2PPt$ (1078.76): calcd. C 48.99, H 4.02, N 2.60; found C 49.12, H 4.08, N 2.68.

Acknowledgments

The authors would like to thank the Volkswagenstiftung, the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and Utrecht University (1.5 year stay of SB) for financial support. Drs. M. Lutz and A. L. Spek are thanked for the X-ray study on **11**.

---

[1] [1a] *Inorganic Materials* (Eds.: D. W. Bruce, D. O'Hare), Wiley, Chichester, **1992**. − [1b] S. R. Marder, J. W. Perry, *Adv. Mater.* **1993**, *5*, 804−815. − [1c] D. Astruc, *Acc. Chem. Res.* **1997**, *30*, 383−391. − [1d] P. J. Stang, B. Olenyuk, *Acc. Chem. Res.* **1997**, *30*, 502−518. − [1e] T. M. Swager, *Acc. Chem. Res.***1998**, *31*, 201−207.[1f] B. Olenyuk, A. Fechtenkötter, P. J. Stang, *Acc. Chem. Res.* **1998**, *31*, 1707−1728.

[2] [2a] D. R. Kanis, P. G. Lacroix, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10089−10102. − [2b] D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* **1994**, *94*, 195−242.[2c] M. B. Sponsler, *Organometallics* **1995**, *14*, 1920−1927. − [2d] P. Belazoni, N. Re, A. Sgamellotti, C. Floriani, *J. Chem. Soc., Dalton Trans.* **1998**, 1825−1835. − [2e] N. Re, A. Sgamellotti, C. Floriani, *J. Chem. Soc. Dalton Trans.* **1998**, 2521−2529.

[3] [3a] M. Brady, W. Weng, Y. Zhou, J. W. Seyler, A. J. Amoroso, A. M. Arif, M. Böhme, G. Frenking, J. A. Gladysz, *J. Am. Chem. Soc.* **1997**, *119*, 775−788. − [3b] S. B. Falloon, S. Szafert, A. M. Arif, J. A. Gladysz, *Chem. Eur. J.* **1998**, *4*, 1033−1042.

[4] [4a] T. Kaharu, H. Matsubara, S. Takahashi, *J. Mater. Chem.* **1991**, *1*, 145−146. − [4b] P. Nguyen, G. Lesley, T. B. Marder, I. Ledoux, J. Zyss, *Chem. Mater.* **1997**, *9*, 406−411. − [4c] W.-Y. Wong, W.-K. Wong, P. R. Raithby, *J. Chem. Soc., Dalton Trans.* **1998**, 2761−2769. − [4d] N. Ohshiro, F. Takei, K. Onitsuka, S. Takahashi, *J. Organomet. Chem.* **1998**, *569*, 195−202.

[5] [5a] P. L. Porter, S. Guha, K. Kang, C. C. Frazier, *Polymer* **1991**, *32*, 1756−1760. − [5b] M.-C. Lagunas, R. A. Gossage, A. L. Spek, G. van Koten *Organometallics* **1998**, *17*, 731−741.

[6] [6a] M. S. Khan, A. K. Kakkar, S. L. Ingham, P. R. Raithby, J. Lewis, B. Spencer, F. Wittmann, R. H. Friend, *J. Organomet. Chem.* **1994**, *472*, 247−255. − [6b] P. Steenwinkel, D. M. Grove, N. Veldman, A. L. Spek, G. van Koten, *Organometallics* **1998**, *17*, 5627−5655. − [6c] M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton, A. H. White *J. Chem. Soc., Dalton Trans.* **1998**, 467−473.

[7] [7a] N. J. Long, A. J. Martin, F. Fabrizi de Biani, P. Zanello, *J. Chem. Soc., Dalton Trans.* **1998**, 2017−2021. − [7b] P. Ceroni, F. Paolucci, C. Paradisi, A. Juris, S. Raffia, S. Serroni, S. Campagna, A. J. Bord, *J. Am. Chem. Soc.* **1998**, *120*, 5480−5487. − [7c] J. Lewis, P. R. Raithby, W.-Y. Wong, *J. Organomet. Chem.* **1998**, *556*, 219−228.

[8] [8a] M. Tamm, A. Grzegorzewski, I. Brüdgam, H. Hartl, *J. Chem. Soc., Dalton Trans.* **1998**, 3523−3528. − [8b] X. Gu, M. B. Sponsler, *Organometallics* **1998**, *17*, 5920−5923. − [8c] M. C. B. Colbert, J. Lewis, P. R. Raithby, M. Younus, A. J. White, D. J. Williams, N. N. Payne, C. Yellowlees, D. Beljonne, N. Chandhury, R. H: Friend, *Organometallics* **1998**, *17*, 3034−3043.[8d] T. Weyland, K. Costuas, A. Mari, J.F. Halet, C. Lapinte, *Organometallics* **1998**, *17*, 5569−5579.

[9] J.-D. Lee, L. M. Vrana, E. R. Bullock, K. J. Brewer, *Inorg. Chem.* **1998**, *37*, 3575−3580.

[10] [10a] Y. Hayashi, M. Osawa, Y. Wakatsuki, *J. Organomet. Chem.* **1997**, *542*, 241−246. − [10b] S. Back, H. Pritzkow, H. Lang, *Organometallics* **1998**, *17*, 41−44. − [10c] S. Back, R.A. Gossage, I. del Río, G. Rheinwald, H. Lang, G. van Koten, *J. Organomet. Chem.* **1999**, *582*, 126.

[11] [11a] T. E. Müller, S. W.-K. Choi, D. M. P. Mingos, D. Murphy, D. J. Williams, V. W.-W. Yam, *J. Organomet. Chem.* **1994**, *484*, 209−224. − [11b] V. W.-W. Yam, S. W.-K. Choi, *J. Chem. Soc., Dalton Trans.* **1996**, 4227−4232. − [11c] I. R. Whittall, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Angew. Chem.* **1997**, *109*, 386−388; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 370−371. − [11d] R. J. Puddephatt, *Chem. Commun.* **1998**, 1055−1062.

[12] [12a] M. M. Bhadbhade, A. Das, J. C. Jefferey, J. A. McCleverty, J. A. Navas Badiola, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1995**, 2769−2778. − [12b] S. Sakanishi, D. A. Bardwell, S. Couchman, J. C: Jefferey, J.A. McCleverty, M. D. Ward, *J. Organomet. Chem.* **1997**, *528*, 35−45.

[13] [13a] J. T. Liu, M.-F. Young, C. Tsai, Y. S. We, *J. Organomet. Chem.* **1998**, *564*, 257−266. − [13b] J. Mata, S. Uriel, E. Peris,

R. Lhusar, S. Houbrechts, A. Persoons, *J. Organomet. Chem.* **1998**, *562*, 197−202.

[14] M. C. B. Colbert, A. J. Edwards, J. Lewis, N. J. Long, N. A. Page, D. G. Parker, P. R. Raithby, *J. Chem. Soc., Dalton Trans.* **1994**, 2589−2598.

[15] S. L. James, G. Verspui, A. L. Spek, G. van Koten, *Chem. Commun.* **1996**, 1309−1310.

[16] S. Back, R. A. Gossage, M. Lutz, I. del Río, A. L. Spek, H. Lang, G. van Koten, *Organometallics* **1999**, submitted.

[17] A. Seebald, C. Stader, B. Wrackmeyer, W. Bensch, *J. Organomet. Chem.* **1986**, *311*, 233−242.

[18] J. Dale, *Properties of Acetylenic Compounds*, in: *Chemistry of Acetylenes* (Ed.: H. G. Viehe), Marcel Dekker, New York, **1969**.

[19] [19a] R. S. Dickson, P. J. Fraser, *Adv. Organomet. Chem.* **1974**, *12*, 323−377. − [19b] D. Seyferth, T. Kugita, A. L. Rheinhold, G. P. A. Yap, *Organometallics* **1995**, *14*, 5362−5366. − [19c] E. C. Constable, O. Eich, C. E. Housecroft, C. A. Johnston, *Chem. Commun.* **1998**, 2661−2662.

[20] H. Lang, S. Blau, K. Köhler, *Coord. Chem. Rev.* **1995**, *143*, 113−168 and ref. cited therein.

[21] S. Back, T. Stein, G. Rheinwald, H. Lang, *Acta Crystallogr., Sect. C* **1999**, submitted.

[22] W. Beck, personal communication.

[23] M. I. Bruce, E. Horn, J. G. Matison, M. R. Snow, *Aust. J. Chem.* **1984**, *37*, 1163−1170.

[24] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627−630.

[25] W. E. Davidson, M. C. Henry, *Chem. Rev.* **1967**, *67*, 73−106.

[26] J. Polin, H. Schottenberger, *Org. Synth.* **1996**, *73*, 262−269.

Received November 24, 1999
[I99427]