Polyhedron 30 (2011) 2704–2710

Contents lists available at SciVerse ScienceDirect

Polyhedron

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

Photoactive building blocks for coordination complexes: Gilding 2,2′:6′,2″-terpyridine

Edwin C. Constable *, Catherine E. Housecroft *, Marzena K. Kocik, Jennifer A. Zampese

Department of Chemistry, University of Basel, Spitalstrasse 51, 4056 Basel, Switzerland

ARTICLE INFO

Article history:
Received 14 June 2011
Accepted 1 August 2011
Available online 5 August 2011

Keywords:
Gold(I)
2,2′:6′,2″-Terpyridine
Phosphane
Alkyne
Photophysics

ABSTRACT

The alkyne unit of 4′-ethynyl-2,2′:6′,2″-terpyridine has been functionalized with Ph_3PAu, $(2\text{-tolyl})_3PAu$ or Au(dppe)Au units to produce compounds **1**–**3**, respectively. These derivatives have been characterized by electrospray mass spectrometry, solution ^1H and ^{13}C NMR, UV–Vis and emission spectroscopies, and single crystal X-ray diffraction. In the solid state, molecules of **1** or **2** pack with separated domains of tpy and R_3PAu units; the tpy units in **2** (but not **1**) exhibit face-to-face π-stacking. Compound **3** crystallizes as $2(\mathbf{3})\cdot CHCl_3$, and the folded conformation of the dppe backbone results in a short (2.9470(8) Å) aurophilic interaction. Folded molecule **3** captures $CHCl_3$, preventing intramolecular face-to-face π-interactions between the tpy units. In CH_2Cl_2 solution, **1**–**3** are emissive when excited between 230 and 300 nm, but over minutes when λ_{ex} = 230 nm, the emission bands decay as the compounds photodegrade.

1. Introduction

Gold(I) alkynyl complexes [1,2] containing gold atoms in linear coordination environments are popular building blocks for polymeric and macrocyclic organometallic assemblies [3–12]. The luminescent properties of gold(I) species [13,14] and the ease of synthesis of gold(I) alkynyls make them attractive candidates for derivatization of other metal-binding domains such as pyridine [15–19], 2,2′-bipyridine (bpy) [16,20,21] and 2,2′:6′,2″-terpyridine (tpy) [21,22]. The combination of a luminescent gold(I) unit and a chelating ligand provides an approach to the design of metal ion sensors.

In gold(I) derivatives, aurophilic interactions (i.e. short Au···Au contact of around 3.00–3.20 Å) [23] are considered important in influencing their emissive behaviour [24–27]. Recently, we reported the solid-state structures of four bis(gold(I) phosphane)-decorated 4,4′-diethynyl-2,2′-bipyridines (Scheme 1) [20]. Changing the phosphane from PEt_3 to P^iPr_3 alters the packing, producing different polymeric chain motifs. In both, Au···Au contacts of less than 3.4 Å are observed. For the more sterically demanding PPh_3 and P(4-tolyl)$_3$ substituents, no short Au···Au contacts are present in the solid state. In CH_2Cl_2 solution, each compound (Scheme 1) is a dual emitter at room temperature. However, with $\lambda_{ex} \approx 238$ nm, the emission spectra decay quite rapidly at the expense of a new set of emission maxima, and we have proposed that this arises from cleavage of the Au–C_{alkyne} bond. We now turn our attention to tpy-based compounds in which the alkynyl substituent is directly attached to the 4′-position of the tpy domain. This is in contrast to previously reported systems in which the tpy and C≡C units are separated by an arene spacer [21,22].

2. Experimental

2.1. General procedures

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer with chemical shifts referenced to residual solvent peaks ($CHCl_3$ = δ 7.24 ppm, TMS = δ 0 ppm). ^{31}P NMR spectra were recorded using a Bruker DRX-400 NMR spectrometer and were referenced with respect to 85% H_3PO_4 = δ 0 ppm. Absorption spectra were recorded using a Varian-Cary 5000 spectrophotometer and emission spectra using a Shimadzu RF-5301 PC spectrofluorometer; excitation/emission slit widths were set at 3/3, 5/3, 3/3, and 5/5 for 4′-ethynyl-2,2′:6′,2″-terpyridine, **1**, **2** and **3**, respectively. Electrospray ionization (ESI) mass spectra were measured with a Bruker esquire 3000^{plus} mass spectrometer.

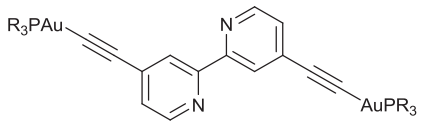
4′-Ethynyl-2,2′:6′,2″-terpyridine was prepared according to the literature procedure starting from 4′-[(trifluoromethylsulfonyl)oxy]-2,2′:6′,2″-terpyridine [28]. R_3PAuCl with R = Ph or 2-tolyl was prepared by a reported route [29] with a reaction temperature of −5 °C. Abbreviation: tht, tetrahydrothiophene.

2.2. {Au(4′-C≡Ctpy)}$_n$

The synthesis of {Au(4′-C≡Ctpy)}$_n$ was based on that described for {Au(4-C≡Cpy)}$_n$ [17]. 4′-Ethynyl-2,2′:6′,2″-terpyridine (50 mg,

* Corresponding author. Fax: +41 61 267 1018.
E-mail address: catherine.housecroft@unibas.ch (C.E. Housecroft).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.08.001



R = Et, ^{i}Pr, Ph, 4-tolyl

Scheme 1. Previously reported bis(gold(I) phosphane)-4,4′-diethynyl-2,2′-bipyridine compounds [20].

190 μmol), [(tht)AuCl] (63.5 mg, 190 μmol) and NaOAc (77.9 mg, 950 μmol) were added to a mixture of THF (5 cm^3) and MeOH (5 cm^3) under argon and with light excluded. The reaction mixture was stirred for 6–12 h after which time a pale yellow precipitate was obtained. This was collected by filtration and washed with MeOH. {Au(4′-C≡Ctpy)}$_n$ was isolated as yellow solid (72 mg, 159 μmol, ca. 82%) and was used without further purification.

2.3. Compound **1**

Ph_3PAuCl (38 mg, 78 μmol), 4′-ethynyl-2,2′:6′,2″-terpyridine (20 mg, 78 μmol), CuI (0.7 mg, 4 μmol) were dissolved in CH_2Cl_2 (8 cm^3) and MeOH (2 cm^3). NaOAc (13 mg, 156 μmol) was then added, and the reaction mixture stirred at room temperature in the dark for 12–16 h. It was then filtered and the solvent removed from the filtrate *in vacuo*. The crude material was purified by preparative plate chromatography in the dark (Al_2O_3, CH_2Cl_2). **1** was isolated as a white solid (39.3 mg, 55.3 μmol, 70.7%). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.66 (d, J = 4.0 Hz, 2H, H^{A6}), 8.54 (d, J = 8.1 Hz, 2H, H^{A3}), 8.52 (s, 2H, H^{B3}), 7.80 (td, J = 7.8, 1.7 Hz, 2H, H^{A4}), 7.54 (m, 6H, $H^{C2/C3}$), 7.49 (m, 3H, H^{C4}), 7.45 (m, 6H, $H^{C2/C3}$), 7.29 (m, 2H, H^{A5}). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ppm 156.5 (C^{A2}), 155.4 (C^{B2}), 149.4 (C^{A6}), 136.8 (C^{A4}), 135.3 (C^{B4}), 134.5 (d, J_{PC} = 14 Hz, $C^{C2/C3}$), 131.8 (d, J_{PC} = 2 Hz, C^{C4}), 129.6 (d, J_{PC} = 56 Hz, C^{C1}), 129.4 (d, J_{PC} = 11 Hz, $C^{C2/C3}$), 124.3 (C^{B3}), 123.7 (C^{A5}), 121.3 (C^{A3}), 102.3 (poorly resolved, *C*≡CAu), signal for C≡*C*Au not observed. ^{31}P NMR (162 MHz, $CDCl_3$) δ/ppm 42.4. UV–Vis λ_{max}/nm (CH_2Cl_2) 229 (ε/dm^3 mol^{-1} cm^{-1} 53 000), 244 (50 000), 277 (54 000), 289 (62 000), 319 (9000), 331 (6000). Emission (CH_2Cl_2, λ_{exc} = 244 nm) λ_{em}/nm 339, 355. ESI MS (CH_2Cl_2/MeOH) *m/z* 1174.4 $[M+AuPPh_3]^+$ (calc. 1174.2), 716.3 $[M+H]^+$ (base peak, calc. 716.2). *Anal.* Calc. for $C_{35}H_{25}AuN_3P$: C, 58.75; H, 3.52; N, 5.87. Found: C, 58.55; H, 3.72; N, 5.92%.

2.4. Compound **2**

The method was as for **1**, starting with (2-tolyl)$_3$PAuCl (42 mg, 78 μmol), 4′-ethynyl-2,2′:6′,2″-terpyridine (20 mg, 78 μmol), NaOAc (13 mg, 156 μmol) and CuI (0.7 mg, 4 μmol). Compound **2** was isolated as a white solid (36.2 mg, 47.8 μmol, 61.6%). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.68 (dd, J = 4.6, 0.8 Hz, 2H, H^{A6}), 8.53 (d, J = 7.9 Hz, 2H, H^{A3}), 8.48 (s, 2H, H^{B3}), 7.79 (td, J = 7.7, 1.8 Hz, 2H, H^{A4}), 7.44 (t, J = 7.5 Hz, 3H, H^{C4}), 7.36 (m, 3H, H^{C3}), 7.26 (ddd, J = 7.4, 4.8, 1.0 Hz, 2H, H^{A5}), 7.17 (t, J = 7.6 Hz, 3H, H^{C5}), 6.93 (dd, J_{PH} = 12.2 Hz, J_{HH} = 7.7 Hz, 3H, H^{C6}), 2.73 (s, 9H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ppm 156.3 (C^{A2}), 155.1 (C^{B2}), 151.1 (C^{A6}), 149.1 (d, J_{PC} = 13 Hz, C^{C2}), 136.6 (C^{A4}), 135.4 (C^{B4}), 133.6 (d, J_{PC} = 8 Hz, C^{C6}), 132.2 (d, J_{PC} = 9 Hz, C^{C3}), 131.6 (d, J_{PC} = 2 Hz, C^{C4}), 126.6 (d, J_{PC} = 9 Hz, C^{C5}), 126.2 (d, J_{PC} = 55 Hz, C^{C1}), 124.0 (C^{B3}), 123.5 (C^{A5}), 121.1 (C^{A3}), 102.4 (d, J_{PC} = 26.6 Hz, *C*≡CAu), 23.7 (d, J = 11 Hz, C^{Me}), signal for C≡*C*Au not observed. ^{31}P NMR (162 MHz, $CDCl_3$) δ/ppm 24.3. UV–Vis λ_{max}/nm (CH_2Cl_2), 251 (ε/dm^3 mol^{-1} cm^{-1} 53 000), 280 (59 000), 288 (64 000), 318 (9000), 332 (6000). Emission (CH_2Cl_2, λ_{exc} = 252 nm) λ_{em}/nm 341, 354. ESI MS (CH_2Cl_2/MeOH) *m/z* 1258.5 $[M+AuP(tolyl)_3]^+$ (calc. 1258.3), 805.2 $[Au\{P(tolyl)_3\}_2]^+$ (calc. 805.2), 758.4 $[M+H]^+$ (base peak, calc. 758.2). *Anal.* Calc. for $C_{38}H_{31}AuN_3P{\cdot}H_2O$: C, 58.84; H, 4.29; N, 5.42. Found: C, 59.14; H, 4.11; N, 5.38%.

2.5. Compound **3**

Bis(diphenylphosphinoethane) (dppe, 22 mg, 55 μmol) and {Au(4′-C≡Ctpy)}$_n$ (50 mg, 110 μmol) were stirred in CH_2Cl_2 (10 cm^3) for 30–60 min. After this time, the solvent was evaporated *in vacuo* and the crude product was purified in the dark by preparative plate chromatography (Al_2O_3, CH_2Cl_2). Compound **3** was isolated as white solid (31.2 mg, 23.9 μmol, 43.4%). ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm 8.68 (d, J = 4.6 Hz, 4H, H^{A6}), 8.56 (d, J = 8.0 Hz, 4H, H^{A3}), 8.55 (s, 4H, H^{B3}), 7.82 (td, J = 7.8, 1.5 Hz, 4H, H^{A4}), 7.72 (m, 8H, H^{C2}), 7.52 (overlapping m, 12H, $H^{C3/C4}$), 7.38 (m, 4H, H^{A5}), 2.69 (s, 4H, H^a). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ppm 156.2 (C^{A2}), 155.3 (C^{B2}), 149.2 (C^{A6}), 136.7 (C^{A4}), 135.0 (C^{B5}), 133.5 (C^{C2}), 132.3 (C^{C4}), 129.7 (t, J_{PC} = 6 Hz, C^{C3}), 124.0 (C^{B3}), 123.7 (C^{A5}), 121.2 (C^{A3}), 102.0 (poorly resolved, *C*≡CAu), 24.0 (J_{PC} = 17 Hz, C^a), signals for C^{C1} and C≡*C*Au not observed. ^{31}P NMR (162 MHz, $CDCl_3$) δ/ppm 40.6. UV–Vis λ_{max}/nm (CH_2Cl_2) 230 (ε/dm^3 mol^{-1} cm^{-1} 122 000), 239 (11 6000), 254 (100 000), 277 (136 000), 289 (156 000), 319 (26 000), 332 (19 000). Emission (CH_2Cl_2, λ_{exc} = 241 nm) λ_{em}/nm 341, 355. ESI MS (CH_2Cl_2) *m/z* 1305.8 $[M+H]^+$ (calc. 1305.3), 1048.6 $[Au(dppe)AuCCtpy]^+$ (calc. 1048.2), 993.7 $[(dppe)_2Au]^+$ (calc. 993.2). *Anal.* Calc. for $C_{60}H_{44}Au_2N_6P_2{\cdot}2H_2O$: C, 53.74; H, 3.61; N, 6.27. Found: C, 53.76; H, 3.41; N, 6.00.

2.6. Crystal structure determinations

Data were collected on a Stoe IPDS diffractometer and the data reduction, solution and refinement used Stoe IPDS software [30] and SHELXL97 [31]. ORTEP figures were drawn using Ortep-3 for Windows [32], and the structures were analysed using Mercury v. 2.4 [33,34].

2.7. Compound **1**

$C_{35}H_{25}AuN_3P$, M = 715.52, colourless plate, monoclinic, space group $P2_1/c$, a = 19.658(4), b = 8.3726(17), c = 17.853(4) Å, β = 105.39(3)°, U = 2833.0(10) Å^3, Z = 4, D_{calc} = 1.678 Mg m^{-3}, μ(Mo Kα) = 5.279 mm^{-1}, T = 173 K. Total 44 788 reflections, 5835 unique, R_{int} = 0.0979. Refinement of 5641 reflections (361 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0426 (R_1 all data = 0.0435), wR_2 = 0.1087 (wR_2 all data = 0.1098), Goodness-of-fit = 1.144.

2.8. Compound **2**

$C_{38}H_{31}AuN_3P$, M = 757.60, colourless plate, triclinic, space group $P\bar{1}$, a = 9.2574(9), b = 17.6618(19), c = 19.504(2) Å, α = 107.172(8)°, β = 96.023(8)°, γ = 91.372(8)°, U = 3024.9(5) Å^3, Z = 4, D_{calc} = 1.664 Mg m^{-3}, μ(Mo Kα) = 4.949 mm^{-1}, T = 173 K. Total 67 142 reflections, 12 533 unique, R_{int} = 0.1018. Refinement of 11 198 reflections (782 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0491 (R_1 all data = 0.0537), wR_2 = 0.1379 (wR_2 all data = 0.1417), Goodness-of-fit = 1.182.

2.9. Compound 2(**3**)·$CHCl_3$

$C_{121}H_{89}Au_4Cl_3N_{12}P_4$, M = 2729.16, colourless needle, monoclinic, space group Pc, a = 10.389(2), b = 17.482(4), c = 15.652(3) Å, β = 98.53(3)°, U = 2811.2(10) Å^3, Z = 1, D_{calc} = 1.612 Mg m^{-3}, μ (Mo Kα) = 5.384 mm^{-1}, T = 173 K. Total 49 946 reflections, 10 592 unique, R_{int} = 0.1933. Refinement of 9643 reflections (669 parameters) with $I > 2\sigma(I)$ converged at final R_1 = 0.0625 (R_1 all