Synthesis and characterization of mono and heteropolynuclear luminescent alkynyl platinum diphenylphosphinous acid/phosphinite complexes

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Dedicated in honor of Professor R. Usón

Abstract

The novel anionic mononuclear *cis*-bis(alkynyl) platinum complexes with a chelated diphenylphosphinous acid/diphenylphosphinite (NBu$_4$)[*cis*-Pt(C≡CR)$_2${(PPh$_2$O)$_2$H}] (R = Bu^t **1a**, Ph **1b**) have been prepared by treatment of [*cis*-Pt(C≡CR)$_2$COD] with PPh$_2$(O)H and (NBu$_4$)(acac) in a 1:2:1 molar ratio. The molecular structure of **1a** has been determined by single-crystal X-ray diffraction. Neutralization reactions of complexes **1** with 1 equiv. of AgClO$_4$ or CuTfO (TfO = triflate) produce tetranuclear dimetallic complexes [*cis*-Pt{(PPh$_2$O)$_2$H}(μ-κC^α:η^2-C≡CR)$_2$M]$_2$ (M = Ag, **2a**, **2b**; M = Cu **3a**, **3b**), in which each anionic fragment {Pt}(C≡CR)$_2^-$ ({Pt} = Pt{(PPh$_2$O)$_2$H}) acts as a μ-η^2:η^2 bridging ligand towards two different silver(I) or copper(I) centres. Finally, the reactions of (NBu$_4$){Pt}(C≡CR)$_2$ **1** with [CuCl]$_n$ produce heterodinuclear platinum(II)–copper(I) complexes (NBu$_4$)[*cis*-Pt{(PPh$_2$O)$_2$H}(μ-κC^α:η^2-C≡CR)$_2$CuCl] (**4a**, **4b**), in which both alkyne units are η^2-coordinated side-on to the copper(I) chloride. All complexes are emissive in frozen CH$_2$Cl$_2$ solutions.
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1. Introduction

σ-Alkynyl complexes of platinum have been the object of continuous interest over the last few years not only for their structural aspect and reactivity [1] but also for their role as building blocks for molecular materials with interesting properties, derived from the presence of delocalized π systems [2]. Although many representative examples with alkyl or aryl phosphines are known [3], similar compounds with phosphinite and related coligands are uncommon [4] in spite of the fact that diphenylphosphinous acid [PPh$_2$(O)H] and its anion phosphinite [PPh$_2$(O)$^-$] have been largely used

as ligands for transition metal complexes [5]. In the coordination chemistry of these ditopic ligands (soft P and hard O donors) particular attention has been paid to complexes containing the strong chelating mixed system R$_2$P(O)···H–OPR$_2$ (easily formed by strong intramolecular hydrogen bonds when both ligands are in a *cis*-disposition about a metal centre) [5a,h,6] since they are important reagents in catalytic processes such as hydrogenation or hydroformylation of alkenes [7] and hydrophosphinylation or hydrophosphorylation of alkynes [8].

Along these lines, we recently reported the first examples of mononuclear monoalkynyl complexes containing both PPh$_2$(O)H and phosphinite ligands [4]. Thus, complexes of stoichiometry [Pt(C≡CR){(PPh$_2$O)$_2$H}(PPh$_2$OH)] (R = Bu^t, Ph), stabilized by the chelated mixed phosphinite/hydroxyphosphine mixed system Ph$_2$P(O)···H–OPPh$_2$, were easily formed

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by treatment of [*cis*-Pt(C≡CR)$_2$COD] with 2 or 3 equiv. of PPh$_2$(O)H; related neutral [Pt(C≡CR){(PPh$_2$O)$_2$H}L] (L = PEt$_3$, PPh$_2$H, CNBu^t) or anionic [Pt(C≡CR)(CN){(PPh$_2$O)$_2$H}]$^-$ derivatives were also generated through simple PPh$_2$OH substitution reactions. We have also shown that these monoalkynyl complexes [Pt(C≡CR){(PPh$_2$O)$_2$H}(PPh$_2$OH)] are good precursors for the preparation of unusual hexanuclear Pt$_2$Li$_4$ sandwiched [{Pt(C≡CR)(PPh$_2$O)$_3$Li$_2$(H$_2$O)(THF)}$_2$] [4,9] and platinum–rhodium or iridium heterobridged (μ-C≡CR)(μ-PPh$_2$O) [{(PPh$_2$O)$_2$H}Pt(μ-κC^α:η^2-C≡CR)(μ-κP:κO-PPh$_2$O)ML$_2$] (ML$_2$ = Rh/Ir(COD), Rh(CO)$_2$) [10] complexes, obtained by deprotonation with lithium hydroxide or with the acetylacetonate species [M(acac)L$_2$], respectively.

In this paper we describe the preparation and characterization of novel anionic mononuclear *cis*-bis(alkynyl)platinum complexes containing the chelating system diphenylphosphinous acid/phosphinite (NBu$_4$)[*cis*-Pt(C≡CR)$_2${(PPh$_2$O)$_2$H}] (R = Bu^t **1a**, Ph **1b**). These complexes increase the small family of anionic mononuclear alkynyl platinum complexes [11]. Likewise, the *cis*-bis(alkynyl) disposition of the ligands and, particularly their anionic nature, facilitates the synthesis of multimetallic complexes in which a metal or metal fragment 'L$_n$M' is assembled through η^2-alkyne or M···M bonding interactions [1c,e,g,11a,c–e,12–14]. This method of forming multimetallic assemblies has been recently employed by us [11c–e,12,13] and others [1c,g,11a,14], and is exemplified by reactions of the anionic [*cis*-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$]$^{2-}$ and [Pt(C≡CR)$_4$]$^{2-}$ derivatives with d^{10} [MX (M = Cu, Ag; X = Cl, Br) [12a,b], AgClO$_4$ [11c,12a,c], HgX$_2$ (X = Cl, Br, I) [12d], CdCl$_2$ [12e], Cd(ClO$_4$)$_2$ [2o]], d^7 (CoCl$_2$) [12f], d^8 ([Pd(η^3-C$_3$H$_5$)$^+$ [12g,h], Rh(COD)$^+$ [12i,j]) or d^{10}s^2 (TlNO$_3$) [12k] metal species. The use of these alkynyl platinate species as mono or double alkynylating reagents towards the cationic Ir(COD)$^+$ [12j,13a], MCp*(PEt$_3$)$^{2+}$ (M = Rh, Ir) [13b,c] or even the neutral Pt(C$_6$F$_5$)$_2$ species [11d,e] has been also reported. These reactions have allowed us to isolate a variety of multimetallic compounds, some of which show interesting luminescent properties [2o,q,12e,k].

Here we also present the synthesis of novel heterotetrametallic {Pt}$_2$(C≡CR)$_4$M$_2$ (M = Ag, Cu) and bimetallic {Pt}(C≡CR)$_2$CuCl derivatives, obtained by reacting the mononuclear tweezer compounds (NBu$_4$){Pt}(C≡CR)$_2$ with AgClO$_4$, CuTfO or CuCl, and the luminescent properties of all complexes.

2. Experimental

All reactions and manipulations were carried out under nitrogen atmosphere using Schlenk techniques and with distilled solvents purified by known proce-

dures. IR spectra were recorded on a Perkin–Elmer FT-IR 1000 Spectrometer from Nujol mulls between polyethylene sheets unless otherwise noted. NMR spectra were recorded on a Bruker ARX 300 spectrometer, and chemical shifts are reported in ppm relative to external standards (SiMe$_4$, and 85% H$_3$PO$_4$). Elemental analyses were carried out with a Perkin–Elmer 2400 CHNS/O microanalyser; the electrospray mass spectra on a HP5989B with interphase API-ES HP 59987A (in the negative ion mode with methanol as the mobile phase), and the FAB mass spectra on a VG Autospec spectrometer. Conductivities of acetone solutions in ca. 5 × 10^{-4} mol l^{-3} solutions were measured with a Crison GLP 31 conductimeter. Luminescence as well as excitation spectra were recorded on a Perkin Elmer luminescence spectrometer (LS 50B). The starting complexes [*cis*-Pt(C≡CR)$_2$COD] (R = Ph [15], Bu^t [11d]) were prepared following literature methods. All other reagents were used as obtained commercially. Caution: some of the following preparations use AgClO$_4$, which is potentially explosive.

2.1. Synthesis of complexes

2.1.1. Synthesis of (NBu$_4$)[cis-Pt(C≡CR)$_2${(PPh$_2$O)$_2$H}] (R = Bu^t 1a, Ph 1b)

A solution of NBu$_4$Br (0.383 g, 1.187 mmol) in CH$_2$Cl$_2$ (40 ml) was treated with Tlacac (0.360 g, 1.187 mmol) and the mixture was stirred for 6 h at room temperature (r.t.), and then filtered through Kieselgurh. The resulting solution, which contains (NBu$_4$)(acac), was cooled (−20 °C) and treated with PPh$_2$(O)H (0.480 g, 2.374 mmol) and [Pt(C≡CBu^t)$_2$(COD)] (0.553 g, 1.187 mmol). The solvent was then evaporated to a small volume (2 ml) and treated with diethyl-ether (10 ml) to give **1a** as a white solid (0.847 g, 71% yield).

Complex **1b** was prepared similarly starting from NBu$_4$Br (0.128 g, 0.396 mmol), Tlacac (0.120 g, 0.396 mmol), PPh$_2$(O)H (0.160 g, 0.791 mmol) and [Pt(C≡CPh)$_2$(COD)] (0.200 g, 0.396 mmol), (0.241, 58% yield).

1a: *Anal.* Found: C, 62.10; H, 7.61; N, 1.32. Calc. for C$_{52}$H$_{75}$NO$_2$P$_2$Pt: C, 62.26; H, 7.54; N, 1.40%. IR (cm^{-1}) KBr: ν(C≡C) not observed, ν(P–O) 1103 (vs), 1029 (m), 1001 (sh), 983 (s). Λ_M: 97 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CDCl$_3$): δ 17.2 (br, O···H···O), 8.07 (m, 8H), 7.22 (m, 12H) Ph, 2.84 (m, 8H, NCH$_2$–, Bu^n), 1.21 (m, 16H, –CH$_2$–, Bu^n), 0.99 (s, 18H, Bu^t), 0.87 (t, 12H, –CH$_3$, Bu^n). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 72.31 (s, ^1J(P–Pt) = 2563 Hz). MS, Es (−): m/z 881 ([Pt(C≡CBu^t){(PPh$_2$O)$_2$H}(PPh$_2$OH)]$^-$, 20%), 760 ([M]$^-$ 100%). Its low solubility precluded its characterization by ^{13}C NMR spectroscopy.

1b: *Anal.* Found: C, 64.13; H, 6.28; N, 1.36. Calc. for C$_{56}$H$_{67}$NO$_2$P$_2$Pt: C, 64.48; H, 6.47; N, 1.34%. IR (cm^{-1}): ν(C≡C) 2102 (m), ν(P–O) 1101 (s), 1026 (m), 1003 (m), 989 (m). Λ_M: 104 ohm^{-1} cm^2 mol^{-1}. ^{1}H

NMR (CDCl$_3$): δ 16.7 (br, O$\cdots$H$\cdots$O), 8.00 (s, 8H), 7.23 (s, br,12H) 7.00 (m, 10H) Ph, 2.82 (m, 8H, NCH$_2$–, Bu^n), 0.99 (m, 16H, –CH$_2$–, Bu^n), 0.69 (t, 12H, –CH$_3$, Bu^n). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 70.04 (s, ^1J(P–Pt) = 2561 Hz). MS, apci (−): m/z 1043 ([M+NBu$_4$]$^-$ 3%), 900 ([Pt(C$\equiv$CPh){(PPh$_2$O)$_2$H}(PPh$_2$OH)−H]$^-$, 13%), 800 ([M]$^-$ 30%), 698 ([M − C$\equiv$CPh]$^-$ 57%), 598 ([Pt(PPh$_2$O)$_2$H]$^-$, 100%). Its low solubility precluded its characterization by ^{13}C NMR spectroscopy.

2.1.2. Synthesis of [cis-Pt{(PPh$_2$O)$_2$H}(μ-κC$^\alpha$:η^2-C≡CR)$_2$Ag]$_2$ (R = Bu^t 2a, Ph 2b)

To a solution of (NBu$_4$)[cis-Pt(C$\equiv$CBu^t)$_2${(PPh$_2$O)$_2$H}] **1a** (0.152 g, 0.151 mmol) in CH$_2$Cl$_2$ (40 ml), was added a solution of AgClO$_4$ (0.031 g, 0.151 mmol) in acetone (10 ml). The mixture, protected from the light, was stirred at r.t. for 24 h, and then filtered through Kieselgurh and evaporated to dryness. The residue was treated with diethyl-ether (70 ml) and the white precipitate (NBu$_4$ClO$_4$) was filtered off. The resulting pale-yellow solution was evaporated to dryness and treated with n-hexane causing the precipitation of **2a** as a white solid (0.060 g, 46% yield).

Complex **2b** was prepared as a yellow solid following a similar procedure. 0.021 g (0.101 mmol) of AgClO$_4$ and 0.106 g (0.101 mmol) of **1b**; (0.021 g, 23% yield).

2a: *Anal.* Found: C, 49.36; H, 4.91. Calc. for Ag$_2$C$_{72}$H$_{78}$O$_4$P$_4$Pt$_2$: C, 49.78; H, 4.53%. IR (cm^{-1}): v(C$\equiv$C) 2027 (m), v(P–O) 1107 (s), 1029 (m), 1010 (s), 996 (m). Λ_M: 20 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.69 (m, 16H), 7.21 (m, 24H) Ph, 0.95 (s, 36H, Bu^t); at −40 °C, a broad signal at 16.7 is seen (O$\cdots$H$\cdots$O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 60.19 (s, ^1J(P–Pt) = 2842 Hz). MS, FAB (+): m/z 1657 ([M−C$\equiv$CBu^t+H]$^+$ 5%), 1465 ([M−2 C$\equiv$CBu^t−Ag−2H]$^+$ 50%), 905 ([Pt{(PPh$_2$O)$_2$H}(PPh$_2$Oag)] 25%), 599 ([Pt{(PPh$_2$O)$_2$-H}+H]$^-$, 37%).

2b: *Anal.* Found: C, 52.32; H, 3.43. Calc. for Ag$_2$C$_{80}$H$_{62}$O$_4$P$_4$Pt$_2$: C, 52.88; H, 3.44%. IR (cm^{-1}) KBr: v(C$\equiv$C) is not obseved, v(P–O) 1107 (m), 1028 (w), 1011 (w). Λ_M: 16 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.65 (m, 16H), 7.21 (m, 4H), 7.10 (m, 32H), 6.80 (d, J(H–H) = 7.6 Hz, 8H) Ph; at −40 °C, a broad signal at 17.0 is seen (O$\cdots$H$\cdots$O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 63.37 (s, ^1J(P–Pt) = 2786 Hz). MS, FAB (+): m/z 1923 ([M+Ag−2H]$^+$ 7%), 1817 ([M]$^+$ 16%), 1614 ([M−PPh$_2$OH−H]$^+$ 45%), 1512 ([Pt$_2$(PPh$_2$O)$_3$-(C$\equiv$CPh)$_3$Ag$_2$]$^+$ 11%), 1411 ([Pt$_2$(PPh$_2$O)$_3$(C$\equiv$CPh)$_2$Ag$_2$]$^+$ 20%), 915 ([Pt(PPh$_2$O)$_2$(C$\equiv$CPh)Ag$_2$]$^+$ 55%).

2.1.3. Synthesis of [cis-Pt{(PPh$_2$O)$_2$H}(μ-κC$^\alpha$:η^2-C≡CBu^t)$_2$Cu]$_2$ (3a)

To a pale-yellow solution of (NBu$_4$)[cis-Pt(C$\equiv$CBu^t)$_2${(PPh$_2$O)$_2$H}] **1a** (0.100 g, 0.100 mmol) in CH$_2$Cl$_2$ (40 ml), was added a solution of CuTfO

(0.0193 g, 0.100 mmol) in acetone (10 ml). The mixture was stirred at r.t. for 1 h, and then evaporated to dryness. The residue was treated with diethyl-ether (50 ml) and the white precipitate (NBu$_4$TfO) was filtered off. The resulting pale-yellow solution was evaporated to dryness and treated with n-hexane affording **3a** as a yellow solid (0.04 g, 49% yield).

3a: *Anal.* Found: C, 53.04; H, 4.53. Calc. for C$_{72}$Cu$_2$H$_{78}$O$_4$P$_4$Pt$_2$: C, 52.46; H, 4.77%. IR (cm^{-1}): v(C$\equiv$C) is not observed, v(P–O) 1107 (s), 1029 (m), 1014 (s), 997 (m). Λ_M: 31 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CDCl$_3$): δ 17.01 (br, O$\cdots$H$\cdots$O), 7.78 (s, br, 16H), 7.08 (m, 24H) Ph, 0.83 (s, 36H, Bu^t). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 67.93 (s, ^1J(P–Pt) = 2813 Hz). MS, FAB (+): m/z 1366 ([Pt$_2${(PPh$_2$O)$_2$H}(PPh$_2$OH)(C$\equiv$CBu^t)$_3$Cu$_2$]$^+$ 15%), 805 ([Pt(PPh$_2$O)$_2$(C$\equiv$CBu^t)Cu$_2$]$^+$ 68%), 603 ([Pt(PPh$_2$O)(C$\equiv$CBu^t)Cu$_2$−H]$^+$ 70%).

2.1.4. Synthesis of [cis-Pt{(PPh$_2$O)$_2$H}(μ-κC$^\alpha$:η^2-C≡CPh)$_2$Cu]$_2$ (3b)

To a pale-yellow solution of (NBu$_4$)[cis-Pt(C$\equiv$CPh)$_2${(PPh$_2$O)$_2$H}] (**1b**) (0.120 g, 0.115 mmol) in CH$_2$Cl$_2$ (40 ml), was added a solution of CuTfO (0.022 g, 0.115 mmol) in acetone (10 ml). The yellow solution was stirred at r.t. for 1 h, the solvent was evaporated to dryness and ethanol (10 ml) was added to afford **3b** as a yellow solid (0.060 g, 61% yield).

3b: *Anal.* Found: C, 55.03; H, 3.96. Calc. for C$_{80}$Cu$_2$H$_{62}$O$_4$P$_4$Pt$_2$: C, 55.56; H, 3.61%. IR (cm^{-1}): v(C$\equiv$C) 2019 (w), v(P–O) 1108 (s), 1028 (m), 998 (m, br). Λ_M: 30 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.86–6.38 (60H, Ph); at −40 °C, a broad signal at 16.5 is seen (O$\cdots$H$\cdots$O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 64.94 (s, ^1J(P–Pt) = 2818 Hz). MS (es+): m/z 903 ([Pt{(PPh$_2$O)$_2$H}(PPh$_2$OH)(C$\equiv$CPh)+H]$^+$ 100%).

2.1.5. Synthesis of (NBu$_4$)[cis-Pt{(PPh$_2$O)$_2$H}(μ-κC$^\alpha$-C≡CBu^t)$_2$CuCl] (4a)

[CuCl]$_n$ (0.012 g, 0.125 mmol) was added to a suspension of **1a** (0.125g, 0.125 mmol) in 40 ml of acetone. After stirring for 4 h, the mixture was filtered through Kieselgurh and the solvent was evaporated to a small volume (2 ml). Diethyl-ether (15 ml) was added to precipitate a pale-green solid, which was identified as a mixture of **3a** and **4a** ($\sim$0.75:0.25). Recrystallization from CHCl$_3$/Isopropyl-ether afforded **4a** as a white solid. (0.063 g, 46% yield).

4a: *Anal.* Found: C, 56.44; H, 6.56; N 1.29. Calc. for C$_{52}$ClCuH$_{75}$NO$_2$P$_2$Pt: C, 56.67; H, 6.86; N, 1.27%. IR (cm^{-1}): v(C$\equiv$C) 2020 (w), v(P–O) 1100 (s), 1030 (sh), 1012 (s), 997 (m). Λ_M: 92 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 17.4 (br, O$\cdots$H$\cdots$O), 7.96 (s, br, 8H), 7.33 (m, 12H) Ph, 3.43 (m, 8H, NCH$_2$–, Bu^n), 1.81 (m, 8H, –CH$_2$–, Bu^n), 1.42 (m, 8H, –CH$_2$–, Bu^n), 1.12 (s, 18H, Bu^t), 0.98 (t, 12H, –CH$_3$, Bu^n). ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$): δ 66.11 (s, ^1J(P–Pt) = 2824 Hz). MS,

FAB ($-$): m/z 956 ($[Pt(PPh_2O)_2(C\equiv CBu^t)_2(CuCl)_2-$ 2H]$^-$, 16%), 859 ($[M]^-$, 55%), 777 ($[M-C\equiv CBu^t-$ H]$^-$, 28%).

2.1.6. Synthesis of $(NBu_4)[cis$-$Pt\{(PPh_2O)_2H\}(\mu$-$\kappa C^\alpha:\eta^2$-$C\equiv CPh)_2CuCl]$ (4b)

$[CuCl]_n$ (0.010 g, 0.096 mmol) was added to a suspension of **1b** (0.100 g, 0.096 mmol) in 40 ml of acetone. The reaction was stirred for 24 h, and filtered through Kieselgurh. Concentration of the yellow solution obtained to a small volume (~ 2 ml) and addition of diethyl-ether (10 ml) led to the precipitation of **4b** as a pale yellow solid (0.047 g, 43% yield).

4b: *Anal.* Found: C, 58.64; H, 5.82; N 1.20. Calc. for $C_{56}ClCuH_{67}NO_2P_2Pt$: C, 58.89; H, 5.91; N 1.23%. IR (cm^{-1}): $v(C\equiv C)$ 2020 (w), $v(P-O)$ 1090 (s,br), 1018 (s,br). Λ_M: 106 ohm^{-1} cm^2 mol^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.87 (s, 8H), 7.27 (m, 14H), 7.06 (s, 8H) Ph, 2.98 (m, 8H, NCH$_2-$, Bu^n), 1.38 (m, 8H, $-$CH$_2-$, Bu^n), 1.27 (m, 8H, $-$CH$_2-$, Bu^n), 0.86 (t, 12H, $-$CH$_3$, Bu^n); at -40 °C, a broad signal at 17.0 is seen (O$\cdots$H$\cdots$O). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 66.59 (s, ^1J(P$-$Pt) = 2852 Hz). MS, Es ($-$): m/z 899 ($[M]^-$, 100%), 797 ($[M-C\equiv CPh-H]^-$, 42%).

2.2. Crystal structure determination of 1a

Crystals of **1a** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a tetrahydrofuran solution of **1a** at -30 °C. Relevant crystal

Table 1
Crystal data and structure refinement for (NBu$_4$)[cis-Pt(C≡CBu^t)$_2$\{(PPh$_2$O)$_2$H\}] **1a**·0.5 thf

Complex	**1a**
Empirical formula	$C_{54}H_{78}NO_{2.50}P_2Pt$
Formula weight	1038.20
Temperature (K)	293(2)
Crystal system	triclinic
Space group	$P\bar{1}$
Crystal size (mm^3)	$0.7 \times 0.2 \times 0.1$
Unit cell dimensions	
a (Å)	11.0968(2)
b (Å)	14.3059(3)
c (Å)	19.7781(4)
α (°)	87.2352(11)
β (°)	76.4810(11)
γ (°)	70.0961(9)
V (Å^3)	2868.73(10)
Z	2
D_{calc} (Mg m^{-3})	1.202
Absorption coefficient (mm^{-1})	2.537
$F(000)$	1074
θ Range for data collection (°)	5.10–25.35
No. of data/restrains/parameters	10396/0/578
Goodness-of-fit on F^2	1.011
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0478$, $wR_2 = 0.1050$
R indices (all data)	$R_1 = 0.0774$, $wR_2 = 0.1187$
Largest difference peak and hole (e A^{-3})	0.824 and -0.686

data and data collection parameters are listed in Table 1. The diffraction measurements were made on a Nonius kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation. An empirical absorption correction was applied using SCALEPACK [16]. All calculations were carried out using the SHELXL-97 program [17]. The structure was solved by direct methods and refined on F^2. All non-hydrogen atoms were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. All hydrogen atoms (except the hydrogen of the O$\cdots$H$\cdots$O system) were constrained to idealized geometries with isotropic displacement parameters equal to 1.2 or 1.5 times the U_{iso} value of their attached carbon.

3. Results and discussion

3.1. Anionic platinum alkynyl complexes

The reaction of [cis-Pt(C≡CR)$_2$COD] with diphenylphosphine oxide PPh$_2$(O)H (1:2 molar ratio) at low temperature (-20 °C) in the presence of 1 equiv. of (NBu$_4$)(acac), prepared 'in situ', leads to the formation of anionic mononuclear alkynyl platinum complexes (NBu$_4$)[cis-Pt(C≡CR)$_2$\{(PPh$_2$O)$_2$H\}] (R = Bu^t **1a**, Ph **1b**), which can be isolated as pure white materials in 71% (**1a**) or 58% (**1b**) yield (Eq. (1)).

$$R = Bu^t\ \textbf{1a};\ Ph\ \textbf{1b}$$

$$(1)$$
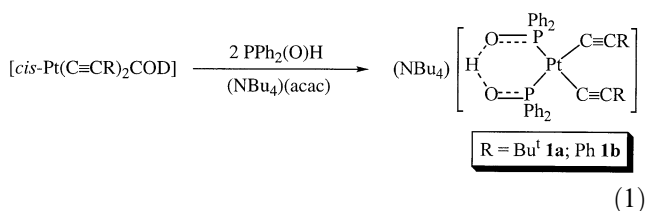
The formulation given agrees with their analytical and spectroscopic data (IR, NMR) and has been confirmed by a single-crystal X-ray diffraction study on complex **1a**. Both compounds behave as 1:1 electrolytes in acetone solutions and the molecular peaks of the anions [Pt(C≡CR)$_2$\{(PPh$_2$O)$_2$H\}]$^-$ (m/z 760 **1a**, 800 **1b**) were detected in their mass spectra (ESI$^-$). Their IR spectra shows absorptions in the P–O stretching region (range 1103–983 cm^{-1}), and the lack of bands due to v(O–H) in the usual spectral region is consistent with the presence of symmetrical hydrogen bond formation, as had been previously noted [4,6,10,18]. The presence of alkynyl terminal groups is only observed in the IR spectrum of **1b** (2102 cm^{-1}), but the proton spectrum of the *tert*-butylderivative **1a** exhibits the expected singlet due to the C≡CBu^t with the appropriate integration ratio. Furthermore, in their ^{1}H NMR spectra both complexes show, in addition to Ph and NBu$_4^+$ signals, a broad downfield resonance (δ 17.2 **1a**, 17.0 **1b**) confirming the presence of strong O$\cdots$H$\cdots$O hydrogen

bonds [4,6c,d,19]. Their $^{31}P\{^1H\}$ NMR spectra show one singlet resonance (δ 72.31 **1a**, 70.04 **1b**) and the value of the coupling to ^{195}Pt [^1J(Pt–P) 2563 **1a**, 2561 Hz **1b**] is higher than those observed in the neutral alkynyl platinum derivatives [*cis*-Pt(C≡CR)$_2$L$_2$] with phosphine ligands *trans* to the C≡CR groups [4,11d,15,20]. Unfortunately, the very low solubility of complexes **1a** and **1b** precluded their characterization by $^{13}C\{^1H\}$ NMR spectroscopy.

An X-ray diffraction study (Fig. 1, Table 2) confirms that **1a** is a square planar Pt(II) complex formed by two mutually *cis*-alkynyl groups and a chelated diphenyl-phophinous acid/diphenylphosphinite ligand. Both Pt–P bond lengths are identical within experimental error [Pt(1)–P(1) 2.2827(15), Pt(1)–P(2) 2.2800(15) Å], and comparable to those found in related compounds containing the chelated PPh$_2$OHOPPh$_2$ ligand [7b,c,8a]. The C–C alkynyl bond distances [C(1)–C(2) 1.205(8), C(7)–C(8) 1.171(8) Å] and the bend back angles at C$_\alpha$ [C(2)–C(1)–Pt(1) 171.6(5)°, C(8)–C(7)–Pt(1) 172.7(6)°] and at C$_\beta$ [C(1)–C(2)–C(3) 174.3(7)°, C(7)–C(8)–C(9) 173.2(8)°] are those expected for terminal alkynyl ligands [1d]. The pseudo-five membered (Pt–POOP) ring is nearly planar, as indicated by the following torsion angles: Pt(1)–P(2)–O(2)···O(1) 5.4°; P(2)–O(2)···O(1)–P(1) 2.6°; O(1)–P(1)–Pt(1)–P(2) 3.9°; P(1)–Pt(1)–P(2)–O(2) 5.9°. The O(1)···O(2) distance (2.385 Å), is shorter than the sum of the van der Waals radii, indicating a strong hydrogen bonding [6d,f,g,j,7,8a]. Although the hydrogen atom of the O–H–O system can not be located in the structure refinement, the system seems to be rather symmetric, as it is mirrored by the symmetry observed in P–O distances [P(1)–O(1) 1.576(4), P(2)–O(2) 1.573(4) Å],
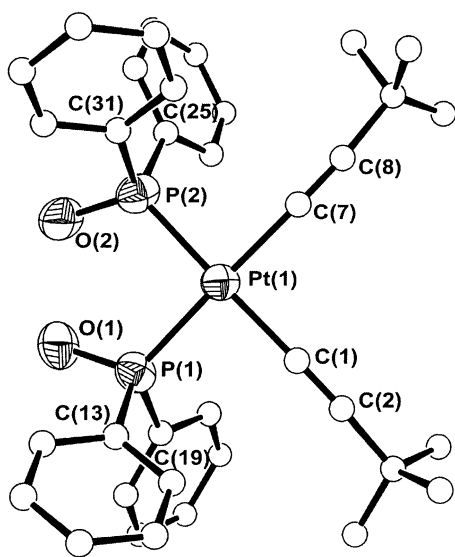
Table 2
Selected bond lengths (Å) and bond angles (°) for (NBu$_4$)[*cis*-Pt(C≡CBu^t)$_2${(PPh$_2$O)$_2$H}] **1a**·0.5 thf

Bond lengths

Pt(1)–C(1)	2.020(6)	P(1)–O(1)	1.576(4)
Pt(1)–C(7)	2.030(6)	P(2)–O(2)	1.573(4)
Pt(1)–P(1)	2.2827(15)	C(1)–C(2)	1.205(8)
Pt(1)–P(2)	2.2800(15)	C(7)–C(8)	1.171(8)

Bond angles

C(1)–Pt(1)–C(7)	90.2(2)	O(2)–P(2)–Pt(1)	115.78(18)
C(7)–Pt(1)–P(2)	87.80(16)	C(2)–C(1)–Pt(1)	171.6(5)
C(1)–Pt(1)–P(1)	88.35(15)	C(1)–C(2)–C(3)	174.3(7)
P(2)–Pt(1)–P(1)	93.53(6)	C(8)–C(7)–Pt(1)	172.7(6)
O(1)–P(1)–Pt(1)	115.65(18)	C(7)–C(8)–C(9)	173.2(8)

which have values between those reported for single and double P–O bonds [21] and comparable to those observed in other complexes chelated by a PPh$_2$PO–H–OPPh$_2$ ligand [5h,6d,f,g,7b,c,8a].

3.2. Heteropolynuclear $\{Pt\}_2M_2$ (M = Ag, Cu) and $\{Pt\}CuCl$ complexes

As commented in the introduction, we have previously described the capability of *cis*-bis(alkynyl)mononuclear platinum species to attach Ag(I) or Cu(I) via η^2-coordination [11c,12a–c,22]. For comparative purposes, we have now studied the reactivity of the mononuclear *cis*-bis(alkynyl) complexes (NBu$_4$)[*cis*-Pt(C≡CR)$_2${(PPh$_2$O)$_2$H}] **1** towards AgClO$_4$, CuTfO and CuCl to generate systems of higher nuclearity.

As is shown in Scheme 1(i), treatment of a CH$_2$Cl$_2$ solution of (NBu$_4$)[*cis*-Pt(C≡CR)$_2${(PPh$_2$O)$_2$H}] (R = Bu^t **1a**, Ph **1b**) with 1 equiv of AgClO$_4$ or CuTfO in acetone results in the formation of white (**2a**) or yellow (**2b**, **3a**, **3b**) solids in moderate or low yield. The tetrametallic formulation for these complexes [*cis*-Pt{(PPh$_2$O)$_2$H}(μ-κC$^\alpha$:η^2-C≡CR)$_2$M]$_2$ (M = Ag, R = Bu^t **2a**, Ph **2b**; M = Cu **3a**, **3b**) was established from their mass spectra (see Section 2 for details) and from a preliminary X-ray crystallographic study on crystals obtained by slow diffusion of *n*-hexane at −30 °C into a saturated solution of **2b** in CH$_2$Cl$_2$. The poor quality of all crystals studied precluded a good characterization by X-ray diffraction, and only the connectivity and the M–M distances are given in this paper. A schematic representation of the structure is given in Fig. 2. The data confirms that two monoanionic square-planar entities [Pt(C≡CPh)$_2${(PPh$_2$O)$_2$H}]$^-$ are connected by two bridging Ag(I) ions through η^2-Ag-alkynyl linkages (Fig. 2). As a whole, the structure of **2b** has some resemblance to that previously found for the tetranuclear dianionic species [Pt$_2$Ag$_2$(C$_6$F$_5$)$_4$(C≡CPh)$_4$]$^{2-}$ [12a]. However, while in the tetranuclear anion both platinum fragments were parallel and disposed in an *anti* fashion, in this platinum–silver complex **2b**, both
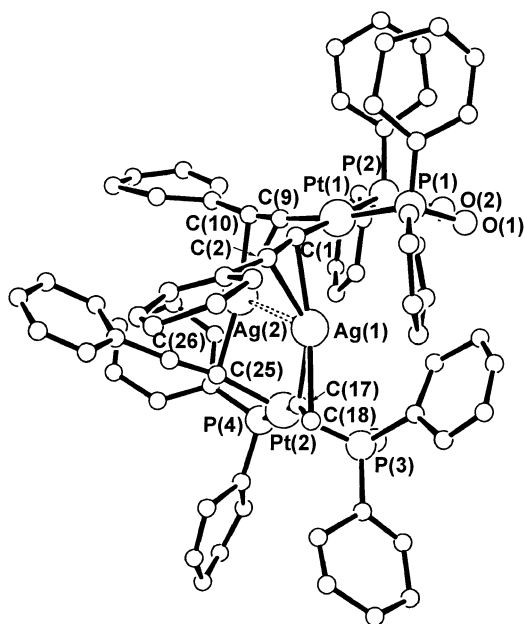

Fig. 1. Molecular structure of the anion [*cis*-Pt(C≡CBu^t)$_2${(PPh$_2$O)$_2$H}]$^-$ in **1a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
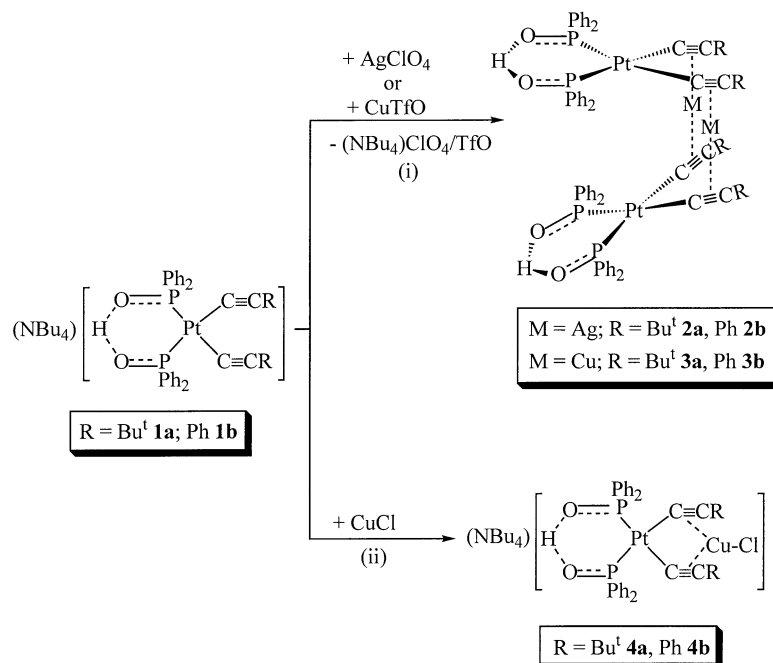
Scheme 1.

Fig. 2. View of the preliminary X-ray diffraction study of **2b** showing the connectivity of atoms.

$[Pt(C{\equiv}CPh)_2\{(PPh_2O)_2H\}]^-$ fragments seem to be staggered and the platinum coordination planes form a dihedral angle of approximately 136°. The Pt–Ag [ca. 3.13 Å] and Ag–Ag [3.00 Å] distances seem to be similar to those previously found in the anion $[Pt_2Ag_2(C_6F_5)_4\text{-}(C{\equiv}CPh)_4]^{2-}$ [12a] (Pt–Ag 3.10 and 3.15 Å; Ag–Ag 2.939(1) Å].

The reactions of polymeric copper halides $[CuX]_n$ with alkynyl metal complexes have been extensively

investigated [1c,g]. The results of these reactions depend on the metal fragments. Thus, depolymerization processes give rise to heteropolynuclear complexes in which CuX, Cu_2X_2 or Cu^+ entities are stabilized by η^2-alkyne interactions and simple alkynyl–halide exchange reactions have been reported [1b,23]. The resulting products also depend on the nature of the alkynyl ligand. We have thus previously shown that while trinuclear species $[\{Pt(C{\equiv}CPh)_4\}(CuX)_2]^{2-}$ are easily formed starting from $[Pt(C{\equiv}CPh)_4]^{2-}$, the analogous reactions using $[Pt(C{\equiv}CBu^t)_4]^{2-}$, produce a partial displacement of the halide ligands from CuX yielding hexametallic complexes $[\{Pt(C{\equiv}CBu^t)_4(CuX)\}_2Cu_2]^{2-}$ [12b]. As is shown in Scheme 1(ii), $[CuCl]_n$ is also readily depolymerized by complexes **1**. Thus, the reactions of complexes **1** with equimolecular amounts of $[CuCl]_n$ in acetone lead, after partial evaporation of acetone and addition of diethyl-ether, to the formation of binuclear anionic (NBu_4)[cis-Pt{(PPh_2O)_2H}(μ-κC^α:η^2-C≡CR)_2CuCl] (R = Bu^t **4a**, Ph **4b**) complexes, which are isolated as white (**4a**) or pale yellow (**4b**) solids in moderate yields. Compound **4a** is always obtained with small amounts of the tetra-nuclear derivative **3a**, as determined by NMR spectroscopy, suggesting that in this system, the affinity of Cu(I) ions towards the C≡CBu^t fragments or to the Cl⁻ ions is quite similar. Recrystallization of the mixture (CHCl_3/isopropyl-ether) gave **4a** as a pure white solid. The binuclear derivatives are less stable in solution and in solid state than the tetranuclear complexes **2**–**3**. The formulation of **4** as bimetallic species, in which the platinum fragment acts as a bidentate chelating ligand via η^2-alkyne coordination to CuCl, is based on

elemental analyses, conductivity measurements in acetone and spectroscopic data (see below).

Compounds **2a**, **3b** and **4** show, in their IR spectra, one $\nu(C\equiv C)$ vibration in the expected region (range 2019–2017 cm^{-1}) for bridging alkynyl ligands [1d] and all complexes show absorptions in the P–O stretching region (1108–994 cm^{-1}). As in the starting materials, the absence of bands due to $\nu(O–H)$ in the normal region is consistent with the presence of a symmetrical hydrogen bond [4,6,10,18]. However, the ^{1}H NMR spectra at −40 °C for **2**, **3b**, **4b** or at room temperature (**3a**, **4a**) confirm the presence of the expected PPh$_2$O-HOPPh$_2$ system (δ O–H–O 17.4–16.5). The most remarkable feature in the ^{1}H NMR spectra is the presence of the expected *tert*-butyl resonance in complexes **2a**, **3a** and **4a** (δ 0.83–1.12). The η^2-coordination of the metallic fragments is clearly inferred from the ^{31}P{^{1}H} NMR spectra. All complexes exhibit a singlet resonance (at 20 °C: δ 60.59–67.93), which is high-field shifted relative to the corresponding precursor (δ 72.32 **1a**, 70.04 **1b**). In the tetranuclear derivatives **2** and **3**, the observation even at low temperature (−40 °C) of only one singlet phosphorous resonance suggests the equivalence of all four atoms in solution. It is worth mentioning that in all compounds the value of the ^1J(Pt–P) coupling constants (2786–2852 Hz) is clearly greater than in the corresponding mononuclear complexes (2563 Hz **1a**, 2561 Hz **1b**), indicating that the *trans* influence of the bridging alkynyl ligands is much smaller than that of the terminal ones [20].

3.3. Optical properties

The luminescence properties of complexes **1**–**4** have been examined and the data of the emission and excitation spectra in frozen (77 K) CH$_2$Cl$_2$ solutions are summarized in Table 3. These complexes are strongly emissive in frozen CH$_2$Cl$_2$ solutions, except **1a** that emits weakly, while at room temperature (KBr pellets, or solution) the emissions are extremely weak.

At 77 K, the mononuclear complex **1b** shows an intense vibronic emission but the emission profile is dependent on the excitation energy. As can be observed in Fig. 3, excitation at high energy (λ_{exc} 320 nm) gives rise to a structured band with maxima at 429, 448, 458, 471 and 497 nm, while the emission spectrum upon excitation at lower energies (λ_{exc} 370 nm) shows only two maxima at 453 and 502 nm, respectively. The corresponding excitation spectrum is also dependent on the monitored emission energy. Thus, the excitation spectrum (by monitoring at 430 nm) shows a continuous in energy with a maximum at 320 nm, while excitation spectra monitoring at lower emission energies, exhibits two clear maxima at ∼320 and ∼360 nm, whose relative intensities change with the energy of the emission monitored. The observed vibrational spacing

Table 3
Excitation and emission spectral data for complexes in frozen (77 K) CH$_2$Cl$_2$ solutions

Compound	$\lambda_{exc\ max}$	$\lambda_{emi\ max}$
1a [a]	356, 372	425, 446, 463, 490, 508, 547
1b	320 [b]	(429, 448, 458, 471, 497) [c]
	(320, 360) [d]	(453, 502) [e]
2a	393	543
2b	392	588
3a	389	573
3b	409	610
4a	332, 390	537
4b	380	543
[*cis*-Pt(C≡CBu^t)$_2$(PPh$_3$)$_2$]	325 [f]	(434, 451, 475) [c]
	(323, 357) [g]	(447, 469, 493) [h]
[*cis*-Pt(C≡CPh)$_2$(PPh$_3$)$_2$]	358	444, 463, 490

[a] The emission is weak.
[b] Monitoring at 430 nm.
[c] λ_{exc} 320 nm.
[d] λ_{emi} 450 nm.
[e] λ_{exc} 370 nm.
[f] λ_{emi} 435 nm.
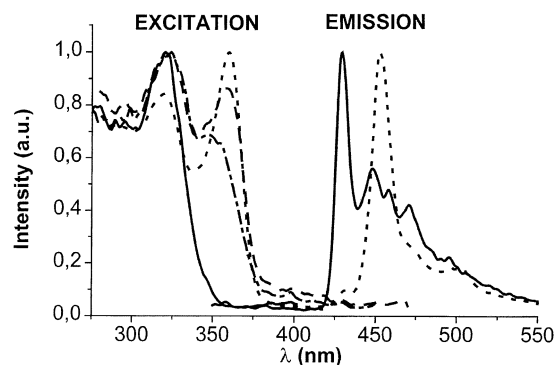[g] λ_{emi} 450 nm.
[h] λ_{exc} 357 nm.

Fig. 3. Excitation spectra, monitoring the emission at 430 nm (—), 450 nm (---), 475 nm (–·–), 500 nm (– – –) and emission spectra, excitation at 320 nm (—), 370 nm (---), of **1b** in CH$_2$Cl$_2$ at 77 K.

in the emission spectra (ca. 1100, 1475, and 2060, 2155 cm^{-1}) are suggestive of a combination of vibrational modes of the C≡C groups and phenyl moieties and the large Stokes shifts (7940 and 5703 cm^{-1}) are indicative of their triplet parentage. The behaviour of this complex could be tentatively attributed to two closely lying emissive states of separate origins, having a mainly intraligand character with an admixture of phenyl and acetylenic character. The nature of metal–π-alkynyl interaction in platinum alkynyl–phosphine complexes has been examined by a number of spectroscopic photoelectron and theoretical studies [2n,24]. These complexes usually exhibit low absorption bands (300–400 nm) arising from both π → π*(C≡CR) IL and d$_\pi$ [Pt → π*(C≡CR)] MLCT transitions. Upon photoexcitation some of these complexes display photoluminescence

which is usually assigned to the admixture ^{3}MLCT/IL [^{5}d(Pt) → π*(C≡CR)/π → π*(C≡CR)] transition with predominant IL character. Recent theoretical calculations on the model bis(alkynyl)bis(phosphine)platinum complexes confirm that the LUMO derive almost exclusively from π* compounds of alkynyl entities, whereas the HOMO, having an antibonding Pt–C_α and bonding C_α–C_β character, results from a pronounced interaction between d-type(π) metallic FMOs and π components of the alkynyl groups [24a–c,25]. Therefore, it is likely that the emissions in **1a** and **1b** would also involve a certain degree of metal to alkynyl MLCT character. In agreement with this assignment, and since the acceptor π*(C≡CBu^t) orbital energy is higher in energy than the π*(C≡CPh), the low temperature emission of **1a** is slightly blue–shifted in energy (425–547 cm^{-1}) from the emission of **1b**. A comparison has been made with the related mononuclear neutral complexes [*cis*-Pt(C≡CR)$_2$(PPh$_3$)$_2$] (R = Bu^t, Ph). The glassy (CH$_2$Cl$_2$, 77K, λ_{ex} = 358 nm) emission spectrum of [*cis*-Pt(C≡CPh)$_2$(PPh$_3$)$_2$] displays an intense vibronically structured emission (444–490 nm), which is at a similar energy to the emission of **1b** upon excitation at lower energies. This fact suggests that the platinum metal fragments have a similar effect on the emission, which is also attributed to a ^{3}(π–π*) excited state with some ^{3}MLCT character. It is interesting to note that the behaviour of *tert*-butylacetylide complex [*cis*-Pt(C≡CBu^t)$_2$(PPh$_3$)$_2$] is reminiscent of **1b**, also showing multiple luminescence. When the complex is excited at λ 357 nm, it exhibits a strong structured emission at low energy (447–493 nm). However, upon excitation at shorter wavelengths (λ = 320 nm), the emission is clearly blue-shifted (peak maxima 434, 451, 475 nm) once again suggesting the presence of two closely different emissive states.

All heterometallic complexes are highly emissive showing broad and unstructured emission profiles with their maxima red shifted from the emission of the corresponding precursors. The increased π-accepting ability of the C≡CR groups upon π-coordination to silver(I) or copper(I) clearly seems to be responsible for the red-shift in the emissions. The emission and excitation spectra of the phenyl complexes **2b**–**4b** are shown in Fig. 4. In all cases, the bands exhibit a large Stokes shifts (7029 **2a**, 8503 **2b**, 7996 **3a**, 8116 **3b**, 6914 **4a**, 6155 **4b**) from the excitation maxima, suggesting that these emissions are probably phosphorescence. In the tetranuclear Pt$_2$M$_2$ derivatives the emission is shifted to lower energy along the series **3b** (Cu, Ph) > **2b** (Ag, Ph) > **3a** (Cu, Bu^t) > **2a** (Ag, Bu^t). The observed lower emission energies for the phenylacetylide derivatives is consistent with the lower π* orbital ligand energy supporting the involvement of the π*(C≡CR) orbitals in the lowest excited state. It is noteworthy that the emissions from the copper complexes (**3**) occur at longer wavelengths than those of silver **2**. This fact, which has
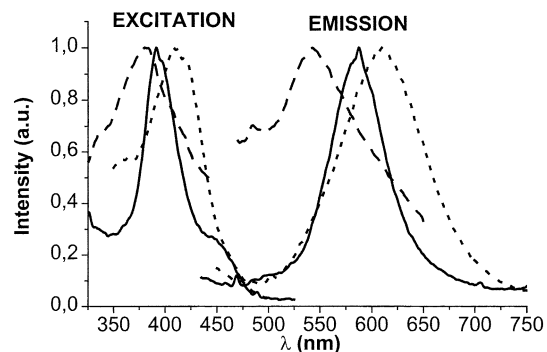

Fig. 4. Excitation and emission spectra of [Ag–Ph] **2b** (—), [Cu–Ph] **3b** (---), [Cu–Cl–Ph] **4b** (– – –) in CH$_2$Cl$_2$ at 77 K.

been previously observed in the hexanuclear clusters [Pt$_2$M$_4$(C≡CR)$_8$] (M = Cu, Ag) [2q,26] derivatives and other Pt–M alkynyl heterometallic complexes [27], could be tentatively related to a stronger π-coordination of acetylide ligands to Cu(I) ions and to the possible participation of the valence orbitals of the d^{10} metal centers in the LUMO [28]. The emission in the binuclear Pt–Cu complexes **4a** and **4b** in glassy solutions (acetone **4a** or CH$_2$Cl$_2$ **4b**) is blue shifted in relation to **3a** and **3b** respectively which could be related to the lower acidity of the neutral CuCl unit.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 186886. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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