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Reactions of Gold(I) Acetylides with 1,1'-Diisocyanoferrocene: From Orthodox to Unorthodox Behavior

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Received June 27, 2008

1,1'-Diisocyanoferrocene (**1**) reacts with the gold(I) acetylides $[\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R})]_n$ (**2a** $\text{R} = \text{CF}_3$, **2b** $\text{R} = \text{H}$, **2c** $\text{R} = \text{OMe}$, **2d** $\text{R} = \text{NMe}_2$) to afford the respective dinuclear gold complexes $[\{\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R})\}_2(\mu\text{-1})]$ (**3**), whose aurophilic aggregation in the solid state depends on the nature of the substituent R . The product of the reaction of **1** with $[\text{Au}(\text{C}\equiv\text{C}-\text{Fc})]_n$ (**2e**, Fc = ferrocenyl) is the hexanuclear gold cluster $[(\text{Fc}-\text{C}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{N}-\text{C}_5\text{H}_4\text{Fe}\{\text{C}_5\text{H}_4\text{-N}=\text{C}(\text{Au})-\text{C}\equiv\text{C}-\text{Fc}\})_3]$, which is composed of three subunits **4** and exhibits an unusual arrangement of gold atoms. The formation of (**4**)₃ is based on a different specific reaction of the two chemically equivalent functional groups of **1** with **2e**, viz., coordination and 1,1-insertion. This “schizoid” behavior apparently is a novel variant of induced reaction asymmetry and constitutes a new phenomenon in chemistry. The reaction of **2e** with 1,1'-bis(diphenylphosphanyl)ferrocene (**5**) affords the expected $[(\text{Au}-\text{C}\equiv\text{C}-\text{Fc})_2(\mu\text{-5})]$ (**6**), which does not exhibit aurophilic interactions.

Introduction

Gold(I) acetylides are oligomeric or polymeric compounds. Structural studies have been hampered by their insoluble nature.¹ Their reaction with suitable ligands L affords monomeric, and usually nicely soluble, complexes of the type $[\text{Au}(\text{C}\equiv\text{CR})\text{L}]$, especially with $\text{L} = \text{PR}'_3$, $\text{P}(\text{OR}')_3$, and $\text{R}'\text{NC}$.² Despite the rapid development of organogold chemistry during the past two decades,³ gold(I) acetylides have not yet found applications in organic synthesis. This is in contrast to the closely related silver(I) acetylides, whose synthetic utility is well documented.⁴ It has been only very recently that the first examples of C–C coupling reactions utilizing gold(I) acetylides were described. Bruce et al. used monomeric complexes of the type $[\text{Au}(\text{C}\equiv\text{CR})(\text{PR}_3)]$ in $\text{Cu}^{\text{I}}/\text{Pd}^0$ -catalyzed reactions with C–X units, which afforded the structure element C–C \equiv CR by elimination of $[\text{AuX}(\text{PR}_3)]$.⁵

Among the complexes of the type $[\text{Au}(\text{C}\equiv\text{CR})\text{L}]$, rigid-rod-like species that contain an isocyanide ligand $\text{R}'\text{NC}$ have received particular attention. This is due, inter alia, to a wide range of interesting properties of this class of compounds,

relevant to applications in the field of materials science. For example, the group of Puddephatt has tested the potential of such complexes for the chemical vapor deposition of gold.⁶ They have also pioneered the study of rigid-rod polymers of the type $[\text{Au}(\mu\text{-CN}-\text{C}_6\text{R}_4-\text{C}\equiv\text{C})]_n$ based on bridging (isocyanatoaryl)acetylides.⁷ The presence of aurophilic interactions⁸ in these materials is indicated by their solid-state luminescence properties.⁹ Aurophilic interactions also govern the photophysical behavior of monomeric complexes of the type $[\text{Au}(\text{C}\equiv\text{CR})(\text{CNR}')]_n$ in the solid state.¹⁰ As another aspect of the optical properties of such rigid-rod-like species, their cubic hyperpolarizabilities have been probed.¹¹ Finally, mesogenic behavior has been observed for such compounds.¹² The formation of mesophases has been attributed in part to aurophilic interactions in these as well as in closely related complexes.¹³

The aurophilic aggregation usually observed in the solid state for linear dicoordinate gold(I) complexes can give rise to three principal structural motifs, viz., a parallel, an antiparallel, and

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a crossed arrangement of neighboring molecules. A recent CSD analysis¹⁴ confirmed the result of an earlier study¹⁵ that $\text{Au}\cdots\text{Au}$ distances are on average shortest for the crossed arrangement. This is perfectly plausible, since at a given $\text{Au}\cdots\text{Au}$ distance steric repulsions between the ligands of neighboring molecules will be least for an essentially staggered orientation, which corresponds to a crossed arrangement with a torsion angle of ca. 90° . It is also plausible that for “asymmetric” (heteroleptic) species $[\text{AuX}(\text{L})]$ a preference exists for the antiparallel over the parallel arrangement on steric as well as on electrostatic grounds. In the case of gold(I) isocyanide complexes, only three examples are known that exhibit a parallel arrangement of neighboring molecules (albeit in combination with the antiparallel motif), viz., the cyano complexes $[\text{Au}(\text{CN})(\text{CNR}')] (\text{R}' = \text{Me}, i\text{-Pr}, n\text{-Bu})$.¹⁶ In view of the isoelectronic nature of cyanide and acetylide ligands, these species are closely related to the acetylide complexes of the type $[\text{Au}(\text{C}\equiv\text{CR})(\text{R}'\text{NC})]$, which are the focus of our present study, where we have used the bidentate organometallic isocyanide 1,1'-diisocyanoferrrocene (**1**)¹⁷ for reactions with a range of gold acetylides. A selected aspect of the present study has already been briefly communicated.¹⁸ We note that the number of oligodentate isocyanides has remained small in comparison to other important ligand families.¹⁹ It is also essential to note that the distance between the two Cp decks of ferrocene is 3.32 Å, which is at the low end of the range typically observed for $\text{Au}\cdots\text{Au}$ distances in gold(I) isocyanide complexes.²⁰ In a preliminary investigation of the coordination chemistry of **1** we have already prepared the dinuclear gold complex $[(\text{AuCl})_2(\mu\text{-1})]$, which exhibits an eclipsed diaura-[6]ferrocenophane-type structure with an intramolecular $\text{Au}\cdots\text{Au}$ distance of ca. 3.34 Å.²¹ The molecules form one-dimensional chains in an antiparallel zipper-like arrangement through intermolecular aurophilic interactions with $\text{Au}\cdots\text{Au}$ distances of 3.35 and 3.48 Å. This structure is related to that of the cyano complexes $[\text{Au}(\text{CN})(\text{CNR}')]$ mentioned above, since a combination of the parallel with the antiparallel arrangement of the rod-like $[\text{AuX}(\text{L})]$ units occurs.

Results and Discussion

The gold(I) acetylides used in this study are $[\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R})]_n$ (**2a** $\text{R} = \text{CF}_3$, **2b** $\text{R} = \text{H}$, **2c** $\text{R} = \text{OMe}$, **2d** $\text{R} =$

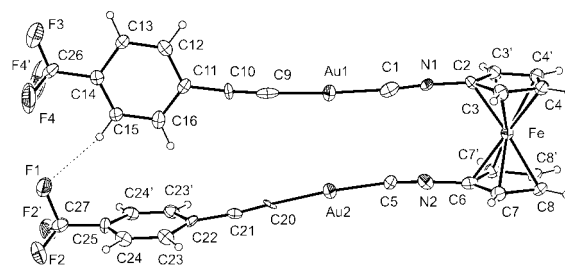


Figure 1. Molecular structure of $[(\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{CF}_3))_2(\mu\text{-1})]$ (**3a**) in the crystal.

NMe_2) and $[\text{Au}(\text{C}\equiv\text{C}-\text{Fc})]_n$ (**2e**, Fc = ferrocenyl¹⁸). These compounds were prepared by an established route from $[\text{AuCl}(\text{SMe}_2)]$ and the respective acetylene derivative in the presence of triethylamine at room temperature.²³ All compounds were isolated from the reaction mixture as insoluble solids and characterized by elemental analyses and IR spectra, where their characteristic $\nu(\text{C}\equiv\text{C})$ vibrational band was observed between ca. 1980 and 2000 cm^{-1} . The reactions worked best for acetylides bearing electron-donating substituents, while with $\text{HC}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{CF}_3$, which contains the strongly electron-withdrawing trifluoromethyl group, the reaction was more sluggish and the yield was only moderate. Furthermore, the product (**2a**) proved to be thermally unstable at room temperature and slowly afforded a violet intractable material.

The reactions of 1,1'-diisocyanoferrrocene (**1**) with $[\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R})]_n$ (**2**, 2/ n equiv) were performed in dichloromethane at room temperature. They proceeded smoothly over the course of several hours, affording the expected $[(\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R}))_2(\mu\text{-1})]$ (**3**) in the case of **2a–d**. The reaction with **2e** turned out to be a special case and will be discussed later. **2a–d** were isolated as yellow, air-stable, microcrystalline solids. Their solubility in common organic solvents proved to be generally poor. Dichloromethane turned out to be the best choice. The solubility in this solvent is highest for the CF_3 bearing compound **3a** and lowest for the NMe_2 bearing analogue **3d**. ^1H NMR spectra could be recorded for all four compounds using CD_2Cl_2 . However, attempts to recrystallize **3a–d** in order to obtain single crystals suitable for an X-ray diffraction study failed in the case of the least soluble compound, **3d**. The $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{N}\equiv\text{C})$ vibrational bands were observed in the IR spectra of **3a–d** at ca. 2115 and 2200 cm^{-1} , respectively. This compares well with values reported for closely related compounds such as $[\text{Au}(\text{C}\equiv\text{CPh})(\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6})]$ [$\nu(\text{C}\equiv\text{C})$ 2119 cm^{-1} , $\nu(\text{N}\equiv\text{C})$ 2211 cm^{-1}]²⁴ and corresponds to a $\nu(\text{N}\equiv\text{C})$ band shift of ca. 100 cm^{-1} with respect to uncoordinated **1** and an even slightly larger $\nu(\text{C}\equiv\text{C})$ band shift with respect to the respective gold(I) acetylide **2**, which is in accord with previous observations.^{2a} These substantial band shifts to higher energy indicate that, in line with the classic study by Cotton and Zingales,²⁵ the isocyanide acts as a strongly σ -donating ligand, whose coordination to $\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R})$ reduces the degree of metal–carbon π -bonding in this moiety.

The crystal structures of **3a–c** were determined by X-ray diffraction. The molecular structures are shown in Figures 1–3.

In each case the quality of the crystal structure determination was affected by the small size of the crystal. It was further compromised by the presence of disordered solvent of crystal-

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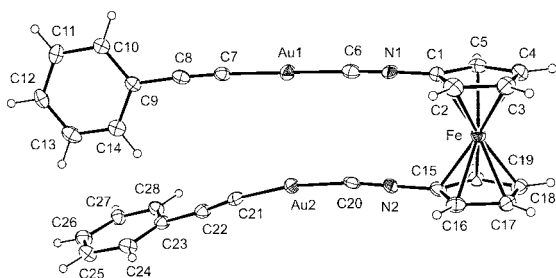


Figure 2. Molecular structure of $[\{\text{Au}(\text{C}\equiv\text{C-Ph})\}_2(\mu\text{-1})]$ (**3b**) in the crystal.

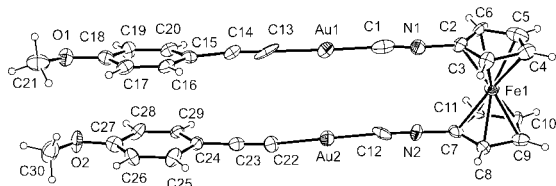


Figure 3. Molecular structure of $[\{\text{Au}(\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{OMe})\}_2(\mu\text{-1})]$ (**3c**) in the crystal.

lization in the case of **3c**. Consequently, a meaningful discussion of bond parameters is possible for the heavy atoms only. The $\text{C-N}\equiv\text{C-Au-C}\equiv\text{C-C}$ chains are nearly linear for all three compounds with bond angles between ca. 171° and 178° , as expected for such rigid-rod-type molecular units. A prominent feature of all three molecular structures is the fact that the molecules adopt an eclipsed conformation with an intramolecular aurophilic contact. This $\text{Au}\cdots\text{Au}$ distance apparently depends on the electronic properties of the acetylide ligand $\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{R}$. It is $3.3011(11)$ Å for **3a** ($\text{R} = \text{CF}_3$), $3.3617(5)$ Å for **3b** ($\text{R} = \text{H}$), and $3.6219(12)$ Å for **3c** ($\text{R} = \text{OMe}$). Correlations between $\text{Au}\cdots\text{Au}$ distances and the “hard” or “soft” character of anionic ligands X in linear dicoordinate gold(I) complexes $[\text{AuX}(\text{L})]$ have been found in previous theoretical and experimental studies. For example, Pyykkö et al. predicted an increase in the strength of the aurophilic interaction for staggered dimers of the phosphane complexes $[\text{AuX}(\text{PH}_3)]$ in the series of halogeno ligands with $\text{F} < \text{Cl} < \text{Br} < \text{I}$.²⁶ This trend was verified by X-ray crystallography for $[\text{AuX}(\text{PPhMe}_2)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) by Balch and co-workers.²⁷ In the case of isocyanide complexes $[\text{AuX}(\text{CNR})]$, an opposite trend was found.²⁸ A theoretical study performed for dimers of $[\text{AuX}(\text{CNMe})]$ ($\text{X} = \text{Cl}, \text{I}$) revealed that in this case the antiparallel, instead of the staggered, arrangement of monomeric units is preferred.²⁰ The major attractive contribution between monomeric units was found to originate from the dipole–dipole interaction. Consequently, the $\text{Au}\cdots\text{Au}$ distance is indicative of the presence, but not commensurate with the strength, of aurophilic interactions. In view of these results, the eclipsed molecular structures of **3a–c**, which correspond to the parallel arrangement of $[\text{AuX}(\text{CNR})]$ units, might appear extraordinary. However, closer inspection of the crystal packing reveals an antiparallel orientation of neighboring molecules (Figures 4–6).

This combination of parallel and antiparallel alignments is reminiscent of the structural motifs observed for the chloro complex $[(\text{AuCl})_2(\mu\text{-1})]$ and the cyano complexes $[\text{Au}(\text{C-}$

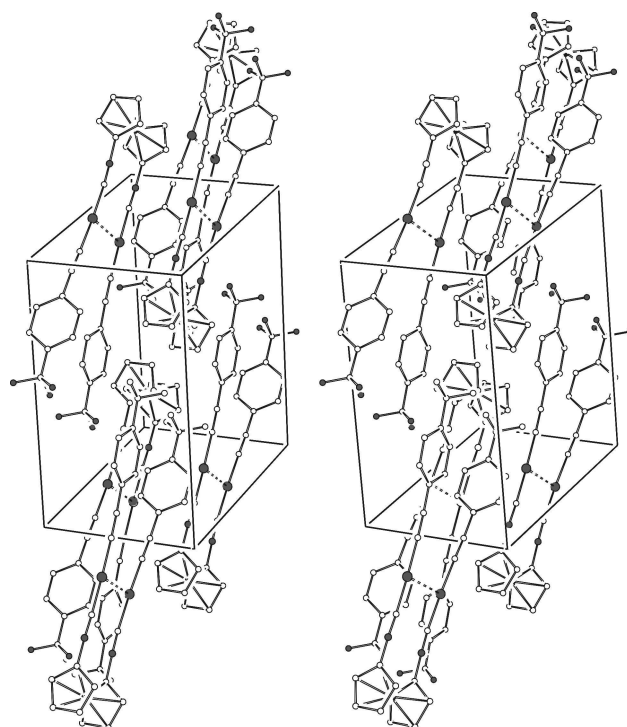


Figure 4. Stereographic representation of the crystal packing of $[\{\text{Au}(\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{CF}_3)\}_2(\mu\text{-1})]$ (**3a**). $\text{Au}\cdots\text{Au}$ distances < 4 Å are indicated by dotted lines.

$\text{N}(\text{CNR}')$ ($\text{R}' = \text{Me}, i\text{-Pr}, n\text{-Bu}$) (vide supra). In the case of **3c**, a one-dimensional chain of antiparallel molecules is formed, whose intermolecular $\text{Au}\cdots\text{Au}$ distances of $3.5576(15)$ and $3.5921(16)$ Å are very similar to the intramolecular distance of $3.6219(12)$ Å. We have previously observed a similarly nice balance between intra- and intermolecular aurophilicity in the case of $[(\text{AuCl})_2(\mu\text{-1})]$, which is aggregated as one-dimensional chains, too.²¹ The insoluble nature of $[(\text{AuCl})_2(\mu\text{-1})]$ is reminiscent of the very low solubility of **3c** and the even poorer solubility of the NMe_2 -substituted analogue **3d**. We therefore assume that **3d** probably also forms such one-dimensional chains in the crystal. In the case of **3b**, the molecules are aggregated as antiparallel dimers with intermolecular $\text{Au}\cdots\text{Au}$ distances of $3.9509(5)$ Å. In the case of **3a**, which exhibits the shortest intramolecular $\text{Au}\cdots\text{Au}$ contact in this series, no such intermolecular contacts are present. In addition to the short intramolecular $\text{Au}\cdots\text{Au}$ contact, an intramolecular $\text{C-F}\cdots\text{H-C}$ interaction is observed for this compound (indicated by a dotted line in Figure 1). The FHC angle of ca. 168.8° and the $\text{F}\cdots\text{C}$ and $\text{F}\cdots\text{H}$ distances of ca. 3.47 and 2.54 Å, respectively, are compatible with a weak hydrogen bond.²⁹ Although their existence, nature, and supramolecular relevance still is a contentious issue, weak intramolecular $\text{C-F}\cdots\text{H-C}$ hydrogen bonds have recently been probed and authenticated by NMR spectroscopic methods in solution and by neutron diffraction in the solid state.³⁰

As already mentioned above, the reaction of $[\text{Au}(\text{C}\equiv\text{C-Fc})]_n$ (**2e**) deserves special attention.¹⁸ In view of the results just described, we anticipated the formation of $[\text{Fe}(\text{C}_5\text{H}_4(\text{NC-Au-C}\equiv\text{C-Fc}))_2]$ (**3e**) in the reaction of **1** with $[\text{Au}(\text{C}\equiv\text{C-Fc})]_n$ ($2/n$

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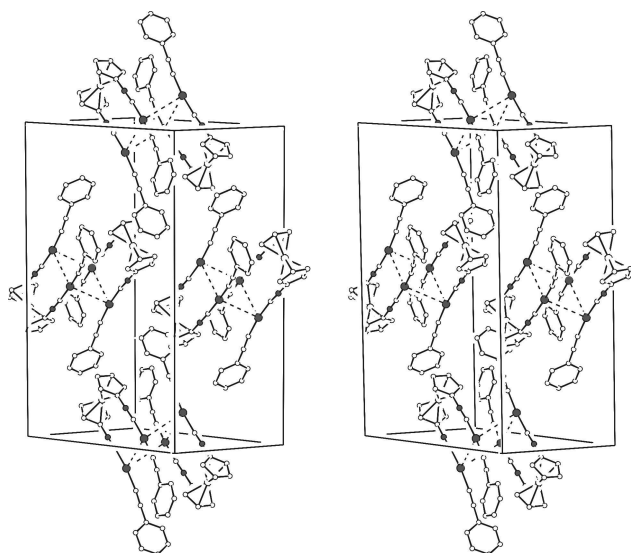
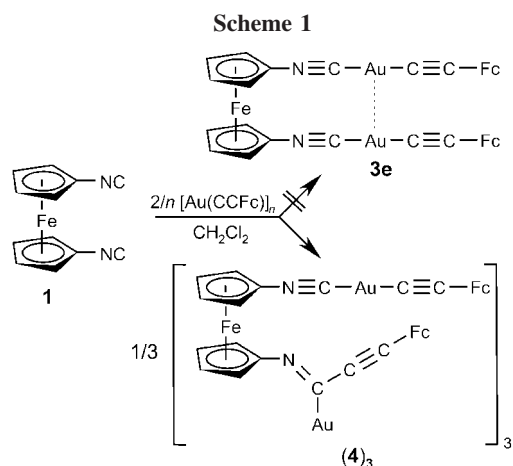


Figure 5. Stereographic representation of the crystal packing of $[\{\text{Au}(\text{C}\equiv\text{C-Ph})\}_2(\mu\text{-1})]$ (**3b**). $\text{Au}\cdots\text{Au}$ distances < 4 Å are indicated by dotted lines.



equiv). Furthermore, we expected that the product would exhibit an eclipsed molecular conformation similar to that found for **3a–c**, so that an efficient communication between the two redox-active terminal ferrocenyl units seemed feasible and might have been probed by cyclic voltammetry. Microanalytical data of the product that we obtained in good yield from this reaction agreed well with the composition of **3e**. However, its ^1H NMR spectrum was incompatible with **3e**, since it exhibited too many signals for a species of such symmetry. Characterization of the product was hampered by its poor solubility in common organic solvents. Again, dichloromethane proved to be the best solvent. We eventually succeeded in obtaining single crystals suitable for an X-ray structure analysis, which proved that the product is not **3e**, but rather the hexanuclear gold cluster $[(\text{Fc-C}\equiv\text{C-Au-C}\equiv\text{N-C}_5\text{H}_4)\text{Fe}\{\text{C}_5\text{H}_4\text{-N}=\text{C}(\text{Au-C}\equiv\text{C-Fc})\}]_3$, which is composed of three subunits **4** (Figure 7, Scheme 1).

IR and NMR spectroscopic data are fully in accord with this result. In particular, due to the presence of the σ,μ_2 -iminoacyl group a $\nu(\text{N}=\text{C})$ vibrational band is observed at 1491 cm^{-1} in addition to the expected $\nu(\text{N}\equiv\text{C})$ and $\nu(\text{C}\equiv\text{C})$ bands at 2201 and 2155 cm^{-1} , respectively. For comparison, the $\nu(\text{C}=\text{N})$ band of $\text{Ph-C}\equiv\text{C-C}(\text{=NPh})\text{Ph}$ is located at 1560 cm^{-1} ,³¹ while it

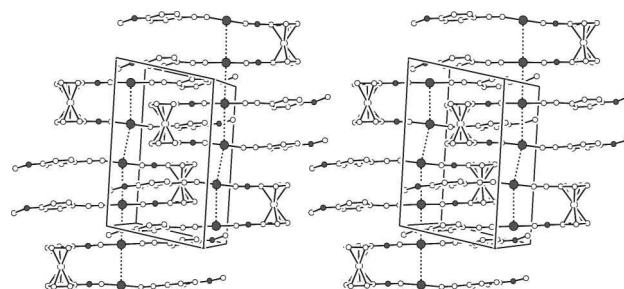


Figure 6. Stereographic representation of the crystal packing of $[\{\text{Au}(\text{C}\equiv\text{C-}p\text{-C}_6\text{H}_4\text{OMe})\}_2(\mu\text{-1})]$ (**3c**). $\text{Au}\cdots\text{Au}$ distances < 4 Å are indicated by dotted lines.

occurs at 1530 cm^{-1} in the case of the mononuclear iminoacyl complex $[\text{Pd}\{\text{C}(\text{C}\equiv\text{C-Ph})(\text{=NPh})\}\text{Cl}(\text{PEt}_3)_2]$.³² It is well documented for binuclear complexes that a σ,μ_2 -iminoacyl coordination leads to a notable energy decrease of this band of ca. 60 cm^{-1} with respect to the parent imine.³³ Due to the poor quality of the crystal, the data/parameter ratio of the X-ray structure analysis is rather low. Consequently, a detailed discussion of bond parameters is meaningful only for the heavy atoms.

The gold cluster exhibits $\text{Au}\cdots\text{Au}$ distances that are typical for auriphilic interactions, ranging from $3.165(2)$ to $3.391(2)$ Å. The cluster core is a triangle of gold atoms whose three sides are each bridged by the $\text{N}=\text{C}$ unit of a single iminoacyl ligand. Such σ,μ_2 -bridging iminoacyl ligands $\text{RN}=\text{CR}'$ are quite common. In fact, even several clusters are known with a side of an M_3 triangle bridged by a σ,μ_2 -iminoacyl ligand, especially in the chemistry of osmium.³⁴ In contrast, clusters with two bridged triangular sides of this type are rare.³⁵ (**4**)₃ is unique since bridging of all three sides of an M_3 triangle with σ,μ_2 - $\text{RN}=\text{CR}'$ ligands has not been described to date. We note, however, that the general structural motif is not unfamiliar in the chemistry of gold. Several triply bridged triangular clusters of the type $[\text{Au}_3\{\sigma,\mu_2\text{-RN}=\text{C}(\text{OR}')\}]_3$ have been reported that contain carbenate ligands $\text{RN}=\text{C}(\text{OR}')$, which are akin to iminoacyl ligands $\text{RN}=\text{CR}'$. These gold clusters were obtained from the reaction of $[\text{AuCl}(\text{L})]$ ($\text{L} = \text{SMe}_2, \text{PPh}_3$) with isocyanides RNC in a suitable alcohol $\text{R}'\text{OH}$ in the presence of KOH .³⁶ They usually aggregate in the solid state due to auriphilic interactions.³⁷ For example, $[\text{Au}_3\{\sigma,\mu_2\text{-}p\text{-TolN}=\text{C}(\text{OEt})\}]_3$ forms dimeric units in the crystal through two intermolecular $\text{Au}\cdots\text{Au}$ contacts.³⁸ A similar motif is observed for (**4**)₃, where two atoms of the Au_3 triangle are each connected with a further gold atom, in this case, however, intramolecularly. This is caused by the Au-Au contact present within two of the three subunits of (**4**)₃. These Au-Au interactions altogether result in an unprecedented chain of five gold atoms with two neighboring atoms being bridged by a sixth one.

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Table 1. Crystal Data and Structure Refinement for 3a, 3b, 3c, and 6

	3a	3b	3c	6
emp. formula	C ₃₀ H ₁₆ Au ₂ F ₆ FeN ₂	C ₂₈ H ₁₈ Au ₂ FeN ₂	C _{30.50} H ₂₃ Au ₂ ClFeN ₂ O ₂	C ₅₈ H ₄₆ Au ₂ Fe ₃ P ₂
fw	968.23	832.23	934.74	1366.37
temp/K	143(2)	173(2)	173(2)	143(2)
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>Pbca</i>
lattice param	<i>a</i> = 11.4667(13) <i>b</i> = 8.5646(8) <i>c</i> = 14.1478(16) β = 98.271(9)	<i>a</i> = 9.0781(7) <i>b</i> = 24.9236(18) <i>c</i> = 13.4933(11) β = 128.191(5)	<i>a</i> = 8.4412(12) <i>b</i> = 11.8387(18) <i>c</i> = 14.197(2) α = 87.290(12) β = 81.080(11) γ = 84.569(12)	<i>a</i> = 14.6431(8) <i>b</i> = 11.7790(5) <i>c</i> = 27.4725(15)
length/Å				
angle/deg				
cell volume/Å ³	1375.0(3)	2399.5(4)	1394.6(4)	4738.5(4)
<i>Z</i>	2	4	2	4
<i>d</i> _{calc} /g cm ⁻³	2.339	2.304	2.226	1.915
μ /mm ⁻¹	11.228	12.813	11.134	7.174
<i>F</i> (000)	896	1536	874	2640
θ range/deg	1.45 to 25.00	1.63 to 25.00	1.45 to 25.23	1.48 to 25.00
index ranges	-13 \rightarrow <i>h</i> \rightarrow 13 -10 \rightarrow <i>k</i> \rightarrow 10 -16 \rightarrow <i>l</i> \rightarrow 16	-10 \rightarrow <i>h</i> \rightarrow 10 -29 \rightarrow <i>k</i> \rightarrow 29 -15 \rightarrow <i>l</i> \rightarrow 16	-9 \rightarrow <i>h</i> \rightarrow 10 -14 \rightarrow <i>k</i> \rightarrow 14 -17 \rightarrow <i>l</i> \rightarrow 16	-9 \rightarrow <i>h</i> \rightarrow 17 -14 \rightarrow <i>k</i> \rightarrow 12 -32 \rightarrow <i>l</i> \rightarrow 32
reflins collected	8971	14 072	9181	15 824
indep reflins	2601 [<i>R</i> _{int} = 0.1376]	4226 [<i>R</i> _{int} = 0.1336]	4698 [<i>R</i> _{int} = 0.0995]	3995 [<i>R</i> _{int} = 0.1162]
reflins obsd	1652	3584	2523	2466
<i>T</i> _{min} / <i>T</i> _{max}	0.08/0.23	0.02/0.75	0.07/0.73	0.28/0.82
data/restraints/params	2601/0/223	4226/0/298	4698/1/349	3995/0/295
GOF on <i>F</i> ²	0.878	1.004	0.820	0.879
final <i>R</i> indices	<i>R</i> ₁ = 0.0455	<i>R</i> ₁ = 0.0457	<i>R</i> ₁ = 0.0614	<i>R</i> ₁ = 0.0430
[<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> ₂ = 0.0819	<i>wR</i> ₂ = 0.1044	<i>wR</i> ₂ = 0.1363	<i>wR</i> ₂ = 0.0808
<i>R</i> indices	<i>R</i> ₁ = 0.0829	<i>R</i> ₁ = 0.0539	<i>R</i> ₁ = 0.1034	<i>R</i> ₁ = 0.0862
(all data)	<i>wR</i> ₂ = 0.0910	<i>wR</i> ₂ = 0.1073	<i>wR</i> ₂ = 0.1478	<i>wR</i> ₂ = 0.0900
largest diff peak/hole/e Å ⁻³	1.758/-1.639	1.853/-2.167	1.679/-2.375	1.579/-0.702

Finally, we focus our attention on the component of **4** that is based on 1,1'-diisocyanoferrrocene (**1**). This unit was formed in a peculiar way. One of the two isocyano groups shows the usual, and expected, coordination of the gold acetylide unit Au(C \equiv C-Fc). In contrast, the other one has undergone a 1,1-insertion reaction with the Au-C bond of the gold acetylide, thus forming an iminoacyl group. 1,1-Insertion or α -addition reactions are common in the chemistry of isocyanides and can occur with a wide range of metal-carbon bonds. For example, metalated aldimines are formed in their reaction with organolithium compounds and Grignard reagents, respectively.³⁹ Analogous reactions are observed with M-C bonds of transition metal complexes, which often lead to the formation of η^2 -iminoacyl complexes, especially in the case of early transition metals.⁴⁰ We note that insertion reactions of isocyanides with transition metal acetylide complexes are currently attracting particular attention. This is primarily due to two reasons. First, multiple and successive insertions have been observed with heterodinuclear complexes of the type [Cl(PR₃)₂Pd-C \equiv C-Pt(PR₃)₂Cl], and even the living polymerization of aryl isocyanides has been described with this system.⁴¹ Second, examples have been reported for the catalytic coupling of isocyanides with terminal alkynes.⁴² These reactions afford 1-aza-1,3-enines, which are useful synthons in organic chemistry.⁴³ Surprisingly, despite the

recent dynamic progress in the chemistry of gold,³ insertion reactions of isocyanides with Au-C bonds are practically unknown. Only two examples have been described to date,⁴⁴ and only one of these involves a gold(I) species,^{44b} viz., the 1,1-insertion of 2,6-dimethylphenylisocyanide into the Au-C bond of the gold(I) enolate [Au{CH₂C(O)Ph}(PPh₃)].

The 1,1-insertion of an isocyanide into an Au-C bond is very unusual as such. It is even more unusual that in the present case this reaction occurs in conjunction with a second, different, reaction. This observation requires some reflection. It is common knowledge that two equivalent groups in a molecule often do not react independently from one another. The fact that the reaction of the first group influences that of an equivalent second group is known as induced reactivity asymmetry.⁴⁵ This effect can be thermodynamic (different equilibrium constants) and/or kinetic (different reaction rates) in origin. Simple examples reflecting a thermodynamic influence are polyprotic acids such as H₃PO₄, where the consecutive decrease in acidity (*pK*_{a1} = 2.16, *pK*_{a2} = 7.21, *pK*_{a3} = 12.32) is mainly due to electrostatic reasons.⁴⁶ Essentially the same holds true for the different redox potentials observed for the two formally identical subunits of 1,1'-biferrocene (Fc-Fc) (*E*⁰₁ = +0.31 V, *E*⁰₂ = +0.64 V vs SCE).⁴⁷ With respect to kinetic effects, a common observation is that the reaction rate slows down in consecutive

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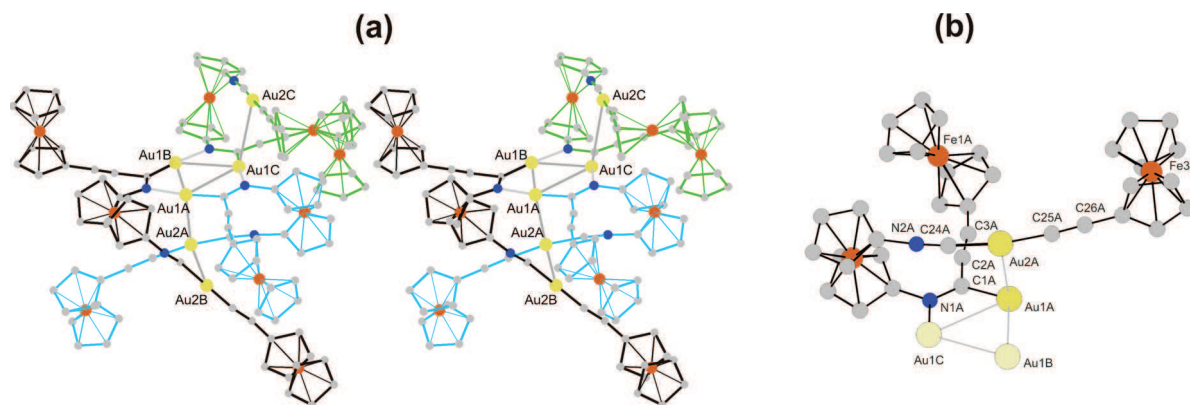


Figure 7. (a) Molecular structure of $(\mathbf{4})_3$ in the crystal (stereographic representation with subunits marked in different colors). Interatomic distances < 4.0 Å in the Au_6 cluster: Au1A–Au1B 3.356(2), Au1A–Au1C 3.278(2), Au1A–Au2A 3.352(2), Au2A–Au2B 3.165(2), Au1B–Au1C 3.284(2), Au1C–Au2C 3.391(2) Å. (b) Molecular structure of the subunit colored blue in (a). Selected bond lengths (Å): C1A–N1A 1.31(3), C1A–C2A 1.40(4), C1A–Au1A 1.98(3), C2A–C3A 1.22(4), C24A–N2A 1.15(3), C24A–Au2A 1.90(3), C25A–C26A 1.25(5), C25A–Au2A 1.95(3), N1A–Au1C 1.99(2).

reactions of equivalent groups. Due to their relevance to polymer chemistry, the kinetics of consecutive reactions of difunctional substrates has been treated theoretically, for both interacting and noninteracting functional groups already half a century ago.⁴⁸ A simple and particularly well-studied example in this context is the reaction of aromatic diisocyanates with alcohols.⁴⁹

Although the induced reactivity asymmetry is a commonly known and widely studied phenomenon in chemistry, the variant we have observed in our work is extraordinary, since the consecutive reactions are not the same. To the best of our knowledge, it has never been observed before that two chemically equivalent groups in a molecule undergo a different specific reaction with the same reagent. This “schizoid” reactivity observed for **1** in its reaction with **2e** apparently constitutes a novel phenomenon in chemistry⁵⁰ and will demand further systematic investigations in the near future. Unfortunately, attempts to study the course of the reaction by ^1H NMR spectroscopy have not been successful so far because of the essentially insoluble nature of both the gold acetylide starting material and the gold cluster product.

While the reaction of **2e** with 1,1'-diisocyanoferrrocene (**1**) proved to be rather peculiar, its reaction with 1,1'-bis(diphenylphosphanyl)ferrocene (**5**, dppf) gave the expected result, viz., the complex $[(\text{Au}-\text{C}\equiv\text{C}-\text{Fc})_2(\mu\text{-}\mathbf{5})]$ (**6**), which was isolated in high yield as a yellow, microcrystalline solid. The $\Delta(\text{C}\equiv\text{C})$ vibrational band is observed at 2110 cm^{-1} in the IR spectrum, which is very similar to the values of 2105 and 2115 cm^{-1} reported for the closely related $[(\text{Au}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)\text{Me})_2(\mu\text{-}\mathbf{5})]$ ⁵¹ and $[(\text{Au}-\text{C}\equiv\text{C}-\text{Ph})_2(\mu\text{-}\mathbf{5})]$,⁵² respectively. It is also in line with the value of ca. 2115 cm^{-1} found in the case of **3a–d**. The $^{31}\text{P}\{^1\text{H}\}$ NMR signal is observed as a singlet at 24.8 ppm, which is very similar to the value of 27.4 ppm reported for the chloro analogue $[(\text{AuCl})_2(\mu\text{-}\mathbf{5})]$.⁵³ A single-crystal X-ray structure determination was performed for $[(\text{Au}-\text{C}\equiv\text{C}-\text{Fc})_2(\mu\text{-}\mathbf{5})]$ (Figure 8).

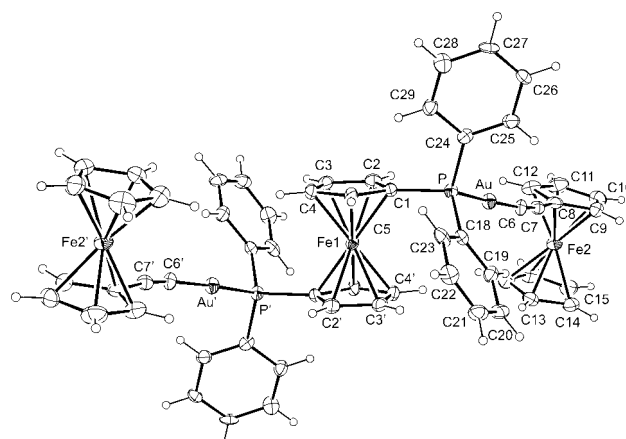


Figure 8. Molecular structure of $[(\text{Au}-\text{C}\equiv\text{C}-\text{Fc})_2(\mu\text{-}\mathbf{5})]$ (**6**) in the crystal.

The molecule exhibits crystallographically imposed inversion symmetry. The P–Au–C≡C–C chain is essentially linear, with bond angles between ca. 173° and 178° . The Au–P bond length of 2.293(2) Å is similar to the values found for closely related compounds such as $[(\text{Au}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)\text{Me})_2(\mu\text{-}\mathbf{5})]$ [2.279(2) Å],⁵¹ $[(\text{Au}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)\text{O})_2-p\text{-C}_6\text{H}_4](\mu\text{-}\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)]$ [2.261(7) and 2.278(7) Å],⁵⁴ and $[(\text{Ph}_3\text{P})_2\text{Au}]_2(\mu\text{-}1,12\text{-}(\text{C}\equiv\text{C})_2\text{-}1,12\text{-C}_2\text{B}_{10}\text{H}_{10})]$ [2.2743(14) Å].⁵⁵ We note that these Au–P bond length are marginally longer than those of the chloro complex $[(\text{AuCl})_2(\mu\text{-}\mathbf{5})]$ [2.239(3) Å],⁵³ which reflects the comparatively higher *trans* influence of an alkynyl ligand as opposed to a chloro ligand. The Au–C bond length of 1.998(10) Å found for $[(\text{Au}-\text{C}\equiv\text{C}-\text{Fc})_2(\mu\text{-}\mathbf{5})]$ compares well with values observed for similar compounds such as the three dinuclear gold(I) acetylide complexes just mentioned; the corresponding values are 2.005(10) Å for $[(\text{Au}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)\text{Me})_2(\mu\text{-}\mathbf{5})]$, 2.03(2) and 2.05(3) Å for $[(\text{Au}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)\text{O})_2-p\text{-C}_6\text{H}_4](\mu\text{-}\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)]$, and 2.007(5) Å for $[(\text{Ph}_3\text{P})_2\text{Au}]_2(\mu\text{-}1,12\text{-}(\text{C}\equiv\text{C})_2\text{-}1,12\text{-C}_2\text{B}_{10}\text{H}_{10})]$.

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1,12-C₂B₁₀H₁₀]]. The structure of $[\{\text{Au}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)\text{Me}\}_2(\mu-5)]$, which seems to be the closest structurally characterized relative of $[(\text{Au}-\text{C}\equiv\text{C}-\text{Fc})_2(\mu-5)]$, also exhibits centrosymmetric molecules. Auophilic interactions are absent in both cases, which is probably due to the steric bulk of the acetylide ligands. In the structure of $[(\text{AuCl})_2(\mu-5)]$, which contains the much less bulky chloro ligand, two crystallographically independent molecules are present. One of them exhibits crystallographically imposed inversion symmetry with exactly staggered cyclopentadienyl rings, too. In contrast to the two acetylide complexes $[(\text{Au}-\text{C}\equiv\text{C}-\text{Fc})_2(\mu-5)]$ and $[\{\text{Au}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)\text{Me}\}_2(\mu-5)]$, particularly short intermolecular Au...Au distances of 3.083(1) Å are observed in this case.⁵³ With the di(acetylide) ligand (C≡C-CH₂O-*p*-C₆H₄)₂SO₂, which is unbranched at the α-carbon atom and therefore “leaner” than C≡C-C(CH₃)Me and C≡C-Fc, auophilic aggregation to dimeric units has been observed.⁵⁶ However, the Au...Au distance of 3.1488(7) Å is still longer than that of the chloro complex $[(\text{AuCl})_2(\mu-5)]$.

Conclusion

The reaction of the gold(I) acetylides $[\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R})]_n$ (**2a** R = CF₃, **2b** R = H, **2c** R = OMe, **2d** R = NMe₂) with 1,1'-diisocyanoferrrocene (**1**) proceeds in an “orthodox” way, affording the respective dinuclear gold complexes $[\{\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R})\}_2(\mu-1)]$ (**3**). The molecules exhibit an eclipsed conformation with an intramolecular auophilic contact in conjunction with an antiparallel orientation of neighboring molecules in the crystal. The intramolecular Au...Au distance correlates with the electron-donating properties of the substituent R (CF₃ < H < OMe), while the corresponding intermolecular distances show the opposite trend. Curiously, the product of the reaction of **1** with $[\text{Au}(\text{C}\equiv\text{C}-\text{Fc})]_n$ (**2e**, Fc = ferrocenyl) is the hexanuclear gold cluster $[(\text{Fc}-\text{C}\equiv\text{C}-\text{Au}-\text{C}\equiv\text{N}-\text{C}_5\text{H}_4)\text{Fe}\{\text{C}_5\text{H}_4-\text{N}=\text{C}(\text{Au})-\text{C}\equiv\text{C}-\text{Fc}\}]_3$, whose formation is based on a different specific reaction of the two chemically equivalent functional groups of **1** with **2e**, viz., coordination and 1,1-insertion. This “unorthodox” behavior appears schizoid and constitutes a novel variant of induced reaction asymmetry. Systematic investigations, including quantum-chemical calculations, are currently underway to shed more light on this phenomenon.

Experimental Section

General Procedures. All reactions were performed in an inert atmosphere (dinitrogen) by using standard Schlenk techniques or a conventional glovebox. 1,1'-Diisocyanoferrrocene (**1**)^{17a} and $[\text{AuCl}(\text{SMe}_2)]$ ⁵⁷ were prepared according to published procedures. The gold(I) acetylides $[\text{Au}(\text{C}\equiv\text{C}-\text{Ph})]_n$ (**2b**)^{2a} and $[\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{OMe})]_n$ (**2c**)²² were prepared by slight variation of a published method,²³ which is detailed below for the new compounds **2a** and **2d**. Preparative details for $[\text{Au}(\text{C}\equiv\text{C}-\text{Fc})]_n$ (**2e**) and (**4**)₃ have already been communicated.¹⁸ Solvents and reagents were procured from standard commercial sources. NMR: Varian Unity INOVA 500

spectrometer operating at 500.13 MHz for ¹H. IR: BIO-RAD FTS-40A. Elemental analyses: microanalytical laboratory of the University of Kassel.

$[\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{CF}_3)]_n$ (**2a**). HC≡C-*p*-C₆H₄CF₃ (255 mg, 1.5 mmol) and NEt₃ (730 mg, 7.3 mmol) were added sequentially to a stirred solution of $[\text{AuCl}(\text{SMe}_2)]$ (442 mg, 1.5 mmol) in dichloromethane (20 mL) at 0 °C. The solution was stirred for 1 h. Cold methanol (20 mL) was added and the mixture was stirred at 0 °C for a further 2 h. The pale yellow precipitate was isolated by centrifugation and dried in vacuo at 0 °C. Yield: 210 mg (38%). Anal. Calcd for C₉H₄AuF₃ (366.1): C, 29.53; H, 1.10. Found: C, 29.31; H, 1.06. IR (cm⁻¹): ν(C≡C) 2003 (w).

$[\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{NMe}_2)]_n$ (**2d**). HC≡C-*p*-C₆H₄NMe₂ (218 mg, 1.5 mmol) and NEt₃ (300 mg, 3.0 mmol) were added sequentially to a stirred solution of $[\text{AuCl}(\text{SMe}_2)]$ (442 mg, 1.5 mmol) in dichloromethane (20 mL). After 30 min the yellow precipitate was filtered off, washed with methanol (5 mL) and diethyl ether (5 mL), and dried in vacuo. Yield: 470 mg (92%). Anal. Calcd for C₁₀H₁₀AuN (341.2): C, 35.21; H, 2.95; N, 4.11. Found: C, 35.28; H, 2.98; N, 3.92. IR (cm⁻¹): ν(C≡C) 1999 (w).

$[\{\text{Au}(\text{C}\equiv\text{C}-p\text{-C}_6\text{H}_4\text{R})\}_2(\mu-1)]$ (**3**). General procedure: A solution of **1** (50 mg, 0.21 mmol) in dichloromethane (10 mL) was added to a stirred suspension of the respective gold(I) acetylide (**2**) (0.42 mmol; **a** 155 mg, **b** 126 mg, **c** 140 mg, **d** 145 mg) in dichloromethane (50 mL). The mixture was stirred for 14 h. The product was isolated by cannula filtration, washed with methanol (10 mL) and diethyl ether (10 mL), and dried in vacuo.

3a. Yield: 115 mg (56%). IR (cm⁻¹): ν(N≡C) 2192 (s), ν(C≡C) 2115 (m). ¹H NMR (CD₂Cl₂): δ 7.32 (d, *J* = 8.0 Hz, 4 H, C₆H₄), 7.28 (d, *J* = 8.0 Hz, 4 H, C₆H₄), 4.93 (s, 4 H, C₅H₄), 4.49 (s, 4 H, C₅H₄). Anal. Calcd for C₃₀H₁₆Au₂F₆FeN₂·0.5CH₂Cl₂ (1010.7): C, 36.25; H, 1.70; N 2.77. Found: C, 35.78; H, 1.54; N 2.48.

3b. Yield: 71 mg (40%). IR (cm⁻¹): ν(N≡C) 2203 (s), ν(C≡C) 2121 (m). ¹H NMR (CD₂Cl₂): δ 7.30 (s, 2 H, Ph), 7.13 (s, 8 H, Ph), 4.94 (s, 4 H, C₅H₄), 4.47 (s, 4 H, C₅H₄). Anal. Calcd for C₂₈H₁₈Au₂FeN₂·0.5CH₂Cl₂ (874.7): C, 39.13; H, 2.19; N, 3.20. Found: C, 39.27; H, 2.81; N, 3.08.

3c. Yield: 117 mg (61%). IR (cm⁻¹): ν(N≡C) 2204 (s), ν(C≡C) 2123 (w). ¹H NMR (CD₂Cl₂): δ 7.24 (d, *J* = 9.0 Hz, 4 H, C₆H₄), 6.65 (d, *J* = 9.0 Hz, 4 H, C₆H₄), 4.93 (s, 4 H, C₅H₄), 4.47 (s, 4 H, C₅H₄), 3.72 (s, 6 H, Me). Anal. Calcd for C₃₀H₂₂Au₂FeN₂O₂·0.5CH₂Cl₂ (934.8): C, 39.19; H, 2.48; N, 3.00. Found: C, 39.26; H, 2.37; N, 2.92.

3d. Yield: 129 mg (66%). IR (cm⁻¹): ν(N≡C) 2192 (s), ν(C≡C) 2115 (m). ¹H NMR (CD₂Cl₂): δ 7.19 (d, *J* = 9.0 Hz, 4 H, C₆H₄), 6.47 (d, *J* = 9.0 Hz, 4 H, C₆H₄), 4.92 (s, 4H, C₅H₄), 4.47 (s, 4 H, C₅H₄), 2.89 (s, 12 H, Me). Anal. Calcd for C₃₂H₂₈Au₂FeN₄·0.5CH₂Cl₂ (960.9): C, 40.62; H, 3.04; N, 5.83. Found: C, 40.58; H, 3.03; N, 5.89.

$[(\text{Au}-\text{C}\equiv\text{C}-\text{Fc})_2(\mu-5)]$ (**6**). Dppf (**5**) (110 mg, 0.2 mmol) was added to a stirred suspension of **2e** (160 mg, 0.4 mmol) in dichloromethane (50 mL). The mixture was stirred for 3 h. The slightly turbid solution was filtered to remove traces of insoluble material. The volume of the filtrate was reduced in vacuo to ca. 10 mL. The product was precipitated by slow addition of diethyl ether (10 mL). Yield: 242 mg (89%). IR (cm⁻¹): ν(C≡C) 2110 (w). ¹H NMR (CDCl₃): δ 7.36–7.28 (m, 20 H, Ph), 4.44 (s, 4 H, C₅H₄), 4.36 (s, 4 H, C₅H₄), 4.21 (s, 10 H, Cp), 4.11 (s, 4 H, C₅H₄), 4.05 (s, 4 H, C₅H₄). ¹³C{¹H} NMR (CDCl₃): δ 133.6 (d, *J* = 15.5 Hz), 131.6, 131.2 (d, *J* = 10.0 Hz), 130.4, 128.6, (d, *J* = 9.5 Hz), 128.2 (d, *J* = 12.1 Hz), 102.2, 98.7, 82.0, 81.6, 74.5 (d, *J* = 12.7 Hz), 73.4 (d, *J* = 12.3 Hz), 71.8, 69.9, 67.8. ³¹P{¹H} NMR (CDCl₃): δ 24.8. Anal. Calcd for C₅₈H₄₆Au₂Fe₃P₂ (1366.4): C, 50.98; H, 3.39. Found: C, 51.56; H, 3.92.

X-ray Crystallography. For each data collection a single crystal was mounted on a glass fiber and all geometric and intensity data were taken from this sample. Data collection using

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Mo K α radiation ($\lambda = 0.71073$ Å) was made on a Stoe IPDS2 diffractometer equipped with a two-circle goniometer and an area detector. Absorption correction was done by integration using X-red.⁵⁸ The data sets were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS97) and refined using alternating cycles of least-squares refinements against F^2 (SHELXL97).⁵⁹ All non H atoms were found in difference Fourier maps and were refined with anisotropic displacement parameters. H atoms were placed in constrained positions according to the riding model with the 1.2-fold isotropic displacement parameters. Pertinent crystallographic data are collected in Table 1. The crystal structure of (**4**)₃ has

already been published elsewhere.¹⁸ Graphical representations were made using ORTEP-3 win.⁶⁰

Acknowledgment. We are grateful to Umicore AG&Co. KG (Hanau, Germany) for a generous gift of precious metal compounds. D.R. thanks the Otto Braun Fonds for a doctoral fellowship.

Supporting Information Available: Crystallographic data of compounds **3a**, **3b**, **3c**, and **6** (CIF file). This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM8005992