Pt-M complexes (M = Ag, Au) as models for intermediates in transmetalation processes

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Abstract: Heteropolynuclear complexes $[(\text{CNC})(\text{PPh}_3)\text{PtM}(\text{PPh}_3)](\text{ClO}_4)$ (M = Au (1), Ag (2)) and $[\{\text{Pt}(\text{CNC})(\text{PPh}_3)_2\text{M}\}(\text{ClO}_4)]$ (M = Ag (3), Au (4); CNC = 2,6-diphenylpyridinate) have been prepared and studied by structural, spectroscopic techniques and DFT calculations. The X-ray crystal structures of 1, 3 and 4 confirm the existence of Pt–M bonds and M–C_{ipso} interactions involving one of the phenyl fragments of CNC. Their NMR spectra confirm the persistence of the Pt–M interactions in solution and also show an intramolecular “metronome-like” dynamic processes consisting of back-and-forth bouncing of the acidic M fragments along the C–Pt–C axis. DFT calculations on these complexes identify two main orbital interactions between the [PtCNC] and [M]⁺ fragments, namely a donation of the former to a vacant orbital of the latter, and a much weaker backdonation from the acidic M to the Pt fragment. Overall, the strength of the [Pt]···M interactions is higher for the gold compounds than for their silver counterparts. The interaction between the acidic center (silver or gold) and the carbon atom of one of the phenylene rings in these heteropolymetallic complexes can be envisaged as the first step in a process of interchange of aryl ligands. However, the ligand exchange cannot progress further due to the polydentate nature of the CNC ligand, and therefore these structures can be considered as frozen “snapshots” of a transmetalation reaction which have been arrested at different steps in the process.

Introduction

The study of heteropolynuclear complexes containing metal-metal interactions between closed or pseudo-closed shell metal ions (d^8 , d^{10} , $d^{10}s^2$) is a field of great interest.^[1] Many of these interactions are dative in nature, and are established between a basic donor metal and an acidic acceptor center. The importance of these dative metallophilic bonds is well recognized since they are behind many unique luminescent properties.^[2] Moreover, metallophilic bonding interactions have also been recognized as a powerful tool in molecular recognition or crystal engineering. In this particular field, there is an abundant chemistry of electron rich Pt(II) complexes being used as basic donors toward a wide array of acidic centers, mainly Ag(I)^[3] and to a lesser extent Au(I),^[4] Cu(I),^[5] Tl(I),^[6] Cd(II),^[7] Hg(II),^[8] Pb(II),^[6b] Zn(II)^[9]... The use of Pt(II) complexes containing cyclometalated ligands in this role is relatively recent.^[2c, 3-4, 8] These ligands can improve the ability of the metal to form Pt→M donor–acceptor bonds, both from the point of view of the lesser steric hindrance, which can favor the approach of the acidic center, as well as from the orbital perspective. The strong ligand field exerted by cyclometalated ligands propitiates a stronger dative bond, typically employing the occupied higher-energy d_{z^2} orbital as the donor moiety. Interest has grown lately as it has been recognized that polymetallic moieties can play a crucial role in bimetallic catalytic processes, especially in C–C or C–X coupling reactions.^[10] These polymetallic species can be formed in situ, starting from mononuclear metallic complexes that at some point join together to act as the catalyst, or can be added as pre-assembled polymetallic complexes. In both cases, the situation in which M–M bonds are present is of special interest, especially when the catalysts are heterobimetallic pairs. In these systems the metals could be chosen according to their reactivity to fine tune their catalytic properties.

In many of the catalytic processes of interest involving bimetallic catalysis the participating couples are formed by a potential donor metal such as Pd(II) or Pt(II) and an acidic center such as Cu(I), Ag(I) or Au(I). These are precisely some of the most typical metals prone to form M→M' donor–acceptor bonds. For example, complexes with Pt–Au, Pt–Cu or Pt–Ag bonds have been identified

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in either gas phase or in solution as intermediates in transmetalation reactions involving methyl groups,^[5a, 11] whereas Pd–Au or Pd–Cu species have been proposed as transition states in aryl ligand interchange processes.^[12] Also, the microscopic reverse of the transmetalation step in the Pd–M (M = Cu, Ag, Au) catalyzed Sonogashira-type reactions has been observed in the gas phase.^[13] Espinet and coworkers have studied the mechanism of Pd/Ni Negishi coupling reactions by means of DFT calculations and have found “the existence, in both transition states and in some intermediates, of Pd···Zn bond interactions between the electron-rich Pd center and the fairly positive Zn center”.^[14] These interactions would account for the decrease in the energy of the transmetalation barriers when using organozinc compounds as nucleophiles.

However, these M→M' donor–acceptor bimetallic complexes have rarely been studied and characterized in depth. Recently, Chen and coworkers have reported the preparation, X-ray structure determination, gas phase and DFT studies of the Pd→Cu complex [(bq)₂PdCuL]⁺ (bq = benzoquinolate, L = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).^[15] This complex is described as a model for the transition state for the transmetalation step in the Negishi coupling. Also from Professor Chen's laboratory, an unprecedented Pd→Zn complex has been structurally characterized,^[16] which can be related to Espinet's studies mentioned above. Furthermore, our group recently reported the preparation, full structural characterization, and NMR and DFT studies of the complex [(CNC)(PPh₃)PtAu(PPh₃)]⁺ (CNC = 2,6-diphenylpyridinate).^[4] This complex is remarkable since it can be regarded as a snapshot of a transmetalation process and presents dynamic behavior in solution, showing the persistence of the Pt→Au bond, and the alternative formation of Au–C bonds. In this paper we expand on this study and present new complexes containing Pt→M (M = Ag, Au) bonds, which again can shed light on the reaction mechanisms of the transmetalation processes involving catalytic bimetallic systems.

Results and Discussion

Preparation of the heterodinuclear complexes [(CNC)(PPh₃)PtM(PPh₃)](ClO₄) (M = Au (1), Ag (2)).

The reaction of equimolecular amounts of complex [Pt(CNC)(PPh₃)] with [AuCl(PPh₃)] and silver perchlorate in tetrahydrofuran at -40°C in the absence of light led to the formation of the dinuclear adduct [(CNC)(PPh₃)PtAu(PPh₃)](ClO₄) (1), which was obtained as an orange solid after workup (Scheme 1).

Scheme 1. Synthesis of complex 1.

The crystal structure of 1 was determined by X-ray diffraction. Figure 1a shows the cation complex of 1 and Table 1 (left) lists some relevant structural parameters. This structure showed an interaction between the Au center and the *ipso* carbon of one of the phenylene rings of the CNC ligands (denoted C_A in Scheme 1), together with the expected Pt–Au interaction. The Au–C_A interaction is strong, causing a noticeable elongation of the Pt–C_A bond length (2.158(3) Å) with respect to the Pt–C_B distance (2.063(3) Å). Moreover, as can be seen in Table 1, the C_A phenylene ring deviates from the coordination plane defined by the square-planar environment of the metal center. The optimized DFT structure for this complex (1-DFT, see supplementary material) presents an excellent agreement with the experimentally determined one.

Figure 1. Molecular structures of the cations of complexes $[(\text{CNC})(\text{PPh}_3)\text{PtAu}(\text{PPh}_3)](\text{ClO}_4)$ (1, a) and $[(\text{CNC})(\text{PPh}_3)\text{PtAg}(\text{PPh}_3)](\text{ClO}_4)$ (2-DFT, b).

Table 1. Selected bond distances (Å) and angles ($^\circ$) for the structures of complexes 1 and 2-DFT.

	1 (M = Au)	2-DFT (M = Ag)
Pt–C(13)	2.063(3)	2.068
Pt–C(7)	2.158(3)	2.167
Pt–M	2.7222(2)	2.791
M–C(7)	2.225(3)	2.245
C(13)–Pt–C(7)	156.30(14)	157.95
C(7)–Pt–M	52.71(9)	52.02
C(7)–M–P(2)	153.25(8)	168.10
P(2)–M–Pt	152.38(2)	125.60

Interestingly the RT ^1H NMR spectrum of 1 was found not to be consistent with its ground-state geometry determined by X-ray diffraction, suggesting a dynamic process. Thus, the phenylene rings are equivalent, and, for example, only one signal corresponding to the CH_{ortho} is observed. However, at lower temperatures the two phenylene rings become inequivalent and in the spectrum at 173K in the 5 to 9 ppm region presents a more complex pattern than that recorded at RT, as a result of the decoalescence of several signals (see Figure 2). We proved that this behavior is related to the operation of an intramolecular “metronome-like” dynamic process at RT (see Scheme 2) involving the 12-valence electron metal fragment $[\text{AuL}]^+$, consisting of a back-and-forth bouncing of the gold-phosphane unit along the C–Pt–C axis.^[4]

The successful use of group-11 metals as co-catalysts in group-10 metal catalyzed cross-coupling reactions^[10] has pushed us to widen our studies to silver. In principle, silver can be expected to be less carbophilic than gold, and also to show a more labile behavior towards coordination to other centers. Thus, we have carried out a procedure related to that leading to 1 but using $[\text{Ag}(\text{OCIO}_3)(\text{PPh}_3)]$ as a silver-phosphane source, in order to prepare an analogous platinum-silver adduct. It has to be remarked that, in contrast to the referred preparation, the atom-economy of the latter process is expected to be 100%, as no by-product should be formed during the course of the reaction.

Figure 2. ^1H NMR spectra of a CD_2Cl_2 solution of **1** at 273K (top) and 173K (bottom).

Scheme 2. Proposed “metronome-like” dynamic process operating in complexes **1**, **2**, **3**, and **4**.

Equimolecular amounts of $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ and the silver salt were dissolved in dichloromethane at -60°C and stirred for five minutes in the absence of light. After evaporation to dryness and subsequent work-up a yellow solid (**2***) is obtained, which has been carefully analyzed by NMR techniques. The isolated solid results in a mixture of three different complexes: the desired binuclear platinum-silver adduct $[(\text{CNC})(\text{PPh}_3)\text{PtAg}(\text{PPh}_3)](\text{ClO}_4)$ (**2**) and equimolecular amounts of the silver-bisphosphane compound $[\text{Ag}(\text{PPh}_3)_2](\text{ClO}_4)$ (**AgP2**) and a heterotrinnuclear platinum-silver-platinum adduct $[\{\text{Pt}(\text{CNC})(\text{PPh}_3)\}_2\text{Ag}](\text{ClO}_4)$ (**3**) (Scheme 3).

Elemental analyses carried out with different preparations of **2*** were fully consistent with a formula $[(\text{CNC})(\text{PPh}_3)\text{PtAg}(\text{PPh}_3)](\text{ClO}_4)$. Attempts to obtain crystalline material from samples of **2*** led invariably to a mixture of crystals. One batch was constituted by well-formed orange specimens, which were identified as the trinuclear **3**. A second group was formed by poor quality yellow crystals, not suitable for X-ray diffraction studies, but whose NMR spectra behaved as **2*** and most probably corresponds to the dinuclear $[(\text{CNC})(\text{PPh}_3)\text{PtAg}(\text{PPh}_3)](\text{ClO}_4)$ (**2**). Finally, a third group of crystals was well-formed, colorless specimens whose structure was determined by X-ray diffraction (see experimental) and which corresponds to the silver complex $[\text{Ag}(\text{PPh}_3)_2](\text{ClO}_4)$. This result pushed us to try the synthesis of the trinuclear **3** through a different method. Such preparation and the structural and spectroscopic characterization of pure **3** will be discussed later on in this work.

Scheme 3. Reaction of $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ with $[\text{Ag}(\text{OCIO}_3)(\text{PPh}_3)]$. Obtaining of the complex mixture 2^* .

In the absence of an X-ray determination for the adduct 2 , we have used DFT calculations to estimate its structure (Figure 1b). A selection of the geometrical parameters obtained is shown in Table 1 (right). The optimized structure 2-DFT shows undeniable similarities to that experimentally determined for 1 . Indeed the silver center presents an interaction with the ipso carbon of one of the phenylene rings and also with the platinum center ($\text{Ag}-\text{C}$ and $\text{Ag}-\text{Pt}$ bond distances of 2.245 and 2.791 Å respectively). Although this interaction causes a deviation on the aromatic ring with regard to the square-planar coordination plane of the platinum center, it has to be remarked that this deviation is less pronounced than that observed for 1 . This may be related to a less marked carbophilicity of silver with regard to gold, and strongly suggests that the Lewis Base - Lewis Acid interaction is less tight for the $\text{Pt}-\text{Ag}$ adduct than for the $\text{Pt}-\text{Au}$ one.

The presence of the three compounds in the isolated 2^* has been further confirmed from the different ^1H , ^{31}P , and ^{195}Pt NMR spectra collected. The RT ^1H NMR spectrum of the solid in dichloromethane- d_2 shows the presence of a collection of broad signals, which at first sight are not very informative. However, at 253 K a well-defined ^1H NMR spectrum is obtained, which presents three sets of signals corresponding to 2 , 3 , and $\text{AgP}2$ (Figure 3). According to the integration of the different signals, the $2:3:\text{AgP}2$ ratio is 3.8:1:1. Thus, the constant of the equilibrium shown in Scheme 3 (K_{253}) is 0.069, which corresponds to a ΔG_{253}^0 of 5.6 kcal/mol.

A careful VT ^1H NMR study unravels the very rich behavior of sample 2^* . In the 313-to-253 K temperature range, a first dynamic process with an estimated coalescence temperature of 298 K is observed (see Figure 4). This process involves the coalescence of the signals corresponding to 2 , 3 , and $\text{AgP}2$, as is highlighted by the three sets of signals apparent in the 5.6-to-6.6 ppm range at 253 K, which at 313 K become one broad, not completely resolved peak centered at 5.90 ppm.

Figure 3. ^1H NMR spectrum of a CD_2Cl_2 solution of 2^* , compared with the ^1H NMR spectra of CD_2Cl_2 solutions of 3 and $\text{AgP}2$ (253K).

Figure 4. Selected VT ^1H NMR spectra of CD_2Cl_2 solutions of 2^* .

At temperatures below 253 K the interconversion equilibrium becomes slow in the NMR timescale, and therefore the behavior of **2** and **3** can be individually observed. A lowering in the temperature of the sample causes a gradual broadening of the signals corresponding to **2**. Oppositely to that observed for **1** the signals do not decoalesce even at 163 K. The behavior of the signals attributable to the trinuclear **3** will be described later on.

Additional information on the dynamic processes occurring in solution for the dinuclear Pt-M complexes can be obtained from the ^{31}P and ^{195}Pt NMR spectra of **1** and 2^* . Remarkably, the RT ^{31}P NMR spectrum of **1** shows two singlets at 22.5 (Pt-P) and 34.6 (Au-P) ppm, each of them accompanied of the corresponding satellites, as a result of the coupling to active ^{195}Pt nuclei ($^1J_{\text{P-Pt}} = 3680$ Hz, $^2J_{\text{P-Pt}} = 254$ Hz). This observation indicates that the Pt-Au interaction is tight, and therefore dissociation of the $[\text{Au}(\text{PPh}_3)]^+$ fragment at room temperature is slow in relation to the NMR timescale. Consistent with this, the ^{195}Pt NMR spectrum at room temperature shows a doublet of doublets at -4017 ppm (See Figures S6 and S7 in supporting information).

The ^{31}P NMR spectra of 2^* also reflect the presence of a mixture of complexes **2**, **3** and AgP2. Thus, at RT the spectrum presents a singlet at 24.1 ppm with its corresponding satellites ($^1J_{\text{P-Pt}} = 3662$ Hz), typical for a phosphane ligand bonded to Pt, and a doublet of broad peaks assigned to the PPh_3 ligand bonded to Ag in **2**, centered at 15.1 ppm and with a coupling constant $^1J_{\text{P-Ag}} = 672$ Hz. Upon lowering the temperature these signals become increasingly sharp. Thus, at 253K an additional shoulder is observed in the sharpest signal. Comparison of this spectrum to that of the pure trinuclear **3** (that will be discussed later) at this temperature allows us to assign this signal to the PPh_3 ligand of **3**. However, at a lower temperature (163K, Figure 5) no shoulder is discernible. The Pt- PPh_3 signal mainly attributable to **2** does not change significantly ($\delta = 23.2$ ppm, $^1J_{\text{P-Pt}} = 3540$ Hz) while the Ag- PPh_3 signal appears much more resolved. Now, two doublets, caused by the coupling with the two active isotopes of Ag (^{107}Ag (abundance 51.8%) and ^{109}Ag (abundance 48.2%)), can be observed with $^1J_{\text{P-Ag}}$ coupling constants of 730 Hz and 623 Hz respectively. Outstandingly, for each of these doublets, platinum satellites can be observed with $^2J_{\text{P(Ag)-Pt}} = 122$ Hz. Along with all these signals, this spectrum also shows a low intensity doublet of doublets, with a typical pattern for a Ag- PPh_3 system, caused by the silver complex AgP2.

Figure 5. ^{31}P NMR spectrum of a CD_2Cl_2 solution of 2^* at 163K.

Besides, the ^{195}Pt NMR spectrum of **2*** at 193K (See Figures S11 and S12, Supporting Information) shows a quite well-resolved main signal corresponding to a doublet of doublet of doublets centered at -4171 ppm. This signal is assigned to the dinuclear **2** and its complex pattern is caused by the coupling with the silver and both P atoms of the PPh_3 ligands ($^1J_{\text{Pt-P}} = 3561 \text{ Hz}$, $^1J_{\text{Pt-Ag}} = 438 \text{ Hz}$ y $^2J_{\text{Pt-P(Ag)}} = 115 \text{ Hz}$). Along with this main signal corresponding to **2**, a much lower intensity signal consisting in a doublet of doublets is also observed and assigned to $[\{\text{Pt}(\text{CNC})(\text{PPh}_3)_2\text{Ag}\}(\text{ClO}_4)]$ (**3**) (see discussion on the NMR spectra of pure **3** below). At RT, the signal corresponding to **2** appears only as a broad doublet with no features, while the intensity of the signal of **3** increases.

The observation of the existence of Pt-Ag coupling both in the ^{31}P and ^{195}Pt NMR spectra indicates that at low temperature the Pt-Ag interaction in **2** still occurs, whereas at temperatures close to RT a dynamic process might be happening at a relatively high rate that causes a loss of magnetic information. Two likely possibilities can be envisaged: first, dissociation-association equilibria involving the breakage of the Pt-Ag interaction and/or, second, rearrangement equilibria between **2**, **3** and AgP2 as depicted in Scheme 3, which involves the additional breakage of the Ag-P interaction.

The spectroscopic observations on the samples of **1** and **2*** highlight a tunable behavior of the Pt-Au and Pt-Ag systems, which may have inspiring implications for the application of coinage metals as co-catalysts in certain reactions. According to NMR evidence the Pt-Au interactions are stronger than those of Pt-Ag. Thus, if we consider the structures under discussion as arrested intermediates or *snapshots* for transmetalation processes, it turns out that the presence of either the $[\text{Ag}(\text{PPh}_3)]^+$ or the $[\text{Au}(\text{PPh}_3)]^+$ fragments gives rise to a different degree of transmetalation, which is more marked for the gold acidic fragment. Besides, in solution the Pt-Ag interactions seem to be more labile and therefore the metal fragments exchange readily, whereas the Pt-Au interactions are tighter and hence the corresponding metal fragments do not show signs of fast exchange at the NMR timescale.

Preparation of the heterotrinnuclear complexes $[\{\text{Pt}(\text{CNC})(\text{PPh}_3)_2\text{M}\}(\text{ClO}_4)]$ ($\text{M} = \text{Ag}$ (**3**), Au (**4**)).

The observation of the above-discussed equilibrium between the platinum-silver heterodinuclear adduct **2**, the silver bisphosphane derivative AgP2 and the platinum-silver-platinum heterotrinnuclear complex **3** has prompted us to look for a convenient way to prepare the latter complex. We have also pursued the synthesis of an analogous platinum-gold-platinum derivative, with the aim of studying and comparing the chemical behavior of these trinnuclear species.

Scheme 4. Synthesis of complexes **3** and **4**.

Treatment of a dichloromethane solution of the starting material $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ with AgClO_4 in a 2:1 molar ratio at room temperature for 2 h in the absence of light leads, after the corresponding work-up, to an orange solid, which was identified as the heterotrinnuclear $[\{\text{Pt}(\text{CNC})(\text{PPh}_3)_2\text{Ag}\}(\text{ClO}_4)]$ (**3**, Scheme 4), in high purity. If the reaction is carried out in a 1:1 molar ratio an equimolecular mixture of **3** and unreacted silver perchlorate is obtained instead.

Preparation of the analogous platinum-gold-platinum complex is slightly different. Treatment of an equimolecular mixture of $[\text{AuCl}(\text{tht})]$ and silver perchlorate in tetrahydrofuran at 0°C afforded a suspension after 60 min of stirring. The precipitate was filtered off and then complex $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ was added. Work-up of this solution led to the isolation of an orange solid corresponding to the heterotrinnuclear $[\{\text{Pt}(\text{CNC})(\text{PPh}_3)_2\text{Au}\}(\text{ClO}_4)]$ (**4**,

Scheme 4) in high purity. The formation of 4 occurs regardless of the Pt/Au ratio used, consistent with the lability of the Au-tht bond.^[17]

Crystals suitable for X-ray analyses have been obtained from both solids, and therefore the molecular structures of 3 and 4 have been determined. Drawings of the complex cations of both complexes are shown in Figure 6, whereas a compared selection of relevant bond distances and angles is included in Table 2. The structures of both complex cations are similar, and can be described as trinuclear moieties in which the acidic Ag/Au center (M) is sandwiched by two square-planar platinum CNC complexes. The dihedral angles between the best square planar environments of the platinum atoms show that they are nearly parallel (4.5(1)° for 3 and 1.1(1)° for 4). The relative rotation of the two “Pt(CNC)(PPh₃)” fragments, taking as reference the Pt—Pt line, is about 90° in all cases, which minimizes steric repulsions between the phosphane ligands.

Figure 6. Molecular structures of the cations of complexes $[\{\text{Pt}(\text{CNC})(\text{PPh}_3)_2\text{Ag}\}(\text{ClO}_4)]$ (3, a) and $[\{\text{Pt}(\text{CNC})(\text{PPh}_3)_2\text{Au}\}(\text{ClO}_4)]$ (4, b).

Table 2. Relevant bond distances (Å) and angles (°) for the structures of complexes 3 and 4

	3 (M = Ag)	4 (M = Au)
Pt–M	2.8549(3), 2.9078(3)	2.7297(2), 2.7426(2)
Pt–C _A	2.128(3), 2.125(3)	2.212(3), 2.244(3)
Pt–C _B	2.055(3), 2.056(3)	2.051(3), 2.045(3)
M–C _A	2.277(3), 2.258(3)	2.174(3), 2.157(3)
C _A –M–C _A	173.96(12)	176.75(12)
Pt–M–Pt	126.83(1)	131.43(1)

The Pt–M distances are short and therefore indicative of the existence of intermetallic bonds (see Table 2). The Pt–Au distances are shorter than the Pt–Ag ones, and, in fact, they are the shortest intermetallic distances found for complexes containing dative Pt(II)→Au(I) bonds,^[2a, 2b, 18] with the exception of the complex $[(\text{PEt}_3)_2(\text{C}_6\text{F}_5)\text{Pt}(\mu\text{-H})\text{Au}(\text{PPh}_3)]$ for which an intermetallic distance of 2.714(1) Å is reported.^[19] Interestingly, the Pt–M lines lean toward one of the CNC carbon atoms (C_A in Scheme 4) bonded to Pt (average value Ag–Pt–C_A angles: 51.17(9)°; Au–Pt–C_A angles: 50.47(8)°), in such a way that the existence of $\eta^1\text{-M-C}$ bond becomes evident. Indeed, the C_A–M–C_A angles in 3 and 4 are considerably closer to 180° than the Pt–M–Pt ones which, considering the tendency of Ag(I) and Au(I) centers to adopt linear dispositions, strongly suggests that the M–C interactions prevail over the M–Pt ones. As can be seen in Table 2, the M–C_A distances are around 0.1 Å longer in 3 than in 4. The shorter distances observed for the Pt–Au complex 4 can be explained by a higher carbophilicity of gold with regard to silver. This fact also suggests that the interaction of the square-planar platinum complex $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ with gold is stronger than that of $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ with silver.

As a consequence of the Pt–M interactions, the two pairs of asymmetric Pt–C bond lengths in 3 and 4 become mutually different. Thus, the Pt–C_A distances are longer than the Pt–C_B ones in both cases. In agreement with a stronger interaction being observed in the Pt–Au complex, this difference becomes especially marked in 4. Indeed, the Au–C_A distances in 4 become even shorter than those of Pt–C_A. The differences in the silver and gold complexes are also apparent in the disposition of the aromatic rings containing C_A and C_B. Both types of rings present significant deviations with regard to the ideal square-planar platinum coordination plane. However, among them, the C_A rings in the Pt–Au complexes 1 and 4 show a more outstanding deviation (see Table 3), which is also consistent with the referred stronger Pt–Au interactions. Thus, if we consider again these two structures as arrested intermediates in transmetalation processes, it can be inferred that the heterotrinuclear Pt-

Au complex 4 is frozen in a more advanced step of transmetalation. This trend is fully consistent with that observed for complexes 1 and 2-DFT.

Table 3. Relevant dihedral angles (°) for complexes 1, 2-DFT, 3 and 4.

Complex	Pt plane — N ring plane	Pt plane — C _A ring plane	Pt plane — C _B ring plane	Pt plane — Pt' plane
1	11.5(1)	23.1(1)	14.3(1)	–
2-DFT	9.8	15.9	11.4	–
3	8.5(1) 7.5(1)	15.0(1) 12.3(1)	14.1(1) 12.2(1)	4.5(1)
4	8.5(1) 9.0(1)	26.2(1) 28.4(1)	11.3(1) 10.4(1)	1.1(1)

In general terms, the NMR behavior of solutions of 3 and 4 in dichloromethane-d₂ are very much alike. The ¹H NMR spectra at 313K are relatively simple, only showing eight groups of signals (Figure 7). However, the solid state structures of both complexes predict the inequivalency of fourteen groups of protons. Thus, this apparent simplicity of the referred spectra is an indicator of a dynamic process operating in solution.

Figure 7. ¹H NMR spectra of CD₂Cl₂ solutions of 3 (top) and 4 (bottom) at 313K.

The VT ¹H NMR spectra confirm the operation of dynamic processes in solution. However, the activation parameters for the exchanges in complexes 3 and 4 seem not to be the same, and slight differences are discernible in the spectra. Thus, whereas the signals in 3 widen slowly (Figure 8, top) and start to become sharp only at 173K, in the case of 4 the sharpening below the coalescence temperatures happens below 243K, and at 203K a well-defined ¹H NMR spectrum shows the predicted fourteen group of signals (Figure 8, bottom). The latter spectrum is fully consistent with the solid state structure.

Figure 8. ¹H NMR spectra of CD₂Cl₂ solutions of 3 at 168 K (top) and 4 at 203 K (bottom).

The dynamic behavior of 4, and most likely that of 3, is consistent with the operation of a double “*metronome-like*” motion of the gold center (or alternatively the silver one), which moves back-and-forth along the two C–Pt–C axis of the trinuclear complex (Scheme 2). This motion explains the observed simplification of the spectra at the fast exchange rate temperatures that gives rise to nine groups of signals (two of them are overlapped so that eight groups are apparent in the spectrum), which at the low-exchange rate temperatures split up into fourteen groups.

The VT ^{31}P NMR spectra of 3 and 4 uniquely show a singlet (24.1 ppm for 3, 21.0 ppm for 4, at 293K), accompanied by the corresponding platinum satellites (P–Pt coupling constants of 3670 and 3802 Hz respectively). No coupling to silver nuclei can be discerned in these spectra. Conversely, the VT ^{195}Pt NMR spectra of 3 are more informative. Both the RT and 193 K spectra show a similar pattern (See Figures S19 and S20, Supporting Information), and present just one signal, indicating the equivalence of the two Pt atoms, that appears as a doublet of doublets centered at -4144 ppm (193K), as a consequence of the coupling of the Pt with the P ($^1J_{\text{Pt-P}} = 3631$ Hz) and the Ag ($^1J_{\text{Pt-Ag}} = 530$ Hz), not being possible to differentiate the two active isotopes of Ag. This observation indicates that the Pt–Ag interactions remain in solution in this temperature range, and therefore dissociation-association equilibria are slow with regard to the technique timescale. Moreover, a downfield shift of the Pt signal with respect to the starting material of around 200 ppm is observed. Such downfield shift has been reported to be a consequence of the presence of the Pt–Ag bonds in solution.^[4, 20] In the case of 4, the ^{195}Pt NMR spectrum (RT) shows a doublet centered at -4006 ppm with coupling constants $^1J_{\text{Pt-P}} = 3813$ Hz (See Figures S26 and S27, Supporting Information). These spectra do not undergo significant changes at lower temperatures. As for the Pt–Ag complex 3, this ^{195}Pt NMR signal is downfield shifted with respect to the starting material (322 ppm (RT) and 331 ppm (193K)), which is consistent with the persistence of Pt–Au bonds in solution.

Structure and bonding of the heterodinuclear and heterotrinuclear Pt–M (M = Ag, Au) complexes. DFT studies.

The X-ray studies have revealed a peculiar bonding situation between the planar Pt fragment and the acidic M that involves not only dative Pt→M bonds but also the participation of the *ipso* carbon of the CNC ligand in the solid state. In order to gain more insight into these interactions, DFT calculations have been carried out (see computational details in the Supporting Information). The optimized structures (1-DFT, 2-DFT, 3-DFT, and 4-DFT) are in very good agreement with the available X-ray data (1, 3, and 4). A selection of structural data is collected in Table S2. The consistency of the experimental and theoretical data obtained has encouraged us to focus more deeply on the study of the Pt···M interaction by means of the Atoms In Molecules (AIM), Natural Bond Analysis (NBO), and Energy Decomposition Analysis (EDA-NOCV) methods.

We first applied the AIM method to compare the topology of the newly observed complex 2-DFT with that of the previously reported gold analogue 1-DFT.^[4] As readily seen in Figure 9 left, which shows the contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ in the Ag–C–Pt plane, the AIM method locates bond critical points (BCPs) between Pt and the adjacent carbon atoms as well as between Ag and the adjacent carbon atom, which are associated with bond paths (BPs) running between these atoms. However, no bond path (or BCP) between the Pt and Ag metal centers was found. This scenario is therefore identical to that found in the analogous heterobimetallic Pt–Au complex 1-DFT.^[4] Indeed, the NBO Wiberg bond indices (WBI) computed for these Pt–M bonds are nearly identical (0.08 and 0.07, for 1-DFT and 2-DFT, respectively). Despite that, the strength of the M–C bond seems to be higher in complex 1-DFT than in 2-DFT in view of the higher WBI computed for the former bond (0.32 and 0.21, respectively). This is qualitatively consistent with the dynamic behavior observed experimentally for complexes 1 and 2.

Figure 9. Contour line diagrams $\nabla^2\rho(r)$ for the cations of complex 2-DFT (left) and 4-DFT (right) in the M–C–Pt plane (Solid lines connecting nuclei: bond paths; Green dots: bond critical points).

Table 4. Results of the EDA-NOCV at the ZORA-BP86-D3/TZ2P level. Energy values in kcal/mol. Fragments: $[\text{Pt}] + \text{ML}^+$

M / L	Au/PPh ₃ (1-DFT)	Ag/[PPh ₃] (2-DFT)	Ag/[Pt] (3-DFT)	Au/[Pt] (4-DFT)
ΔE_{int}	-94.3	-80.2	-88.1	-100.2
$\Delta E_{\text{Pauli}}^{\text{a}}$	168.5	113.9	142.4	200.6
$\Delta E_{\text{elstat}}^{\text{a}}$	-137.4 (52.3%)	-95.9 (49.4%)	-105.1 (45.6%)	-152.2 (50.6%)
$\Delta E_{\text{orb}}^{\text{a}}$	-88.4 (33.6%)	-63.0 (32.5%)	-63.8 (27.7%)	-89.1 (29.6%)
$\Delta E(\rho_1)^{\text{b}}$	-45.0 (50.9%)	-26.0 (41.3%)	-22.4 (35.1%)	-40.6 (45.6%)
$\Delta E(\rho_2)^{\text{b}}$	-11.1 (12.6%)	-7.6 (12.1%)	-8.6 (13.5%)	-13.8 (15.5%)
$\Delta E_{\text{disp}}^{\text{a}}$	-37.0 (14.1%)	-35.2 (18.1%)	-61.5 (26.7%)	-59.5 (19.8%)
WBI (M–C) ^c	0.32	0.21	0.16	0.35
WBI (M–Pt) ^c	0.08	0.07	0.08	0.09
WBI (C–Pt) ^c	0.32	0.40	0.41	0.32

^a Percentages indicate the contribution to the total attractive interactions ($\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$). ^b Percentages indicate the contribution to the total orbital interactions (ΔE_{orb}). ^c Computed Wiberg Bond Indices for the selected bonds.

More quantitative insight into the bonding situation in these species can be gained by means of the EDA-NOCV method. To this end, the interaction between the $[\text{PtCNC}] \cdots [\text{M-PPh}_3]^+$ moieties has been analyzed. According to the data gathered in Table 4, and reinforcing the experimental observations discussed above, the interaction between these fragments is clearly stronger in complex 1-DFT. This is mainly due to the larger electrostatic and orbital attractions, and also to the dispersion interactions (albeit to a much lesser extent) computed for 1-DFT, in spite of this system exhibiting a more destabilizing Pauli repulsion. These results agree with the lower M–C WBI computed for 2-DFT. The partitioning of the orbital term (ΔE_{orb}) by means of the NOCV method in the Pt–Ag complex shows two main orbital interactions, namely the $[\text{PtCNC}] \rightarrow [\text{Ag}]^+$ donation ($\Delta E(\rho_1)$) and the $[\text{Ag}]^+ \rightarrow [\text{PtCNC}]$ backdonation ($\Delta E(\rho_2)$), the latter being significantly weaker than the former. Although qualitatively the bonding situation is analogous in both heterobimetallic species, the referred orbital interactions are significantly weaker in complex 2-DFT, which is translated into the lower ΔE_{orb} value computed for this species as compared to 1-DFT.

The bonding situation in the trinuclear complexes 3-DFT and 4-DFT was also investigated. The topology of the electron density of these complexes strongly resembles those computed for the binuclear complexes 1-DFT and 2-DFT. Thus, the AIM method (see Figure 9 right for 4-DFT) also locates bond critical points (BCPs) between M and the adjacent aryl carbon atom but not between the Pt and M metal centers (which agrees with the rather low WBI values computed for the Pt–M bond, 0.08 and 0.09 for 3-DFT and 4-DFT, respectively). Once again, the computed WBI for the M–C bond is higher for the gold-complex 4-DFT than for 3-DFT (0.35 vs 0.16, respectively) thus confirming the higher carbophilicity of Au(I) as compared to Ag(I).

According to the EDA-NOCV method, the replacement of the PPh₃ ligand by a $[\text{PtCNC}]$ unit results in stronger $[\text{PtCNC}] \cdots [\text{M}(\text{PtCNC})]^+$ interactions for complexes 3-DFT and 4-DFT as compared to 1-DFT and 2-DFT (see Table 4). This is very likely to be due to the lower donating ability of the $[\text{PtCNC}]$ fragment as compared to PPh₃, which makes the M(I) center more electrophilic. This is qualitatively confirmed by the computed NBO charges on the M center (for instance, a value of +0.34e was computed for the gold atom in 1-DFT whereas a higher positive value of +0.51e was found in complex 4-DFT), which in turn is reflected in the higher electrostatic attractions (ΔE_{elstat}) computed for the trinuclear complexes.

Not surprisingly, the scenario in the trinuclear complexes resembles that found for the binuclear systems. Thus, the $[\text{PtCNC}] \cdots [\text{M}(\text{PtCNC})]^+$ interaction is higher in the gold complex 4-DFT than in 3-DFT as a consequence of much higher electrostatic and orbital interactions, which is consistent with the observed experimental findings. Once again, the NOCV method identifies two main orbital interactions, the donation from an occupied π -molecular orbital of the $[\text{PtCNC}]$ fragment to a vacant orbital mainly located the $[\text{M}(\text{PtCNC})]^+$ moiety (ρ_1) and the reverse backdonation from the $[\text{M}(\text{PtCNC})]^+$ fragment (ρ_2), as shown in Figure 10. Similarly to what was found for

the bimetallic systems 1-DFT and 2-DFT, the former interaction is stronger than the latter and both are higher in the gold-complex 4-DFT than in the analogous silver complex 3-DFT.

The different importance of the Pt···M interactions in complexes 1-DFT, 2-DFT, 3-DFT, and 4-DFT can be also estimated by computing the deformation energy of the Lewis basic platinum fragment [PtCNC] on the resulting polynuclear compounds with regard to its ground state geometry. According to our calculations, the deformation energies are 9.0 (1-DFT), 3.4 (2-DFT), 5.4 (3-DFT), and 9.1 (4-DFT) kcal/mol. Once again these energies are in good agreement with the higher strength of the Au–C interactions, with regard to the Ag–C ones.

Figure 10. EDA-NOCV computed main deformation densities ($\Delta\rho$) for complex 4-DFT. Charge flows from red to blue.

Conclusions

We have synthesized a series of novel heteropolymetallic derivatives that conceptually can be considered as the result of Lewis acid-Lewis base interactions among metallic fragments of different chemical properties. Thus, these fragments assemble together forming more complex molecular architectures. The resulting compounds are notable from different perspectives, ranging from supramolecular/cluster chemistry to bimetallic catalysis.

The combination of the structural, spectroscopic and computational data collected has shed light on the intrinsic properties and behavior of the M···(Pt–C) interactions (M = Ag, Au). The structural data highlight the different importance of these interactions as a function of the group-11 metal, suggesting stronger ones in the Pt–Au complexes (1 and 4). Besides, DFT calculations provide quantitative descriptions of the referred M···(Pt–C) interactions, remarking the prevalence of the M–C bonds in the whole picture. The combination of the electronic, geometric and steric features of the involved metallic fragments determines the final structures, which can be interpreted as arrested intermediates or “snapshots” of transmetalation reactions. Therefore, it can be concluded that these structures constitute real photographs of aryl ligand exchange processes which have been frozen at different degrees of transfer.

Furthermore, the NMR studies on the heteropolymetallic derivatives prove the occurrence of dynamic processes in solution with reasonably low energy barriers. These consist of the intramolecular back-and-forth bouncing of the Lewis acidic [M–L]⁺ fragments over the C–Pt–C axis of the Lewis basic [Pt(CNC)] fragment (“metronome-like” dynamics), together with Pt–Ag and Ag–P bond-forming and bond-breaking processes in the Pt–Ag complexes (2 and 3).

Experimental Section

General Comments. Literature methods were used to prepare the starting material [Pt(CNC)(PPh₃)] (CNC = 2,6-diphenylpyridinate).^[4] Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer (ATR in the range 250–4000 cm^{–1}). Mass spectrometry was performed with the Microflex matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) Bruker or an Autoflex III MALDI-TOF Bruker instruments. ¹H, ¹³C{¹H}, ³¹P{¹H} and ¹⁹⁵Pt{¹H} NMR spectra were recorded on Bruker AV-400 and AV-500 spectrometers using the standard references: SiMe₄, 85% H₃PO₄ and Na₂PtCl₆ in D₂O for references for ¹H and ¹³C, ³¹P and ¹⁹⁵Pt respectively. The signal attributions and coupling constant assessment was made on the basis of a multinuclear NMR analysis of each compound including, besides 1D spectra, ¹H COSY, ¹H–¹³C HMQC, ¹H–¹³C HMBC and APT.

Safety Note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with great caution.

Chart 1. ^1H and ^{13}C numbering scheme for the $[\text{Pt}(\text{CNC})]$ fragment (CNC = 2,6-diphenylpyridinate).

Preparation of the complex $[(\text{CNC})(\text{PPh}_3)\text{PtAu}(\text{PPh}_3)](\text{ClO}_4)$ (1). Synthesis was carried out under a strict argon atmosphere. To a solution of $[\text{AuCl}(\text{PPh}_3)]$ (0.076 g, 0.150 mmol) in tetrahydrofuran (20 mL) at -40°C , AgClO_4 (0.032 g, 0.150 mmol) was added. After 75 minutes of stirring in the absence of light the suspension was filtered. To the collected solution, complex $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ (0.100 g, 0.150 mmol) was added. After 3 hours of stirring at room temperature, the resulting solution was evaporated to dryness. Addition of methanol (5 mL) caused a precipitate which was decanted, washed with diethyl ether (10 mL), and air dried (Yield: 0.116 g, 64 %). Anal. Found: C, 50.88; H, 3.21; N, 1.26. Anal. Calcd for $\text{C}_{53}\text{H}_{41}\text{AuClN}_2\text{O}_4\text{P}_2\text{Pt}$: C, 51.12; H, 3.32; N, 1.12. IR (ATR, cm^{-1}): 1597 (w, u(N-C)), 1562 (vw, u(N-C)), 1079 (s, u(ClO_4^-)), 689 (s, u(P-C)), 621 (m, u(ClO_4^-)), 536 (vs, u(P-C)), 513 (vs, u(P-C)), 497 (vs, u(P-C)). ^1H NMR (400.132 MHz, CD_2Cl_2 , 293K, see Chart 1 for the H numbering scheme): δ = 7.92 (1H, t, $^3J_{\text{H7-H6}}$ = 8.0 Hz, H7), 7.72 (2H, dd, $^3J_{\text{H5-H4}}$ = 7.6 Hz, $^4J_{\text{H5-H3}}$ = 1.3 Hz, H5), 7.70-7.67 (6H, m, $^3J_{\text{H6-H5}}$ = 8.3 Hz, $^4J_{\text{H6-Hp}}$ = 1.2 Hz, o-Ph(PPh_3)(Pt)), 7.62 (2H, d, $^3J_{\text{H6-H7}}$ = 8.0 Hz, H6), 7.53-7.47 (6H, m, overlapped signals of p-Ph(PPh_3)(Pt) and p-Ph(PPh_3)(Au)), 7.32 (6H, td, $^3J_{\text{Hm-Ho}}$ = 8.3 Hz, $^3J_{\text{Hm-Hp}}$ = 2.7 Hz, m-Ph(PPh_3)(Au)), 7.26 (2H, ddd, $^3J_{\text{H4-H5}}$ = 7.6 Hz, $^3J_{\text{H4-H3}}$ = 7.6 Hz, $^4J_{\text{H4-H2}}$ = 1.0 Hz, H4), 7.21 (6H, td, $^3J_{\text{Hm-Ho}}$ = 8.3 Hz, $^3J_{\text{Hm-Hp}}$ = 2.5 Hz, m-Ph(PPh_3)(Pt)), 7.11-7.08 (6H, td, $^3J_{\text{H6-H5}}$ = 8.3 Hz, $^4J_{\text{H6-Hp}}$ = 1.2 Hz, o-Ph(PPh_3)(Au)), 6.84 (2H, ddd, $^3J_{\text{H3-H4}}$ = $^3J_{\text{H3-H2}}$ = 7.6 Hz, $^4J_{\text{H3-H5}}$ = 1.3 Hz, H3), 6.08 (2H, dd, $^3J_{\text{H2-H3}}$ = 7.6 Hz, $^4J_{\text{H2-H4}}$ = 1.0 Hz, $^3J_{\text{H2-Pt}}$ = 25.9 Hz, H2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.624 MHz, CD_2Cl_2 , 293K, see Chart 1 for the C numbering scheme): δ = 164.4 (s, C8), 154.2 (s, C9), 146.1 (s, $^1J_{\text{C-Pt}}$ = 654 Hz, C1), 143.0 (s, C7), 142.1 (s, C2), 136.1 (d, $^1J_{\text{C-P}}$ = 11.5 Hz, $^3J_{\text{C-Pt}}$ = 25.4 Hz, o-C-PPh₃(Pt)), 134.1 (d, $^1J_{\text{C-P}}$ = 13.9 Hz, o-C-PPh₃(Au)), 132.8-132.4 (d, $^4J_{\text{C-P}}$ = 2.1 Hz, d, $^4J_{\text{C-P}}$ = 1.6 Hz, p-C-PPh₃(Au) and p-C-PPh₃(Pt)), 130.5 (s, $^3J_{\text{C-Pt}}$ = 33.2 Hz, C3), 129.9 (d, overlapped signals of m-C-PPh₃(Au) and C5), 129.3 (d, $^1J_{\text{C-P}}$ = 11.1 Hz, m-C-PPh₃(Pt)), 125.9 (s, $^4J_{\text{C-Pt}}$ = 22.9 Hz, C4), 117.6 (d, $^4J_{\text{C-P(Pt)}}$ = 3.1 Hz, C6) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (161.923 MHz, CD_2Cl_2): δ = 34.6 (s, $^2J_{\text{P(Au)-Pt}}$ = 254 Hz) (293K), 22.5 (s, $^1J_{\text{P-Pt}}$ = 3680 Hz) (293K); 35.8 (s, $^2J_{\text{P(Au)-Pt}}$ = 242 Hz) (193K), 22.1 (s, $^1J_{\text{P-Pt}}$ = 3660 Hz) (193K) ppm. $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.679 MHz, CD_2Cl_2): δ = -4017 (dd, $^1J_{\text{Pt-P}}$ = 3680 Hz, $^2J_{\text{Pt-P(Au)}}$ = 254 Hz) (293K), -4060 (dd, $^1J_{\text{Pt-P}}$ = 3660 Hz, $^2J_{\text{Pt-P(Au)}}$ = 242 Hz) (193K) ppm. Mass spectra MALDI+ DCTB: m/z = 1145 $[(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})\text{PtAu}(\text{C}_{18}\text{H}_{15}\text{P})]^+$.

Obtaining of the mixture 2*. The reaction was carried out under a strict argon atmosphere. To a solution of $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ (0.150 g, 0.219 mmol) in CH_2Cl_2 (20 mL) at -70°C , $[\text{Ag}(\text{OCIO}_3)(\text{PPh}_3)]$ (0.102 g, 0.219 mmol) was added. After 30 minutes of stirring in the absence of light the the solution was evaporated dryness. n-hexane (10 mL) was added to the orange solid and the resulting suspension was filtered off and air dried (Yield: 0.207 g, 82 %). Anal. Found: C, 55.02; H, 3.96; N, 1.31. Anal. Calcd for $\text{C}_{53}\text{H}_{41}\text{AgClN}_2\text{O}_4\text{P}_2\text{Pt}$: C, 55.06; H, 3.57; N, 1.21. IR (ATR, cm^{-1}): 1598 (m, u(N-C)), 1564 (w, u(N-C)), 1547 (w, u(N-C)), 1088 (s, u(ClO_4^-)), 690 (vs, u(P-C)), 620 (s, u(ClO_4^-)), 539 (vs, u(P-C)), 514 (vs, u(P-C)), 499 (vs, u(P-C)). ^1H NMR (500.130 MHz, CD_2Cl_2 , 243K): δ = 7.87 (1H, t, $^3J_{\text{H7-H6}}$ = 8.0 Hz, H7), 7.72 (6H, m, $^3J_{\text{H6-H5}}$ = 7.8 Hz, $^3J_{\text{H6-Hp}}$ = 1.0 Hz, o-Ph(PPh_3)), 7.64 (2H, d, $^3J_{\text{H5-H4}}$ = 7.6 Hz, H5), 7.56 (2H, d, $^3J_{\text{H6-H7}}$ = 8.0 Hz, H6), 7.54-7.40 (6H, m, Ph(PPh_3)), 7.31 (6H, t, $^3J_{\text{Hp-Hm}}$ = 7.2 Hz, p-Ph(PPh_3)), 7.22 (6H, m, Ph(PPh_3)), 7.18 (2H, t, $^3J_{\text{H4-H5}}$ = 7.6 Hz, $^3J_{\text{H4-H3}}$ = 7.6 Hz, H4), 6.91 (6H, m, Ph(PPh_3)), 6.81 (2H, t, $^3J_{\text{H3-H4}}$ = 7.6 Hz, $^3J_{\text{H3-H2}}$ = 7.6 Hz, H3), 6.04 (2H, d, $^3J_{\text{H2-H3}}$ = 7.6 Hz, H2) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.461 MHz, CD_2Cl_2): δ = 24.1 (s, $^1J_{\text{P-Pt}}$ = 3662 Hz) (293K), 15.1 (d, $^1J_{\text{P-Ag}}$ = 672 Hz) (293K); 23.6 (s, $^1J_{\text{P-Pt}}$ = 3548 Hz) (183K), 15.3 (dd, $^1J_{\text{P-Ag}}$ = 717 Hz, $^1J_{\text{P-Ag}}$ = 624 Hz, $^2J_{\text{P(Ag)-Pt}}$ = 122 Hz) (183K) ppm. $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.679 MHz, CD_2Cl_2 , 193 K): δ = -4171 (ddd, $^1J_{\text{Pt-P}}$ = 3561 Hz, $^1J_{\text{Pt-Ag}}$ = 438 Hz, $^2J_{\text{Pt-P(Ag)}}$ = 115 Hz) ppm. Mass spectra MALDI+ DCTB: m/z = 1055 $[(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})\text{PtAg}(\text{C}_{18}\text{H}_{15}\text{P})]^+$, 793 $[\text{Pt}(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})\text{Ag}]^+$, 687 $[\text{Pt}(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})+\text{H}]^+$, 389 $[\text{Ag}(\text{C}_{18}\text{H}_{15}\text{P})]^+$.

Preparation of the complex $[(\text{CNC})(\text{PPh}_3)\text{Pt}_2\text{Ag}](\text{ClO}_4)$ (3). To a solution of $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ (0.100 g, 0.146 mmol) in CH_2Cl_2 (20 mL) at room temperature, AgClO_4 (0.015 g, 0.146 mmol) was added. After 120 minutes of stirring in absence of light the solution was evaporated dryness. iPrOH (3 mL) was added to the orange solid and the resulting suspension was filtered off, washed with n-hexane (10 mL) and air dried (Yield: 0.090 g, 78 %). Anal. Found: C, 52.79; H, 3.24; N, 1.44. Anal. Calcd for $\text{C}_{70}\text{H}_{52}\text{AgClN}_2\text{O}_4\text{P}_2\text{Pt}_2$: C, 53.19; H, 3.32; N, 1.77. IR (ATR, cm^{-1}): 1598 (m, u(N-C)), 1564 (w, u(N-C)), 1547 (w, u(N-C)), 1090 (m, u(ClO_4^-)), 693 (s, u(P-C)), 622 (m, u(ClO_4^-)), 539 (vs, u(P-C)), 513 (m, u(P-C)), 501 (m, u(P-C)). ^1H NMR (500.130 MHz, CD_2Cl_2 , 293K): δ = 7.64 (2H, t, $^3J_{\text{H7-H6}}$ = 7.9 Hz, H7), 7.51-7.43 (18H, m, overlapped signals of protons m-Ph(PPh_3) and p-Ph(PPh_3)), 7.39 (4H, d, $^3J_{\text{H5-H4}}$ = 7.6 Hz, H5), 7.29 (4H, d, $^3J_{\text{H6-H7}}$ = 7.9 Hz, H6), 7.23 (12H, m, o-Ph(PPh_3)), 6.97 (4H, t, $^3J_{\text{H4-H5}}$ = 7.6 Hz, $^3J_{\text{H4-H3}}$ = 7.6 Hz, H4), 6.51 (4H, t, $^3J_{\text{H3-H4}}$ = 7.6 Hz, $^3J_{\text{H3-H2}}$ = 7.6 Hz, H3), 5.83 (4H, d, $^3J_{\text{H2-H3}}$ = 7.6 Hz, H2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.624 MHz, CD_2Cl_2 , 293K): δ = 165.5 (s, C8), 152.8 (s, C9), 149.6 (s, C1), 142.2 (s, C7), 139.7 (s, C2), 135.5 (d, $^1J_{\text{C-P}}$ = 11.4 Hz, $^2J_{\text{C-Pt}}$ = 34.5 Hz, C-PPh₃), 132.1 (s, C-PPh₃), 130.5 (s, C3), 129.2 (d, $^1J_{\text{C-P}}$ = 10.9 Hz, C-PPh₃), 127.5 (s, C4), 125.6 (s, C5), 116.7 (s, C6) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.461 MHz, CD_2Cl_2): δ = 24.1 (s, $^1J_{\text{P-Pt}}$ = 3670 Hz) (293K), 23.6 (s, $^1J_{\text{P-Pt}}$ = 3617 Hz)

(193K) ppm. $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.679 MHz, CD_2Cl_2): $\delta = -4102$ (dd, $^1J_{\text{Pt-P}} = 3711$ Hz, $^1J_{\text{Pt-Ag}} = 513$ Hz) (293K), -4144 (dd, $^1J_{\text{Pt-P}} = 3631$ Hz, $^1J_{\text{Pt-Ag}} = 530$ Hz) (193K) ppm. Mass spectra MALDI+ DIT: $m/z = 1479$ $[\text{Pt}(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})]_2\text{Ag}^+$, 793 $[\text{Pt}(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})\text{Ag}]^+$, 687 $[\text{Pt}(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})+\text{H}]^+$.

Preparation of the complex $[\{(\text{CNC})(\text{PPh}_3)\text{Pt}\}_2\text{Au}](\text{ClO}_4)$ (4) To a solution of $[\text{AuCl}(\text{tht})]$ ($\text{tht} = \text{SC}_4\text{H}_8$, tetrahydrothiophene) (0.052 g, 0.162 mmol) in THF (20 mL) at 0°C and under an Ar atmosphere, tht (15 μL , 0.162 mmol) and AgClO_4 (0.033 g, 0.162 mmol) was added. After 60 minutes of stirring in absence of light, the complex $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ (1) (0.212 g, 0.308 mmol) was added to the solution. After 2 hours of stirring, the resulting solution was concentrated to ca. 5 mL and kept to -30°C to give an orange precipitate that was filtered off, washed with diethyl ether (10 mL) and finally air dried (Yield: 0.153 g, 60 %). Anal. Found: C, 49.94; H, 3.05; N, 1.80. Anal. Calcd for $\text{C}_{70}\text{H}_{52}\text{AuClN}_2\text{O}_4\text{P}_2\text{Pt}_2$: C, 50.35; H, 3.14; N, 1.68. IR (ATR, cm^{-1}): 1597 (w, $\nu(\text{N-C})$), 1576 (vw, $\nu(\text{N-C})$), 1563 (vw, $\nu(\text{N-C})$), 1544 (vw, $\nu(\text{N-C})$), 1092 (s, $\nu(\text{ClO}_4^-)$), 692 (s, $\nu(\text{P-C})$), 620 (m, $\nu(\text{ClO}_4^-)$), 540 (vs, $\nu(\text{P-C})$), 513 (s, $\nu(\text{P-C})$), 507 (s, $\nu(\text{P-C})$). ^1H NMR (500.130 MHz, CD_2Cl_2 , 293K): $\delta = 7.58$ (2H, t, $^3J_{\text{H7-H6}} = 7.9$ Hz, H7), 7.50 (6H, t, $^3J_{\text{H6-H5}} = 7.1$ Hz, $p\text{-Ph}(\text{PPh}_3)$), 7.34 (12H, t, $^3J_{\text{Hm-Ho}} = 7.0$ Hz, $m\text{-Ph}(\text{PPh}_3)$), 7.33-7.27 (20H, m, overlapped signals H5 and H6 of ligand CNC and $o\text{-Ph}(\text{PPh}_3)$), 6.98 (4H, t, $^3J_{\text{H4-H5}} = 7.4$ Hz, $^3J_{\text{H4-H3}} = 7.4$ Hz, H4), 6.64 (4H, t, $^3J_{\text{H3-H4}} = 7.4$ Hz, $^3J_{\text{H3-H2}} = 7.4$ Hz, H3), 5.98 (4H, broad singlet signal, H2) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.624 MHz, CD_2Cl_2 , 293K): $\delta = 165.3$ (s, C8), 154.2 (s, C9), 146.1 (s, C1), 142.7 (s, C2), 141.9 (s, C7), 135.6 (d, $^1J_{\text{C-C}} = 11.4$ Hz, C-PPh₃), 131.8 (d, $^1J_{\text{C-C}} = 2.4$ Hz, C-PPh₃), 129.0 (d, $^1J_{\text{C-Pt}} = 25.9$ Hz, $^1J_{\text{C-C}} = 11.0$ Hz, overlapped signals of $o\text{-C-PPh}_3$ and C3 and C4), 125.6 (s, C5), 116.8 (d, $^1J_{\text{C-C}} = 3.2$ Hz, C6) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.461 MHz, CD_2Cl_2 , 203K): $\delta = 20.8$ (s, $^1J_{\text{P-Pt}} = 3794$ Hz) ppm. $^{195}\text{Pt}\{^1\text{H}\}$ NMR (85.679 MHz, CD_2Cl_2): $\delta = -4006$ (d, $^1J_{\text{Pt-P}} = 3813$ Hz) (293K), -4018 (d, $^1J_{\text{Pt-P}} = 3773$ Hz) (193K) ppm. Mass spectra MALDI+ DCTB: $m/z = 1569$ $[(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})\text{PtAuPt}(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})]^+$, 1307 $[(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})\text{PtAuPt}(\text{C}_{17}\text{H}_{11}\text{N})]^+$, 1145 $[(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})\text{PtAu}(\text{C}_{18}\text{H}_{15}\text{P})]^+$, 893 $[(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})\text{PtAu}]^+$, 687 $[\text{Pt}(\text{C}_{17}\text{H}_{11}\text{N})(\text{C}_{18}\text{H}_{15}\text{P})+\text{H}]^+$.

X-ray structure determinations. Crystal data and other details of the structure analyses are presented in Table S1. Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of n -hexane into concentrated solutions of the complexes in 3 mL of CHCl_3 or Me_2CO . Crystals were mounted at the end of quartz fibres. The radiation used in all cases was graphite monochromated Mo K α ($\lambda = 0.71073$ Å). X-ray intensity data were collected on an Oxford Diffraction Xcalibur diffractometer. The diffraction frames were integrated and corrected from absorption by using the CrysAlis RED program.^[21] The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 with SHELXL-97.^[22] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the values of their attached parent atoms (1.5 times for the methyl hydrogen atoms). In the structure of 4-0.5 $\text{Me}_2\text{CO} \cdot 0.5n\text{-C}_6\text{H}_{14}$, the n -hexane solvent molecule is disordered over to positions close to an inversion center, sharing the methyl carbon atom. Each set of disordered atoms were refined with 0.5 occupancy. Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table S1. CCDC 1452240 (1), 1841242 (3), 1841243 (4) and 1841244 (AgP2) contain the supplementary crystallographic data for this paper, which can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational details. See Supporting Information.

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