Discrete Triangle, Square and Hexametallic Alkynyl Cyano-Bridged Compounds Based on [*cis*-Pt(C≡CR)$_2$(CN)$_2$]$^{2-}$ Building Blocks

Juan Forniés,*[a] Julio Gómez,[b] Elena Lalinde,*[b] and M. Teresa Moreno[b]

Dedicated to the memory of Dr. M. Teresa Pinillos Martínez

Abstract: Novel mixed bis(alkynyl)-bis(cyano)platinate(II) species [*cis*-Pt(C≡CR)$_2$(CN)$_2$]$^{2-}$ (**1a**: R = *t*Bu, **1b**: R = Ph) have been prepared and their potential as building blocks in the generation of self-organized systems with a variable molecular architecture has been studied. The reaction of **1** with the ditopic acceptor species [{*cis*-Pt(C$_6$F$_5$)$_2$S}$_2$(dppa)] (dppa = diphenylphosphinoacetylene) gave the dianionic cyanide/dppa bridged molecular platinotriangles (NBu$_4$)$_2$[(C$_6$F$_5$)$_2$Pt(μ-dppa){(μ-CN)$_2$Pt(C≡CR)$_2$}Pt(C$_6$F$_5$)$_2$] (**2**). X-ray analysis of **2a** confirmed that the "Pt$_2$(C$_6$F$_5$)$_4$(μ-dppa)" binuclear moiety is connected to the dianionic "Pt(C≡CR)$_2$(CN)$_2$" unit by two bridging cyanide ligands. Moreover, treatment of **1** with the solvent cationic species [M(cod)(acetone)$_2$]$^+$ afforded heterometallic molecular squares Pt$_2$M$_2$ (M = Rh, Ir) containing cyanide bridges and terminal alkynyl ligands, (NBu$_4$)$_2$-[cyclo{[*cis*-Pt(C≡CR)$_2$(μ-CN)$_2$][M(cod)]}$_2$] (**3**: M = Rh, **4**: M = Ir). The solid-state structures of phenyl derivatives have been determined by X-ray crystallography. The terminal alkynyl ligands in these cyanide-bridged molecular squares **3** and **4** have been used in the assembly of higher multimetallic complexes. Thus, very unusual bis(double-alkynide)-cyanide-bridged hexametallic compounds (NBu$_4$)$_2$[{(C$_6$F$_5$)$_2$Pt(μ-C≡CPh)$_2$(μ-CN)$_2$}$_2${M(cod)}$_2$] (**5b**: M = Rh, **6b**: M = Ir) were easily formed by simple reactions of **3b** and **4b** with two equivalents of [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$]. An X-ray diffraction study on complex **5b** indicated that the derivative was formed by a simultaneous migration of one σ-alkynyl group from each "Pt(C≡CPh)$_2$(μ-CN)$_2$" corner of the square to both "Pt(C$_6$F$_5$)$_2$" units, resulting in bent σ,π-double-alkynyl bridging systems. Finally, the novel supramolecular anionic assemblies (NBu$_4$)$_4$[cyclo{[*cis*-Pt(C≡CR)$_2$(μ-CN)$_2$][SnPh$_3$]}$_4$] **7** have been obtained by self-assembly of **1** and [SnPh$_3$(acetone)$_2$]$^+$.

Keywords: alkyne ligands · cyanides · heterometallic complexes · platinum · self-assembly

Introduction

In recent years, coordination-driven self-assembly has been employed in the synthesis of a large number of metallocyclic polygons and polyhedra[1] and a variety of methodologies and connectors have been proposed and used in their preparation. However, although cyanide ions have the potential to bridge a variety of metal ions forming multinuclear complexes or extended infinite one, two or three-dimensional systems,[2] comparatively few discrete cyano-bridged rings with three or more than three metal atoms have been described.[3–8] In particular, the number of metal-containing cyano-bridged molecular triangles is surprisingly small[3] and discrete molecules with square cyano-bridged structures are relatively scarce.[4] Recently, the design of molecular entities has yielded big rings,[5] stars,[6] boxes and cages[4j,k,7] and clusters[8] involving cyanide bridging ligands, but only a few examples with platinum centers in their structure have been reported.[4f,5a]

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Platon plots and refine structure studies of each structure in three different ways (Model 1: with the identities of C and N as presented in the article; Model 2: with the elements types reversed; Model 3: with a 50/50 hybrid scattering factor at each of the affected atomic sites).

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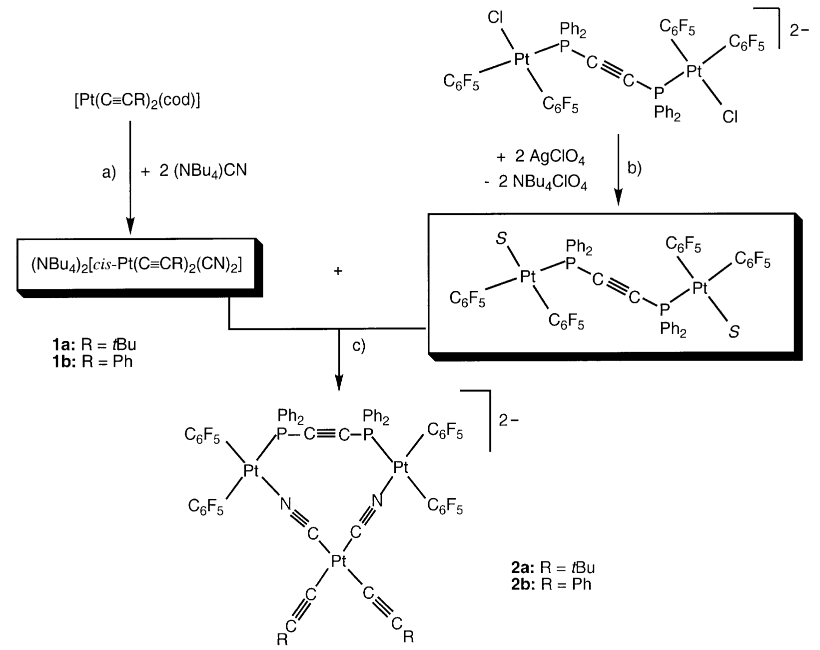
For several years we have been studying the chemistry of alkynyl bridging platinum complexes with regard not only to structural aspects and reactivity but also to their potential interest for material science due to interesting properties such as luminescence[9] or ionic conductivity.[10] We have shown that neutral *cis*- or *trans*-bis(alkynyl)platinum complexes of type $[Pt(C{\equiv}CR)_2L_2]$[11,12a] and, particularly, mixed $[cis/trans\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$[9f,12] and homoleptic $[Pt(C{\equiv}CR)_4]^{2-}$[9a,b,d,13] (R = Ph, *t*Bu, $SiMe_3$) anionic species are excellent precursors to the synthesis of polymetallic species stabilized via η^2-alkyne–metal and in some cases Pt⋯metal bonding interactions. We have also found that anionic platinum substrates are able to act as mono-[12a,d,e,13a,d] or even dialkynylating[12c,d,13c] reagents towards very acidic d^8 or d^6 metal fragments. Continuing our research in this field we considered the preparation of novel mixed bis(alkynyl)bis(cyano)platinate(II) species $[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]^{2-}$ of interest since the combination of CN and C≡CR ligands allowed us to observe the competition between the nitrogen and the acetylenic density to coordinate other ML_n fragments. In this paper we describe the synthesis of these $[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]^{2-}$ stabilized with NBu_4^+ as a counterion and report the results of the interactions of these species with several metal fragments. We report the building up of discrete dianionic cyano-bridged platinum triangle species **2** based on reaction of the ditopic acceptor neutral organometallic fragment $[\{cis\text{-}Pt(C_6F_5)_2S\}_2(dppa)]$ (dppa = diphenylphosphinoacetylene; S = acetone) with the ditopic dianionic donor $[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]^{2-}$ (**1a**: R = *t*Bu, **1b**: R = Ph) building blocks. In addition, we report the synthesis of heteronuclear square cyano-bridged compounds **3** and **4** by combining **1** with 90° acceptor metal solvent entities, $[M(cod)S_2]^+$ (M = Rh, Ir). These complexes still contain two terminal alkynyl ligands bonded to each one of Pt centers and therefore the possibility of forming higher multimetallic assemblies has been investigated. The reaction of these complexes with two equivalents of $[cis\text{-}Pt(C_6F_5)_2(thf)_2]$ yields very unusual hexametallic cyano-bridged σ,π-bis(double-alkynyl)cyanide-bridged rhodium or iridium/platinum M_2Pt_4 (**5b**, **6b**) formed via migration of one alkynyl group from each Pt center of the cyanide ring to Pt atoms of both "$Pt(C_6F_5)_2$"units. Finally, $[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]^{2-}$ units have been employed in the construction of macrocyclic Pt_2Sn_4 square assemblies **7** by combination with $SnPh_3^+$ cations.

Abstract in Spanish: *Se han preparado nuevas especies bis(alquinilo)bis(ciano)platinato(II) $[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]^{2-}$ (**1 a**: R = tBu, **1 b**: R = Ph) y se ha estudiado su potencial como unidades constructoras en la formación de sistemas con arquitectura molecular variable. La reacción de **1** con las especies aceptoras ditópicas $[\{cis\text{-}Pt(C_6F_5)_2S\}_2(dppa)]$ (dppa = difenilfosfinoacetileno) produce triángulos moleculares de platino con puentes cianuro/dppa $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}dppa)\{(\mu\text{-}CN)_2Pt(C{\equiv}CR)_2\}Pt(C_6F_5)_2]$ **2**. El análisis por difracción de Rayos X de **2 a** confirma que la unidad binuclear "$Pt_2(C_6F_5)_4(\mu\text{-}dppa)$" se conecta a la unidad dianiónica "$Pt(C{\equiv}CR)_2(CN)_2$" a través de dos ligandos cianuro puente. Por otro lado, el tratamiento de **1** con las especies catiónicas solvatadas $[M(cod)(acetona)_2]^+$ produce cuadrados moleculares heterometálicos de Pt_2M_2 (M = Rh, Ir) que contienen puentes cianuro y ligandos alquinilo terminales, $(NBu_4)_2[ciclo\{[cis\text{-}Pt(C{\equiv}CR)_2(\mu\text{-}CN)_2][M(cod)]\}_2]$ (**3**: M = Rh, **4**: M = Ir) como se ha confirmado mediante difracción de Rayos X en los derivados de fenilo (**3 b**, **4 b**). Estos cuadrados moleculares, que contienen ligandos alquinilo terminales, se han empleado para generar complejos de mayor nuclearidad. Así, se forman fácilmente especies hexametálicas con puentes bis(doble-alquinilo)-cianuro $(NBu_4)_2[\{(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2(\mu\text{-}CN)_2\}_2\{M(cod)\}_2]$ (**5 b**: M = Rh, **6 b**: M = Ir) mediante reacción de los derivados **3 b** y **4 b** con 2 equivalentes de $[cis\text{-}Pt(C_6F_5)_2(thf)_2]$. El estudio por difracción de Rayos X sobre el complejo **5 b** indica que su formación se produce mediante migración simultánea de un grupo σ-alquinilo de cada uno de los grupos "$Pt(C{\equiv}CR)_2(\mu\text{-}CN)_2$", situado en las esquinas del cuadrado, a ambas unidades "$Pt(C_6F_5)_2$" dando lugar a sistemas con doble puente acetiluro de tipo σ/π. Finalmente, se generan sistemas supramoleculares aniónicos $(NBu_4)_4[ciclo\{[cis\text{-}Pt(C{\equiv}CR)_2(\mu\text{-}CN)_2][SnPh_3]\}_4]$ (**7**) por reacción de **1** con $[SnPh_3(acetona)_2]^+$.*

Results and Discussion

Mononuclear building block complexes: The synthesis of the bis(alkynyl)bis(cyano)platinate(II) complexes $(NBu_4)_2[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]$ (**1a**: R = *t*Bu, **1b**: R = Ph) were carried out by reaction of the neutral platinum derivatives $[Pt(C{\equiv}CR)_2(cod)]$ (R = *t*Bu,[12a] Ph[14]) with two equivalents of $(NBu_4)CN$ in acetone (Scheme 1a). This synthetic strategy, previously used by us and others with phosphine ligands,[11b,12a,15] caused the displacement of the cyclooctadiene by the cyanide ligands and led to the formation of the dianionic species quantitatively, as observed by NMR spectroscopy. However, all attempts to obtain these compounds as solid samples failed. Evaporation of the solvent followed by prolonged vacuum to eliminate the COD ligand gave **1a** and **1b** as oily samples, which were characterized spectroscopically. The most noticeable feature in the IR spectra is the presence of one broad, strong absorption at 2101 cm^{-1}, which is assigned to $\tilde{\nu}(C{\equiv}C)$ vibrations (see below), together with a shoulder in the region 2131–2125 cm^{-1} tentatively attributed to $\tilde{\nu}(C{\equiv}N)$ vibrations.[2a] It is interesting to note that the $\tilde{\nu}(C{\equiv}C)$ absorption in both complexes appears at higher frequencies than those previously observed in other anionic alkynylplatinate(II) species, in accordance with a better π-acceptor capability of the isoelectronic CN groups, which effectively compete in these systems for the electron density of the Pt atom. The ^1H NMR spectra show, in addition to the NBu_4^+ cation signals, the expected resonances due to *t*Bu (δ 1.13, s, **1a**) or phenyl groups (**1b**). For complex **1a**, the C_α and C_β resonances were observed at δ 87.6 and 109.6, respectively but ^{195}Pt satellites were not observed; the CN signal appeared as a singlet at 132.5 ppm. For comparative purposes with complex **3a′** (see below) $(NBu_4)_2[cis\text{-}Pt(C{\equiv}CtBu)_2(^{13}CN)_2]$ (**1a′**) was also prepared (see Experimental



Scheme 1. Synthesis of the complexes **1** and the triangular platinum species **2**.

Section for details); a J^{195}Pt,C(cyanide) coupling constant of 916 Hz was observed for this complex.

Molecular triangles: Complexes $(NBu_4)_2[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]$ **1** can be used as a ditopic donor unit to make triangular species. Thus, treatment of $(NBu_4)_2[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]$ (**1a**: R = *t*Bu, **1b**: R = Ph) with the neutral ditopic acceptor dinuclear species $[\{cis\text{-}Pt(C_6F_5)_2S\}_2(\mu\text{-dppa})]$ (dppa = diphenylphosphinoacetylene; S = acetone), prepared in situ by treatment of $(NBu_4)_2[\{cis\text{-}Pt(C_6F_5)_2Cl\}_2(\mu\text{-dppa})]$[16] with 2 equiv of $AgClO_4$ in acetone (Scheme 1b) led to novel anionic molecular triangles $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-dppa})\{(\mu\text{-}CN)_2Pt(C{\equiv}CR)_2\}Pt(C_6F_5)_2]$ (**2a**: R = *t*Bu, **2b**: R = Ph; Scheme 1c) which were obtained as white solids in moderate yields (40–42 %). The new complexes **2** have been characterized by the usual spectroscopic and analytical methods and the triangle constitution confirmed by a single X-ray analysis on complex **2a**. Their IR spectra exhibit one $\tilde{\nu}(C{\equiv}C)$ absorption at 2117 cm^{-1} (**2a**) and at 2120 cm^{-1} (**2b**), respectively; this confirms the presence of terminal alkynyl ligands, and two strong $\tilde{\nu}(C{\equiv}N)$ bands which, in accordance with the bridging nature of the CN groups,[2a] are shifted towards higher energy in relation to that seen in the precursors **1** (range 2184–2157 **2** vs 2131–2125 cm^{-1} **1**). In accordance with the formulation given in Scheme 1, their ^{19}F NMR spectra exhibit two multiplets in the *o*-fluorine region (4 *o*-F:4 *o*-F), two different signals at high field for the *para*-fluorine and two multiplets due to the *meta*-fluorine (4*m*-F:4*m*-F), thus unequivocally confirming the presence of two nonequivalent C_6F_5 rings (C_6F_5 *trans* to N and C_6F_5 *trans* to P). As expected, only one singlet signal (δ −4.28 to 2.95) was observed in their $^{31}P\{^1H\}$ NMR spectra, the ^1J(Pt,P) (2454 **2a**, 2490 Hz **2b**) being slightly smaller than in the precursor[16] (2564 Hz), probably reflecting a worse bonding interaction between platinum and phosphorous as the result of higher steric constraint.

Slow diffusion of *n*-hexane into a solution of **2a** in benzene leads to the formation of colorless crystals suitable for X-ray crystal structure analysis. A view of the molecular structure of the trinuclear complex anion $[(C_6F_5)_2Pt(\mu\text{-dppa})\{(\mu\text{-}CN)_2Pt(C{\equiv}CtBu)_2\}Pt(C_6F_5)_2]^{2-}$ (**2a**) is shown in Figure 1. Selected bond lengths and angles are given in Table 1. The structure confirms that the reaction has taken place with stereoretention. Thus, the triplatinum anion consists of a “*cis,cis*-$Pt_2(C_6F_5)_4(\mu\text{-dppa})$” binuclear fragment and a “*cis*-$Pt(C{\equiv}CtBu)_2(CN)_2$” moiety linked by the cyanide ligands, with the

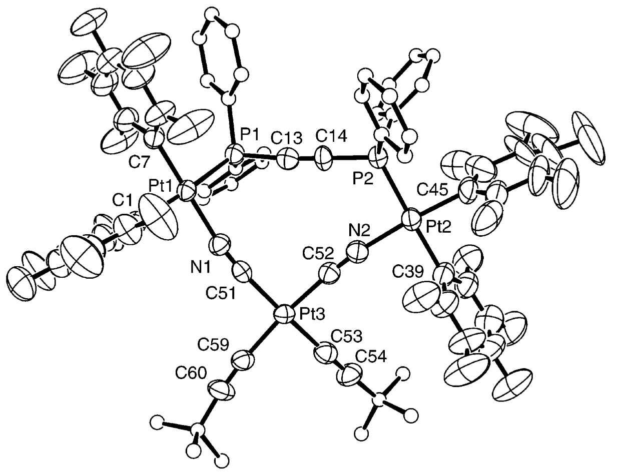


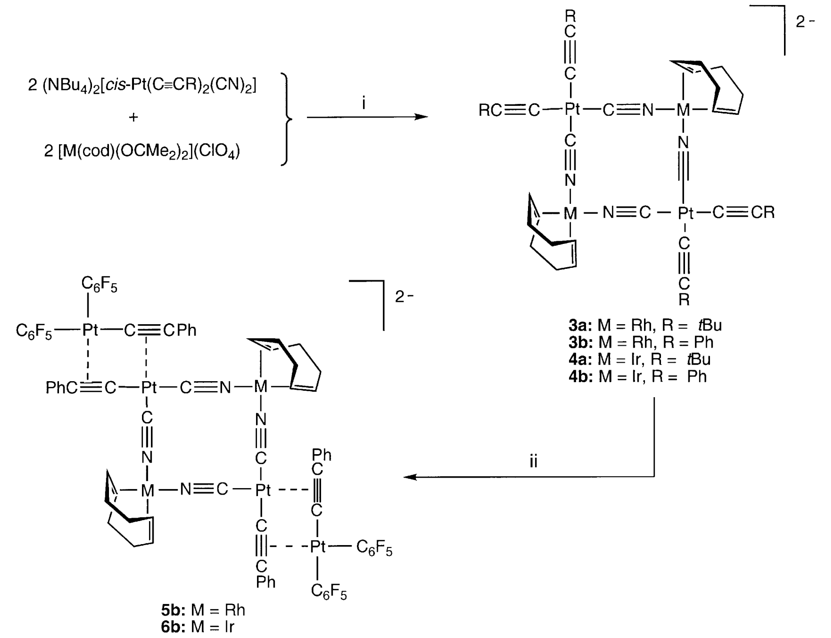
Figure 1. Molecular structure of the anion $[(C_6F_5)_2Pt(\mu\text{-dppa})\{(\mu\text{-}CN)_2Pt(C{\equiv}CtBu)_2\}Pt(C_6F_5)_2]^{2-}$ in complex **2a**, with the hydrogen atoms omitted.

Table 1. Selected bond lengths [Å] and angles [°] for $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-dppa})\{(\mu\text{-}CN)_2Pt(C{\equiv}CtBu)_2\}Pt(C_6F_5)_2]\cdot C_6H_6$ ($2a\cdot C_6H_6$).

Pt1–N1	2.045(4)	N1–C51	1.139(6)
Pt1–P1	2.2692(14)	N2–C52	1.151(6)
Pt2–N2	2.033(4)	C13–C14	1.191(6)
Pt2–P2	2.2753(14)	C53–C54	1.204(7)
P1–C13	1.773(5)	C59–C60	1.186(7)
P2–C14	1.760(5)		
C52-Pt3-C51	90.2(2)	C52-N2-Pt2	172.5(4)
N1-Pt1-P1	90.39(13)	C14-C13-P1	174.0(5)
N2-Pt2-P2	93.61(13)	C13-C14-P2	175.3(5)
C13-P1-Pt1	117.6(2)	N1-C51-Pt3	173.3(5)
C14-P2-Pt2	115.4(2)	N2-C52-Pt3	173.6(5)
C51-N1-Pt1	172.1(4)		

carbon ends bound to Pt3 and the nitrogen ends to Pt1 and Pt2. Alternative refinements with the C and N atoms changed and with a 50:50 factor of occupancy give worse results (see Supporting Information). The platinum(II) centers adopt slightly distorted square-planar coordination geometries, the dihedral angles between the Pt_3 plane and the corresponding best square-planar coordination planes being 36.54 Å Pt1, 8.60 Å Pt2, 8.10 Å Pt3. The coordination geometry around the platinum atoms is only slightly distorted from its ideal angle of 90° [90.2(2)–93.61(13)°]. The presence of the two phosphorous atoms at Pt2 and Pt1 seems to minimize steric constraint, the CN connectors and P–C–C entities being essentially linear [range 172.1(4)–175.3(5)°]. The observed Pt···Pt distances are Pt1–Pt3 5.160 Å, Pt2–Pt3 5.143 and Pt1–Pt2 7.223 Å. Recently, a cyclic trimer of a neutral Pt–bis(phosphine) complex, $[PtCl_2(\mu\text{-}\kappa P,P'\text{-}PPh_2\text{-}C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CPPh_2)]_3$, has been structurally characterized.[17]

Molecular squares: As previously commented, the ability of alkynyl ligands to bind metal atoms has now been firmly established. In fact, we have previously shown that the dianionic mixed substrates $[cis\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ act as a monoalkynylating agent towards the cationic solvent iridium fragment $[Ir(cod)S_2]^{+}$[12e] while similar reactions with $[Rh(cod)S_2]^{+}$ (S = acetone) yield simple 1:1 adducts, formally zwitterionic, in which the rhodium is unusually stabilized by two η^2-alkyne interactions.[12e] With these precedents and considering that the terminal CN groups still also have a potentially N atom donor, we considered it of interest to explore the reactivity of the novel mixed bis(alkynyl)bis(cyano)platinate(II) derivatives **1** towards the same cationic substrates $[M(cod)S_2]^{+}$. The results of this study are summarized in Scheme 2. As can be observed, using $(NBu_4)_2[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]$ (**1**) as building blocks, the hard nitrogen end of the CN ligand is always the preferred bridging ligand regardless of the unsaturated metal fragment employed. This has allowed us to synthesize a new kind of anionic heteronuclear cyanide-bridged molecular squares **3** and **4**, which also display four terminal alkynyl ligands. Thus, the reactions in acetone of $(NBu_4)_2[cis\text{-}Pt(C{\equiv}CR)_2(CN)_2]$ (**1a**: R = *t*Bu, **1b**: R = Ph) with the solvent species $[M(cod)(acetone)_2]^{+}$ (M = Rh, Ir) (1:1 molar ratio) prepared "in situ" by treating $[M(\mu\text{-}Cl)(cod)]_2$ (M = Rh, Ir) with $AgClO_4$ (2 equiv) in acetone, produced the immediate precipitation of yellow solids formulated as $(NBu_4)_2[cyclo\{[cis\text{-}Pt(C{\equiv}CR)_2(\mu\text{-}CN)_2][M(cod)]\}_2]$ (**3a**: M = Rh, R = *t*Bu; **3b**: M = Rh, R = Ph; **4a**, **4b**: M = Ir) (Scheme 2i) (see Experimental Section). The products, which are stable in solid state, are very insoluble in common organic solvents, thus precluding conductivity measurements. However, the FAB(−) MS data for the squares **3** and **4** are strongly supportive of the formulation of the square structures with detection of the monoanion tetranuclear parent ion in **3a** (*m*/*z* 1483), **3b** (*m*/*z* 1562) and **4b** (*m*/*z* 1741), whose isotopic distribution patterns matched the calculated compositions, and additional peaks were easily assignable to their fragmentation. In accordance with the bridging nature of the cyano ligands,[2a] the IR spectra show two strong $\tilde{\nu}(C{\equiv}N)$ stretching vibrations at higher frequencies (2170–2150 cm^{-1}) than those found for the corresponding terminal CN groups in the starting materials **1**. Moreover, one additional $\tilde{\nu}(C{\equiv}C)$ band is also observed in the expected region (2113–2107 cm^{-1}) for terminal C≡CR ligands. The planar formulation is consistent with their proton NMR spectra which, at room temperature, exhibit only one olefinic signal (δ 4.22–3.88, 8H) and two aliphatic resonances [δ 2.37–1.49 8H:8H, one for **4b** (δ 2.16, 16H)], due to the equivalent COD ligands. For complex **4b**, the spectrum was also recorded at low temperature exhibiting a similar pattern. In order to confirm that the reactions take place with retention of the σ-C(CN) coordination of the cyanide ligands to Pt atoms, complex $(NBu_4)_2[cyclo\{[cis\text{-}Pt(C{\equiv}CtBu)_2(\mu\text{-}^{13}CN)_2][Rh(cod)]\}_2]$ (**3a′**) was also prepared in a similar manner starting from $(NBu_4)_2[cis\text{-}Pt(C{\equiv}CtBu)_2(^{13}CN)_2]$ (**1a′**). In former complex (**3a′**), the μ-^{13}CN resonance is downfield shifted to 138.7 ppm with respect to the value observed in **1a′** (δ 132.5). The observed shift (Δ6.2 ppm) is comparable to those reported for other heteropolynuclear Rh-μ-CN–Co–CN systems containing terminal and bridging cyanide ligands.[4i] In agreement with the Pt–CN bond, the magnitude of the $^1J(Pt,^{13}C)$ (973 Hz) is even slightly larger than in **1a′** with terminal ^{13}CN ligands



Scheme 2. Self-assembly of heterometallic Pt_2Rh_2, Pt_2Ir_2 alkynyl cyanide-bridged molecular squares **3** and **4**, i) $-2\,NBu_4ClO_4$. Synthesis of hexametallic complexes **5b** and **6b** by reaction with ii) $2\,[cis\text{-}Pt(C_6F_5)_2(thf)_2]$.

(916 Hz) probably reflecting a better π-back donor component in the Pt–C(cyanide) bond as a consequence of the coordination of the nitrogen centers. After many attempts X-ray quality crystals of **3b** and **4b** were finally obtained by slow diffusion of diisopropyl ether into saturated dichloromethane solutions (−30 °C **3b**, room temperature **4b**) of both complexes and, thus, their solid-state structures were determined by X-ray crystallographic analyses. Figures 2 (top) and 3 (top) show a view of the dianions [cyclo{[*cis*-Pt(C≡CPh)$_2$(μ-CN)$_2$][M(cod)]}$_2$]$^{2-}$ (M = Rh, Ir) and Tables 2 and 3 summarize selected bond lengths and angles. Both nearly square anions are formed by two "Pt(C≡CPh)$_2$(μ-CN)$_2$" fragments and two M(cod) (M = Rh or Ir) moieties held together by the CN bridges (For modifications of C/N atoms see Supporting Information). The observed Pt–C(cyanide) [1.979(10)–1.900(18) Å] and M–N(cyanide) [2.056(8)–1.986(14) Å] distances and the corresponding C-Pt-C [90.9(3)° **3b**, 89.4(7)° **4b**] and N-M-N (cyanide C and N) [90.3(3)° **3b**, 90.1(5)° **4b**] angles are in line with the expected values. As is observed in Figures 2 (top) and 3 (top), the anions show a different degree of bending at the M-NC-Pt edges (see Tables 2 and 3), being closer to a linear arrangement in the Rh derivative than in the Ir one. The geometrical details of the two terminal alkynyl groups and the η^2-bonded COD ligands are unexceptional.[12e,13b,13d,18] The edge-to-edge distances (Pt···M) are 5.166 and 5.167 Å for **3b** and 5.110 and 5.048 Å for **4b**. The macrocycles are practically planar, the dihedral angles between the Pt$_2$M$_2$ plane and the corresponding coordination planes of each metal are within the range 2.62 to 6.93°. Notably the crystal packing pattern of these compounds is different (see Figures 2, bottom and 3, bottom). Thus, whereas the anions of the Pt$_2$Rh$_2$ derivative are offset (see Figure 2, bottom), in the anion of complex **4b**, the arrangement of the different layers of squares is essentially eclipsed, forming an extended

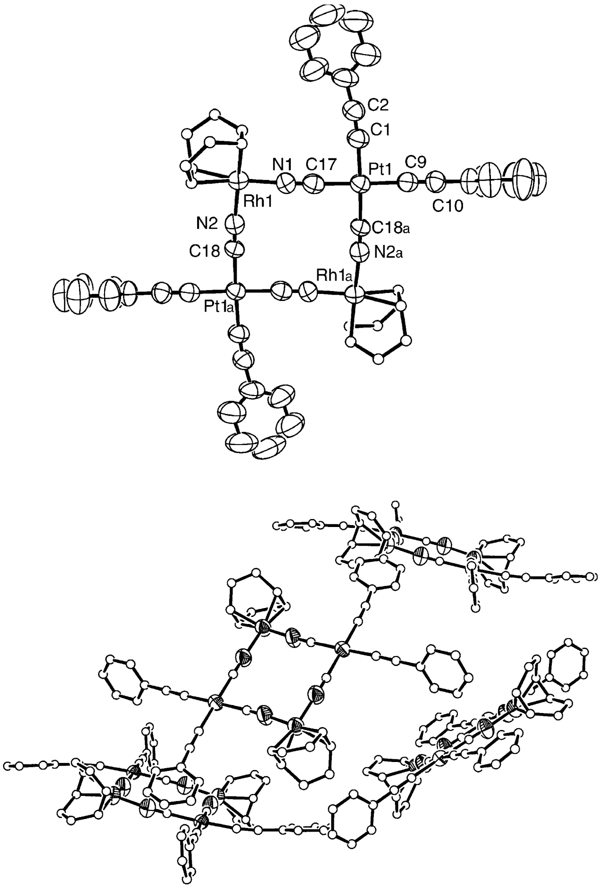


Figure 2. View of the molecular structure of the anion [cyclo{[*cis*-Pt(C≡CPh)$_2$(μ-CN)$_2$][Rh(cod)]}$_2$]$^{2-}$ in complex **3b**. Hydrogen atoms are omitted for clarity (top); simplified packing diagram of **3b**. Note how the squares are offset, preventing the formation of channels (bottom).

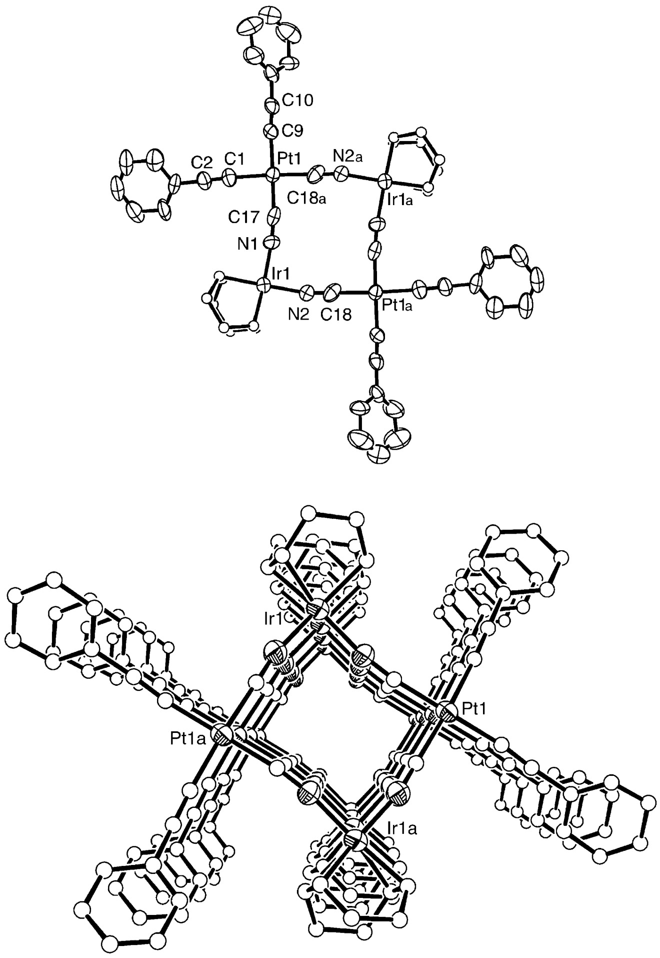


Figure 3. Structure of the anion [cyclo{[*cis*-Pt(C≡CPh)$_2$(μ-CN)$_2$][Ir(cod)]}$_2$]$^{2-}$ in complex **4b** (top); packing diagram of **4b** showing how the cores of the molecular squares stack forming an infinite tunnel (bottom).

Table 2. Selected bond lengths [Å] and angles [°] for (NBu$_4$)$_2$[cyclo{[*cis*-Pt(C≡CPh)$_2$(μ-CN)$_2$][Rh(cod)]}$_2$] (**3b**·CH$_2$Cl$_2$).

Pt1–C18a	1.972(8)	C17–N1	1.165(10)
Pt1–C17	1.979(10)	C18–N2	1.147(9)
Rh1–N1	2.027(8)	C1–C2	1.210(11)
Rh1–N2	2.056(8)	C9–C10	1.196(11)
C18a-Pt1-C17	90.9(3)	C1-C2-C3	173.7(10)
N1-Rh1-N2	90.3(3)	C10-C9-Pt1	177.8(8)
C17-N1-Rh1	176.4(7)	C9-C10-C11	179.1(10)
C18-N2-Rh1	175.1(7)	N1-C17-Pt1	178.3(8)
C2-C1-Pt1	172.2(8)	N2-C18-Pt1a	177.6(8)

Table 3. Selected bond lengths [Å] and angles [°] for $(NBu_4)_2$[cyclo{[*cis*-Pt(C≡CPh)$_2$(μ-CN)$_2$][Ir(cod)]}$_2$] (**4b**).

Pt1–C18a	1.971(18)	C17–N1	1.20(2)
Pt1–C17	1.900(18)	C18–N2	1.150(19)
Ir1–N1	1.986(14)	C1–C2	1.162(19)
Ir1–N2	2.012(13)	C9–C10	1.172(19)
C17-Pt1-C18a	89.4(7)	C1-C2-C3	174.4(18)
N1-Ir1-N2	90.1(5)	C10-C9-Pt1	173.8(13)
C17-N1-Ir1	169.7(13)	C9-C10-C11	176.6(16)
C18-N2-Ir1	168.6(15)	N1-C17-Pt1	173.5(14)
C2-C1-Pt1	176.9(16)	N2-C18-Pt1a	177.6(16)

channel in the solid (Figure 3, bottom). Similar packing patterns with extended channels in the solid state have been previously found in related complexes,[4h,19] but the driving force behind their formation is not clear at this moment.

Hexametallic derivatives: Complexes **3** and **4** are remarkable because bi- or polynuclear species containing terminal alkynyl ligands are scarce.[13a,c,d,15,16,20] As far as we know, these species are unique since they are the first examples of polynuclear derivatives containing four terminal alkynyl groups. In these complexes, each platinum atom still has two mutually *cis* σ-bonded alkynyl ligands. This structural arrangement as well as the dianionic nature of the square core are essential requirements for its further application in the assembly of higher multimetallic assemblies. All efforts to prepare neutral defined products of stoichiometry {Pt_2(C≡CR)$_2$(CN)$_2$$M_4(cod)_4$} containing two additional cationic $[M(cod)]^+$ fragments have been unsuccessful. Thus, treatment of **3** and **4** with one additional equiv of $[M(cod)(acetone)_2]^+$ or alternatively $(NBu_4)_2$[Pt(C≡CR)$_2$(CN)$_2$] **1** with 2 equiv $[M(cod)(acetone)_2]^+$ in acetone afforded insoluble solids, whose ^{1}H NMR spectra in [D$_6$]DMSO clearly suggest that they are complex mixtures probably of tetranuclear complexes (with NBu_4^+ cations) and the expected neutral hexanuclear species.

In an effort to expand the supramolecular motif of tetrametallic complexes, and to continue our studies of platinum alkynyl derivatives, we decided to examine the reactivity of the phenyl derivatives towards the fragment "*cis*-Pt$(C_6F_5)_2$". The stabilization of "*cis*-Pt$(C_6F_5)_2$" units by two η^2-alkyne or metallalkyne fragments is now well documented.[11b,12a,12c,12d,13a,13c,13d,16] In addition, previous work has also shown that, in particular, mononuclear anionic systems such as $[PtX_2$(C≡CR)$_2]^{2-}$ (X = C_6F_5, C≡CR) act as monoalkynylating agent of this acidic "*cis*-Pt$(C_6F_5)_2$" synthon yielding σ/π doubly alkynyl diplatinum complexes.[12a,13a] Accordingly, suspensions of $(NBu_4)_2$[cyclo{[*cis*-Pt(C≡CPh)$_2$(μ-CN)$_2$][M(cod)]}$_2$] (M = Rh **3b**, Ir **4b**) were treated in CH_2Cl_2 with two equivalents of the bis(solvent) neutral complex [*cis*-Pt$(C_6F_5)_2$(thf)$_2$] (THF = tetrahydrofuran). This caused the slow solubilization of the precursor yielding turbid solutions from which, after the usual work-up, the expected hexametallic dianionic species $(NBu_4)_2$[{$(C_6F_5)_2$Pt(μ-C≡CPh)$_2$(μ-CN)$_2$}$_2${M(cod)}$_2$] (**5b**: M = Rh, **6b**: M = Ir) were obtained as yellow solids in moderate yields (ca. 60%).

Crystals of **5b** were grown at low temperature from CH_2Cl_2/diisopropyl ether. The structure of the anion (Figure 4, Experimental Section and Supporting Information) confirms the formulation given in Scheme 2ii, which implies the formal, simultaneous migration of one of the σ-C≡CPh groups from each corner of the square to both "Pt$(C_6F_5)_2$" fragments forming two novel σ/π double alkynyl bridging systems. We have recently reported the first unusual examples of double-alkynyl migration processes between the homoleptic species $[Pt(C{\equiv}CR)_4]^{2-}$ and the very acidic dicationic d^6 metal fragments $[MCp^*(PEt_3)S_2]^{2+}$ (M = Rh, Ir)[13c] but, in this case, the final formation of **5b** and **6b** is remarkable because it represents the first occasion in which a polynuclear precursor acts as an alkynylating agent. The formation of these species recall the unusual synthesis of hexametallic zirconium based σ/π species {1,3,5-(Cp_2Zr-C≡C)$_3$$C_6H_3$}[$Cp_2$Zr(μ-$\eta^2$-C≡C*t*Bu)]$_3$ generated by simultaneous activation of three C–C bonds on [1,3,5-(*t*BuC≡CC≡C)$_3$$C_6H_3$] by "Zr$Cp_2$" recently reported by Rosenthal et al.[21] As can be seen in Figure 4 (see Table 4 for details), the structure establishes the formation of two slightly bent (dihedral angle 35.7°) σ/π doubly alkynyl bridging systems connecting the platinum atoms as consequence of the simultaneous σ-alkynyl migration from each Pt1 to each Pt2 (Pt···Pt 3.36 Å). The structural details of the bridging system are similar to those found in comparable homo[11a,12a,22] or heterobinuclear[12d,e,13d,22b] systems. The η^2-metal acetylenic linkages are slightly asymmetric with the M–C$_\beta$ bond lengths perceptibly shorter than the corresponding M-C$_\alpha$

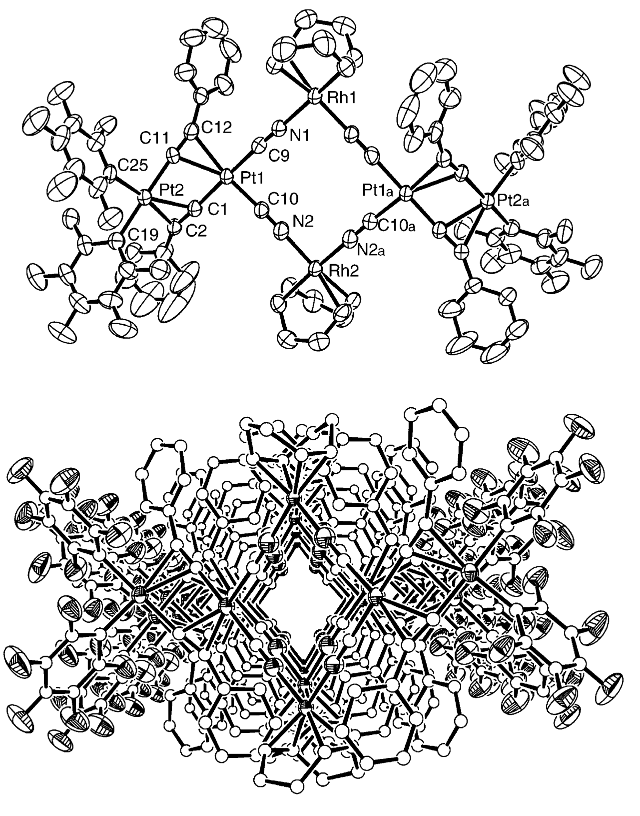


Figure 4. Crystal structure of the anion [{$(C_6F_5)_2$Pt(μ-C≡CPh)$_2$Pt(μ-CN)$_2$}$_2${Rh(cod)}$_2]^{2-}$ in complex **5b**. Hydrogen atoms are omitted for clarity (top); packing diagram of **5b** showing the channel created by the stacking of molecules in the crystal (bottom).

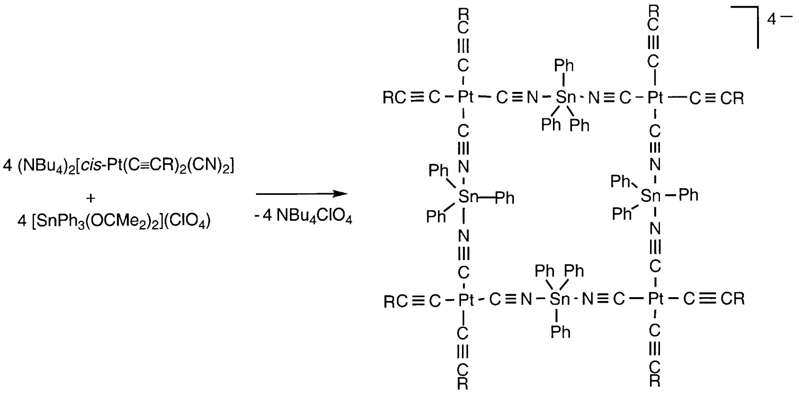
Table 4. Selected bond lengths [Å] and angles [°] for $(NBu_4)_2\{(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(\mu\text{-}CN)_2\}_2\{Rh(cod)\}_2]$ (**5b**).

Pt1–C10	1.935(5)	Pt2–C1	2.271(5)
Pt1–C1	1.982(5)	Rh1–N1	2.048(4)
Pt1–C9	1.985(6)	Rh2–N2	2.049(5)
Pt1–C12	2.269(5)	N1–C9	1.154(7)
Pt1–C11	2.291(5)	N2–C10	1.152(7)
Pt2–C11	2.000(5)	C1–C2	1.232(7)
Pt2–C2	2.261(5)	C11–C12	1.213(7)
C10-Pt1-C9	89.3(2)	C2-C1-Pt1	176.9(5)
C1-Pt1-C12	96.4(2)	C1-C2-C3	155.1(6)
C11-Pt2-C2	97.5(2)	N1-C9-Pt1	176.9(5)
N1-Rh1-N1a	90.1(2)	N2-C10-Pt1	177.0(5)
N2a-Rh2-N2	88.9(3)	C12-C11-Pt2	174.4(5)
C9-N1-Rh1	177.6(5)	C11-C12-C13	157.2(6)
C10-N2-Rh2	177.1(5)		

and accordingly the M–$C_\alpha{\equiv}C_\beta$ backbones remain almost linear [174.4(5), 176.9(5)°], while units $C_\alpha{\equiv}C_\beta$–C(Ph) exhibit a marked deviation from linearity [157.2(6), 155.1(6)°]. In spite of the extended polymetallic assembly, the square shape of the central core remains essentially identical to the precursor with Rh–N, Pt–C bond lengths and C-N-Rh, N-C-Pt, C-Pt-C or N-Rh-N bond angles comparable to those found in **3b**. Only the Pt–CN distances are slightly asymmetric, the Pt–C *trans* to C≡C bond [1.935(5) Å] being perceptibly shorter than the corresponding one *trans* to the C_α carbon donor [1.985(6) Å], consistent with the stronger *trans* influence of the σ-donor C_α carbon atom. The dihedral angles between the Pt1-Pt1a-Rh_2 and the best coordination planes at each metal center [Pt1 4.75°, Rh2 7.69°, Rh1 1.43°] gives again an idea of the planarity of the square. The most remarkable feature is the change observed in the final stacking pattern in the solid state (Figure 4, bottom). Thus, in contrast to **3b**, where the molecular squares are not stacked in the hexametallic Pt_4Rh_2 derivative (**5b**), the squares are stacked in an eclipsed way along the *c* axis, resulting in long channel-like cavities (Figure 4, bottom). The repeating units are 10.2 Å apart excluding bonding interactions.

The IR spectra of **5b** and **6b** confirm the activation of one σ-Pt–C bond in the precursor. Thus, they show one weak $\tilde{\nu}$(C≡C) band shifted to lower wavenumbers (Δ90 cm^{-1}) in relation to that observed in the precursor [2020 cm^{-1} in **5b**, **6b** vs 2110 (**3b**), 2113 cm^{-1} (**4b**)], which is consistent with a σ/π double alkynyl bridging system.[11a,d,12a,d,e,13d,22a] As expected, the hexametallic complexes **5b** and **6b** also show two strong high-frequency bands (range 2175–2164 cm^{-1}), which appear at similar positions to those observed in the molecular squares (**3**, **4**), and which are assigned to the bridging cyanide groups. The FAB(−) MS data for these derivatives are strongly supportive of the hexametallic nature with detection of the parent ion in **5b** (*m*/*z* 2864). As is typical in double-alkynyl bridging systems, the ^{19}F and ^{1}H NMR spectra confirm that these complexes are dynamic on their respective time scales. Thus, only one type of C_6F_5 ring is observed with a typical AA′MXX′ pattern (2*o*-F, *p*-F, 2*m*-F) and only one olefinic environment evidencing the existence of an apparent C_{2v} symmetry. These patterns, which do not change for complex **6b** at low temperature (−50 °C), can be explained by a fast σ/π intramolecular exchange of both alkynyl bridging ligands, which equilibrates the corresponding corners followed by a very fast inversion of the central puckered diplatinacycles to account for the apparent time-averaged plane of symmetry containing the metal centers.

In an attempt to extend the size of the molecular squares we considered the possibility of coordination of the cyanide ligands to well known organotin cations. Transition metal cyano complexes have been studied in combination with R_3Sn^+ cations.[23] The synthetic strategy employed (Scheme 3) is based on the displacement of the acetone molecules from the fragments $[SnR_3(S)_2]^+$, which present the solvent molecules in the apical positions of a trigonal bipyramide, by two nitrogen atoms of two cyano ligands belonging to different "*cis*-Pt(C≡CR)$_2$(CN)$_2$" fragments. Thus, treatment of $(NBu_4)_2$[*cis*-Pt(C≡CR)$_2$(CN)$_2$] (**1a**: R = *t*Bu, **1b**: R = Ph) with 1 equivalent of the bis(solvent) cationic species $[SnPh_3(acetone)_2]^+$ prepared "in situ" in acetone, results in the immediate precipitation of white solids formulated as $(NBu_4)_4$[cyclo{[*cis*-Pt(C≡CR)$_2$(μ-CN)$_2$][SnPh$_3$]}$_4$] (**7a**: R = *t*Bu, **7b**: R = Ph) (Scheme 3). Despite many attempts we have not been successful in obtaining crystals for X-ray studies and, unfortunately, their extreme insolubility precludes their complete characterization. However, the formulation given is in accordance with their IR spectra, which confirm the presence of cyanide bridge (one high-frequency band at 2143 cm^{-1} **7a**, 2154 cm^{-1} **7b**) and terminal alkynyl ligands (one $\tilde{\nu}$(C≡C) band at 2116 cm^{-1} **7a**, 2115 cm^{-1} **7b**). In addition, the ^{1}H NMR spectrum of **7a** shows, as expected, one resonance for the equivalent *t*Bu groups (δ 1.16) besides the signals due to the NBu_4^+ cation. In order to obtain more soluble species, the possibility of further reaction of



7a: R = *t*Bu
7b: R = Ph

Scheme 3. Self-assembly of Pt_2Sn_4 alkynyl cyanide-bridged molecular squares **7**.

these complexes with "*cis*-$Pt(C_6F_5)_2$" was investigated. Unfortunately, all efforts to prepare a defined product by reacting complexes **7** with [*cis*-$Pt(C_6F_5)_2(thf)_2$] in acetone were fruitless.

Conclusion

We have prepared novel anionic mixed bis(alkynyl)bis(cyano)platinate(II) species $(NBu_4)_2[Pt(C{\equiv}CR)_2(CN)_2]$ (**1**) and we have examined their reactivity towards several fragments. Novel anionic supramolecular assemblies (molecular triangle, square and hexametallic species) can be readily constructed by self-assembly between solvent species and the square-planar [*cis*-$Pt(C{\equiv}CR)_2(CN)_2]^{2-}$ anions as building blocks. These species are remarkable for several reasons. Firstly, there are few examples of heteronuclear cyanide-bridged molecular triangles and squares;[3,4] In addition, the reported Pt triangles and square molecules are usually cationic with a very high charge.[1] In our systems, the successful synthesis of anionic triangles and squares can be attributed to the well-recognized ability of cyanide to accommodate high negative charge.[4k,24] Finally, the coordination ability of the two bis(alkynyl) corners in the squares **3b** and **4b** has allowed us to form higher multimetallic assemblies; we have shown that **3b**, **4b** act as polynuclear unprecedented dialkynylating agents towards two different d^8 "*cis*-$Pt(C_6F_5)_2$" units yielding hexametallic compounds **5b**, **6b** stabilized by two σ/π double alkynyl bridged systems.

Experimental Section

General methods: All reactions and manipulations were carried out under nitrogen atmosphere using Schlenk techniques and distilled solvents purified by known procedures. IR spectra were recorded on a Perkin-Elmer FT-IR 1000 Spectrometer as Nujol mulls between polyethylene sheets. NMR spectra were recorded on Bruker ARX 300 or Bruker Avance 400 spectrometers and chemical shifts are reported in ppm relative to external standards ($SiMe_4$ and $CFCl_3$). Elemental analyses were performed with a Perkin Elemer 2400 CHNS/O or a Carlo Erba EA 1110 CHNS/O microanalyzer. Mass spectra were recorded on a VG Autospec double-focusing (FAB) or HP-5989(B) (ES) mass spectrometers (in these complexes, M refers to the cyclic anionic entity). *cis*-$[Pt(C{\equiv}CR)_2(cod)]$ (R = *t*Bu,[12a] Ph[14]), $(NBu_4)_2$[*cis*-$\{Pt(C_6F_5)_2Cl\}_2(\mu\text{-}dppa)]$,[16] $[M(\mu\text{-}Cl)(cod)]_2$ (M = Rh,[25a] Ir[25b]) and [*cis*-$Pt(C_6F_5)_2(thf)_2]$[26] were prepared according to literature methods. All other reagents were used as obtained commercially.

CAUTION: Some of the following preparations use $AgClO_4$, which is potentially explosive.

Preparation of $(NBu_4)_2$[*cis*-$Pt(C{\equiv}CR)_2(CN)_2$] (1a: R = *t*Bu, 1b: R = Ph): $(NBu_4)CN$ (0.207 g, 0.772 mmol) was added to a suspension of $[Pt(C{\equiv}C\textit{t}Bu)_2(cod)]$ (0.180 g, 0.386 mmol) in acetone (20 mL) and the solution obtained was stirred for 5 min. Evaporation of the solution to dryness gave an oily residue, which was characterized by ^1H NMR and IR spectroscopy. ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 3.57$ (m, 16H; N-CH_2, *n*Bu), 1.84 (m, 16H; CH_2, *n*Bu), 1.52 (m, 16H; CH_2, *n*Bu), 1.13 (s, 18H; *t*Bu), 1.00 (t, 24H; CH_3, *n*Bu); IR: $\tilde{\nu} = 2125$ (sh) (C≡N), 2101 cm^{-1} (s) (C≡C); $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 20 °C): $\delta =$ 132.5 (s, CN), 109.6 (s, $C_\alpha{\equiv}C_\beta$-), 87.6 (s, $C_\alpha{\equiv}C_\beta$-), 58.7 (s, N-CH_2-$(CH_2)_2$-CH_3), 32.6 (s, $C(CH_3)_3$), 28.9 (s, CMe_3), 24.0, 19.3 (s, N-CH_2-$(CH_2)_2$-CH_3), 13.4 (s, N-$(CH_2)_3$-CH_3).

Complex **1b** was prepared similarly as an oil by using the appropriate starting materials, $(NBu_4)CN$ (0.106 g, 0.396 mmol), $[Pt(C{\equiv}CPh)_2(cod)]$ (0.100 g, 0.198 mmol). ^1H NMR (300.1 MHz, CD_3COCD_3, 20 °C): $\delta =$ 7.19 (d, $J = 7.2$ Hz, 4H), 7.09 (m, 4H), 6.94 (t, $J = 7.2$ Hz, 2*p*-H) (Ph), 3.52 (m, 16H; N-CH_2, *n*Bu), 1.81 (m, 16H; CH_2, *n*Bu), 1.47 (m, 16H; CH_2, *n*Bu), 0.97 (t, 24H; CH_3, *n*Bu); IR: $\tilde{\nu} = 2131$ (m, sh) (C≡N), 2101 cm^{-1} (vs) (C≡C).

Preparation of $(NBu_4)_2$[*cis*-$Pt(C{\equiv}C\textit{t}Bu)_2(^{13}CN)_2$] (1a′): $[Pt(C{\equiv}C\textit{t}Bu)_2(cod)]$ (0.15 g, 0.297 mmol) was treated with $K^{13}CN$ (0.0392 g, 0.594 mmol) in acetone (20 mL) and the solution was stirred for 10 min. After evaporation to dryness, the residue was treated with a solution of $(NBu_4)Br$ (0.191 g, 0.594 mmol) in CH_2Cl_2 (20 mL) and the mixture was stirred for 24 h. The KBr formed was filtered off, and the filtrate was evaporated to dryness giving **1a′** as oily residue. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta =$ 132.5 (s, $^1J(^{195}Pt,^{13}C) = 916$ Hz, CN).

Synthesis of $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}dppa)\{(\mu\text{-}CN)_2Pt(C{\equiv}CR)_2\}Pt(C_6F_5)_2]$ (2a: R = *t*Bu, 2b: R = Ph): A solution of $(NBu_4)_2$[*cis*-$\{Pt(C_6F_5)_2Cl\}_2(\mu\text{-}dppa)]$ (0.400 g, 0.199 mmol) in acetone (20 mL) was treated with $AgClO_4$ (0.0826 g, 0.398 mmol) and the mixture, protected from the light, was stirred at room temperature for 1 h. The final suspension was evaporated to dryness and the residue treated with diethyl ether (30 mL) and filtered. The filtrate was again evaporated to dryness and the residue which contains [*cis*,*cis*-$\{Pt(C_6F_5)_2(acetone)\}_2(\mu\text{-}dppa)]$ [$\delta(P) = 0.80$ s, $^1J(P,Pt) = 2570$ Hz; $\delta(F) = -117.6$ (dd, $^3J(Pt,o\text{-}F) = 497$ Hz, 4*o*-F), −118.8 (m, $^3J(Pt,o\text{-}F) = 375$ Hz, 4*o*-F), −161.7 (t, 2*p*-F), −163.1 (t, 2*p*-F), −164.3 (m, 4*m*-F), −165.5 (m, 4*m*-F)] was treated with a solution of $(NBu_4)_2$[*cis*-$Pt(C{\equiv}C\textit{t}Bu)_2(CN)_2]$ (0.178 g, 0.199 mmol) in acetone (20 mL). The mixture was stirred for 15 min and evaporated to dryness. The addition of EtOH (10 mL) rendered **2a** as a white solid (0.185 g, 40 %).

Compound **2b** was obtained as a white solid similarly by starting from $(NBu_4)_2$[*cis*-$\{Pt(C_6F_5)_2Cl\}_2(\mu\text{-}dppa)]$ (0.151 g, 0.075 mmol), $AgClO_4$ (0.031 g, 0.150 mmol) and an acetone solution of $(NBu_4)_2$[*cis*-$Pt(C{\equiv}CPh)_2(CN)_2]$ (0.070 g, 0.0.75 mmol) (0.075 g, 42 %).

Data for **2a**: ^1H NMR (300.1 MHz, CD_3COCD_3, 20 °C): $\delta = 7.79$ (m, 8H), 7.45 (m, 12H), 3.43 (m, 16H; N-CH_2, *n*Bu), 1.77 (m, 16H; CH_2, *n*Bu), 1.47 (m, 16H; CH_2, *n*Bu), 0.99 (t, 24H; CH_3, *n*Bu), 0.96 (s, 18H; CH_3, *t*Bu); ^{19}F NMR (282.4 MHz, CD_3COCD_3, 20 °C): $\delta = -116.5$ (dd, $^3J(Pt,o\text{-}F) = 389$ Hz, 4*o*-F), −117.1 (m, $^3J(Pt,o\text{-}F) = 370$ Hz, 4*o*-F), −164.9 (t, 2*p*-F), −165.7 (m, 4*m*-F), −166.0 (m, 2*p*-F), −166.6 (m, 4*m*-F); $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3COCD_3, 20 °C): $\delta = -4.28$ (s, $^1J(P,Pt) = 2454$ Hz); IR: $\tilde{\nu} = 2176$ (s), 2157 (s) (C≡N), 2117 (m) (C≡C), 802 (vs), 787 cm^{-1} (m) (X-sens C_6F_5); MS (ES−): *m*/*z* (%): 1865 (100) $[M+3H]^-$, 1479 (15) $[Pt_2(C_6F_5)_4(CN)(dppa)]^-$; elemental analysis calcd for $C_{96}F_{20}H_{110}N_4P_2Pt_3$ (2347.15): C 49.13, H 4.72, N 2.39; found: C 49.21, H 4.57, N 2.39.

Data for **2b**: ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.66$ (m, 8H), 7.37–7.25 (m, 12H), 7.16–6.98 (m, 10H), 3.13 (m, 16H; N-CH_2, *n*Bu), 1.46 (m, 16H; CH_2, *n*Bu), 1.29 (m, 16H; CH_2, *n*Bu), 0.82 (t, 24H; CH_3, *n*Bu); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -117.9$ (dm, $^3J(Pt,o\text{-}F) = 435$ Hz, 4*o*-F), −118.7 (m, $^3J(Pt,o\text{-}F) = 352$ Hz, 4*o*-F), −163.1 (t, 2*p*-F), −164.9 (m, 2*p*-F + 4*m*-F), −166.0 (m, 4*m*-F); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 2.95$ (s, $^1J(P,Pt) = 2490$ Hz); IR: $\tilde{\nu} = 2184$ (s), 2168 (s) (C≡N), 2120 (s) (C≡C), 819 (s), 802 cm^{-1} (vs) (X-sens C_6F_5); MS (FAB−): *m*/*z* (%): peak molecular not observed, 1453 (15) $[Pt_2(C_6F_5)_4(dppa)]^-$, 1148 (25) $[Pt(C_6F_5)(dppa)_2-2H]^-$; elemental analysis calcd for $C_{100}F_{20}H_{102}N_4P_2Pt_3$ (2387.12): C 50.32, H 4.31, N 2.35; found: C 49.82, H 4.02, N 2.23.

Synthesis of $(NBu_4)_2$[cyclo{[*cis*-$Pt(C{\equiv}CR)_2(\mu\text{-}CN)_2][M(cod)]\}_2]$ (3a: M = Rh, R = *t*Bu, 3b: M = Rh, R = Ph; 4a: M = Ir, R = *t*Bu, 4b: M = Ir, R = Ph): $AgClO_4$ (0.080 g, 0.385 mmol) was added to a solution of $[Rh(\mu\text{-}Cl)(cod)]_2$ (0.095 g, 0.193 mmol) in acetone (20 mL), and the mixture was stirred for 5 h, protected from the light. After filtration of the mixture through Celite, the solution obtained was added to a solution of $(NBu_4)_2$[*cis*-$Pt(C{\equiv}C\textit{t}Bu)_2(CN)_2]$ **1a** (0.345 g, 0.385 mmol) in acetone (5 mL), causing the precipitation of **3a** as a yellow solid (0.196 g, 59 %).

Complexes **3b**, **4a** and **4b** were obtained as yellow solids following a similar process to that described for **3a** using the corresponding starting materials:

Compound **3b**: $(NBu_4)_2$[*cis*-$Pt(C{\equiv}CPh)_2(CN)_2]$ (**1b**; 0.312 g, 0.333 mmol), $AgClO_4$ (0.069 g, 0.333 mmol), $[Rh(\mu\text{-}Cl)(cod)]_2$ (0.082 g, 0.166 mmol) (0.195 g, 65 %).

Compound **4a**: $(NBu_4)_2[\textit{cis}\text{-}Pt(C\equiv C\textit{t}Bu)_2(CN)_2]$ (**1a**; 0.352 g, 0.394 mmol), $AgClO_4$ (0.082 g, 0.394 mmol), $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.132 g, 0.197 mmol) (0.220 g, 59 %).

Compound **4b**: $(NBu_4)_2[\textit{cis}\text{-}Pt(C\equiv CPh)_2(CN)_2]$ (**1b**; 0.353 g, 0.378 mmol), $AgClO_4$ (0.078 g, 0.378 mmol), $[Ir(\mu\text{-}Cl)(cod)]_2$ (0.127 g, 0.189 mmol) (0.195 g, 52 %).

Data for **3a**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta=$ 4.11 (brs, 8H; =CH, COD), 3.51 (m, 16H; N-CH_2, *n*Bu), 2.26 (brs, 8H; CH_2, COD), 1.78 (m, 16H; CH_2, *n*Bu), 1.70 (m, 16H; CH_2, *n*Bu + 8H; CH_2, COD), 1.15 (s, 36H; *t*Bu), 1.08 (t, 24H; CH_3, *n*Bu); IR: $\tilde{\nu}=2163$ (s), 2151 (s) ($C\equiv N$), 2107 cm^{-1} (s) ($C\equiv C$); MS (FAB−): *m*/*z* (%): 1483 (100) $[M+NBu_4]^-$, 620 (73) $[PtRh(C\equiv C\textit{t}Bu)_2(CN)_2cod]^-$, 538 (36) $[PtRh(C\equiv C\textit{t}Bu)_2(CN)_3]^-$; elemental analysis calcd for $C_{76}H_{132}N_6Pt_2Rh_2$ (1725.84): C 52.89, H 7.71, N 4.87; found: C 52.94, H 7.38, N 4.92.

Data for **3b**: ^{1}H NMR (300.1 MHz, CD_3COCD_3, 20 °C): $\delta=7.24$ (d, 8H), 7.14 (t, 8H), 7.00 (t, 4H) Ph, 4.22 (brs, 8H; =CH, COD), 3.60 (m, 16H; N-CH_2, *n*Bu), 2.37 (brs, 8H; CH_2, COD), 1.91 (m, 16H; CH_2, *n*Bu), 1.79 (m, 8H; CH_2, COD), 1.60 (m, 16H; CH_2, *n*Bu), 1.02 (t, 24H; CH_3, *n*Bu); IR: $\tilde{\nu}=2170$ (m), 2154 (s) ($C\equiv N$), 2111 cm^{-1} (s) ($C\equiv C$); MS (FAB−): *m*/*z* (%): 1562 (20) $[M+NBu_4]^-$; elemental analysis calcd for $C_{84}H_{116}N_6Pt_2Rh_2$ (1805.88): C 55.87, H 6.47, N 4.65; found: C 55.48, H 6.32, N 4.58.

Data for **4a**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta=3.88$ (brs, 8H; =CH, COD), 3.49 (m, 16H; N-CH_2, *n*Bu), 2.07 (brm, 8H; CH_2, COD), 1.77 (m, 16H; CH_2, *n*Bu), 1.65 (m, 16H; CH_2, *n*Bu), 1.49 (m, 8H; CH_2, COD), 1.15 (s, 36H; *t*Bu), 1.06 (t, 24H; CH_3, *n*Bu); IR: $\tilde{\nu}=2160$ (sh), 2150 (s), ($C\equiv N$), 2107 cm^{-1} (m) ($C\equiv C$); MS (FAB−): *m*/*z* (%): 1687 (16) $[Pt_2Ir_2(C\equiv C\textit{t}Bu)_4(CN)_4(NBu_4)_2]^-$, 767 (30) $[Pt_2(C\equiv C\textit{t}Bu)_4(CN)_2]^-$; elemental analysis calcd for $C_{76}H_{132}Ir_2N_6Pt_2$ (1904.47): C 47.93, H 6.99, N 4.41; found: C 47.65, H 7.00, N 4.29.

Data for **4b**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta=7.30$, 7.14, 7.05 (3 m, 20H; Ph), 4.00 (brs, 8H; =CH, COD), 3.41 (m, 16H; N-CH_2, *n*Bu), 2.16 (brs, 16H; CH_2, COD), 1.70 (m, 16H; CH_2, *n*Bu), 1.24 (m, 16H; CH_2, *n*Bu), 0.95 (t, 24H; CH_3, *n*Bu); similar pattern at −50 °C; IR: $\tilde{\nu}=2168$ (s), 2153 (s) ($C\equiv N$), 2113 cm^{-1} (m) ($C\equiv C$); MS (FAB−): *m*/*z* (%): 1741 (27) $[M+NBu_4]^-$, 1198 (6) $[M-Ir-cod]^-$, 954 (15) $[Pt_2(C\equiv CPh)_4(CN)_2(cod)]^-$, 423 (23) $[Pt(C\equiv CPh)_2(CN)]^-$, 300 (100) $[Ir(cod)]^-$; elemental analysis calcd for $C_{84}H_{116}Ir_2N_6Pt_2$ (1984.51): C 50.84, H 5.89, N 4.23; found: C 50.43, H 5.83, N 4.14.

Synthesis of $(NBu_4)_2[cyclo\{[\textit{cis}\text{-}Pt(C\equiv C\textit{t}Bu)_2(\mu\text{-}^{13}CN)_2][Rh(cod)]\}_2]$ (3a′): This complex was prepared starting from $[Rh(cod)(acetone)_x]ClO_4$ (0.297 mmol) and $(NBu_4)_2[\textit{cis}\text{-}Pt(C\equiv C\textit{t}Bu)_2(^{13}CN)_2]$ (**1a′**; 0.266 g, 0.297 mmol) in a similar way to **3a** (0.15 g, 60 %). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C): $\delta=138.7$ (s, $^1J(^{195}Pt,^{13}C)=973$ Hz, CN), C_α and C_β not observed, 79.4 (s, COD, olefinic), 59.7 (s, N-CH_2-$(CH_2)_2$-CH_3), 32.9 (s, $C(CH_3)_3$), 30.8 (s, COD, methylene), 28.9 (s, CMe_3), 24.9, 20.1 (s, N-CH_2-$(CH_2)_2$-CH_3), 14.1 (s, N-$(CH_2)_3$-CH_3); *g*-HMBC experiment ($CDCl_3$) indicates that the C_β appears at δ 112.0 (C_α not observed).

Synthesis of $(NBu_4)_2[\{(C_6F_5)_2Pt(\mu\text{-}C\equiv CPh)_2Pt(\mu\text{-}CN)_2\}_2\{M(cod)\}_2]$ (5b: M = Rh, 6b: M = Ir): $[\textit{cis}\text{-}Pt(C_6F_5)_2(thf)_2]$ (0.074 g, 0.110 mmol) was added to a yellow suspension of **3b** (0.100 g, 0.055 mmol) in CH_2Cl_2 (20 mL) and the mixture stirred at room temperature for 30 min. The mixture was filtered through Celite and the solvent removed in vacuo. Addition of EtOH (5 mL) to the residue afforded **5b** as a yellow solid (0.068 g, 63 %).

Compound **6b** was obtained as a yellow solid following the same procedure as for **5b** but using the precursors: **4b** (0.100 g, 0.050 mmol) and $[\textit{cis}\text{-}Pt(C_6F_5)_2(thf)_2]$ (0.068 g, 0.100 mmol) (0.093 g, 61 %).

Data for **5b**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta=7.31$ (d, 8H), 7.12 (m, 12H) Ph, 4.10 (s, 8H; =CH, COD), 3.23 (m, 16H; CH_2, *n*Bu), 2.32 (brs, 8H; CH_2, COD), 1.76 (m, 8H; CH_2, COD), 1.65 (m, 16H; CH_2, *n*Bu), 1.48 (m, 16H; CH_2, *n*Bu), 0.97 (t, 24H; CH_3, *n*Bu); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta=-117.0$ (d, $^3J(Pt,o\text{-}F)=388$ Hz, 8*o*-F), −164.7 (t, 4*p*-F), −166.4 (m, 8*m*-F); IR: $\tilde{\nu}=2175$ (s), 2166 (s) ($C\equiv N$), 2020 (w) ($C\equiv C$), 795 cm^{-1} (m, br) (X-sens C_6F_5); MS (FAB−): *m*/*z* (%): 2864 (15) $[M+2NBu_4]^-$, 2626 (40) $[M+2NBu_4-Rh(CN)(cod)]^-$, 555 (100) $[Pt(C_6F_5)_2(CN)]^-$, 413 $[Pt(C_6F_5)(CN)_2-H]^-$; elemental analysis calcd for $C_{108}F_{20}H_{116}N_6Pt_4Rh_2$ (2864.26): C 45.29, H 4.08, N 2.93; found: C 44.77, H 3.64, N 2.93.

Data for **6b**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta=7.33$–7.17 (m, 20 H; Ph), 3.93 (brs, 8H; =CH, COD), 3.27 (m, 16H; CH_2, *n*Bu), 2.16 (brs, 8H; CH_2, COD), 1.68 (m, 24H; CH_2, COD, *n*Bu), 1.25 (m, 16H; CH_2, *n*Bu), 0.86 (t, 24H; CH_3, *n*Bu); a similar spectrum is observed at −50 °C; ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta=-117.0$ (d, $^3J(Pt,o\text{-}F)=410$ Hz, 8*o*-F), −164.5 (t, 4*p*-F), −166.4 (m, 8*m*-F); at −50 °C the *o*-F and *m*-F signals broaden but do not split; IR: $\tilde{\nu}=2172$ (s), 2164 (s) ($C\equiv N$), 2020 (w) ($C\equiv C$), 803 (m), 793 cm^{-1} (m) (X-sens C_6F_5); MS (FAB−): *m*/*z* (%): 2816 (30) $[M+2NBu_4-2C\equiv CPh-CN]^-$, 555 (100) $[Pt(C_6F_5)_2(CN)]^-$, 413 $[Pt(C_6F_5)(CN)_2-H]^-$; elemental analysis calcd for $C_{108}F_{20}H_{116}Ir_2N_6Pt_4$ (3042.91): C 42.63, H 3.84, N 2.76; found: C 42.63, H 3.71, N 2.54.

Synthesis of $(NBu_4)_4[cyclo\{[\textit{cis}\text{-}Pt(C\equiv CR)_2(\mu\text{-}CN)_2][SnPh_3]\}_4]$ (7a: R = *t*Bu, 7b: R = Ph): $AgClO_4$ (0.062 g, 0.298 mmol) was added to a solution of $[SnPh_3Cl]$ (0.121 g, 95 %, 0.298 mmol) in acetone (20 mL) and the mixture was stirred for 6 h in absence of the light. The AgCl formed was separated by filtration through Celite and the resulting solution was added to a solution of $(NBu_4)_2[\textit{cis}\text{-}Pt(C\equiv C\textit{t}Bu)_2(CN)_2]$ (**1a**; 0.267 g, 0.298 mmol) in acetone (2 mL) causing the precipitation of **7a** as a white solid (0.158 g, 54 %).

Complex **7b** was obtained starting from $(NBu_4)_2[\textit{cis}\text{-}Pt(C\equiv CPh)_2(CN)_2]$ (**1b**; 0.293 g, 0.314 mmol), $SnPh_3Cl$ (0.127 g, 0.314 mmol) and $AgClO_4$ (0.065 g, 0.314 mmol) (0.167 g, 51 %).

Complex **7a**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta=7.71$, 7.44 (2m, 60 H; Ph), 3.30 (m, 32H; N-CH_2, *n*Bu), 1.46 (m, 32H; CH_2, *n*Bu), 1.24 (m, 32H; CH_2, *n*Bu), 1.16 (s, 72H; *t*Bu), 0.95 (t, 48H; CH_3, *n*Bu); IR: $\tilde{\nu}=$ 2143 (s) ($C\equiv N$), 2116 cm^{-1} (vs) ($C\equiv C$); no peaks were observed in the FAB (−) mass spectrum; elemental analysis calcd for $C_{192}H_{276}N_{12}Pt_4Sn_4$ (4007.59): C 57.54, H 6.94, N 4.19; found: C 57.22, H 6.61, N 4.13.

Complex **7b**: ^{1}H NMR (300.1 MHz, CD_3COCD_3, 20 °C): $\delta=$ 8.32–6.98 (m, 100H; Ph), 3.40 (m, 32H; N-CH_2, *n*Bu), 1.74 (m, 32H; CH_2, *n*Bu), 1.36 (m, 32H; CH_2, *n*Bu), 0.88 (t, 48H; CH_3, *n*Bu); IR: $\tilde{\nu}=2154$ (s) ($C\equiv N$), 2115 cm^{-1} (vs) ($C\equiv C$); MS (FAB−): *m*/*z* (%): 423 (35) $[Pt(C\equiv CPh)_2(CN)]^-$, 348 (100) $[Pt(C\equiv CPh)(CN)_2+H]^-$, 323 (55) $[Pt(C\equiv CPh)(CN)]^-$; elemental analysis calcd for $C_{208}H_{244}N_{12}Pt_4Sn_4$ (4167.51): C 59.95, H 5.90, N 4.03; found: C 60.14, H 5.62, N 3.71.

Crystallography: A summary of crystal data and refinement parameters is given in Table 5. For all the complexes, X-ray intensity data were collected with a Nonius κ-CCD area-detector diffractometer, using graphite-monochromated $Mo_{K\alpha}$ radiation. Images were processed using the Denzo-Scalepack suite of programs,[27] the absorption correction was performed using SORTAV.[28] The structures were solved by Direct Methods and refined by full-matrix least squares on F^2 using SHELXL-97 program.[29] All non-hydrogen atoms were assigned anisotropic displacement parameters, and all hydrogen atoms were assigned anisotropic displacement parameters of 1.2 times the U_{iso} value of their attached carbon for the phenyl and CH_2 and 1.5 times for the methyl groups. In order to establish the identities of the C and N atoms of the bridging cyanide ligands, each structure was refined three different ways—with the identities of C and N as presented here, with the element types reversed, and with a 50/50 hybrid scattering factor at each of the affected atomic sites. Examination of the ΔMSDA values for bonds involving these atoms revealed the correct assignments[30,31] (Supporting Information). The crystals obtained for **4b** and **5b** did not contain lattice solvent, however in **3b** one molecule of CH_2Cl_2, and one molecule of benzene for **2a** were found for the asymmetric unit. Residual peaks close to the heavy atoms were observed for **4b**.

CCDC-206328–206331 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12Union Road, Cambridge CB2 1EZ (UK); fax: (+44)1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk).

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Table 5. Crystallographic data for compounds $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-dppa})\{(\mu\text{-CN})_2Pt(C\equiv C\mathit{t}Bu)_2\}Pt(C_6F_5)_2]\cdot C_6H_6$ (**2a**$\cdot C_6H_6$), $(NBu_4)_2[cyclo\{[\mathit{cis}\text{-}Pt(C\equiv CPh)_2(\mu\text{-CN})_2][Rh(cod)]\}_2]\cdot CH_2Cl_2$ (**3b**$\cdot CH_2Cl_2$), $(NBu_4)_2[cyclo\{[\mathit{cis}\text{-}Pt(C\equiv CPh)_2(\mu\text{-CN})_2][Ir(cod)]\}_2]$ (**4b**) and $(NBu_4)_2[\{(C_6F_5)_2Pt(\mu\text{-}C\equiv CPh)_2Pt(\mu\text{-CN})_2\}_2\{Rh(cod)\}_2]$ (**5b**).

	2a$\cdot C_6H_6$	**3b**$\cdot CH_2Cl_2$	**4b**	**5b**
empirical formula	$C_{102}H_{114}F_{20}N_4P_2Pt_3$	$C_{43}H_{60}Cl_2N_3PtRh$	$C_{42}H_{58}IrN_3Pt$	$C_{108}H_{116}F_{20}N_6Pt_4Rh_2$
M_w	2423.18	987.84	992.20	2864.25
T [K]	293(2)	293(2)	293(2)	173(1)
$\lambda(Mo_{K\alpha})$ [Å]	0.71070	0.71073	0.71073	0.71073
crystal system	triclinic	hexagonal	monoclinic	monoclinic
space group	$P\bar{1}$	$R\bar{3}$	$P2_1/c$	$C/2c$
crystal dimensions	$0.5\times0.2\times0.17$	$0.7\times0.7\times0.8$	$0.4\times0.25\times0.25$	$0.1\times0.08\times0.15$
a [Å]	16.5980(2)	34.8347(7)	14.1259(4)	22.2237(3)
α [°]	85.8700(10)	90	90	90
b [Å]	18.4930(3)	34.8348(7)	8.7764(3)	25.2650(4)
β [°]	89.2230(10)	90	95.9022(13)	106.6087(9)
c [Å]	19.2290(2)	23.5951(7)	32.6353(13)	20.1086(3)
γ [°]	63.8010(6)	120	90	90
V [Å^3]	5281.07(12)	24795.8(10)	4024.5(2)	10819.6(3)
Z	2	18	4	4
ρ_{calcd} [Mg m^{-3}]	1.524	1.191	1.638	1.758
μ [mm^{-1}]	4.074	2.957	6.806	5.532
$F(000)$	2396	8928	1944	5552
θ range for data collection [°]	5.10 to 26.37	4.14 to 26.37	4.17 to 26.37	1.81 to 27.93
index ranges	$0\leq h\leq 20$ $-20\leq k\leq 23$ $-23\leq l\leq 24$	$-43\leq h\leq 33$ $-43\leq k\leq 41$ $-27\leq l\leq 29$	$-16\leq h\leq 17$ $-7\leq k\leq 10$ $-27\leq l\leq 40$	$-29\leq h\leq 29$ $-33\leq k\leq 32$ $-26\leq l\leq 26$
reflns colld	21336	52346	7248	45137
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	21336/0/1181	11209/0/455	5240/0/428	12850/0/637
GoF on F^2 [a]	1.255	1.108	0.899	1.157
final R indices $[I>2\sigma(I)]$[a]				
$R1$	0.0463	0.0635	0.0633	0.0444
$wR2$	0.0805	0.1572	0.1400	0.0987
R indices (all data)[a]				
$R1$	0.0872	0.1155	0.1278	0.0704
$wR2$	0.0909	0.1874	0.1599	0.1051
largest diff peak and hole [e Å^{-3}]	0.771 and −0.905	1.144 and −0.825	1.943 and −1.606	1.279 and −1.035

[a] $R1=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^2]^{1/2}$; goodness of fit $=\Sigma w(F_o^2-F_c^2)^2/(N_{obs}-N_{param})]$; $w=[\sigma^2(F_o)+(g_1P)^2+g_2P]^{-1}$; $P=[\max(F_o^2,0+2F_c^2]/3$.

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