Inorganica Chimica Acta 374 (2011) 171-174

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Gold(I) alkynyl complexes containing a flexible, biphenyl-derived bis(alkyne)

Michael Weishäupl^a, Christian Robl^a, Wolfgang Weigand^{a,*}, Sebastian Kowalski^b, Fabian Mohr^{b,*}

^a Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, 07743 Jena, Germany ^b Fachbereich C, Anorganische Chemie, Bergische Universität Wuppertal, 42119 Wuppertal, Germany

ARTICLE INFO

Article history: Available online 11 March 2011

Professor Dr. Wolfgang Kaim zum 60. Geburtstag gewidmet.

Keywords: Gold Alkyne X-ray structure analysis Luminescence Rotationally chiral ligand

ABSTRACT

2,2'-Diethynylbiphenyl was prepared in a three step sequence from commercially available 2,2'-bis(bromomethyl)biphenyl and subsequently reacted with the phosphinegold(I) complexes [AuCl(P)] (P = PEt₃, PCy₃, P^fBu₃, PPh₃, PTA) in the presence of base to give the bis(alkynyl) gold(I) complexes [(P)Au(deb)Au(P)] in good yields as air-stable solids. The compounds were fully characterized spectroscopically and the solid state structures of 2,2'-diethynylbiphenyl as well as the PEt₃ complex were determined by X-ray diffraction. Both solution and solid-state luminescence spectra of the gold complexes were recorded.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Alkynyl complexes of gold have long been investigated due to their interesting photophysics, non-linear optical properties, liquid crystal behavior, their application in homogenous catalysis as well as their fascinating supramolecular architectures [1–7]. In particular, dinuclear gold complexes containing bridging bis(alkynes) are of interest, since linking two linear Au-alkyne-Au units may lead to enhancement of luminescence and also give rise to further interesting structural features. An example of this, albeit with another metal, is the recent report from the group of Wong who reported the self assembly and luminescence of some platinum(II) complexes containing various bis(alkynes) [8]. Given our past interest in the structures and properties of gold alkynyl complexes [9–14], we wished to study some gold(I) phosphine complexes containing bis(alkynes) with a flexible biphenyl-based backbone, the results of this study are presented herein.

2. Results and discussion

2,2'-Diethynylbiphenyl **1** (abbreviated here as H_2 deb or deb after deprotonation) was prepared in a three step sequence from commercially available 2,2'-bis(bromomethyl)biphenyl following the procedure by Staab [15]. By slow evaporation of an ether

* Corresponding authors.

solution of compound **1** crystals suitable for X-ray diffraction were obtained. There are two crystallographically independent molecules of **1** (Fig. 1) lying on a twofold axis which were identified as the P- and M-enantiomers. The bond lengths and angles in both molecules are virtually identical and are similar to other aromatic dialkynes such as 1,4-diethynylbenzene [16] or 1,4-diethynylnaphthalene [17]. The planes of the two phenyl rings are rotated against each other by angles of 115.2° (P-enantiomer) and 112.7° (M-enantiomer), respectively.

 H_2 deb reacts with two equivalents of the chlorogold(I) phosphine complexes [AuCl(P)] (P = PEt₃, PCy₃, P^tBu₃, PPh₃, PTA) in the presence of base to give the bis(alkynyl) gold(I) complexes [(P)Au(deb)Au(P)] (**1a** P = PEt₃, **1b** PCy₃, **1c** P^tBu₃, **1d** PPh₃, **1e** PTA) in good yields as air-stable solids (Scheme 1).

Apart from the PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) derivative **1e** which is insoluble in all common solvents, complexes **1a–1d** were soluble in chlorinated solvents and acetone. Our experience with gold(I) complexes containing PTA has shown that in some cases very soluble (also in water) complexes form, in other cases they are insoluble in all common solvents [9,18,19]. Compounds **1a–1d** were fully characterized by spectroscopic techniques and, in the case of **1a**, by single crystal X-ray diffraction. Complexes **1a–1d** show singulet resonances in their ³¹P{¹H} NMR spectra with chemical shifts typical for alkynylgold(I) phosphine complexes. Deprotonation of the alkyne is evident from the absence of the acetylenic proton signal in the ¹H NMR spectra of compounds **1a–1d** as well as the disappearance of the \equiv C–H band in the IR spectrum of **1a–1e**. In addition, the IR spectra of complexes



E-mail addresses: wolfgang.weigand@uni-jena.de (W. Weigand), fmohr@uni-wuppertal.de (F. Mohr).

^{0020-1693/\$ -} see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2011.03.019



Fig. 1. Molecular structure of compound 1. Ellipsoids show 50% probability levels and hydrogen atoms are shown as spheres with arbitrary radii.





1a–1e show a shift of the C=C stretching frequency to *ca*. 2100 cm⁻¹, as is typically observed in gold(I) alkynyl complexes. Given the good solubility of compounds **1a–1d** in halogenated solvents, we were able to also record ¹³C{¹H} NMR spectra and could unambiguously identify the signals from the acetylenic carbon atoms. The signal due to the carbon atom attached to the gold atom appears as a doublet (${}^{2}J_{P-C}$ of 140 (**1a**), 133 (**1b**), 129 (**1c**), 144 (**1d**) Hz) at in the range of 138–143 ppm, whilst the other acetylenic carbon resonance is seen at around 100 ppm as a doublet with a much smaller ${}^{3}J_{P-C}$ coupling constant of 27 (**1a**), 25 (**1b**), 24 (**1c**), 27 (**1d**) Hz. The molecular structure of the PEt₃ derivative **1a** was determined by single crystal X-ray diffraction (Fig. 2). **1a** is situated on a twofold axis running through the C–C single bond of the biphenyl group. The molecule consists of the deprotonated deb ligand bridging two Et₃PAu units. The C1–Au–P angle is almost

linear (*ca.* 178°), as expected for a gold(I) compound. The two aryl rings of the biphenyl unit are twisted by about 110° with respect to each other, thus preventing any aurophilic Au…Au interactions [20,21]. Furthermore, there are also no intermolecular Au…Au interactions between adjacent molecules. Bond lengths and angles of **1a** (given in the figure caption) are typical for phosphine gold(I) alkynyl complexes.

Room temperature luminescence spectra of gold complexes **1a–1e** were recorded in solution (where possible) as well as in the solid-state (Table 1).

In the case of the complexes **1a–1d**, the solution emission spectra show a broad peak around 390 nm as well as a shoulder at *ca*. 430–450 nm, the position and intensity of the latter varies with solvent. In CH_2Cl_2 the shoulder is more intense than in benzene, which could be due to a stronger interaction (π – π type



Fig. 2. Molecular structure of complex 1a. Ellipsoids show 50% probability levels and hydrogen atoms are shown as spheres with arbitrary radii. Selected bond lengths (Å): Au-P 2.272(1), Au-C1 1.998(5), C1-C2 1.197(7). Selected bond angles (°): P-Au-C1 178.3(2), Au-C1-C2 176.7(5).

 Table 1

 Luminescence data for complexes 1a-1e.

	-	
	λ_{em} (nm) ^{a,b} solution	λ_{em} (nm) ^{a,b} solid-state
1a	CH ₂ Cl ₂ 390, 442 (s) ^c C ₆ H ₆ 390, 433 (s)	459
1b	CH ₂ Cl ₂ 387, 431 (s) C ₆ H ₆ 388, 433 (s)	527
1c	CH ₂ Cl ₂ 388, 427 (s) C ₆ H ₆ 389, 429 (s)	482
1d	CH ₂ Cl ₂ 388, 447 (s) C ₆ H ₆ 390, 430 (s)	484
1e	-	577

^a Excitation at 350 nm.

^ь At 25 °С.

 $^{\rm c}\,$ s denotes shoulder.

interactions) between benzene and the complexes, thus affecting the rotation about the biphenyl axis. This is further supported by the fact that the intensity of the shoulder in CH₂Cl₂ decreases with increasing steric bulk of the phosphine. In the solid-state, the major broad band in the room temperature emission spectra of all five complexes is shifted to higher wavenumbers (450–480 nm); in complex **1e** the band appears at 577 nm. The observed emission bands may be assigned (based on comparison to similar phosphine gold(I)alkynyl species [22,23]) to arise from a mixture of metalperturbed π – π * IL and σ – π * MLCT states. The variation of the emission maxima depending on the nature of the phosphines can be explained by the fact that stronger donor ligands make the gold(I) center more electron rich, thus increasing the energy level of the σ (Au–P) orbital which results in a slightly lower σ – π * emission energy.

In conclusion, we present here the preparation, structures and luminescence studies of some phosphine gold(I)alkynyl complexes containing a rotationally chiral bis(alkyne) in the backbone.

3. Experimental

All reactions were carried out under dry, oxygen free dinitrogen using standard schlenk techniques. Solvents were dried over LiAlH₄ and distilled under dinitrogen before use. 2,2'-Diethynylbiphenyl (1) was prepared following the method of Staab [15]. The gold complexes [AuCl(P)] (P = PEt₃, P^tBu₃, PCy₃, PPh₃, PTA) were prepared by treating [AuCl(tht)] (tht = tetrahydrothiophene) [24] with equimolar amounts of the phosphine. All other chemicals were sourced commercially and used as received. ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on Jeol EX 400 or Bruker Avance 600 instruments using residual solvent signals as reference. Mass spectra (FAB positive ion mode) were measured on a Finigan MAT 90 spectrometer and IR spectra on a Nicolet 520 FT-IR instrument as KBr disks. Luminescence spectra were measured on a Perkin Elmer LS50B instrument. Elemental analyses were carried out by staff of the microanalytical laboratory in house. Labels used in the assignment of proton NMR data are shown below:

3.1. Preparation of the deb gold complexes

 $P_{Au} H^{A} H^{D} Au$

A suspension of [AuCl(P)] (0.20 mmol) in MeOH (20 mL) was treated with sodium metal (*ca.* 30 mg). After *ca.* 30 min at room

3.2. [(Et₃P)Au(deb)Au(PEt₃)] 1a

following complexes were prepared:

Pale brown solid 91% yield. ¹H NMR (CD₂Cl₂): δ 7.50 (part of ABCD spin system, ³ $J_{H^{D}-H^{C}} = 7.8$, ⁴ $J_{H^{D}-H^{B}} = 1.3$ Hz, 2H^D, dep), 7.41 (part of ABCD spin system, ³ $J_{H^{A}-H^{B}} = 7.7$, ⁴ $J_{H^{A}-H^{C}} = 1.4$ Hz, 2H^A, deb), 7.21 (part of ABCD spin system, ³ $J_{H^{A}-H^{B}} = 7.7$, ⁴ $J_{H^{A}-H^{C}} = 1.4$ Hz, 2H^A, deb), 7.21 (part of ABCD spin system, ³ $J_{H^{B}-H^{A}} = 7.7$, ³ $J_{H^{B}-H^{C}} = 7.4$, ⁴ $J_{H^{A}-H^{C}} = 1.4$, ³ $J_{H^{C}-H^{D}} = 7.8$, ⁴ $J_{H^{A}-H^{C}} = 1.3$ Hz, 4H^{B,C}, deb), 1.78 (m, 12H, PCH₂), 1.15 (m, 18H, PCH₂CH₃); ¹³C{¹H} NMR (CD₂Cl₂): δ 143.68, 134.16, 131.06, 127.23, 126.09, 125.12 (d, ⁴ $J_{P-C} = 2.5$ Hz) deb, 141.77 (d, ² $J_{P-C} = 140$ Hz, C=CAu), 102.31 (d, ³ $J_{P-C} = 27$ Hz, C=CAu), 18.21 (d, ¹ $J_{P-C} = 33$ Hz, P-C), 9.17 (P-C-C); ³¹P{¹H} NMR (CD₂Cl₂): δ 37.22; IR (KBr disk): 2107 cm⁻¹ ν (C=C); *Anal.* Calc. for C₂₈H₃₈Au₂P₂ (830.49)%: C, 40.50; H, 4.61. Found: C, 40.50; H, 4.81%.

3.3. [(Cy₃P)Au(deb)Au(PCy₃)] **1b**

Colorless solid 82% yield. ¹H NMR (CD₂Cl₂): δ 7.51 (m, 2H, dep), 7.44 (m, 2H, deb), 7.21 (m, 4H, deb), 1.20–2.00 (m, 66H, PCy₃); ¹³C{¹H} NMR (CD₂Cl₂): δ 143.56, 134.19, 131.16, 127.21, 125.95, 125.24 (d, ⁴J_{P-C} = 2.7 Hz) deb, 143.24 (d, ²J_{P-C} = 133 Hz, C=CAu), 101.01 (d, ³J_{P-C} = 25 Hz, C=CAu), 33.71, 31.26, 27.72, 26.53 (PCy₃); ³¹P{¹H} NMR (CD₂Cl₂): δ 56.53; IR (KBr disk): 2107 cm⁻¹ ν (C=C); *Anal.* Calc. for C₅₂H₇₄Au₂P₂ (1155.05)%: C, 54.06; H, 6.46. Found: C, 54.06; H, 6.62%.

3.4. [(^tBu₃P)Au(deb)Au(P^tBu₃)] **1c**

Colorless solid 89% yield. ¹H NMR (CD₂Cl₂): δ 7.52 (m, 4H, dep), 7.19 (m, 4H, deb), 1.48 (s, 54H, P^tBu₃); ¹³C{¹H} NMR (CD₂Cl₂): δ 142.81, 133.57, 130.95, 126.65, 125.28, 124.64 (d, ⁴*J*_{P-C} = 3.0 Hz) deb, 141.73 (d, ²*J*_{P-C} = 129 Hz, C=CAu), 101.45 (d, ³*J*_{P-C} = 24 Hz, C=CAu), 38.94 (d, ¹*J*_{P-C} = 17 Hz, P^tBu₃), 32.21 (P^tBu₃); ³¹P{¹H} NMR (CD₂Cl₂): δ 92.32; IR (KBr disk): 2108 cm⁻¹ ν (C=C); *Anal.* Calc. for C₄₀H₆₂Au₂P₂ (998.82)%: C, 48.10; H, 6.26. Found: C, 47.71; H, 6.08%.

3.5. [(Ph₃P)Au(deb)Au(PPh₃)] 1d

Cream colored solid 86% yield. ¹H NMR (CD₂Cl₂): δ 7.4–7.6 (m, 34H, dep, Ph₃P), 7.24 (m, 4H, deb); ¹³C{¹H} NMR (CD₂Cl₂): δ 143.73, 134.29, 131.17, 127.34, 126.37, 124.90 (d, ⁴*J*_{P-C} = 2.8 Hz) deb, 134.87, 132.01, 130.55, 129.65 (PPh₃), 137.99 (d, ²*J*_{P-C} = 144 Hz, C=CAu), 102.69 (d, ³*J*_{P-C} = 27 Hz, C=CAu); ³¹P{¹H} NMR (CD₂Cl₂): δ 41.74; IR (KBr disk): 2114 cm⁻¹ ν (C=C); *Anal.* Calc. for C₅₂H₃₈Au₂P₂ (1118.76)%: C, 55.83; H, 3.42. Found: C, 55.71; H, 3.56%.

3.6. [(PTA)Au(deb)Au(PTA)] 1e

Cream colored solid 96% yield. IR (KBr disk): 2098 cm⁻¹ $v(C \equiv C)$; *Anal.* Calc. for C₂₈H₃₂N₆Au₂P₂ (908.47)%: C, 37.02; H, 3.55; N, 9.25. Found: C, 36.93; H, 3.76; N, 9.41%.

3.7. X-ray structure determination

X-ray diffraction intensities were recorded at 213 K with a Siemens P4 diffractometer using graphite monochromatized Mo K α radiation. An empirical absorption correction was applied for **1a**

Table 2

Crystallographic data data for 1 and 1a.

	1	1a
Formula	C ₁₆ H ₁₀	C28H38Au2P2
Mr	202.24	830.46
Crystal size (mm ³)	$0.6\times0.7\times0.9$	$0.2\times0.3\times0.4$
Crystal system	monoclinic	monoclinic
Space group	C2	C2/c
a (Å)	10.379(2)	22.705(3)
b (Å)	9.643(2)	10.4254(14)
<i>c</i> (Å)	11.895(2)	15.968(2)
β(°)	96.68(1)	131.00(1)
V (Å ³)	1182.4(4)	2852.5(7)
Ζ	4	4
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.136	1.934
μ (Mo K $lpha$) (mm ⁻¹)	0.064	10.400
<i>F</i> (000)(e)	424	1576
T (K)	213	213
hkl range	$-14 \leqslant h \leqslant$ +14	$-26 \leqslant h \leqslant$ +26
	$-13 \leqslant k \leqslant$ + 13	$-12\leqslant k\leqslant 0$
	$-16 \leqslant l \leqslant$ +16	$-18\leqslant l\leqslant$ +18
Reflections measured	3451	5007
Reflections unique	3130	2517
R _{int}	0.0272	0.0432
Parameters refined	148	149
$R(F)/wR(F ^2)$ (all reflexions)	0.0420/0.0680	0.0400/0.0478
Goodness-of-fit (GOF) on $ F ^2$	2.704	1.023
$\Delta ho_{ m fin}$ (maximum/minimun), (e Å $^{-3}$)	+0.164/-0.156	+0.721/-0.631

and an empirical extinction correction for both compounds. The phase problem was solved by direct methods and the structural model was completed by subsequent difference Fourier syntheses. Hydrogen atoms were put into calculated positions and introduced into the final cycles of refinement with common isotropic displacement parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters [25]. Further crystallographic details are compiled in Table 2.

Acknowledgments

M.W. thanks the Hanns-Seidel-Stiftung e.V. for a scholarship. We also thank the Fonds der Chemischen Industrie for support of this work.

Appendix A. Supplementary material

CCDC 777705 and 777706 contain the supplementary crystallographic data for **1** and **1a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.019.

References

- For some recent reviews see: N. Meyer, E. Schuh, F. Mohr, Annu. Rep. Prog. Chem., Sect. A 106 (2010) 255.
- [2] F. Mohr (Ed.), Gold Chemistry. Applications and Future Directions in the Life Sciences, Wiley-VCH, Weinheim, 2009.
- [3] A. Laguna (Ed.), Modern Supramolecular Gold Chemistry, Wiley-VCH, Weinheim, 2009.
- [4] For orther important papers on these topics see: V.W.W. Yam, K.K.W. Lo, K.M.C. Wong, J. Organomet. Chem. 578 (1999) 3.
- [5] C.E. Powell, M.G. Humphrey, Coord. Chem. Rev. 248 (2004) 725.
- [6] S. Sanz, L.A. Jones, F. Mohr, M. Laguna, Organometallics 26 (2007) 952.
- [7] R.J. Puddephatt, Coord. Chem. Rev. 216-217 (2001) 313.
- [8] F. Lin, H.Y. Peng, J.X. Chen, D.T.W. Chik, Z. Cai, K.M.C. Wong, V.W.W. Yam, H.N.C. Wong, J. Am. Chem. Soc. 132 (2010) 16383.
- [9] F. Mohr, E. Cerrada, M. Laguna, Organometallics 25 (2006) 644.
- [10] N.C. Habermehl, M.C. Jennings, C.P. McArdle, F. Mohr, R.J. Puddephatt, Organometallics 24 (2005) 5004.
- [11] L.A. Méndez, J. Jiménez, E. Cerrada, F. Mohr, M. Laguna, J. Am. Chem. Soc. 127 (2005) 852.
- [12] F. Mohr, M.C. Jennings, R.J. Puddephatt, Angew. Chem., Int. Ed. Engl. 43 (2004) 969.
- [13] F. Mohr, D.J. Eisler, C.P. McArdle, K. Atieh, M.C. Jennings, R.J. Puddephatt, J. Organomet. Chem. 670 (2003) 27.
- [14] F. Mohr, M.C. Jennings, R.J. Puddephatt, Eur. J. Inorg. Chem. (2003) 217.
- [15] H.A. Staab, H. Mack, A. Nissen, Chem. Ber. 105 (1972) 2310.
- [16] N.A. Ahmed, A.I. Kitaigorodsky, M.I. Sirota, Acta Crystallogr., Sect. B 28 (1972) 2875.
- [17] V. Enkelmann, O. Rohde, Acta Crystallogr., Sect. B 33 (1977) 3531.
- [18] F. Mohr, S. Sanz, E. Vergara, E. Cerrada, M. Laguna, Gold Bull. 39 (2006) 212.
- [19] E. Vergara, S. Miranda, F. Mohr, E. Cerrada, E.R.T. Tiekink, P. Romero, M. Laguna, Eur. J. Inorg. Chem. (2007) 2926.
- [20] H. Schmidbaur, Chem. Soc. Rev. 24 (1995) 391.
- [21] H. Schmidbaur, A. Schier, Chem. Soc. Rev. 37 (2008) 1931.
- [22] D. Li, X. Hong, C.M. Che, W.C. Lo, S.M. Peng, J. Chem. Soc., Dalton Trans. (1993) 2929.
- [23] XFIT for Windows, Australian Synchrotron Research Program, 1996.
- [24] R. Usón, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 85.
- [25] G.M. Sheldrick, Acta Cryst. A64 (2008) 412.