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Synthesis and Coordination Chemistry of Gold(I) Acetylides. The Solid-State Structure of $\{[\eta^2\text{-}(Ph_3P)AuC{\equiv}CFc]Cu(\mu\text{-}Cl)\}_2$

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The gold(I) acetylide $(Ph_3P)AuC{\equiv}CC_6H_3(CH_2NMe_2)_2$-3,5 (**3**) is accessible by the reaction of $(Ph_3P)AuCl$ (**1**) with $HC{\equiv}CC_6H_3(CH_2NMe_2)_2$-3,5 (**2**) in a 1:1 molar ratio. Base-catalyzed desilylation of $(Ph_3P)AuC{\equiv}CSiMe_3$ (**4**) produces the homobimetallic gold(I) species $(Ph_3P)AuC{\equiv}CAu(PPh_3)$ (**5**). However, the intermediate formation of $(Ph_3P)AuC{\equiv}CH$ could not be evidenced, but is most likely. The coordination chemistry of **5** and $(Ph_3P)AuC{\equiv}CFc$ (**6**) toward different copper(I) halides $[CuX]_n$ (**7a**, X = Cl; **7b**, X = Br) is presented. While heterodinuclear **6** affords with equimolar amounts of **7a** hexanuclear $\{[\eta^2\text{-}(Ph_3P)AuC{\equiv}CFc]Cu(\mu\text{-}Cl)\}_2$ (**8**), homobinuclear **5** produces with **7b** in a 1:1 molar ratio via ligand exchange polymeric $[Cu\text{-}C{\equiv}C]_n$ (**10**) and mononuclear $(Ph_3P)AuBr$ (**11**). A feasible reaction mechanism for the formation of the latter species is presented. The solid-state structure of **8** is reported. It exhibits a linear array around the gold(I) center and a coplanar arrangement of the Cu_2Cl_2 and the gold(I) acetylide entities.

Introduction

In the search for new material properties a manifold of different organometallic complexes were prepared.[1] In this context, the chemical and physical properties of gold(I) acetylides have recently been the subject of thorough studies.[2−15] Besides their nonlinear optical (NLO) properties also the liquid crystalline behavior of gold(I) acetylides is of interest.[9,16]

Moreover, mixed-metal gold(I) acetylides containing a late transition metal (TM) complex fragment, such as Fc or {Pt} (Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$; {Pt} = Pt-$[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$), were prepared.[17] The study of their electrochemical behavior revealed that a remotely

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present late TM center, e.g., Fe(II), shifts the Au(I)/Au(0) reduction potential to a more negative value.[17]

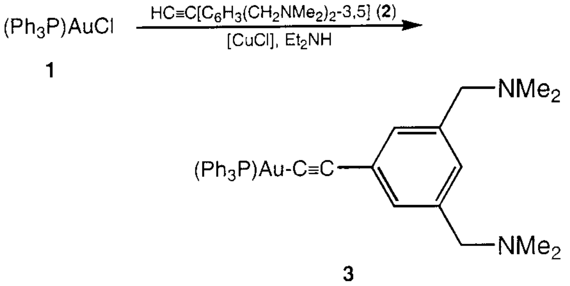
A variety of TM monoacetylides have been studied with respect to their ability to form σ,η^2-complexes.[18] Prominent representative species have been prepared with, for example, $Re(CO)_5$ end groups.[19] Also, Pt(II) σ-acetylide-containing coordination polymers were reported.[20] Moreover, η^2-acetylene complexes of copper(I) salts are of interest due to their applicability in the deposition of thin copper films for electronic devices, e.g., by using chemical vapor deposition techniques (CVD).[21]

In view of our earlier studies in this area[18c,22] we set out to study the synthesis of mono- as well as homo- and heterobimetallic gold(I) acetylides of the general type $(Ph_3P)AuC\equiv CR$ (R = singly bonded organic or organometallic group) and their coordination behavior toward copper(I) halides.

Results and Discussion

Synthesis and Spectroscopy. In the course of our studies toward the synthesis and reaction chemistry of gold(I) acetylides we choose as starting material the gold(I) acetylide $(Ph_3P)AuC\equiv CR$ [**3**, R = $C_6H_3(CH_2NMe_2)_2$-3,5; **4**, R = $SiMe_3$;[5c] **6**, R = Fc; Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$[17]].

As shown by Vicente et al., complex **4** can easily be prepared by the reaction of $(PPh_3)AuCl$ (**1**) with $HC\equiv C\text{-}SiMe_3$ in diethylamine as solvent.[5c] However, it appeared that in the synthesis of **3** the reaction of **1** with $HC\equiv C[C_6H_3(CH_2NMe_2)_2\text{-}3,5]$ (**2**) in Et_2NH as solvent requires the addition of catalytic amounts of $[CuCl]_n$ to obtain **3** in high yields. The latter procedure was first published by Bruce and co-workers.[3c]



(1)

The IR spectrum of **3** reveals the stretching frequency of the C$\equiv$C triple bond at 2112 cm^{-1}, in a region that is typical for this type of molecules.[2-15]

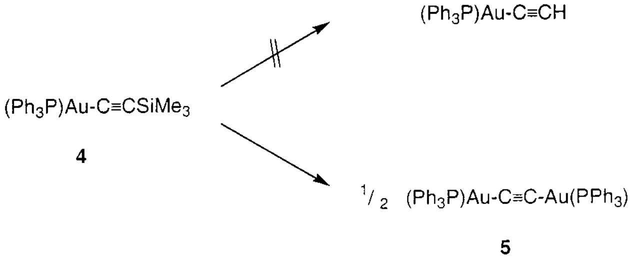
The same is true for the ^1H NMR spectrum of **3**, showing resonance signals due to the respective organic groups present.[17,22] However, it must be noted that in the $^{13}C\{^1H\}$ NMR spectrum of **3** only one resonance signal for the C$\equiv$C carbon atoms was found at 103.5 ppm. The phenomenon of low detectability of the sp-hybridized carbon atoms of gold(I) acetylides has already been described earlier.[3]

A suitable tool to monitor the successful formation of **3** is given by $^{31}P\{^1H\}$ NMR spectroscopy. While the ^{31}P resonance signal for $(Ph_3P)AuCl$ (**1**) is found at 33.8 ppm,[22] the phosphorus signal of **3** is low-field shifted by approximately 10 ppm to 43.6 ppm.

The FAB mass spectrum of **3** shows the peak of the respective molecular ion M^+ at the expected m/z value (675). Further fragments are $M^+ - NMe_2$ (m/z = 631) and $M^+ - 2\ NMe_2$ (m/z = 587). As base peak $AuPPh_3^+$ (m/z 459) is found.

To desilylate the $Me_3SiC\equiv C$ entity in $(PPh_3)AuC\equiv CSiMe_3$ (**4**)[5c] to obtain $(Ph_3P)AuC\equiv CH$, this complex was treated with a methanolic K_2CO_3 solution at 25 °C. However, instead of mononuclear $(Ph_3P)AuC\equiv CH$,[5c] the homodinuclear gold(I) complex $(Ph_3P)AuC\equiv CAu(PPh_3)$ (**5**)[6b] was formed in quantitative yield (Scheme 1), which probably is caused by the application of the basic desilylation procedure.

Scheme 1. Formation of 5 by Treatment of 4 with K_2CO_3/MeOH



Presumably in the reaction of **4** with K_2CO_3/MeOH as intermediate $[(Ph_3P)AuC\equiv C]^-$ is formed, which, however, reacts with further **4** under ligand substitution

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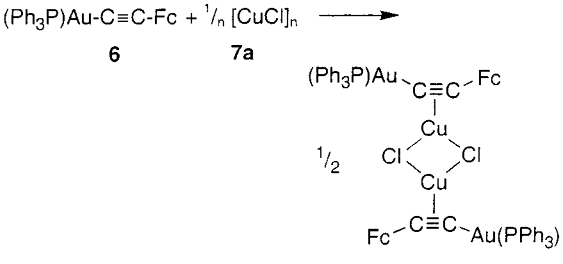
to **5**. The direct synthesis of a similar species was described by Cross et al. using a NaOEt/EtOH solution containing $(Ph_3P)AuCl$ (**1**) and acetylene gas. The analytical and spectroscopic data of **5** are consistent with the reported values.[3b]

Complexes $(PPh_3)AuC{\equiv}CR$ [**3**, R = $C_6H_3(CH_2NMe_2)_2$-3,5; **4**, R = $SiMe_3$;[5c] **6**, R = Fc; Fc = $(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$[17]] as well as $(PPh_3)AuC{\equiv}CAu(PPh_3)$ (**5**) contain a C≡C unit, which allows the preparation of oligonuclear TM species. As an example, the homo- and heterobimetallic complexes **5** and **6** were reacted with copper(I) halides in an attempt to synthesize $Cu_2(\mu-X)_2$-bridged oligonuclear complexes. The copper(I) salts $[CuX]_n$ (**7a**, X = Cl; **7b**, X = Br) were chosen because of their well-studied reaction chemistry toward C≡C triple bonds.[18c,23] For example, η^2-alkyne complexes of general type $[(\eta^2-RC{\equiv}CR)Cu(\mu-X)]_2$ (R = Me_3Si, ...; X = Cl, Br, CO_2R, ...) are of fundamental interest, since these species can successfully be applied as organometallic precursors for growing thin copper films on different substrates by applying the chemical vapor deposition process.[21,23]

In the case of $(Ph_3P)AuC{\equiv}CFc$ (**6**), reaction with $1/n[CuCl]_n$ in a 1:1 molar ratio in dichloromethane as solvent affords the hexanuclear complex **8** in 70% yield.



6 7a

8

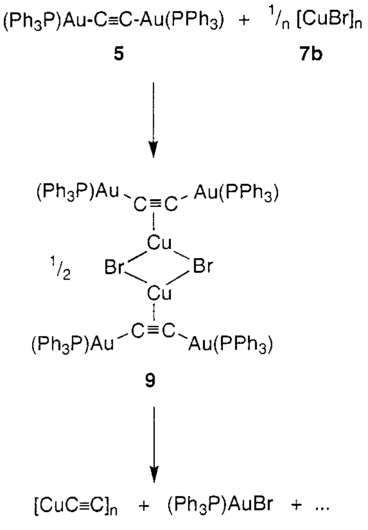
(2)

Solid orange **8**, which is stable to air for several days, is poorly soluble in unpolar organic solvents, but dissolves readily in, for example, dichloromethane and tetrahydrofuran. However, in dichloromethane solutions it starts to decompose after several days, even under inert gas atmosphere.

The IR spectrum of **8** exhibits the expected absorption band for the C≡C triple bond at 1924 cm^{-1}. Compared to the starting material **6**, it is shifted by almost 190 cm^{-1} to lower wavenumbers, which is typical for the η^2-coordination of a C≡C building block to a TM complex fragment such as CuCl[17] and hence the formation of **8**.

^1H as well as $^{13}C\{^1H\}$ NMR spectroscopic studies on **8** do not reveal significant changes in the chemical shifts of the organic groups present, when compared to **6**.[17] For the Fc entities a singlet at 4.22 ppm and two pseudotriplets at 4.11 and 4.44 ppm with a coupling constant of J_{HH} = 3.6 Hz are found.

Scheme 2. Preparation of 10 and 11 via Intermediate Formation of 9



5 7b

9

10 11

To obtain another hexanuclear species, $(Ph_3P)Au-C{\equiv}C-Au(PPh_3)$ (**5**) was reacted with equimolar amounts of $1/n[CuBr]_n$ (**7b**) in dichloromethane at 25 °C. However, in the course of the reaction the colorless reaction mixture developed an intense red color and a red precipitate was formed. After appropriate workup, the red precipitate could be identified by its spectroscopic data as polymeric $[CuC{\equiv}C]_n$ (**10**).[24] As a further product, $(Ph_3P)AuBr$ (**11**) could be characterized by $^{31}P\{^1H\}$ NMR spectroscopic studies and by X-ray crystallography.[25]

An explanation for the formation of **10** and **11** in the reaction of **5** with **7b** is given by the assumption of the formation of the heterobimetallic intermediate **9** (Scheme 2).

The hexanuclear intermediate **9** provides the possibility for an intramolecular ligand exchange, which finally yields polymeric **10** and mononuclear **11**. A similar observation was made when $\{Pt\}C{\equiv}CSiMe_3$ ($\{Pt\}$ is the bis(orthoamino)aryl unit $Pt[C_6H_3(Me_2NCH_2)_2-2,6]$) was reacted with copper(I) halides, yielding $\{Pt\}Cl$ along with $[CuC{\equiv}CSiMe_3]_n$; that is, in this reaction the Pt−C bond rather than the C−Si bond is selectively broken.[22] However, this behavior contrasts with that of $(CO)_5ReC{\equiv}CRe(CO)_5$.[19]

Solid-State Structure of $\{[\eta^2-(Ph_3P)AuC{\equiv}CFc]Cu(\mu-Cl)\}_2$ (8). Single crystals of **8** could be obtained by diffusion-controlled crystallization of a *n*-pentane solution into a dichloromethane solution containing **8** at 25 °C. The solid-state structure of **8** is depicted in Figure 1. Important structural details are given in Table 1, and crystal and intensity collection data are summarized in Table 2 (Experimental Section).

Hexanuclear **8** crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell. Molecules of **8** exhibit a center of inversion; all symmetry-generated atoms are marked with the suffix a. The best planes through the atoms Cu(1)−C(1)−C(2) and through the $Cu_2(\mu-Cl)_2$ entity, Cu(1)−Cl(1)−Cl(1a)−Cu(1a), are tilted by only 1.22°. Thus, the coordination sphere around Cu(1) is

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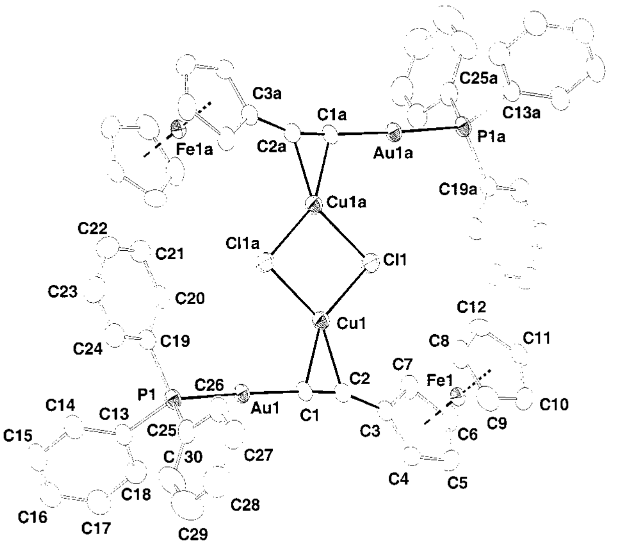

Figure 1. ZORTEP drawing (50% probability level) and atom-numbering scheme of **8**.

Table 1. Selected Distances (Å) and Angles (deg) for 8^{a,b}

bond lengths		angles	
Au(1)−P(1)	2.2804(16)	P(1)−Au(1)−C(1)	176.90(19)
Au(1)−C(1)	2.020(6)	Au(1)−C(1)−C(2)	176.3(5)
C(1)−C(2)	1.227(9)	C(1)−C(2)−C(3)	162.4(6)
C(2)−C(3)	1.438(9)	C(1)−Cu(1)−C(2)	35.4(2)
C(1)−Cu(1)	2.014(6)	Cl(1a)−Cu(1)−Cl(1)	94.03(6)
C(2)−Cu(1)	2.205(6)	Cu(1a)−Cl(1)−Cu(1)	85.97(6)
Cu(1)−Cl(1)	2.2711(17)		
Cu(1)−Cl(1a)	2.3107(18)		
Cl(1)−Cu(1a)	2.3107(18)		
D(1)-Fe(1)^c	1.6475(29)		
D(2)-Fe(1)^c	1.6513(31)		

[a] Symmetry transformations used to generate equivalent atoms: $1 - x$, $-y + 1$, $-z + 2$. [b] Standard deviations are given as the last significant figure in parentheses. [c] D(1), D(2): centroids of the cyclopentadienyl ligands.

Table 2. Crystal and Intensity Collection Data for 8

empirical formula	$C_{31}H_{26}AuCl_3CuFeP$
chemical formula	$C_{60}H_{48}Au_2Cl_2Cu_2Fe_2P_2$, 2 CH_2Cl_2
fw	852.19
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	10.4288(1)
b (Å)	11.6962(1)
c (Å)	14.3504(2)
α (deg)	67.6206(5)
β (deg)	82.2386(6)
γ (deg)	64.5716(7)
V (Å^3)	2889.6(11)
ρ_{calc} (g cm^{-3})	1.937
F(000)	824
Z	1
cryst dimens (mm)	0.4 × 0.2 × 0.1
diffractometer model	Bruker Smart CCD
radiation (λ, Å)	0.71073
max., min. transmn	0.350855, 0.138235
abs coeff (μ, mm^{-1})	6.569
temperature (K)	173(2)
scan mode	ω-scan
scan range (deg)	$1.54 \le \theta \le 30.45$
index ranges	$-8 \le h \le 14$ $-14 \le k \le 16$ $-19 \le l \le 19$
total no. of reflns	11 535
no. of unique reflns	7643
no. of obsd reflns [$I \ge 2\sigma(I)$]	6089
no. of refined params	344
completeness to θ_{max}	86.3%
R1, wR2^a [$I \ge 2\sigma(I)$]	0.0494, 0.1152
R1, wR2^a (all data)	0.0611, 0.1194
R(int), S	0.0484, 0.978
max., min. peak in final Fourier map (e Å^{-3})	4.328, −4.360

[a] $R1 = [\Sigma(||F_o| - |F_c|)/\Sigma|F_o|)]$; $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2}$; $P = [F_o^2 + 2F_c^2]/3c)$; $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0443P)^2 + 0.00005P]$; n = number of reflections, p = parameters used.

trigonal-planar and comprises the η^2-bonded acetylide and the μ-bridging chloro ligands. A similar feature has been observed for other $Cu_2(\mu\text{-}X)_2$-containing complexes (X = halide), e.g., $[(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)_2Cu_2(\mu{-}Br)_2]$,[23a] $[(\eta^2\text{-}PhC{\equiv}CSiMe_3)Cu(\mu\text{-}Br)]_2$,[26] or $[(\eta^2\text{-}FpC{\equiv}CPh)Cu(\mu\text{-}Cl)]_2$ [Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$][18a] or the copper(I) tmtch complexes prepared by Weiss and Behrens (tmtch = 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne).[27] The C≡C triple bond distance C(1)−C(2) amounts to 1.227(9) Å and lies in the range of bond lengths encountered in related η^2-bonded organic or organometallic alkynes to copper(I) salts; for example, in $[(\eta^2\text{-}FpC{\equiv}CPh)Cu(\mu\text{-}Cl)]_2$ the C≡C bond length is 1.27(2) Å.[18a] Compared to known C≡C bond lengths reported for other gold(I) acetylides,[3−15] the η^2-coordination of copper(I) does not cause a significant change of the C≡C distance. The Au(1)−P(1) bond [2.2804(16) Å] resembles values reported for this bond in other organo gold(I) phosphorus complexes, e.g., $(Ph_3P)AuC{\equiv}CC_6H_4NO_2\text{-}4$ [2.277(1) Å].[9a] The Au(1)−C(1) distance of 2.020(6) Å is slightly longer than found, for example, in complex **5** [1.988(6) Å][3b] or (nmdpp)AuC≡CPh [2.00(2) Å] [nmdpp = (neomenthyl)-diphenylphosphine].[9c] This elongation can be assigned to the η^2-coordination of the C≡C entity to copper(I).[18c] The latter type of bonding also causes the deviation of the C1−C2−C3 array from linearity [C(1)−C(2)−C(3) 162.4(6)°]. However, the Au(1)−C(1)−C(2) as well as the P(1)−Au(1)−C(1) angles [176.3(5)°, 176.90(19)°] are almost linear.[9a,c]

The structural features of **8** additionally provide a possible explanation for the instability of $\{[\eta^2\text{-}(Ph_3P)AuC{\equiv}CAu(PPh_3)]Cu(\mu\text{-}Br)\}_2$ (**9**), owing to steric crowding.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of purified nitrogen (O_2 traces: Cu catalyst, BASF AG, Ludwigshafen; H_2O: molecular sieve 4 Å) using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were purified by distillation from sodium/benzophenone ketyl; dichloromethane and n-pentane were purified by distillation from calcium hydride. Infrared spectra were recorded on a Perkin-Elmer FT-IR 1000 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300.130 MHz in the Fourier transform mode; $^{13}C\{^1H\}$ NMR spectra were recorded at 75.323 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal ($CDCl_3$: ^{1}H NMR, δ 7.27; $^{13}C\{^1H\}$ NMR, δ 77.0). $^{31}P\{^1H\}$ NMR were recorded at 121.506 MHz in $CDCl_3$ with $P(OMe)_3$ (δ 139.0 ppm) as external reference relative to H_3PO_4 (δ 0.0 ppm). FD and

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FAB mass spectra were recorded on a Finnigan 8400 mass spectrometer operating in the positive-ion mode. Melting points were determined using sealed nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by H. Kolbe, Mülheim/Ruhr.

General Remarks. $(Ph_3P)AuCl$ (**1**),[3c] $C_6H_3(CH_2NMe_2)_2$-3,5-$(C{\equiv}CH)$-1,[28] $(Ph_3P)AuC{\equiv}CSiMe_3$,[5c] and $(Ph_3P)AuC{\equiv}CFc$ (**6**)[17] were prepared by published procedures. All other chemicals were purchased from commercial sources and were used as received.

1. Synthesis of $(Ph_3P)Au[C{\equiv}C\text{-}1\text{-}C_6H_3(CH_2NMe_2)_2\text{-}3,5]$ (3). At 25 °C $1/n[CuCl]_n$ (**7a**) (20 mg, 0.02 mmol) was added in one portion to a stirring mixture of **1** (480 mg, 1 mmol), $C_6H_3(CH_2NMe_2)_2$-3,5-$(C{\equiv}CH)-1$ (**2**) (270 mg, 1.25 mmol), and 30 mL of $HNEt_2$. After 4 h of stirring, all volatiles were removed in an oil-pump vacuum. The residue was suspended in H_2O (15 mL), and the suspension was extracted with dichloromethane (3 × 10 mL). The combined dichloromethane extracts were dried over Na_2SO_4 and then filtered off. After drying in an oil-pump vacuum, **3** (610 mg, 0.9 mmol, 85% relative to **1**) could be obtained as a colorless solid. Mp: [°C] 148. IR (KBr): [cm^{-1}] 2112 [$\nu_{C\equiv C}$]. ^1H NMR ($CDCl_3$): [δ] 2.18 (s, 12 H, NMe_2), 3.41 (s, 4 H, CH_2), 7.09 (s, 2 H, C_6H_3), 7.10 (s, 1 H, C_6H_3), 7.3−7.7 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 43.9 (NMe_2), 62.7 (CH_2), 103.5 ($AuC{\equiv}C$), 127.6 (d, J_{PC} = 50 Hz, $^iC/C_6H_5$), 127.7 (d, J_{PC} = 11 Hz, CH/C_6H_5), 128.9 ($^iC/C_6H_3C{\equiv}C$), 130.1 (CH/C_6H_3), 130.1 (CH/C_6H_5), 130.6 (CH/C_6H_3), 132.9 (d, J_{PC} = 15 Hz, CH/C_6H_5), 137.2 ($^iC/C_6H_3CH_2$-NMe_2).[a] $^{31}P\{^1H\}$ NMR ($CDCl_3$): [δ] 43.6 (PPh_3). FAB MS [m/z (rel intensity)]: 675 (40) $[M]^+$, 631 (30) $[M - NMe_2]^+$, 587 (50) $[M - 2NMe_2]^+$, 459 (100) $[AuPPh_3]^+$. Anal. Calcd for $C_{32}H_{34}AuN_2P$ (674.61): C, 56.97; H, 5.08. Found: C, 56.51; H, 5.01. [a]The second signal for the $C{\equiv}C$ entity could not be assigned unequivocally.

2. Synthesis of $(Ph_3P)AuC{\equiv}CAu(PPh_3)$ (5) by the Reaction of $(Ph_3P)AuC{\equiv}CSiMe_3$ with $MeOH/K_2CO_3$. At 25 °C, 400 mg of $(Ph_3P)AuC{\equiv}CSiMe_3$ (0.7 mmol) was dissolved in 20 mL of methanol, and 0.5 g of K_2CO_3 (3.3 mmol) was added in one portion. After 10 h of stirring at this temperature all volatiles were evaporated. Then, the residue was extracted with dichloromethane (4 × 5 mL). The combined dichloromethane extracts were concentrated to 5 mL, and 30 mL of n-pentane was added. After decantation of the supernatant solution and drying of the residue in an oil-pump vacuum, **5** (220 mg, 65% based on $(Ph_3P)AuC{\equiv}CSiMe_3$) could be isolated as a colorless solid.

The spectroscopic data of **5** are in agreement with the data reported for this homobimetallic complex.[3b]

3. Synthesis of $\{[\eta^2\text{-}(Ph_3P)AuC{\equiv}CFc]Cu(\mu\text{-}Cl)\}_2$ (8). At 25 °C, 40 mg of $1/n[CuCl]_n$ (**7a**) (0.4 mmol) was added to **6** (130 mg, 0.2 mmol) dissolved in 30 mL of dichloromethane. After 3 h of stirring, all volatiles were evaporated in an oil-pump vacuum, and the residue was extracted with dichloromethane (3 × 10 mL). The combined dichloromethane extracts were evaporated to yield orange **8** (110 mg, 0.07 mmol, 70% based on **6**). Mp: [°C] 145. IR (KBr): [cm^{-1}] 1924 [$\nu_{C\equiv C}$]. ^1H NMR ($CDCl_3$): [δ] 4.11 (pt, J_{HH} = 3.6 Hz, 4 H, C_5H_4), 4.22 (s, 10 H, C_5H_5), 4.44 (pt, J_{HH} = 3.6 Hz, 4 H, C_5H_4), 7.4−7.6 (m, 30 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 67.8 (CH/C_5H_4), 68.7 ($^iC/C_5H_4$), 70.0 (C_5H_5), 71.9 (CH/C_5H_4), 129.1 (d, J_{PC} = 11.3 Hz, CH/C_6H_5), 129.9 (d, J_{PC} = 62.7 Hz, $^iC/C_6H_5$), 131.5 (CH/C_6H_5), 134.3 (d, J_{PC} = 13.8 Hz, CH/C_6H_5).[a] Anal. Calcd for $C_{60}H_{48}Au_2Cl_2Cu_2Fe_2P_2$ (1534.57): C, 46.96; H, 3.15. Found: C, 47.15; H, 3.36. [a]Signals for the $C{\equiv}C$ entity were not detected.

X-ray Structure Determination. The structure of **8** was determined by single-crystal X-ray diffraction. The preparation of single crystals was done in perfluoro alkyl ether from ABCR GmbH & Co KG (viscosity 1600 cSt). Data were collected on a Bruker Smart CCD diffractometer using Mo Kα radiation. The unit cell was determined with the program SMART.[29] For data integration and refinement of the unit cell the program SAINT[29] was used. The space group was determined using the program or ABSEN,[30] and the empirical absorption correction was done with SADABS.[31] In the structure solution by direct methods the program SIR97[32] was employed, and the structure refinement was based on least-squares methods based on F^2 with SHELX97.[33] The plots of the molecular structures were visualized using the program ZORTEP.[34] All non-hydrogen atoms were fully refined in their located positions; the hydrogen atoms were positioned as riding models to their neighboring atom and refined depending on their position.

Crystallographic data of **8** are given in Table 2.

4. Reaction of 5 with 7b. To **5** (200 mg, 0.2 mmol) dissolved in 30 mL of dichloromethane was added 60 mg of **7b** (0.4 mmol). After 5 min a red precipitate was formed, which subsequently was identified by its IR spectrum as $[CuC{\equiv}C]_n$ (**10**)[24] (isolated yield: 30 mg, 90% based on **5**). After 1 h of stirring at 25 °C, all volatiles were evaporated in an oil-pump vacuum, and the residue was extracted with dichloromethane (3 × 10 mL). The combined dichloromethane extracts were evaporated (oil-pump vacuum) to yield colorless **11** (230 mg, 90% based on **5**).

$(Ph_3P)AuBr$ (**11**) was identified by FAB-MS and X-ray crystallography.[25]

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Supporting Information Available: Tables containing final atomic coordinates for non-hydrogen atoms and equivalent isotopic temperature displacement parameters, a complete list of bond lengths and angles, and anisotropic displacement parameters for **8** have been deposited as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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