

Oligomerization of Digoldacetylide Complexes through Angular Head-to-Tail Auophilic Bonding

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The concept of auophilic bonding predicts an extended supramolecular chemistry of mono- and dinuclear gold acetylide complexes, but examples of the type $(R_3P)AuC\equiv CAu(PR_3)$ reported in the literature were all found to be monomeric owing to the influence of the auxiliary phosphine ligands employed. Compounds prepared with small tertiary phosphines have now been shown to exhibit the expected oligomerization: Complexes of the type $(R_3P)AuC\equiv CAu(PR_3)$ with $R_3P = Me_3P$ and Me_2PhP were found to have one-dimensional zigzag chain structures in which the molecular units are linked head-to-tail through short α, ω Au–Au contacts. By contrast, $(Et_3P)AuC\equiv CAu(PEt_3)$, with its more bulky phosphines, shows monomeric units of D_3 symmetry in the crystal. The mononuclear complex $(MePh_2P)AuC\equiv CH$ is a dimer in the solid state, with one short Au–Au contact. This angular dimeric unit (C_2 symmetry) resembles the connectivity pattern in the zigzag chains of the aggregates of the dinuclear complexes. The compounds have also been characterized through their vibrational (IR/Raman), multinuclear NMR, and mass spectra.

Introduction

Gold acetylide Au_2C_2 (“explosive gold”) was discovered by Berthelot¹ in 1866, and this early work on the first binary compound of gold and carbon marks the start of extensive research in organogold chemistry, which still continues to attract great interest.² While there has been a steady growth in organogold chemistry quite generally in recent years, gold alkynyl compounds have remained a particularly active field. This special position of gold acetylides is based on a set of interesting chemical and physical properties which suggest extensive applications in a variety of modern technologies including nonlinear optics, mesogenic phases, sensors (photoluminescence), crystal engineering, etc.

These properties are based (a) on the thermal and chemical stability of gold acetylide derivatives, e.g., toward oxidation and hydrolysis, which is quite remarkable considering the lability of ligand-free Au_2C_2 ; (b) on their rodlike structures, which can be modified extensively both by substituents at the alkyne unit or in the auxiliary ligands provided for the gold atoms; and (c) on the ready formation of intermolecular auophilic interactions, which can influence greatly the configuration, conformation, and HOMO–LUMO characteristics of the monomers.

Recent literature reflects this potential in a series of highly successful experimental studies.² Regarding the specific area of the present paper, alkynyl gold complexes of the types $LAuC\equiv CAuL$ (**A**) and $LAuC\equiv CH$ (**B**, $L = PR_3$), the following investigations made fundamental contributions: Initial preparative studies by Cross et al. led to the characterization of the first complexes, **A** and **B**, obtained from the corresponding R_3PAuCl complexes, acetylene gas, and a strong base in alcohol.³ This work was paralleled by studies of Bruce et al.⁴ on these and substituted acetylides $R_3PAuC\equiv CR'$ (**C**) following up previous investigations by Coates et al.^{2,5} and Puddephatt et al.⁶ In the mid-1990s the photophysical properties of these complexes were investigated by Mingos, Yam, et al. using a set of specific substituents for the phosphine ligands.⁷ Vicente, Chicote, et al. developed a new strategy for the synthesis of pure monoaurated acetylenes **B**⁸ and gold acetylide complexes with ylidic components.⁹

(1) Berthelot, M. P. *Liebigs Ann. Chem.* **1866**, 139, 150.
 (2) (a) Schmidbaur, H. Organogold Compounds. In *Gmelin Handbuch der Anorganischen Chemie*, 8th ed.; Slawisch, A., Ed.; Springer-Verlag: Berlin, 1980. (b) Schmidbaur, H.; Grohmann, A.; Olmos, M. E., Organogold Chemistry. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley & Sons Ltd.: Chichester, 1999. (c) Yam, V. W.-W.; Choi, S. W.-K. *J. Chem. Soc., Dalton Trans.* **1996**, 4227. (d) Yam, V. W.-W.; Choi, S. W.-K.; Cheung, K.-K. *Organometallics* **1996**, 15, 1734. (e) Chao, H.-Y.; Lu, W. L.; Chan, M. C. W.; Che, C.-M.; Cheung, K.-K.; Zhu, N. J. *Am. Chem. Soc.* **2002**, 124, 14696. (f) Shieh, S.-J.; Hong, X.; Peng, S.-M.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 3067. (g) Li, D.; Hong, X.; Che, C.-M.; Lo, W.-C.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1993**, 2929.

(3) (a) Cross, R. J.; Davidson, M. F.; McLennan, A. J. *J. Organomet. Chem.* **1984**, 265, C37. (b) Cross, R. J.; Davidson, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411.
 (4) (a) Bruce, M. I.; Horn, E.; Matison, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, 37, 1163. (b) Bruce, M. I.; Duffy, D. N. *Aust. J. Chem.* **1986**, 39, 1697. (c) Bruce, M. I.; Grundy, K. R.; Lidell, M. J.; Snow, M. R.; Tiekink, R. T. *J. Organomet. Chem.* **1988**, 344, C49. (d) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Smith, M. E.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 995.
 (5) Coates, G. E.; Parkin, C. *J. Chem. Soc.* **1962**, 3220.
 (6) (a) Johnson, A.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1384. (b) Irwin, M. J.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, 16, 3541.
 (7) (a) Müller, T. E.; Choi, S. W.-K.; Mingos, D. M. P.; Murphy, D.; Williams, D. J.; Yam, V. W.-W. *J. Organomet. Chem.* **1994**, 484, 209. (b) Hurst, S. K.; Lucas, N. T.; Humphrey, M. G.; Asselberghs, I.; Boxel, R. V.; Persoons, A. *Aust. J. Chem.* **2001**, 54, 447, and references therein.
 (8) Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D.; Jones, P. G. *Organometallics* **1997**, 16, 5628.
 (9) Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D. *J. Chem. Soc., Dalton Trans.* **1995**, 497.

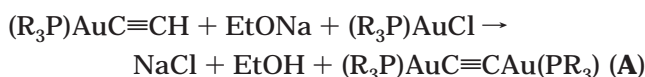
Structural studies on compounds of types **A** and **C** are limited, and only few prototypes have been investigated, e.g., bis[(triphenylphosphine)gold]acetylene, bis[tri(*m*-tolyl)phosphinegold]acetylene;⁴ bis[(diphenyl-1-naphthyl)phosphinegold]acetylene, bis[(phenyldi-1-naphthylphosphine)gold]acetylene, bis[(diferrocenylphenylphosphine)gold]acetylene (all **A**);⁷ [(triphenylphosphine)gold]phenylacetylene,⁴ [(diferrocenylphenylphosphine)gold]phenylacetylene, [(triphenylphosphine)gold]pentafluorophenylacetylene (all **C**); and others.⁷ No structure of a representative example for series **B** has been reported.

An inspection of these structures shows that all molecules of types **A** and **C** are monomeric in the crystal except for (Ph₃P)AuC≡CPh (**C**), which is a dimer with a relatively long Au–Au contact [3.379(1) Å].⁴ For the other examples the monomeric nature is of no surprise since in all cases very bulky ligands and substituents were employed, which rule out any close intermolecular gold–gold contacts. The large number of more complex multinuclear acetylide systems and aurated polyacetylenes are not considered here.

Extensive experimental and theoretical studies related to the aurophilicity concept¹⁰ have clearly demonstrated that this type of bonding should be and actually is ubiquitous in gold(I) chemistry provided that the coordination sphere of the metal atoms is sufficiently open such that aggregation of neighboring molecules is not impeded.¹¹ It therefore appears that phosphine complexes of Au₂C₂ should have a rich supramolecular chemistry. The potential for aggregation is even particularly great due to the α,ω -difunctionality, which should give rise to extended oligomerization. In the present paper we describe the results of our efforts to verify this prediction.

Preparations

To ensure free access to the linearly two-coordinate gold atoms in the molecules of the types **A** and **B**, the smallest tertiary phosphines were chosen in this work. The preparative work followed the published procedures employing the corresponding R₃PAuCl complexes.^{3–5} These were dissolved or suspended in ethanol, and a stream of gaseous acetylene was passed into the solutions, which also contained slightly more than 1 equiv of sodium ethanolate as a base. NMR and Raman spectroscopic investigations of the products showed that in most cases (except for R = Et) mixtures of the products **A** and **B** were obtained the ratio of which was difficult to govern by changes of the reaction time or the sequence of addition of the reagents. Workup of the products by fractional crystallization generally gave one pure single complex which has the lowest solubility.



With the phosphines Me₃P, Et₃P, and Me₂PhP, only the symmetrical dinuclear compounds (**A**) were crystallized, while for MePh₂P the unsymmetrical mononuclear complex (**B**) was isolated. Single crystals could be grown of all four products. It should be noted that several symmetrical triarylphosphine complexes (**A**) have already been reported which also include the (Ph₃P)AuC≡CAu(PPh₃) prototype.⁴

Analytical and spectroscopic identification of the products was not always straightforward. It was observed previously that, for example, the mass spectroscopic characteristics are quite intriguing.^{4c} The spectra show a surprising variety of multinuclear species which indicate the presence of oligomers undergoing multi-branch fragmentation. The expected molecular ions represent only a small minority in the list of ions. Note that this result suggests association of the compounds in the solid state and in solution.

Infrared and Raman spectroscopic data were found to be not always unambiguous. While the C≡C stretching vibration for the symmetrical compounds (**A**, point group *C*₂) is expected to be Raman-active and IR-silent, for the unsymmetrical species of type **B** (point group *C*₃) this vibration should also be IR-active. Mixtures of complexes **A** and **B** described in this paper did not exhibit C≡C stretching bands in the IR spectra and in most cases gave only a single Raman line in the C≡C triple bond range. The differences between the frequencies of two authentic samples (**A** and **B**) are small and may preclude definite assignments to **A** or **B**. This finding is also in agreement with literature reports.^{2c,3,4,7,8}

NMR spectroscopy was elusive in all cases because it was found that the resonances of the acetylene carbon atoms of the symmetrical compounds of type **A** are difficult to detect even at low temperatures, and this is also true for the carbon atom of the unsymmetrical species **B**, which carries no hydrogen atom. Previous tentative assignments⁸ of the C–H resonance in the range 85–95 ppm was finally confirmed by the *proton-coupled* ¹³C spectrum of (MePh₂P)AuC≡CH, which showed the expected doublet splitting ¹*J*(¹³C–¹H) = 228.6 Hz. The range for the resonances of the other acetylene carbon atoms spreads over a large region from 120 to as much as 210 ppm, where quite generally only very weak signals (if any) are detectable. There is also an overlap of this region with the low-field part of the range for aryl resonances which may mask the low-intensity acetylene resonances. Assignments are therefore most unambiguous for the fully alkylated complexes (with Me₃P and Et₃P ligands).

Structures

Symmetrical compounds of type **A** with triarylphosphine ligands were shown to have “wheel-and-axle” type structures, where the rigid digold acetylene rod connects the two 3-fold phosphine rotors.⁴ Even more extended “weight-lift gear” (dumbbell) structures have been found for the anionic bis-isocyanide gold complexes [(RNC)₂Au][–]

(10) (a) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11. (b) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, *24*, 391. (c) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3.

(11) Recent examples: (a) Schmidbaur, H.; Hamel, A.; Mitzel, N. W.; Schier, A.; Nogai, S. *Proc. Natl. Acad. Sci. (Washington)* **2002**, *99*, 4916. (b) Ehlich, H.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **2002**, *41*, 3721.

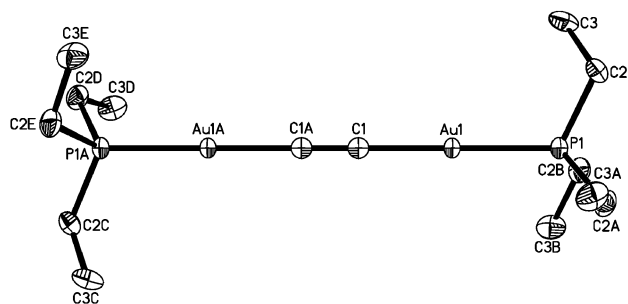


Figure 1. Molecular structure of compound $[(\text{Et}_3\text{P})\text{AuC}\equiv\text{CAu}(\text{PET}_3)]$ (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1–P1 2.283(2), Au1–C1 1.994(8), C1–C1A 1.21(2); P1–Au1–C1 180, Au1–C1–C1A 180.

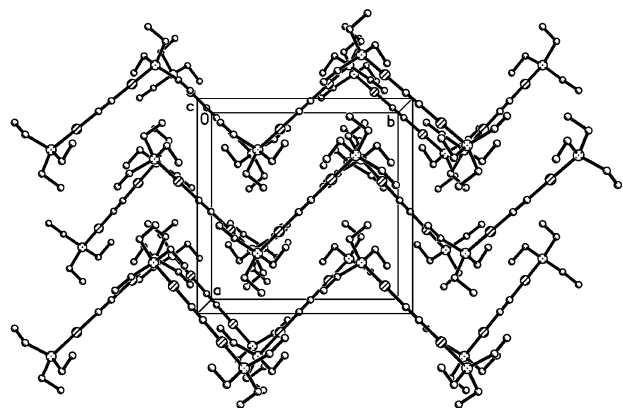


Figure 2. Packing of $[(\text{Et}_3\text{P})\text{AuC}\equiv\text{CAu}(\text{PET}_3)]$ in the cubic cell.

and related combinations of isocyanide and other ligands with linear geometry.¹²

The same structure type has now been confirmed for bis[(triethylphosphine)gold]acetylene, $[(\text{Et}_3\text{P})\text{AuC}\equiv\text{CAu}(\text{PET}_3)]$. This compound crystallizes in the rare cubic space group $Pa\bar{3}$ with $Z = 4$ molecules in the unit cell. The individual molecule has point group D_3 symmetry as shown in Figure 1. The crystals are free of solvent and have an efficient packing of the molecules (Figure 2), but there is no evidence for any aurophilic interactions. The shortest intermolecular Au–Au distance is 6.959 Å. It should be noted that the packing of the triphenylphosphine and tri(*m*-tolyl)phosphine complexes is much less dense and leaves room for solvent inclusion.⁴

The molecular axis comprising six atoms is linear with C≡C, C–Au, and Au–P distances of 1.211(17), 1.994(8), and 2.283(2) Å, respectively. The Au–P–C angles are larger and the C–P–C angles smaller than the tetrahedral standard as observed for most metal complexes of tertiary phosphines.

Crystals of bis[(trimethylphosphine)gold]acetylene, $[(\text{Me}_3\text{P})\text{AuC}\equiv\text{CAu}(\text{PMe}_3)]$, are tetragonal, space group $P4/ncc$, with $Z = 8$ molecules in the unit cell. The individual dinuclear complex has point group C_i symmetry with C≡C, C–Au, and Au–P distances of 1.21(2), 2.010(10), and 2.277(3) Å, respectively, very similar to those of the PET_3 analogue. The angles P–Au–C1

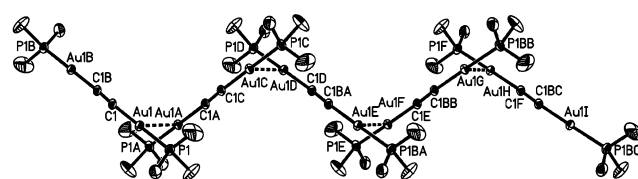


Figure 3. Zigzag chain association of molecules $[(\text{Me}_3\text{P})\text{AuC}\equiv\text{CAu}(\text{PMe}_3)]$ (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1–P1 2.277(3), Au1–C1 2.01(1), C1–C1B 1.21(2), Au1⋯Au1A 3.0747(8); P1–Au1–C1 176.0(3), Au1–C1–C1B 177(1), P1–Au1⋯Au1A–P1A 118.2(3).

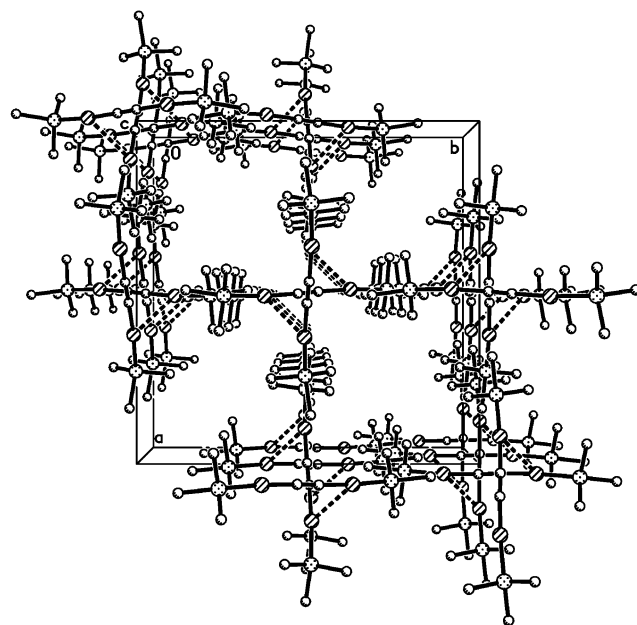


Figure 4. Packing of $[(\text{Me}_3\text{P})\text{AuC}\equiv\text{CAu}(\text{PMe}_3)]$, view down the c -axis of the tetragonal cell.

[176.0(3)°] and C1'–C1–Au [177(1)°] show small deviations from linearity.

Contrary to the findings for the PET_3 complex, the monomers of the PMe_3 complex are clearly associated into zigzag chain oligomers via aurophilic bonding [Au–Au' 3.0747(8) Å] (Figure 3). The head-to-tail connectivity follows a pattern that relates neighboring molecules by a 2-fold axis passing through the midpoint of the Au–Au linkage. The folding of the zigzag chain is determined by a dihedral angle P–Au–Au'–P' of 118.2° at either end of the molecule. Required by the C_i symmetry, for each molecule the α,ω -connections occur at opposite sides of the molecular axis. Together with the dihedral angle relation this leads to a nonparallel orientation of the molecular axis of neighboring molecules, which is obvious from a view down the c -axes of the unit cell (Figure 4).

Crystals of bis[(dimethylphenylphosphine)gold]acetylene, $[(\text{Me}_2\text{PhP})\text{AuC}\equiv\text{CAu}(\text{PhMe}_2)]$, are orthorhombic, space group $Pbca$, with $Z = 8$ molecules in the unit cell. The individual molecule has no crystallographically imposed symmetry but approaches quite closely the requirements of point group C_2 (Figure 5). Its axis is puckered quite significantly with all its angles (C1–C2–Au2 176.4(4)°, C2–C1–Au1 175.6(4)°, P1–Au1–C1 176.5(2)°, and P2–Au2–C2 173.0(1)°) deviating mark-

(12) Ehlich, H.; Schier, A.; Schmidbaur, H. *Z. Naturforsch.* **2002**, *57b*, 890.

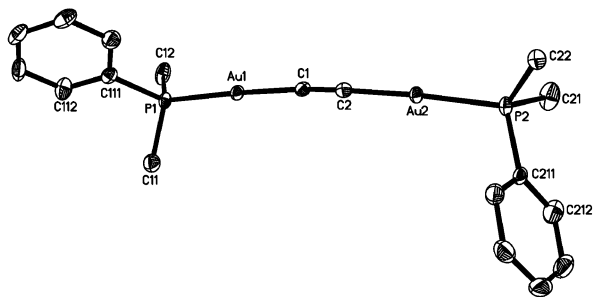


Figure 5. Molecular structure of compound $[(\text{Me}_2\text{PhP})\text{-AuC}\equiv\text{CAu}(\text{PPhMe}_2)]$ (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1–P1 2.284(1), Au1–C1 2.001(5), C1–C2 1.216(7), Au2–P2 2.2849(1), Au2–C2 2.011(5); P1–Au1–C1 176.5(2), Au1–C1–C2 175.6(4), C1–C2–Au2 176.4(4), C2–Au2–P2 173.0(1).

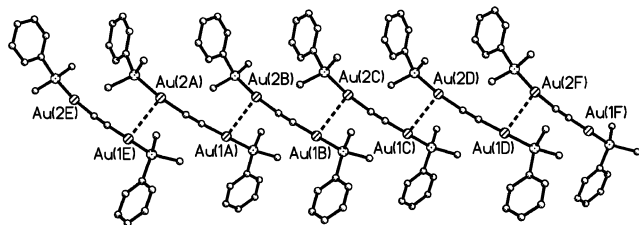


Figure 6. Zigzag chain formation through head-to-tail auriphilic interaction between molecules $[(\text{Me}_2\text{PhP})\text{-AuC}\equiv\text{CAu}(\text{PPhMe}_2)]$ (Au1...Au2 3.1680(3) Å).

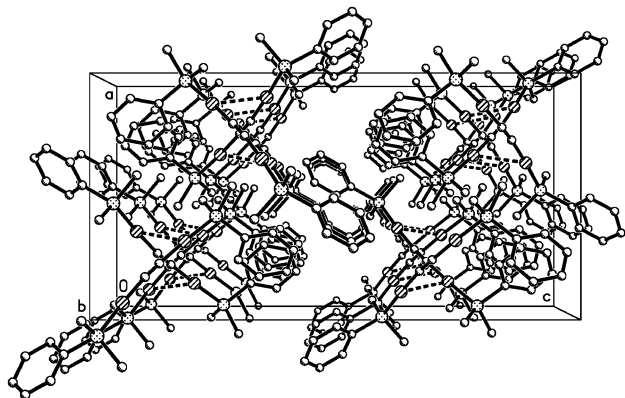


Figure 7. Projection of the chains of molecules $[(\text{Me}_2\text{PhP})\text{-AuC}\equiv\text{CAu}(\text{PPhMe}_2)]$ along the b -axis of the orthorhombic cell.

edly from 180°. The distances C1≡C2 1.216(7), Au1–C1 2.001(5), Au2–C2 2.011(5), Au1–P1 2.284(1), and Au2–P2 2.285(1) Å show no anomalies.

Like the $[(\text{Me}_3\text{P})\text{Au}]_2\text{C}_2$ molecules, the monomers of the Me_2PhP complex are also associated into zigzag strings through head-to-tail auriphilic interactions [Au1–Au2' 3.1680(3) Å] (Figure 6). The projection of the chain along the b -axis of the crystal reveals a connectivity pattern very similar to that of the Me_3P analogue (Figure 7). The dihedral angle P1–Au1–Au2'–P2' is 112.0°.

Although analytical and spectroscopic data have shown that both type **A** and **B** molecules are obtained in the reaction of $(\text{MePh}_2\text{P})\text{AuCl}$ with acetylene in EtOH/EtONa, only $[(\text{methyl}(\text{diphenylphosphine})\text{gold})\text{-acetylene}, (\text{MePh}_2\text{P})\text{AuC}\equiv\text{CH}]$, could be crystallized (monoclinic, space group $C2/c$, $Z = 8$). The asymmetric

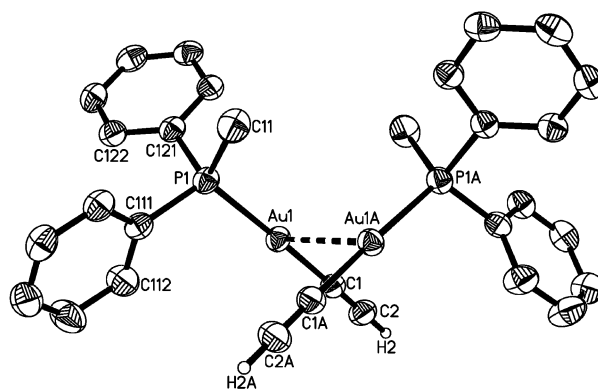


Figure 8. Dimeric unit of $[(\text{MePh}_2\text{P})\text{AuC}\equiv\text{CH}]$ (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1–P1 2.2812(9), Au1–C1 2.008(4), C1–C2 1.187(6), Au1...Au1A 3.0316(3); P1–Au1–C1 174.8(1), Au1–C1–C2 178.9(4), P1–Au1...Au1A–P1A 112.0(3).

unit contains one molecule that is part of a dimer with the second molecule related by a 2-fold axis (Figure 8). The dimer features an auriphilic contact Au1–Au1' of 3.0316(3) Å and a dihedral angle P1–Au1–Au1'–P1' of 111.7°. The packing of these dimers in the crystal shows no further sub-van der Waals contacts. The molecular axis P1–Au1–C1 is slightly bent [174.77–(12)°]. The position of the acetylene hydrogen atom H1 was localized and its position refined with fixed isotropic parameters. The C≡C, Au–C, and Au–P distances [1.187(6), 2.008(4), and 2.2812(9) Å, respectively] are all similar to those in the three compounds of type **A** (above), indicating that the structure of a $(\text{R}_3\text{P})\text{AuC}\equiv\text{C}$ unit is not influenced significantly by H/Au substitution at the other end of the acetylene group.

Discussion and Conclusions

The auriphilicity concept¹⁰ suggests that mono- and dinuclear gold acetylide complexes $\text{LAuC}\equiv\text{CH}$ (**B**) and $\text{LAuC}\equiv\text{CAuL}$ (**A**, L = tertiary phosphine donor ligand) should have a rich supramolecular chemistry. The dinuclear species in particular are to be considered as rigid difunctional building blocks for the construction of oligo- or polymeric aggregates. All compounds of the type **A** reported in the literature were found to be monomers, however, probably owing to the presence of bulky ligands L. In the present work therefore complexes of gold acetylide with four ligands featuring a variety of cone angles (PEt₃, PMe₃, PMe₂Ph, PMePh₂) were prepared and structurally characterized.

In the preparations (following literature methods) product mixtures of types **A** and **B** were obtained and identified by the spectral data of the components. The prominent and least soluble component was isolated by fractional crystallization and its structure determined.

The dinuclear complex with the largest phosphine (PEt₃) was found to be a monomer with a "weight-lifting gear" structure of D_3 symmetry. By contrast, the complex with the smallest phosphine (PMe₃) could be shown to be a zigzag chain polymer in which molecular units with inversion symmetry are linked in a head-to-tail pattern via auriphilic contacts [3.047(8) Å]. The folding of the chain arises from a dihedral angle P–Au–Au'–P' of 118.2°, which minimizes steric interference of the

Table 1. Crystal Data, Data Collection, and Structure Refinement

	(Et ₃ P)AuC≡CAu(PEt ₃)	(Me ₃ P)AuC≡CAu(PMe ₃)	(Me ₂ PhP)AuC≡CAu(PPhMe ₂)	(MePh ₂ P)AuC≡CH
	Crystal Data			
formula	C ₁₄ H ₃₀ Au ₂ P ₂	C ₈ H ₁₈ Au ₂ P ₂	C ₁₈ H ₂₂ Au ₂ P ₂	C ₁₅ H ₁₄ AuP
<i>M_r</i>	654.25	570.10	694.23	422.20
cryst syst	cubic	tetragonal	orthorhombic	monoclinic
space group	<i>Pa</i> $\bar{3}$	<i>P4/ncc</i>	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> (Å)	12.3718(1)	15.8161(2)	12.848(1)	22.0202(3)
<i>b</i> (Å)	12.3718(1)	15.8161(2)	11.433(1)	7.0904(1)
<i>c</i> (Å)	12.3718(1)	10.9850(2)	25.581(1)	17.7718(7)
α (deg)	90	90	90	90
β (deg)	90	90	90	96.550(1)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	1893.7(1)	2747.9(1)	3757.6(5)	2756.6(1)
ρ_{calc} (g cm ⁻³)	2.295	2.756	2.454	2.035
<i>Z</i>	4	8	8	8
<i>F</i> (000)	1208	2032	2544	1584
μ (Mo K α) (cm ⁻¹)	156.31	215.21	157.63	107.64
	Data Collection			
no. of measd reflns	53 486	67 236	93 336	38 989
no. of unique reflns	704 [<i>R</i> _{int} = 0.076]	1540 [<i>R</i> _{int} = 0.080]	4169	2862 [<i>R</i> _{int} = 0.042]
abs corr	DELABS ^{14b}	DELABS ^{14b}	DELABS ^{14b}	DELABS ^{14b}
<i>T</i> _{min} / <i>T</i> _{max}	0.468/0.827	0.389/0.790	0.438/0.814	0.503/0.842
	Refinement			
no. of refined params	28	55	199	155
final <i>R</i> values [<i>I</i> = 2 σ (<i>I</i>)]				
<i>R</i> 1	0.0245	0.0448	0.0252	0.0217
w <i>R</i> 2 ^a	0.0537	0.0990	0.0610	0.0560
ρ_{fin} (max./min.) (e Å ⁻³)	0.727/−1.208	2.686/−1.101	0.964/−1.031	2.032/−0.772

^a w*R*2 = { $[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]$ }^{1/2}; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0075$ [(Et₃P)AuC≡CAu(PEt₃)], 0.0081 [(Me₃P)AuC≡CAu(PMe₃)], 0.0000 [(Me₂PhP)AuC≡CAu(PPhMe₂)], 0.0195 [(MePh₂P)AuC≡CH]; $b = 12.45$ [(Et₃P)AuC≡CAu(PEt₃)], 57.73 [(Me₃P)AuC≡CAu(PMe₃)], 20.97 [(Me₂PhP)AuC≡CAu(PPhMe₂)], 11.50 [(MePh₂P)AuC≡CH].

PMe₃ ligands. A closely related structure has been found for the dimethylphenylphosphine complex (Me₂PhP) with the Au–Au contact slightly longer at 3.1680(3) Å and the dihedral angle P–Au–Au′–P′ at 112.0°. Similar angular units are found for the complex [(Me₂PhP)AuC≡CH] of type **B**, which forms dimers with an Au–Au′ distance of 3.0316(3) Å and a dihedral angle of 111.7°. The dinuclear complex with PMePh₂ ligands could not be crystallized.

The observations made during the preparations suggest that an efficient dimerization and/or low solubility of the mononuclear complexes (**B**) may retard the formation of the dinuclear complexes (**A**) quite considerably. This seems to be true, for example, for (MePh₂P)AuC≡CH, which was obtained almost without any dinuclear byproduct. By contrast, under similar experimental conditions the reaction with (Et₃P)AuCl gave the dinuclear complex exclusively. This complex is not associated, and the monomer is auroated further without steric hindrance. Unfortunately we have no quantitative data to support this qualitative observation.

In summary it could be shown that complexes of monogold and digold acetylide (AuC≡CH and AuC≡CAu) with small tertiary phosphine ligands undergo oligomerization to form dimers or polymers, respectively, through short aurophilic bonding. The compounds have a common structural pattern with very similar angular units in the dimers and in the zigzag one-dimensional supramolecular aggregates. The energy associated with the aurophilic interactions is estimated to be on the order of 8–11 kcal,¹⁰ comparable to the energy of hydrogen bonds. The Au–Au contacts are therefore significant in determining the solid state structure. The photophysical properties of the new compounds, under standard conditions and under pressure, are presently under investigation.

Experimental Part

All experiments were routinely carried out in an atmosphere of dry and pure nitrogen. Solvents were dried and kept under nitrogen, and glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. The tertiary phosphines are commercially available. Their gold chloride complexes were obtained following literature procedures.¹³

General Preparative Method. A suspension of ca. 10 mmol of the (phosphine)gold chloride in ethanol (100 mL) is saturated with acetylene gas at −60 °C for 1 h. Subsequently a solution of sodium ethanolate [prepared by dissolving sodium metal (11 mmol) in ethanol (20 mL)] is added slowly with stirring. Acetylene is bubbled through the reaction mixture for another 3 h. On warming the mixture clears up briefly and then a precipitate is formed, which is filtered off, washed with water, and dried in a vacuum. This product is a mixture of compounds (**A** and **B**) for R₃P = Me₃P, Me₂PhP, and MePh₂P, but only pure **A** for R₃P = Et₃P. The major component can be separated by fractional crystallization from dichloromethane/*n*-pentane. Single crystals can be grown for the pure components from dichloromethane carefully layered with *n*-pentane.

Characterization of the Products. (Me₃P)AuC≡CAu(PMe₃): yield 58.1%, pale yellow solid, mp 206–207 °C; Raman (powder sample) $\nu(\text{C}\equiv\text{C})$ 1974.6 cm⁻¹; MS (FAB) *m/z* = 571.5 [M + H]⁺. Anal. Calcd for C₈H₁₈Au₂P₂ (570.11): C 16.85, H 3.18, P 10.87. Found: C 16.77, H 3.21, P 9.98. NMR (CD₂Cl₂, 25 °C): ¹H, 1.49 ppm, d, *J* = 9.9 Hz; ¹³C (H-coupled), 15.81, dq, *J* = 130.9 and 35.9 Hz, Me; 206.7, dd, *J* = 12.0 and 5.5 Hz (AuC); ³¹P{¹H}, 1.03, s.

(Me₃P)AuC≡CH: isolated from the filtrate, Smp 111–112 °C. Anal. Calcd for C₅H₁₀AuP (298.08): C 20.15, H 3.38, P 10.39. Found: C 20.12, H 3.37, P 10.01. NMR (CD₂Cl₂, 25 °C): ¹H, 1.48, d, *J* = 9.9 Hz, 9H, Me; 2.09, s, 1H, CH; ¹³C (H-coupled), 31.0, qd, *J* = 128.2 and 35.0 Hz, Me; 90.4, dd, *J* = 227.3 and 12.9 Hz, CH; 128.3, dd, *J* = 143.4 and 38.7 Hz, AuC.

(13) (a) Schmidbaur, H.; Brachthäuser, B.; Steigelmann, O.; Beruda, H. *Chem. Ber.* **1992**, *125*, 2705. (b) Mann, F. G.; Wells, A. F.; Purdie, D. *J. Chem. Soc.* **1937**, 1828.

(Et₃P)AuC≡CAu(PEt₃): yield 72.6%, white solid, mp 180–181 °C; Raman (powder) $\nu(\text{C}\equiv\text{C})$ 2009.1 cm⁻¹; MS (FAB) 655.7 [M + H]⁺. Anal. Calcd for C₁₄H₃₀Au₂P₂ (654.27): C 25.70, H 4.62, P 9.47. Found: C 25.25, H 4.38, P 8.87. NMR (CD₂Cl₂, 25 °C): ¹H, 1.05, dt, *J* = 18.0 and 7.6 Hz, 3H, Me; 1.70, dq, *J* = 8.1 and 7.5 Hz, 2H, CH₂; ¹³C (¹H-coupled), 8.90, qd, *J* = 128.2 and 4.6 Hz, Me; 18.04, td, *J* = 130 and 32.3 Hz, CH₂; 150.0, br s AuC; ³¹P{¹H}, 39.2, s.

(Et₃P)AuC≡CH was not detected in the product mixture.

(Me₂PhP)AuC≡CAu(PPhMe₂): yield 71.8%, mp 181–182 °C, white solid; Raman (powder) $\nu(\text{C}\equiv\text{C})$ 1998.2 cm⁻¹; MS (FAB) 695.3 [M + H]⁺. Anal. Calcd for C₁₈H₂₂Au₂P₂ (694.25): C 31.14, H 3.19, P 8.92. Found: C 31.16, H 3.27, P 8.77. NMR (CD₂-Cl₂, 25 °C): ¹H, 1.73, d, *J* = 7.6 Hz, 6H, Me; 7.46–7.75, m, 5H, Ph; ¹³C (¹H-coupled/decoupled), 15.70, qdq, *J* = 131.0, 34.6 and 3.1 Hz, Me; 129.5, 131.7, and 132.5, all dd, *J*(PC) = 10.8, 2.3, and 13.1, respectively, with *J* = 150 for m-, p- and o-C(Ph); 134.2, d, *J* = 53.0 Hz, *i*-C(Ph); 148.3, br s, AuC.

(Me₂PhP)AuC≡CH: not isolated, spectral data from solutions of the product mixture; ¹³C NMR (¹H-coupled, CD₂Cl₂) 90.5, d, *J* = 228.4 Hz, CCH; 127.9, s, AuC; Me₂PhP ligand resonances are overlapping with those of the dinuclear complex.

(MePh₂P)AuC≡CH: yield 71.8%, mp 106–107 °C, white solid; Raman (powder) $\nu(\text{C}\equiv\text{C})$ 1981.8 cm⁻¹; MS (FAB) *m/z* 423.4 [M + H]⁺. Anal. Calcd for C₁₅H₁₄AuP (422.22): C 42.67, H 3.34, P 7.34. Found: C 42.50, H 3.32, P 7.06. NMR (CD₂-Cl₂, 25 °C): ¹H, 2.06, d, *J* = 8.8 Hz, 3H, Me; 1.62, s, 1H, CCH; 7.45–7.63, m, 10H, Ph; ¹³C (¹H-coupled), 14.1, dq, *J* = 132.8 and 34.5 Hz, Me; 90.1, dd, *J* = 228.6 and 2.3 Hz, CCH; 127.8, d, *J* = 39.7 Hz, AuC; 129.3, 131.5, 132.2, and 133.1, for m-, p-, *i*-, and o-CH(Ph), *J*(PC) = 10.8, 7.0, 54.6, and 13.8 Hz, and *J*(CH) = ca. 150 Hz for o-, m-, and p-CH.

(MePh₂P)AuC≡CAu(PPh₂Me): not isolated, spectroscopic data are given for the product mixture; Raman (powder) $\nu(\text{C}\equiv\text{C})$ 2003.1 cm⁻¹; MS (FAB) *m/z* = 819.2 [M + H]⁺; ¹³C NMR (¹H-coupled) 147.4, small br s, AuC; MePh₂P ligand resonances are overlapping with those of the dinuclear complex.

Crystal Structure Determinations. The crystalline samples were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected using a Nonius DIP2020 system with monochromated Mo K α (λ = 0.71073 Å) radiation at –130 °C. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares calculations on *F*² (SHELXL-97).^{14a} Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions. The acetylenic hydrogen in (MePh₂P)AuC≡CH was located and refined using a riding model with fixed isotropic contributions. Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions. Complete lists of displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC 213306–213309.

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Supporting Information Available: A listing of the atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and torsion angles for the crystal and molecular structures of (Et₃P)AuC≡CAu(PEt₃), (Me₃P)-AuC≡CAu(PMe₃), (Me₂PhP)AuC≡CAu(PPhMe₂), and (MePh₂P)-AuC≡CH. This material can be obtained, free of charge, via the Internet at <http://pubs.acs.org>.

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(14) (a) Sheldrick, G. M. *SHELX-97*, Programs for crystal structure analysis; University of Göttingen: Germany, 1997. (b) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, 194.