Synthesis, characterisation and NMR study of paramagnetic heteropolynuclear anionic Pt–Co species. Crystal structures of [NBu4]2[{cis-Pt(C6F5)2(C≡CSiMe3)2}CoCl2]·0.5(CH3)2CO and [NBu4]2[{Pt(C≡C'Bu)4}{CoCl2}2]·1.5(CH3)2CO

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Abstract

The reactions of [NBu4]2[cis-Pt(C6F5)2(C≡CR)2] (R = 'Bu or SiMe3) with CoCl2·6H2O in a 1:1 molar ratio yielded the paramagnetic binuclear species [NBu4]2[{cis-Pt(C6F5)2(C≡CR)2}CoCl2] (R = 'Bu (1a), SiMe3 (1b)) in which the cobalt(II) chloride is coordinated η²-side on to both alkynyl ligands of the platinum fragment. Similar treatment of [NBu4]2[Pt(C≡CR)4]·2H2O (R = 'Bu or SiMe3) with CoCl2·6H2O in a 1:2 molar ratio gave the corresponding trinuclear 1:2 adducts [NBu4]2[{Pt(μ-C≡CR)4}{CoCl2}2] (2). The compounds were characterised by analytical and spectroscopic data and, in addition, the crystal structures of a representative complex of each category were determined: 1b·acetone and 2a·acetone. Surprisingly, whilst in the binuclear anion [{Pt(C6F5)2(C≡CSiMe3)2}CoCl2]²⁻ the cobalt atom is well embedded by the alkynyl fragments giving a precisely planar PtC4Co core and a very long Pt···Co separation (3.446(3) Å), in the trinuclear derivative [{Pt(C≡C'Bu)4}{CoCl2}2]²⁻ the PtC2Co cores are hinged imposing significantly shorter Pt···Co distances (3.077(3) Å). © 1997 Elsevier Science S.A.

Keywords: Paramagnetic complexes; Platinum complexes; Cobalt complexes; Alkynyl complexes; Heteropolynuclear complexes; Crystal structures
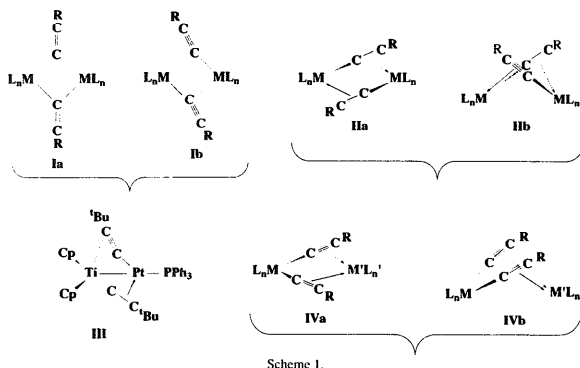
1. Introduction

Since it was reported in 1972 that Cp2Ti(C≡CPh)2 reacts with Ni(CO)4 to give the side-on bridged chelate complex [{Cp2Ti(C≡CPh)2}NiCO] [1a] many binuclear complexes, stabilised through bridging C≡CR, have been prepared [1b,c]. One of the reasons for the interest in these organometallic systems stems from their relevance in C–C coupling alkynide processes [2], as well as C–C bond cleavage on butadiynes induced by metal centres [3]. The driving force behind these processes could be related to the factors that govern the preferred geometries in these binuclear systems which are still a matter of debate [1b,c]. It is surprising, in fact, that in some complexes the alkynide carbon–carbon coupling reaction has been found to be a reversible process in solution [2h,f]. This suggests that even important variations in the (μ-C≡CR)2 system can have a small energetic

cost and could explain why asymmetric and hinged derivatives (II, III and IVb, Scheme 1) may show the easy fluxionality associated with fast alkynyl migration and/or central ring inversion [2b,3d,e,4].

In these species the alkynyl bridging groups exhibit different bonding situations which seem to depend mainly on electronic and/or steric factors of the metal fragments (MLn) and the R substituents on the alkynyl ligands. The classification presented in Scheme 1 is based on the analysis of geometrical data of structurally characterised compounds. Complexes containing an M2C2 ring in which the alkynyl ligands behave as two electron donors (μ.σ-C≡CR, Ia and Ib) are characteristic of electrophillic metal centres (main-group [1c,5] and f-orbital metals [6]), however, recent reports show that this bonding situation has also been found in the Ti–Pt [Cp2Ti(C≡C'Bu)2Pt(C6F5)2] [7] derivative, in several yttrium complexes [2h,8] and in some dicopper systems [9]. Examples of type II (σ, π; IIa and IIb) in which each metal atom is both σ- and η²-bonded to two alkynyl ligands which act as four electron donors have been

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Scheme 1.

reported for early $(d^1–d^1)$ [2b,3b,c,e,4a,10] and late $(d^8–d^8)$ [4a,b,11] homo- and heterobimetallic systems. While structural characterisation of early-early binuclear systems reveals that they are all seen to have flat M_2C_4 cores, structural data for d^8 binuclear species indicates that two possible structural patterns are observed, hinged or planar. Thus, while the anion $[Pt(\mu,\sigma:\eta^2-C\equiv CPh)(C_6F_5)_2]_2^{2-}$ [4b] and the neutral derivative $[Ir(\mu,\sigma:\eta^2-C\equiv CSiMe_3)-(COD)]_2$ [11a] show a significant distortion from planarity, the related neutral complex $[Pt(\mu,\sigma:\eta^2-C\equiv CPh)(C_6F_5)-(PPh_3)]_2$ [11b] displays a planar central PtC_4Pt core. Interestingly, variable temperature ^{19}F NMR data suggest that in solution the analogous $[Pt(C\equiv C^tBu)(C_6F_5)(PPh_3)]_2$ [11b] also exhibits a non-planar structure, thus indicating that this folding cannot be ascribed to crystal-packing forces but rather to electronic or steric effects of the tert-butylalkynide groups. A very asymmetric double alkynyl bridging system (type III) approximately halfway between types I and II has also been recently found in the mixed complex $[Cp_2Ti(C\equiv C^tBu)_2Pt(PPh_3)]$ [4d]. Finally, type IV complexes (Scheme 1) in which one metal centre is σ bonded to both alkynyl ligands and the other one is stabilised by η^2-alkyne interactions have been reported. In these derivatives one of the metal fragments, the 3-metalla-1,4-diyne unit $[M](C\equiv CR)_2$, acts as a didentate metalloligand towards the other $M'L_{n'}$ fragment. The structures found for this type of complexes also include planar and hinged geometries, i.e. the chelated metal centre M' can be located in (**IVa**, tweezer-like) or out (**IVb**, V-shape) of the 3-metalla-1,4-diyne plane (MC_4). In this context, we have recently reported several binuclear doubly alkynyl bridging derivatives which belong to this latter group of complexes **IV** [12]. The structural data for $[\{L_2Pt(C\equiv CPh)_2\}M(C_6F_5)_2]$ (L_2=dppe, M = Pt [4b]; L = PPh₂C≡C′Bu, M = Pd [13]), $[(C_6F_5)_2Pt(C\equiv C-SiMe_3)_2Pd(\eta^3-C_3H_5)]^{2-}$ [14], $[(PPh_3)_2Pt(C\equiv C^tBu)_2-Pd(\eta^3-C_3H_5)]^+$ [4e] and $[Cp^*(PEt_3)Ir(C\equiv CPh)_2M-(C_6F_5)_2]$ (M = Pt [15], Pd [13]) show that in all these cases

the chelated metal centre is clearly out of the 3-metalla-1,4-diyne plane (MC_4) giving non-planar dimetallacycle MC_4M' cores (**IVb**). The preference for this structural disposition must be obviously attributed to both steric and electronic requirements of the chelated monomeric $M'L_n$ fragments. The known tendency of alkynes to coordinate almost perpendicularly to both metal coordination plane makes sterically hindered an in-plane coordination. Surprisingly, a similar structural disposition has been found by Yamazaki and Deeming in the neutral complex $[\{(PMe_2Ph)_2Pt-(C\equiv C^tBu)_2\}CuCl]$ [16] and also by us in the anion $[\{(C_6F_5)_2Pt(C\equiv CPh)_2\}(AgPPh_3)]^-$ [17], in spite of the fact that a planar PtC_4M core would be expected in these cases. In fact this occurs in many other very similar species in which the M' centre of unsaturated $M'L_n$ ($M' =$ Ag, Cu or Au [18]) units is well embedded by bis(alkynyl)titanocene fragments displaying almost planar TiC_4M' cores. Recently, Van Koten and co-workers have reported extended Hückel calculations on $Cp_2Ti(C\equiv CH)_2Cu(CH_3)$ [18a] as a model system. This study indicates that the back-bonding component from filled d orbitals on the metal ($Cu(I),Ag(I)$) to empty π^* orbitals on the alkynes is quite significant, and is to be found in the in-plane interaction [1].

The only reported structure in which a bis-alkynyl platinum fragment forms a tweezer-like adduct (**IVa**, Scheme 1) corresponds to $[\{(C_6F_5)_2Pt(C\equiv CSiMe_3)_2\}HgBr_2]^{2-}$ [19]. In this anion the mercury centre acquires a distorted tetrahedral environment with lower steric requirements and, probably due to this, it is well embedded between both alkynyl groups.

In order to test this idea, we decided to explore the reactivity of the anionic substrates $[PtX_2(C\equiv CR)_2]^{2-}$ ($X = C_6F_5$ (*cis*) or $C\equiv CR$), whose ability to stabilise unusual η^2-

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[1] In these types of complexes the η^2-alkynyl–metal interaction arises from two major components: (i) a σ donation from a filled π orbital on the alkyne to a suitable empty orbital on M; (ii) a back-donating component involving donation from an adequate filled d-orbital on the metal to an empty π^* orbital on the alkyne.

alkyne–M interactions has been reported [12], towards other M'L_n' fragments with potential tetrahedral coordination at the M' centre. In this paper we describe the results obtained with CoCl$_2$, including the single-crystal structure determination of [NBu$_4$]$_2$[{cis-Pt(C$_6$F$_5$)$_2$-(C≡CSiMe$_3$)$_2$}CoCl$_2$]·0.5(CH$_3$)$_2$CO (**1b**·acetone), and [NBu$_4$]$_2$[{Pt(C≡C^{t}Bu)$_4$}{CoCl$_2$}]·1.5(CH$_3$)$_2$CO (**2a**·acetone) which, in our opinion, are a valuable addition to the collection of the previously reported examples. These structures provide the first examples in which the CoCl$_2$ unit is stabilised by η^2-alkyne interactions.

Numerous studies involving η^2-alkyne interactions to cobalt centres have been published but most of them are hexacarbonyldicobalt species bridged by acetylenic fragments (RC≡CR [20] or L$_n$MC≡CR [21]). As far as we know, only three examples of heteropolynuclear cobalt compounds with a double alkynyl bridged system between the metal centres have been reported: [Cp'M(C≡CPh)$_2$CoL$_n$] (M = Ti, L$_n$ = Cl$_2$ [22a]; M = Ti [22b], Hf [22c], L = CO) and only the complexes containing cobalt in the formal oxidation state zero have been structurally characterised.

2. Experimental

2.1. General procedures

The C, H and N analyses were determined with a Perkin-Elmer 240C microanalyser. IR spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 spectrometer and ^{1}H and ^{19}F NMR on a Bruker ARX 300 spectrometer. Chemical shifts are given in ppm and refer to external standards (SiMe$_4$ and CFCl$_3$). Conductivities were measured in ~5 × 10^{-4} M acetone or acetonitrile solutions using a Philips 950/01 conductimeter and mass spectra were obtained in a VG Autospec spectrometer using the FAB(−) technique. Magnetic susceptibilities were obtained by the Evans method [23] using a Sherwood Scientific Magnetic Susceptibility balance. The starting complexes [NBu$_4$]$_2$[Pt(C≡CR)$_4$]·nH$_2$O (n = 0, R = Ph; n = 2, R = ^{t}Bu [24a], R = SiMe$_3$ [24b]), [NBu$_4$]$_2$[cis-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$] (R = Ph, ^{t}Bu [25], SiMe$_3$ [14]) were prepared according to literature methods.

2.2. Syntheses

2.2.1. Preparation of (NBu$_4$)$_2$[{cis-Pt(C$_6$F$_5$)$_2$-(μ-C≡C^{t}Bu)$_2$}CoCl$_2$] (1a)

0.04 g (0.17 mmol) of CoCl$_2$·6H$_2$O was added to a solution of (NBu$_4$)$_2$[cis-Pt(C$_6$F$_5$)$_2$(C≡C^{t}Bu)$_2$] (0.20 g, 0.17 mmol) in 10 ml of acetone and the mixture was stirred for 10 min. The blue solution was evaporated to dryness and the resulting blue solid was treated with Et$_2$O (5 ml) yielding **1a** as a blue solid which was filtered off and washed with Et$_2$O (3 ml) and H$_2$O (5 ml). Yield: 81%.

Anal. Calc. for C$_{56}$H$_{90}$Cl$_2$CoF$_{10}$N$_2$Pt: C, 51.49; H, 6.94; N, 2.14. Found: C, 51.33; H, 7.48; N, 2.14%. IR (cm^{-1}): ν(C≡C) 2051(s); ν(C$_6$F$_5$)$_{x-sensitive}$ 785(vs), 777(vs). ^{1}H NMR (CDCl$_3$): δ 8.57 (s br, 16H, N–CH$_2$, ^{n}Bu); 5.39 (s br, 16H, –CH$_2$–, ^{n}Bu); 2.95 (s br, 16H, –CH$_2$–, ^{n}Bu); 1.81 (s, 24H, –CH$_3$, ^{n}Bu); −3.22 (vbr, 18H, –C≡C^{t}Bu). ^{19}F NMR (CDCl$_3$): δ −102.8 (m, o-F); −162.24 (s br, m-F); −170.08 (s br, p-F). FAB mass spectrum: m/z 786 [M−Cl]$^-$ (82%) (M = [{Pt(C$_6$F$_5$)$_2$(C≡C^{t}Bu)$_2$}CoCl$_2$]). Λ_M (acetone): 182 ohm^{-1} cm^2 mol^{-1}. μ_{eff} (18°C): 4.46 BM.

2.2.2. Preparation of (NBu$_4$)$_2$[{cis-Pt(C$_6$F$_5$)$_2$-(μ-C≡CSiMe$_3$)$_2$}CoCl$_2$] (1b)

Complex **1b** was prepared following the same method described for **1a** but starting from 0.20 g (0.165 mmol) of [NBu$_4$]$_2$[cis-Pt(C$_6$F$_5$)$_2$(C≡CSiMe$_3$)$_2$] and 0.039 g (0.165 mmol) of CoCl$_2$·6H$_2$O. Yield: 81%.

Anal. Calc. for C$_{54}$H$_{90}$Cl$_2$CoF$_{10}$N$_2$PtSi$_2$: C, 48.46; H, 6.78; N, 2.1. Found: C, 47.81; H, 6.85; N, 2.02%. IR (cm^{-1}): ν(C≡C) 1976(s), 1952(s); ν(C$_6$F$_5$)$_{x-sensitive}$ 786(s), 764(s). ^{1}H NMR (CDCl$_3$): δ 8.81 (s br, 16H, N–CH$_2$, ^{n}Bu); 5.14 (s br, 16H, –CH$_2$–, ^{n}Bu); 2.07 (s br, 16H, –CH$_2$–, ^{n}Bu); 1.49 (s, 24H, –CH$_3$, ^{n}Bu); −10.22 (br, 18H, –C≡CSiMe$_3$). ^{19}F NMR (CDCl$_3$): δ −95.24 (d, o-F); −166.65 (t, p-F); −167.43 (m, m-F). FAB mass spectrum: m/z 818 [M−Cl]$^-$ (100%) (M = [{Pt(C$_6$F$_5$)$_2$(C≡CSiMe$_3$)$_2$}-CoCl$_2$]). Λ_M (acetone): 163 ohm^{-1} cm^2 mol^{-1}. μ_{eff} (18°C): 3.43 BM.

2.2.3. Preparation of (NBu$_4$)$_2$[{Pt(μ-C≡C^{t}Bu)$_4$}{CoCl$_2$}$_2$] (2a)

To a colourless solution of [NBu$_4$]$_2$[Pt(C≡C^{t}Bu)$_4$]·2H$_2$O (0.30 g, 0.25 mmol) in 5 ml of acetone 0.14 g (0.5 mmol) of CoCl$_2$·6H$_2$O was added giving a blue solution, which was stirred for 5 min. The blue solid precipitated was filtered off and washed with cold acetone (5 ml). Yield: 85%.

Anal. Calc. for C$_{56}$H$_{108}$Cl$_4$Co$_2$N$_2$Pt: C, 53.20; H, 8.61; N, 2.22. Found: C, 52.99; H, 9.36; N, 2.24%. IR (cm^{-1}): ν(C≡C) 2058(m). ^{1}H NMR (HDA): δ 7.48 (s br, 16H, N–CH$_2$, ^{n}Bu); 5.56 (s br, 16H, –CH$_2$–, ^{n}Bu); 2.65 (s br, 16H, –CH$_2$–, ^{n}Bu); 1.65 (s, 24H, –CH$_3$, ^{n}Bu); −8.99 (vbr, 36H, –C≡C^{t}Bu). FAB mass spectrum: m/z 743 [M−Cl]$^-$ (100%) (M = [{Pt(C≡C^{t}Bu)$_4$}{CoCl$_2$}$_2$]). Λ_M (acetonitrile): 198 ohm^{-1} cm^2 mol^{-1}. μ_{eff} (18°C, value refered to χ_M/Co): 3.37 BM.

2.2.4. Preparation of (NBu$_4$)$_2$[{Pt(μ-C≡CSiMe$_3$)$_4$}-{CoCl$_2$}$_2$] (2b)

Complex **2b** was prepared in a similar way to **2a**. [NBu$_4$]$_2$[Pt(C≡CSiMe$_3$)$_4$]·2H$_2$O (0.28 g, 0.25 mmol); CoCl$_2$·6H$_2$O (0.12 g, 0.50 mmol). Yield: 58%.

Anal. Calc. for C$_{52}$H$_{108}$Cl$_4$Co$_2$N$_2$PtSi$_4$: C, 47.01; H, 8.2; N, 2.1. Found: C, 47.22; H, 8.75; N, 2.04%. IR (cm^{-1}): ν(C≡C) 1984(vs). ^{1}H NMR (HDA): δ 8.69 (s br, 16H, N–CH$_2$, ^{n}Bu); 6.49 (s br, 16H, –CH$_2$–, ^{n}Bu); 2.68 (s br,

16H, –CH$_2$–, ^{n}Bu): 1.61 (s, 24H, –CH$_3$, ^{n}Bu); − 12.66 (vbr, 36H, –C≡CSiMe$_3$). FAB mass spectrum: m/z 839 $[M]^-$ (17%) $\{M = [\{Pt(C≡CSiMe_3)_4\}\{CoCl_2\}_2]\}$. Λ_M (acetonitrile): 188 ohm^{-1} cm^2 mol^{-1}. μ_{eff} (18°C, value refered to χ_M/Co): 3.86 BM.

2.3. X-ray studies

2.3.1. X-ray crystal structure determination of [NBu$_4$]$_2$[{cis-Pt^{r}C$_6$F$_5$)$_2$(C≡CSiMe$_3$)$_2$}CoCl$_2$]·0.5(CH$_3$)$_2$CO (1b·acetone)

Suitable crystals of complex **1b** were obtained from a saturated solution of this complex in acetone at − 30°C. A crystal was fixed with epoxy on top of a glass fibre and mounted on a Siemens P4 automated four circle diffractometer. Graphite monochromated Mo Kα radiation was used. Routine procedures were used to determine the lattice dimensions, Laue group and to collect data. The measurement of diffraction data was undertaken at 200 K using the ω–2θ scan technique. The intensities of three standard reflections re-measured at regular intervals showed no appreciable change as a function of time. An absorption correction based on psi scans was applied (max. and min. transmission factors = 1.000 and 0.699).

The positions of the heavy atoms were determined by the Patterson map and the remaining non-hydrogen atoms were located and refined with anisotropic displacement parameters in succeeding Fourier syntheses. H atoms were added at calculated positions and refined with a common isotropic displacement parameter for the methylenic and ethylenic groups, respectively. Residual electron density was modelled as an acetone group refining at half occupancy. A final difference map did not show any peaks above 1 e Å^{-3}. More than half of the data were weak (mean $I/\sigma = 6.41$), which is reflected in the large values of the final R parameters (see Table 1).

2.3.2. X-ray crystal structure determination of [NBu$_4$]$_2$[{Pt(C≡C^{t}Bu)$_4$}{CoCl$_2$}$_2$]·1.5(CH$_3$)$_2$CO (2a·acetone)

A saturated solution of complex **2a** in acetone at − 30°C afforded suitable crystals for single crystal X-ray analysis. The crystals were found to lose solvent very rapidly, to the extent that several attempts to mount crystals for diffraction proved fruitless. Crystals covered with silicon or lithium grease did not survive the few seconds needed to transfer them into the cold stream of the low temperature device of the diffractometer. Finally, a crystal protected with highly viscous perfluorpolyether was rapidly mounted on a Siemens STOE/AED2 four circle automated diffractometer. Preliminary measurements showed that reflections were weak and broad but since we were very interested in the structure we proceeded with the analysis of this crystal, even though we were aware that the precision of the results would be diminished because of the poor quality of the crystal. The collection of geometrical and intensity data was conducted via common techniques. Data were collected at 173 K by the ω–2θ scan

method. The intensities of three monitor reflections remained nearly constant throughout the course of the data collection, which indicates that the poor crystalline quality of the sample was due to the partial loss of solvent before the crystal was mounted in the diffractometer. No absorption correction was applied because of the very low intensities of the psi scans. Heavy atoms were located by the Patterson method and the remaining non-hydrogen atoms were located and refined by different Fourier syntheses. H atoms were added at calculated positions and refined with a common isotropic displacement parameter for all methylenic and ethylenic groups, respectively. Residual electron density was modelled as two acetone groups, one of them with full occupancy and the other one with half occupancy. Several peaks above 1 e Å^{-3} remained in the final density map which can be attributed to absorption effects, which always occur for heavy atoms like platinum, since the model has not been corrected for absorption. These peaks are located close to the heavy atoms, with no chemical significance. The specific volume for non-hydrogen atoms is 25.4 Å^3, unusually large. This is consistent with the crystal having lost part of its interstitial solvent, with some degree of physical decomposition, so that a lot of empty space is left in the crystal. This fact along with the high absorption and the weak intensity of the data (mean $I/\sigma = 5.67$) explain the large values of the R parameters, the presence of residual electron density and the large standard deviations in some distances and angles found in the structure.

Crystallographic parameters for both structures are shown in Table 1. All calculations were carried out on a Local Area VAX cluster (VAX/VMS V5.5) with the commercial package SHELXTL-PLUS [26] and the SHELXL-93 program [27].
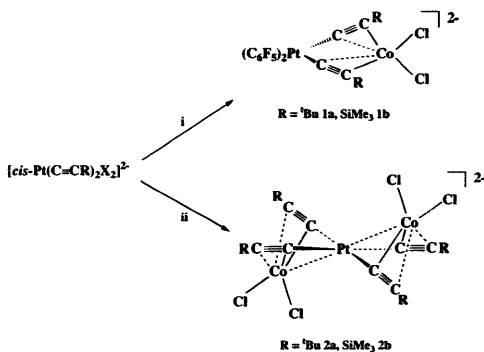
3. Results and discussion

Addition of the stoicheometric amount of CoCl$_2$·6H$_2$O to the colourless solutions of the compounds [NBu$_4$]$_2$[cis-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$] (R = ^{t}Bu or SiMe$_3$) in acetone at room temperature affords the expected 1:1 adducts [NBu$_4$]$_2$[{cis-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$}CoCl$_2$] (R = ^{t}Bu (**1a**), SiMe$_3$ (**1b**)) in high yield. Similar treatment of [NBu$_4$]$_2$[Pt(C≡CR)$_4$]·2H$_2$O (R = ^{t}Bu or SiMe$_3$) with 2 equiv. of CoCl$_2$·6H$_2$O causes the immediate precipitation of the corresponding 1:2 adducts [NBu$_4$]$_2$[Pt(C≡CR)$_4$(CoCl$_2$)$_2$] (R = ^{t}Bu (**2a**), SiMe$_3$ (**2b**)). Both processes are shown in Scheme 2. Unfortunately, analogous reactions with [NBu$_4$]$_2$[cis-Pt(C$_6$F$_5$)$_2$-(C≡CPh)$_2$] or [NBu$_4$]$_2$[Pt(C≡CPh)$_4$] evolve with extensive decomposition and do not allow the preparation of any stable heterometallic compound.

Compounds **1** and **2** have been isolated as blue solids which are stable for months if stored in the freezer; nevertheless, in solution they decompose in very short periods of time. All of them have satisfactory elemental analyses and conductivity data (see Section 2). The mass spectra recorded using the FAB(−) technique for complexes **1a**, **1b** and **2a** exhibit a

Table 1
Crystal data and structure refinement parameters for complexes **1b** and **2a**

	1b	**2a**
Empirical formula	$C_{55.5}H_{93}Cl_2CoF_{10}N_2O_{0.5}PtSi_2$	$C_{60.5}H_{117}Cl_3Co_2N_2O_{1.5}Pt$
Formula weight	1367.42	1351.31
Colour and habit	blue plates	blue plates
Temperature (K)	200(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
Unit cell dimensions		
a (Å)	20.410(8)	12.54(2)
b (Å)	14.912(7)	16.020(11)
c (Å)	23.479(10)	19.877(14)
α (°)	90	84.40(4)
β (°)	98.51(4)	73.21(5)
γ (°)	90	70.38(4)
Volume (Å³)	7076(5)	3600(6)
Z	4	2
Density (calc.) (Mg m⁻³)	1.285	1.247
Absorption coefficient (mm⁻¹)	2.380	2.577
$F(000)$	2084	1412
Crystal size (mm)	$0.14 \times 0.30 \times 0.36$	$0.15 \times 0.26 \times 0.26$
θ Range for data collection (°)	2.02–23.49	2.14–24.03
Index ranges	$-1 \leq h \leq 21$	$-14 \leq h \leq 5$
	$-1 \leq k \leq 16$	$-18 < k \leq 18$
	$-26 \leq l \leq 226$	$-22 \leq l \leq 22$
Reflections collected	9615	14217
Independent reflections	9257 ($R_{int} = 0.1088$)	11315 ($R_{int} = 0.1090$)
Refinement method	full-matrix l.s. on F^2	full-matrix l.s. on F^2
Data/restraints/parameters	7418/73/625	9569/5/619
Weighting parameters: g_1, g_2	0.0763, 0.000	0.1429, 0.000
Goodness-of-fit on F^2	1.007	1.000
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0886$, $wR_2 = 0.1588$	$R_1 = 0.0946$, $wR_2 = 0.2173$
R indices (all data)	$R_1 = 0.2294$, $wR_2 = 0.2352$	$R_1 = 0.1852$, $wR_2 = 0.2738$

$R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. Goodness-of-fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. $w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2; 0) + 2F_c^2]/3$.

i) $X = C_6F_5$, + $CoCl_2$; ii) $X = C\equiv CR$, + $2CoCl_2$
Scheme 2.

strong peak at m/z 786, 818 and 743, respectively, which can be easily attributed to the molecular anion less a chlorine atom. In all cases there is a good degree of coincidence between the isotopomer distribution observed and that calculated for $[M-Cl]^-$ anions. In complex **2b** a very weak peak at m/z 839 can be tentatively assigned to a parent anion $[M]^-$. The IR spectra show one (2051, **1a**; 2058, **2a**; 1984, **2b** cm^{-1}) or two (1976, 1952, **1b** cm^{-1}) ν(C≡C) stretching vibrations, which, as expected, are shifted to lower wavelengths compared with the corresponding ones in the precursors. This shifting, $\Delta\nu$, is slightly greater for the binuclear anions (36, **1a**; 55, **1b** cm^{-1}) than for the trinuclear ones (22, **2a**; 28, **2b** cm^{-1}) suggesting that the η^2-alkyne interaction is stronger in the former. Similar behaviour has been observed in the related platinum–mercury heterobinuclear (NBu$_4$)$_2$[{cis-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$}HgX$_2$] ($\Delta\nu$, 53–74 cm^{-1}) and heterotrinuclear adducts (NBu$_4$)$_2$[{Pt-(C≡CR)$_4$}{HgX$_2$}$_2$] ($\Delta\nu$, 42–49 cm^{-1}) [19], suggesting that these species could display the same structure. As expected, these decreases are small compared with those reported for [{Cp'M(C≡CPh)$_2$}Co(CO)] (Cp' = C$_5$H$_4$-SiMe$_3$; M = Ti, 206; Hf, 208 cm^{-1}) [22b,c] which contain the low valent metal fragment Co(CO). However, it is worth mentioning that they are also significantly smaller than the value of 174 cm^{-1} reported for complex [{Cp'Ti(C≡C-SiMe$_3$)$_2$}CoCl$_2$] [22a] suggesting that in **1** and **2** the η^2-alkynyl bonding interaction is probably weaker.

Solid-state susceptibilities of powdered samples of the four complexes were measured at 291 K, giving the effective magnetic moments 4.46 (**1a**), 3.43 (**1b**), 3.37 (**2a**) and 3.86 (**2b**) BM. In the four cases values refer to χ_M/Co and they are satisfactorily in line with the spin-only value for three unpaired electrons (μ_{eff} = 3.87 BM) of an $^4A_2$ term of Co(II) in a pseudotetrahedral environment ($e^4t_2^3$) [28].

The ^{1}H NMR spectra of complexes **1** and **2** have been recorded. In all cases, the presence of the paramagnetic centres causes the broadening of the signals and leads to chemical shifts in the range δ 8.81 to -12.66 ppm at room temperature (Fig. 1(a) for complex **1b**). Thus, in the spectra of the four complexes a set of four signals appear due to the NBu$_4$$^+$ cation around 8.5 ppm for N–CH$_2$, 5.5 ppm for β-CH$_2$, 2.5 ppm for γ-CH$_2$ and 1.5 ppm for CH$_3$. In complexes **1a** and **2a** a broad signal due to the methyl hydrogens of the ^{t}Bu group appears at -3.22 and -8.99 ppm. The resonances due to the trimethylsilyl groups in compounds **1b** and **2b** are, indeed, shown at higher fields (δ -10.22 ppm for **1b**, -12.66 for **2b**).

We have also been able to obtain the corresponding ^{19}F NMR spectra of complexes **1** in CDCl$_3$ (Fig. 1(b) for complex **1b**). Both spectra show a set of three signals as would be expected in the presence of only one type of C$_6$F$_5$ group. The signal assigned to o-F atoms in both complexes is the most paramagnetically shifted as it appears at an unusually low field for terminal C$_6$F$_5$ groups [4b,c,e,7,11b] (-102.8, **1a**; -95.24, **1b** ppm). Another important observation is that this signal does not show platinum satellites due to the three
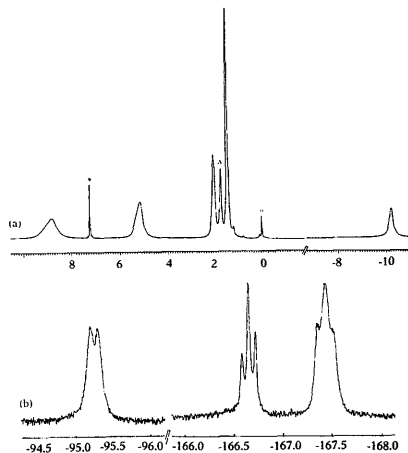

Fig. 1. ^{1}H (a) and ^{19}F (b) NMR spectra of complex **1b** at room teperature. *, CHCl$_3$; △, H$_2$O; ○, grease.

bond coupling between the o-F and the active ^{195}Pt isotope ($I = 1/2$, 33%) which are usual in pentafluorophenyl complexes of platinum. In these derivatives it seems reasonable to attribute this absence both to the presence of the paramagnetic centre and to its quadrupolar magnetic moment (^{59}Co, $I = 7/2$, 100%). The chemical shifts of the *meta* and *para* fluorine resonances which are observed at a higher field are clearly less affected (see Section 2). The analysis of the NMR spectra indicates that the unpaired electrons are essentially located at the cobalt centres and hence it is not surprising that none of them exhibit any observable signal in the EPR spectra. An efficient relaxation mechanism is probably provided by the quadrupolar magnetic moment of the cobalt centre.

In order to ascertain the structural features of the alkynyl bridging systems in these adducts, complexes **1b** and **2a** were characterised by single-crystal X-ray diffraction. Fractional atomic coordinates and selected bond distances and angles are given in Tables 2–4. Figs. 2 and 3 show molecular diagrams for both structures. The crystal structure of **2a** reveals that this compound crystallises with two crystallographically independent but chemically very similar trinuclear [NBu$_4$]$_2$[Pt(C≡CR)$_4$(CoCl$_2$)$_2$] molecules in the asymmetric unit. Discussion of the structure will therefore be limited to only one of the molecules.

As expected, whilst the anion on complex **1b** (Fig. 2) is formed by the mixed dianionic [(C$_6$F$_5$)$_2$Pt(C≡CSi-Me$_3$)$_2$]$^{2-}$ fragment acting as a bis(η^2-alkyne) chelate towards the CoCl$_2$ unit, the heterotrinuclear anion (**2a**, Fig. 3) is formed by the complexation of two identical CoCl$_2$ units (as required by crystallography symmetry) by the

Table 2

Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1b**

	x	y	z	U_{eq} [a]
Pt(1)	385(1)	625(1)	2487(1)	40(1)
Co(1)	−749(1)	2289(2)	2636(1)	44(1)
Cl(1)	−1858(3)	2057(3)	2447(3)	57(2)
Cl(2)	−527(3)	3729(3)	2928(3)	68(2)
Si(1)	−942(3)	2814(4)	1126(3)	55(2)
Si(2)	−626(3)	1849(4)	4170(3)	54(2)
F(2)	383(6)	−1373(8)	1892(5)	70(4)
F(3)	970(7)	−2036(9)	1043(6)	100(5)
F(4)	1734(6)	−981(10)	468(6)	104(5)
F(5)	1936(6)	774(12)	785(6)	103(5)
F(6)	1356(6)	1481(9)	1632(6)	76(4)
F(8)	−181(6)	−887(7)	3270(6)	69(4)
F(9)	415(7)	−2116(9)	4017(6)	98(5)
F(10)	1756(8)	−2242(10)	4253(6)	109(6)
F(11)	2533(6)	−1149(9)	3647(6)	92(5)
F(12)	1954(5)	72(8)	2894(5)	68(4)
N(1)	1770(9)	3121(13)	3237(8)	63(5)
N(2)	−1834(7)	−891(11)	1892(8)	56(5)
C(1)	817(9)	98(15)	1826(8)	43(5)
C(2)	774(10)	−794(15)	1632(9)	49(6)
C(3)	1041(11)	−1174(17)	1199(10)	54(6)
C(4)	1437(11)	−657(21)	906(10)	73(7)
C(5)	1552(10)	221(19)	1068(10)	62(7)
C(6)	1239(9)	591(18)	1503(10)	59(6)
C(7)	861(9)	−293(13)	3048(8)	39(5)
C(8)	491(11)	−910(13)	3350(10)	52(6)
C(9)	787(12)	−1546(15)	3746(10)	58(6)
C(10)	1447(13)	−1645(14)	3870(9)	55(6)
C(11)	1842(12)	−1103(17)	3546(10)	65(7)
C(12)	1542(10)	−450(12)	3168(8)	36(5)
C(13)	−119(9)	1524(14)	1963(9)	47(4)
C(14)	−468(9)	2139(14)	1745(9)	50(6)
C(15)	−1736(10)	2241(16)	847(9)	77(8)
C(16)	−1160(10)	3965(14)	1377(11)	86(9)
C(17)	−437(10)	2908(14)	535(10)	90(9)
C(18)	−42(9)	1157(14)	3092(9)	47(4)
C(19)	−352(9)	1560(12)	3449(8)	39(5)
C(20)	−67(14)	2705(18)	4513(11)	126(12)
C(21)	−1485(10)	2329(16)	4066(10)	91(9)
C(22)	−540(13)	817(14)	4611(9)	92(9)
C(23)	1232(12)	3262(15)	2717(12)	82(9)
C(24)	1341(10)	4096(17)	2353(10)	76(9)
C(25)	877(14)	4067(17)	1817(13)	103(11)
C(26)	915(13)	4926(22)	1434(13)	138(14)
C(27)	1792(12)	3942(15)	3630(10)	74(8)
C(28)	1153(12)	4239(18)	3818(12)	103(10)
C(29)	1256(13)	5050(17)	4221(11)	89(9)
C(30)	647(15)	5412(20)	4421(13)	150(9)
C(31)	1546(12)	2302(16)	3524(12)	77(8)
C(32)	2038(15)	1955(20)	4025(12)	122(13)
C(33)	1748(15)	1209(18)	4363(13)	115(11)
C(34)	2275(16)	696(21)	4730(14)	150(9)
C(35)	2446(10)	3033(14)	3045(10)	66(7)
C(36)	2515(11)	2314(14)	2614(10)	72(8)
C(37)	3230(11)	2124(16)	2559(11)	79(8)
C(38)	3314(13)	1513(15)	2065(12)	103(10)
C(39)	−1320(10)	−503(15)	1539(10)	71(5)
C(40)	−1289(14)	−906(16)	966(12)	101(10)
C(41)	−733(13)	−336(19)	668(11)	101(7)
C(42)	−612(15)	−945(18)	307(14)	146(10)

(*continued*)

Table 2 (*continued*)

	x	y	z	U_{eq} [a]
C(43)	−1766(12)	−1903(13)	1955(10)	73(8)
C(44)	−1092(13)	−2230(15)	2242(13)	97(7)
C(45)	−1067(12)	−3216(19)	2329(11)	101(7)
C(46)	−435(14)	−3591(18)	2594(14)	146(10)
C(47)	−1753(11)	−423(14)	2470(10)	71(5)
C(48)	−2269(12)	−580(17)	2847(12)	97(7)
C(49)	−2036(15)	−299(20)	3470(12)	120(12)
C(50)	−1718(15)	−1124(22)	3746(15)	156(11)
C(51)	−2540(9)	−767(12)	1562(9)	55(6)
C(52)	−2727(10)	220(16)	1421(10)	77(8)
C(53)	−3470(10)	279(17)	1114(11)	81(9)
C(54)	−3650(15)	1191(22)	919(15)	156(11)
O(1)	−1599(16)	−3254(22)	742(15)	89(11)
C(55)	−1298(19)	−3505(22)	463(18)	40(11)
C(56)	−1512(23)	−3321(32)	−97(21)	96(18)
C(57)	−757(23)	−3780(30)	588(21)	83(16)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

homoleptic tetradentate metalloligand $[Pt(C\equiv C^tBu)_4]^{2-}$ through bridging alkynyl ligands ($\mu,\sigma:\eta^2$).

In both anions coordination around the cobalt atom is pseudotetrahedral and is formed by the two chlorine atoms and the midpoints of the respective *cis* (η^2-alkyne) fragments (M_1 and M_2). The CoCl(1)Cl(2) fragment is almost perpendicular to their respective platinum coordination plane (the interplanar angle is 85.2(5)° for **1b** and 86.6(5)° for **2a**). The angles between the planes M_1,M_2,Co and Co(1)Cl(1)Cl(2) are not very different (84.7(2)°, **1b**; 86.1(3)°, **2a**), respectively, and the Co–Cl distances are comparable within the experimental error (2.269(6) and 2.279(6) Å, **1b**; 2.244(5) and 2.253(5) Å, **2a**).

The most remarkable difference is that while the binuclear anion exhibits in-plane bis(η^2-alkyne)cobalt bonding interactions and a flat PtC(13)C(14)C(18)C(19)Co central core (maximum deviation 0.076(3) Å for Co atom), in **2a** (Fig. 3(b)) the cobalt centres are displaced 0.719(4) Å above and below the 3-metalla-1,4-diyne plane [PtC(1)-C(2)C(7)C(8)], generating a non-planar trinuclear anion. Consequently, the central PtC$_4$Co cores are bent. The dihedral angle formed by the M_1M_2Co and the platinum coordination plane is 33.3(5)°, thus implying that the bis(η^2-alkyne) interaction takes place outside the plane (Scheme 1, type **IVb**). This structural difference seems to have a notable influence on other geometric parameters. Thus, the folding along the $M_1 \cdots M_2$ axis (M_1 and M_2 midpoints of alkyne fragments) clearly imposes shorter Pt $\cdots$ Co separation: 3.077(3) Å in **2a** versus 3.446(3) Å in **1b**. The value of 3.077 Å observed in the trinuclear derivative (**2a**) is significantly longer than those found in most clusters with Pt–Co bonds (2.50–2.87 Å) [29] but is comparable to the unbridged Pt–Co bonds seen in the hexanuclear cluster $[Co_3Pt_3(\mu-CO)_4(CO)_5(P^iPr_3)_3(\mu-C)(\mu-H)]$ [30]. Moreover, it is noteworthy that the type of asymmetry observed for the (η^2-alkyne)cobalt interaction is also different. In **1b** the mean values of the Co–C$_\beta$ distances (2.26(2), 2.24(2) Å) are

Table 3
Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for **2a**

	x	y	z	U_{eq} [a]
Pt(1)	0	0	0	22(1)
Pt(2)	0	5000	5000	25(1)
Co(1)	1145(2)	-1784(2)	646(1)	28(1)
Co(2)	-784(2)	3760(2)	4283(1)	33(1)
Cl(1)	976(5)	-1422(3)	1743(2)	37(1)
Cl(2)	2080(5)	-3256(3)	549(3)	42(1)
Cl(3)	-697(6)	3278(3)	3239(3)	48(2)
Cl(4)	-1788(6)	3081(4)	5131(3)	61(2)
N(1)	-972(13)	1234(9)	2169(7)	26(3)
N(2)	-1839(14)	4027(9)	7067(7)	29(4)
C(1)	-467(19)	-1098(12)	326(8)	39(4)
C(2)	-742(20)	-1742(13)	519(10)	46(6)
C(3)	-1294(19)	-2437(11)	756(9)	38(5)
C(4)	-766(23)	-3205(14)	218(11)	62(7)
C(5)	-2617(20)	-2007(15)	773(14)	60(7)
C(6)	-1205(23)	-2778(14)	1471(10)	58(7)
C(7)	1593(20)	-708(12)	-60(8)	39(4)
C(8)	2645(19)	-1198(13)	-60(9)	34(5)
C(9)	3952(17)	-1631(11)	-139(9)	33(5)
C(10)	4505(18)	-2310(14)	-730(11)	49(6)
C(11)	4129(20)	-2046(14)	547(11)	49(6)
C(12)	4479(18)	-859(14)	-306(12)	53(6)
C(13)	271(16)	1032(11)	1687(9)	32(5)
C(14)	1011(18)	1556(14)	1818(10)	36(5)
C(15)	2290(18)	1168(14)	1400(10)	47(6)
C(16)	2888(20)	312(14)	1707(12)	54(6)
C(17)	-1675(17)	2207(11)	2098(9)	30(4)
C(18)	-1796(19)	2502(11)	1365(9)	33(5)
C(19)	-2547(26)	3506(14)	1373(11)	71(9)
C(20)	-1962(33)	4110(13)	1564(13)	113(15)
C(21)	-1501(14)	626(11)	1945(8)	29(3)
C(22)	-2804(17)	752(13)	2310(10)	38(5)
C(23)	-3175(20)	72(14)	2044(11)	44(6)
C(24)	-4450(21)	127(18)	2387(13)	72(8)
C(25)	-1004(16)	1099(11)	2932(8)	29(3)
C(26)	-175(19)	225(12)	3109(9)	38(5)
C(27)	-362(17)	71(13)	3914(9)	39(5)
C(28)	592(21)	-688(15)	4093(11)	59(7)
C(29)	-1228(18)	5183(11)	4532(9)	27(3)
C(30)	-2006(17)	5272(12)	4225(9)	30(4)
C(31)	-3008(23)	5533(13)	3945(11)	55(7)
C(32)	-2638(21)	5708(17)	3138(11)	63(7)
C(33)	-3650(19)	4880(16)	4053(14)	65(7)
C(34)	-3905(22)	6387(17)	4297(13)	68(8)
C(35)	768(16)	3833(11)	4523(9)	27(3)
C(36)	1273(18)	3116(13)	4238(9)	35(5)
C(37)	2043(19)	2213(12)	3926(10)	39(5)
C(38)	2524(22)	2276(14)	3128(10)	55(7)
C(39)	1378(25)	1557(13)	4086(14)	70(8)
C(40)	3081(23)	1889(13)	4265(14)	69(8)
C(41)	-698(16)	3504(12)	6574(9)	32(4)
C(42)	161(19)	2830(14)	6880(10)	45(6)
C(43)	1213(20)	2290(13)	6286(11)	48(6)
C(44)	2123(23)	1593(15)	6542(12)	66(7)
C(45)	-2497(17)	4719(11)	6622(10)	36(5)
C(46)	-3705(21)	5361(13)	6971(10)	50(7)
C(47)	-4122(19)	5992(15)	6428(12)	57(5)
C(48)	-5270(20)	6702(14)	6724(13)	63(7)
C(49)	-2559(20)	3430(13)	7440(10)	46(6)
C(50)	-2971(22)	2981(14)	6988(10)	54(6)

(continued)

Table 3 *(continued)*

	x	y	z	U_{eq} [a]
C(51)	-3698(20)	2424(16)	7442(12)	57(5)
C(52)	-4170(31)	1963(19)	7040(16)	99(11)
C(53)	-1626(19)	4450(13)	7661(8)	44(6)
C(54)	-928(21)	5068(14)	7436(10)	52(6)
C(55)	-797(30)	5454(22)	8071(13)	87(11)
C(56)	-1833(33)	5964(23)	8546(16)	124(15)
O(1)	-3715(20)	803(14)	4191(10)	97(7)
C(57)	-3783(21)	1077(16)	4764(13)	58(7)
C(58)	-4317(39)	751(22)	5449(17)	147(19)
C(59)	-3301(23)	1779(17)	4797(13)	72(8)
O(2)	-4472(47)	5646(34)	1563(27)	141(19)
C(60)	-4494(43)	5409(28)	985(27)	104(22)
C(61)	-5283(44)	4929(34)	843(28)	80(17)
C(62)	-3771(51)	5513(42)	262(30)	115(25)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Selected interatomic distances (Å) and angles (°) for complexes **1b** and **2a**

1b		**2a**	
Distances			
Pt(1)-C(1)	2.05(2)	Pt(1)-C(1)	2.03(2)
Pt(1)-C(7)	2.04(2)	Pt(1)-C(7)	1.91(2)
Pt(1)-C(13)	2.00(2)	Co(1)-C(1)	2.19(2)
Pt(1)-C(18)	1.94(2)	Co(1)-C(2)	2.43(2)
Co(1)-C(13)	2.46(2)	Co(1)-C(7)	2.23(2)
Co(1)-C(14)	2.26(2)	Co(1)-C(8)	2.41(2)
Co(1)-C(18)	2.37(2)	Co(1)-Cl(1)	2.244(5)
Co(1)-C(19)	2.24(2)	Co(1)-Cl(2)	2.253(5)
Co(1)-Cl(1)	2.269(6)	C(1)-C(2)	1.19(3)
Co(1)-Cl(2)	2.279(6)	C(7)-C(8)	1.29(3)
C(13)-C(14)	1.23(2)	Pt(1)···Co(1)	3.077(3)
C(18)-C(19)	1.27(2)		
Pt(1)···Co(1)	3.446(3)		
Angles			
C(1)-Pt(1)-C(7)	90.8(7)	C(1)-Pt(1)-C(7)	88.0(8)
C(1)-Pt(1)-C(13)	91.8(8)	C(1a)-Pt(1)-C(7)	92.0(8)
C(1)-Pt(1)-C(18)	177.8(8)	Cl(1)-Co(1)-Cl(2)	106.1(2)
C(7)-Pt(1)-C(18)	91.4(8)	C(1)-Co(1)-C(7)	76.4(8)
C(7)-Pt(1)-C(13)	177.0(8)	C(2)-Co(1)-C(8)	132.4(7)
C(13)-Pt(1)-C(7)	177.0(8)	C(2)-Pt(1)-C(1)	180(2)
Cl(1)-Co(1)-Cl(2)	110.5(2)	C(8)-C(7)-Pt(1)	175.5(14)
C(18)-Co(1)-C(13)	67.6(7)		
C(19)-Co(1)-C(14)	129.1(8)		
C(14)-C(13)-Pt(1)	167(2)		
C(19)-C(18)-Pt(1)	174(2)		

Symmetry transformation used to generate equivalent atoms in **2a**: $-x$, $-y$, $-z$.

shorter than the corresponding Co–C_α (2.46(2), 2.37(2) Å), while the opposite is found in the trinuclear anion **2a** with Co–C_α (2.19(2), 2.23(2) Å) shorter than those observed for Co–C_β distances (2.43(2), 2.41(3) Å). Interestingly, this structural feature coincides with the asymmetry we previously found in the structurally related anions [{Pt(C$_6$F$_5$)$_2$(C≡CSiMe$_3$)$_2$}HgBr$_2$]²⁻ (planar PtC$_4$Hg) [19], [{Pt(C$_6$F$_5$)$_2$(C≡CPh)$_2$}Ag(PPh$_3$)]⁻ (hinged PtC$_4$-
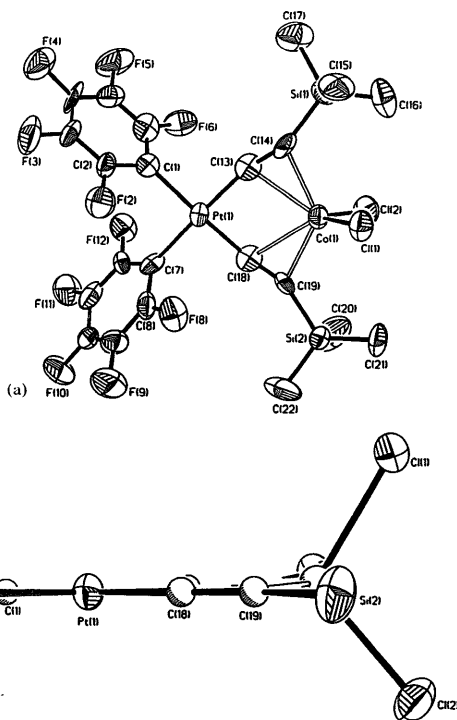
Fig. 2. (a) Structure of the anion of **1b** with the atomic numbering scheme. (b) Schematic view of the planar 'tweezer-like' structure of the PtC₄Co core.

Ag core) [17] and $[\{Pt(C\equiv CPh)_4\}(CuBr)_2]^{2-}$ (hinged PtC₄Cu cores) [31].

As expected, the Pt–C≡C–X units deviate slightly from linearity in both anions (X = Si (**1b**), C (**2a**)), the bending-back angles in **2a** (C_α 180(2), 176.5(14)°; C_β 170(3), 169(2)°) being smaller than those observed in **1b** (167(2) and 174(2)° at C_α; 156(2) and 158(2)° at C_β). In any case these distortions are, however, significantly less pronounced than those reported for $[Cp'M(C\equiv CPh)_2Co(CO)]$ (C_α/C_β M = Ti 160.4(2)/152.1(3)° [22b]; M = Hf 159.9(3)/ 149.7(3)° [22c]), in line with the stronger π-back electron donation that could be expected in the latter, due to the presence of formally Co(O) centres.

As shown in Table 4 the C≡C bond distances in both anions range from 1.19(3) to 1.29(3) Å, but it is noted that, due to the large standard deviations in both structures, no accurate comparisons with structurally related derivatives can be made.

4. Conclusions

We have demonstrated that paramagnetic anionic hetero-polynuclear alkynyl-bridged platinum–cobalt complexes can be synthesised easily by the simple complexation of CoCl₂ with suitable σ-alkynyl anionic platinum substrates. X-ray analyses have shown that while the binuclear anion $[\{Pt(C_6F_5)_2(C\equiv CSiMe_3)_2\}CoCl_2]^{2-}$ (**1b**) exhibits a flat PtC₄Co core due to the in-plane bis(η^2-alkyne) bonding interactions, both PtC₄Co central cores in **2a** $[\{Pt(C\equiv C-Ph)_4\}\{CoCl_2\}_2]$ are bent. As a consequence, the η^2-alkyne–cobalt interactions take place outside the plane of the 'Pt(C≡C)₂' entities. Obviously, the reasons for this structural preference cannot be attributed either to the complexed unit 'CoCl₂' nor to the coordination environment (which are the same in both cases) but rather to the formal differences of the homoleptic anionic alkynyl platinum fragment $[Pt(C\equiv CR)_4]^{2-}$ with regard to the mixed $[cis\text{-}Pt(C_6F_5)_2\text{-}$

(a)

(b)

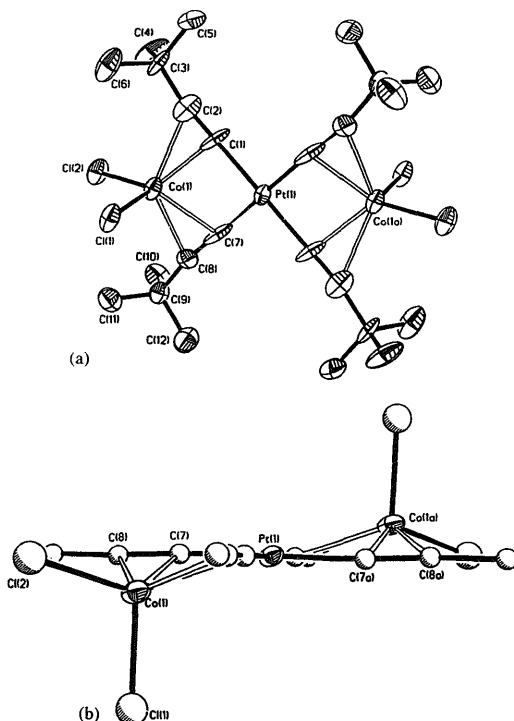Fig. 3. (a) Structure of the anion of **2a** with the atomic numbering scheme. (b) Schematic view showing the bent PtC₄Co cores.

$(C≡CR)_2]^{2-}$. There appears to be no obvious explanation for this preference apart from the shorter metal–metal interaction thus obtained (3.077(3) Å in **2a** versus 3.446(3) Å in **1b**). The donor properties of the metal centre in d^8 square-planar complexes using its occupied d_{z^2} orbital and its ability to react with Lewis-acidic metal complexes yielding heterobimetallic compounds with metal–metal bonds are now firmly established [32]. Many heterometallic platinum complexes with this type of donor–acceptor bond have in fact been isolated and characterised [33]. On this basis, the final structures of **1b** and **2a** could be rationalised as the result of an overall optimisation of all interactions. For the trinuclear anion (**2a**), the enhanced donor properties of the basic centre in $[Pt(C≡C^tBu)_4]^{2-}$ seem to compete with the alkynyl ligands to bind the acidic cobalt centre. The foreseeable stronger interaction between platinum and cobalt with folding could be the dominant factor that causes this complex to be hinged.

On the contrary, the expected reduced donor properties on platinum in the mixed anion $[cis\text{-}Pt(C_6F_5)_2(C≡CSi\text{-}Me_3)_2]^{2-}$, due to the presence of electron-withdrawing C₆F₅ ligands, could account for the weaker platinum–cobalt interaction in the binuclear anion (**1b**) and the final preference for essentially in-plane bis($η^2$-alkynyl)cobalt interactions leading to a flat PtC₄Co core. As suggested by Van Koten and co-workers [18a] in the in-plane interaction the π-back-bonding component takes place to a greater extent, which in turn explains: (i) the lower C≡C stretching frequencies observed in **1** and (ii) the higher distortion of the Pt–C≡C–SiMe₃ entities from linearity.

5. Supplementary material

All the crystallographic material (atomic coordinates, bond lengths, bond angles and anisotropic displacement parameters) is available from the authors on request.

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