A dinuclear Pt–Au complex showing an unusual metal-metal bonding situation: A snapshot of a transmetalation process

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Abstract: The dinuclear Pt–Au complex $[(CNC)(PPh_3)PtAu(PPh_3)](ClO_4)$ (**2**) ($CNC = 2,6$ -diphenylpyridinate) has been prepared. Its crystal structure shows a rare metal-metal bonding situation, with very short Pt–Au and Au–C_{ipso}(CNC) distances and dissimilar Pt–C_{ipso}(CNC) bonds. Multinuclear NMR spectra of **2** show the persistence of the Pt–Au bond in solution and the operation of an unusual fluxional behavior involving the $[Pt^{II}]$ and $[Au^I]$ metal fragments. The $[Pt^{II}] \cdots [Au^I]$ interaction has been thoroughly studied by means of DFT calculations. The observed bonding situation in **2** can be regarded as a model for an intermediate in a transmetalation process.

The study of complexes containing intermetallic interactions between closed or pseudo-closed shell transitions metals (d^8 , d^{10} , $d^{10}s^2$) is a field which is attracting a considerable attention in chemistry. These interactions have proven to be a powerful tool for crystal engineering,^[1-5] and the complexes containing them show interesting photophysical and photochemical properties related to the occurrence of M–M bonds.^[6, 7] Besides, the interest on these systems has increased lately because species containing this kind of interactions play a central role in cooperative catalysis.^[8] For example, complexes with Pt–Au, Pt–Cu or Pt–Ag bonds have been identified in either gas phase or in solution as intermediates in transmetalation reactions involving methyl groups,^[9-11] whereas Pd–Au or Pd–Cu species have been proposed as transition states in aryl ligand interchange processes.^[12, 13] However, scarce experimental evidences supporting this

kind of intermediates have been provided, and the nature and properties of them remains unexplored so far. Indeed, in the context of bimetallic catalysis, Casares and Espinet have stated that “*it is crucial to better understand the exchange reactions within the well-behaved Pd/Au and Pd/Cu couples, but also in other less well-behaved metal combinations*”.^[8]

The M-M interactions described above are of dative nature and are established between a basic donor metallic center and an acidic acceptor metal. A number of metals are known to fulfill this role but $\text{Pt}^{\text{II}}(\text{d}^8)$ is the donor center *par excellence*,^[1, 4, 9, 14-18] while among the acceptors, $\text{Ag}^{\text{I}}(\text{d}^{10})$ is by far the most representative example.^[19, 20] In contrast, very few examples of $\text{Pt}^{\text{II}} \rightarrow \text{Au}^{\text{I}}(\text{d}^{10})$ have been fully characterized.^[21-24] From a structural point of view, several binding modes for the coordination of platinum (II) fragments to Lewis acidic metals are known. The most frequent consists of a metal–metal interaction in which the bond axis lies perpendicular to the coordination plane of the d^8 metal.^[4, 25] A less common binding mode shows additional interaction of the acidic metal with one or two of the ligand atoms directly attached to platinum.^[15, 17, 19, 26-28]

This latter kind of interaction resembles that occurring in most of the key intermediate species proposed in heterobimetallic catalysis. In this communication we report the synthesis and characterization of a rare heterobimetallic Pt-Au complex having an unusual metal-metal bonding mode and a surprising dynamic behaviour in solution. Such bonding situation can be regarded as a model for the transmetalation step of the above-mentioned cooperative bimetallic catalytic systems.

Complex $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ ($\text{CNC} = 2,6\text{-diphenylpyridinate}$, **1**) has been prepared by replacing the dimethyl sulfoxide ligand in $[\text{Pt}(\text{CNC})(\text{dms})]$ ^[29] with PPh_3 . The crystal structure of **1** has been determined by X-ray diffraction and shows the expected square planar coordination around the platinum (see Figure S3 and Table S1 in the Supporting Information). The reaction of equimolecular amounts of complex **1** with $[\text{AuCl}(\text{PPh}_3)]$ and AgClO_4 in THF at $-40\text{ }^\circ\text{C}$ leads to the formation of $[(\text{CNC})(\text{PPh}_3)\text{PtAu}(\text{PPh}_3)](\text{ClO}_4)$ (**2**), which can be obtained as an orange solid after work up (see experimental details in the Supporting Information).

The crystal structure of **2** has been determined by X-ray diffraction (see Supporting Information for details). A drawing of its complex cation is shown in Figure 1, and a selection of relevant bond distances and angles is included in the caption. The

cation of **2** is a dinuclear complex in which the Pt–Au distance is 2.7222(2) Å and the Au atom is also bonded to a PPh₃ ligand. This distance is among the shortest reported for Pt(II)–Au(I) bonds,^[30] only comparable to those of the hydride bridged complexes [(PR₃)(C₆X₅)(μ-H)PtAu(PPh₃)]⁺ (R = PEt₃, X = F, 2.714(1) Å^[21]; R = PPh₃, X = Cl, 2.792(1) Å).^[23] Moreover, a striking feature of **2** is the interaction between the Au center and the *ipso* carbon of one of the phenylene rings of the CNC ligands. Thus, the Au–C7 distance is intriguingly short. Concomitantly, the Pt–C7 distance becomes significantly longer than the Pt–C13 one, the later being in the typical range found for Pt(II) complexes containing this or quite similar CNC ligands.^[15, 16, 31, 32] The C7 phenylene ring remains perfectly planar. However, while the rest of the CNC ligand remains coplanar with the square planar environment of the Pt center, the C7 ring remarkably deviates from this plane (23.1(1)°).

The bonding situation involving Pt, Au and C7 atoms found in the solid state for **2** does not fit into the traditional model of square planar Pt(II)→M donor acceptor complexes. Thus, the Pt–Au line deviates considerably from the perpendicular to the Pt–N–C13 plane and the Pt–Au–P2 line bends 152.38(2)°, with the result of the Au atom leaning towards C7 (Au–Pt–C₇ angle of 52.7(1)°). This kind of situation, although reported in some examples,^[9, 15] remained unstudied so far.^[33]

Figure 1. Molecular structure of the cation of complex **2**. Selected bond distances (Å) and angles (°): Pt–Au 2.7222(2), Pt–C7 2.158(3), Pt–C13 2.063(3), Pt–N 2.036(3), Pt–P 2.2433(9), Au–C7 2.225(3), Pt–Au–P2 152.38(2), C7–Au–P2 153.25(8).

The bonding situation of complex **2** was analysed by means of Density Functional Theory (DFT) calculations at the BP86-D3/6-31G(d)&SDD+f(Pt, Au) level using the Atoms In Molecules (AIM), Natural Bond Orbital (NBO) and Energy Decomposition Analysis (EDA-NOCV) methods (see the Supporting Information). Figure 2 shows the contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ in the plane of the three-membered heterobimetalacycle. Interestingly, the AIM method locates bond critical points (BCPs) between Pt and the adjacent carbon atoms as well as between Au and the adjacent carbon atom which are associated with bond paths (BPs) running between these atoms. On the contrary, no bond path (or BCP) linking Pt and Au metal centers has been found in the topological analysis of the electron density. The NBO-Wiberg Bond Indexes computed for these Pt–C and Au–C bonds (WBI of 0.46 and 0.31, respectively), suggest that the strength of the Pt–C bond is slightly higher than that of the Au–C bond. The existence of a Pt–Au interaction is backed by the NBO analysis, as illustrated by the significant WBI of 0.25. In agreement with this, a remarkable two-electron delocalization from a doubly occupied d(Pt) atomic orbital to a vacant p(Au) atomic orbital is located by applying the Second-Order Perturbation Theory (SOPT) of the NBO method (associated SOPT-energy, $\Delta E^{(2)}$, of -61.4 kcal/mol). This result agrees with a dative nature of the [PtCNC]→Au interaction.

Further quantitative information on the nature of the [PtCNC]...[Au]⁺ interaction in complex **2** can be gained by means of the EDA-NOCV method. As shown in Table 1, the interaction shows a prevalent ionic character, according to the contribution of the electrostatic term (ΔE_{elstat} , 52% to the total attractive interactions). This is not surprising if we take into account that the [PtCNC] moiety and the positively charged [Au]⁺ cation were used as fragments in the bonding analysis. Despite that, the covalent character is also very significant, as the orbital term (ΔE_{orb}) contributes 34% to the total attractive interactions. In addition, interactions coming from dispersion forces (measured by the ΔE_{disp} term) are not negligible as they contribute 14% to the total interaction energy.

Figure 2. Contour line diagrams $\nabla^2\rho(r)$ for the cation of complex **2** in the Au–C–Pt plane (Solid lines connecting nuclei: bond paths; black small spheres: bond critical points).

Figure 3. EDA-NOCV computed main deformation densities ($\Delta\rho$) for complex **2**. Charge flows from dark grey to light grey.

Table 1. EDA-NOCV values (kcal/mol) computed for complex **2** (ZORA-BP86-D3/TZVP//BP86-D3/6-31G(d)&SDD+f level).

ΔE_{int}	ΔE_{Pauli}	$\Delta E_{\text{elstat}}^{[a]}$	$\Delta E_{\text{orb}}^{[a]}$	$\Delta E_{\text{disp}}^{[a]}$
-94.3	168.5	-136.3 (51.9%)	-89.5 (34.0%)	-37.0 (14.1%)

[a] The percentage values in parentheses give the contribution to the total attractive interactions ($\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$)

The ΔE_{orb} can be further partitioned by means of the EDA-NOCV method into pairwise energy contributions for each pair of interacting orbitals. Figure 3 shows the NOCV-deformation densities computed for complex **2**, where the charge flow takes place in the direction from dark grey to light grey. The most important contribution to ΔE_{orb} comes from the $\Delta\rho(1)$ interaction, which can be viewed as the donation of electron density from an occupied π -molecular orbital involving the Pt(CNC) moiety to a vacant orbital mainly located at the Au(I) atom. This interaction ($\Delta E(\rho 1) = -44.6$ kcal/mol) is responsible for the 50% of the total orbital attractions, which highlights the importance of the Au-C bond in the stabilization of the molecule. Additional $[\text{Au}]^+ \rightarrow [\text{PtCNC}]$ backdonation is also found within this analysis, although this interaction is significantly lower ($\Delta E(\rho 2) = -11.4$ kcal/mol, 13% of ΔE_{orb}). This supports the existence of a Pt-Au interaction, although weaker than the Au-C one, which nicely agrees with the computed WBIs (see above).

In solution the existence of $\text{Pt}^{\text{II}} \rightarrow \text{M}$ interactions is often uncertain, since they can be easily broken and participate in quick association-dissociation equilibria.^[34] Nevertheless, a remarkable feature of complex **2** is the persistence of the Pt–Au bond in solution. In agreement with this, the RT ^{31}P NMR spectrum of **2** (see Figure 4a) shows two signals corresponding to the two phosphorus of the PPh_3 ligands, both of them showing ^{195}Pt - ^{31}P couplings. The signal corresponding to the P atom bonded to Pt appears as a singlet at 22.5 ppm with Pt satellites ($^1J_{\text{P-Pt}} = 3680$ Hz), whereas the one corresponding to the P atom bonded to Au appears as a singlet at 34.6 ppm, also with Pt satellites ($^2J_{\text{P-Pt}} = 254$ Hz). Furthermore, the RT ^{195}Pt NMR spectrum of **2** (see Figure 4b) shows a doublet of doublets centered at -4017 ppm, with coupling constants of 3680 ($^1J_{\text{Pt-P}}$) and 254 ($^2J_{\text{Pt-P}}$) Hz. Thus, the presence of remote Pt–Au–P coupling, revealed by the $^2J_{\text{Pt-P}}$ constant, provides evidence of the persistence of the Pt–Au interaction in

dichloromethane- d_2 solutions of **2**. Besides, the corresponding ^{195}Pt NMR chemical shift is downfield with respect to that of the monometallic precursor **1** ($\Delta\delta = +317$ ppm). This downfield shift is consistent with the formation of a $[\text{Pt}] \rightarrow [\text{M}]^+$ dative bond in solution and is caused by the decrease of electron density around the Pt center upon coordination to M^+ . [15, 16, 32]

Figure 4. Room temperature $^{31}\text{P}\{^1\text{H}\}$ (a) and $^{195}\text{Pt}\{^1\text{H}\}$ NMR (b) spectra of a CD_2Cl_2 solution of **2**.

A striking feature of the NMR behavior of **2** in solution is that, despite the persistence of the Pt–Au bond, the phenylene rings are equivalent in both their RT ^1H and ^{13}C NMR spectra. Thus, for example, only one signal corresponding to the CH_{ortho} of the referred phenylene rings is observed, namely a doublet at 6.07 ppm. This is in sharp contrast with the solid state structure of **2** and is a proof of a singular dynamic behavior that deserves further study. A view of the complete VT ^1H NMR spectra performed is shown in Figure 5. Interestingly, the spectrum at 163K 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. Most notably, the doublet at 6.07 ppm splits into two broad peaks centered at 6.43 and 5.16 ppm, respectively. The temperature of coalescence of this process is 203K. According to the Gutowski equation, the estimation of $\Delta\delta$ and T_{coal} values (650 Hz and 203K respectively) affords an approximate activation

free energy, $\Delta G^\ddagger$, of 8.8 kcal/mol for this dynamic process, which can be described as a “metronome-like” exchange process (see Scheme 1) where the Pt–Au bond acts as an anchor of the two metallic fragments.^[35] DFT modelling of this process supports this proposal and estimates an activation barrier of 8.9 kcal/mol (see Supporting Information).

Figure 5. Collected VT ¹H NMR spectra of a CD₂Cl₂ solution of **2**, in the 163 to 273K temperature range.

Scheme 1. Dynamic exchange process (“metronome-like”) in solution proposed for **2**.

The combined experimental observations and calculated data illustrate the robustness and flexibility of the interaction between the original $[\text{Pt}(\text{CNC})(\text{PPh}_3)]$ and $[\text{Au}(\text{PPh}_3)]^+$ metal fragments and highlights the subtle equilibrium of the different forces taking place in the dinuclear system. In this context, it should be remarked that the formation of **2** formally results from an electrophilic attack onto a Pt-R bond of a Pt(II) square-planar system, which can proceed via either attack onto the metal center or onto the carbon atom of R. Thus, the well-known isolobal relation between the $[\text{Au}(\text{PPh}_3)]^+$ fragment and a proton^[36] suggests that **2** can be alternatively viewed as a model for a frozen intermediate of the protonation of a Pt(II)-R species,^[37] a very relevant process in connection with the functionalization of hydrocarbons by Pt complexes.^[38]

In conclusion, we report herein a novel heterobimetallic complex that exhibits a peculiar bonding situation involving Pt–Au and Au–C bonds. DFT calculations have shown that both features are not independent but related, and that the model of a “conventional” dative Pt→Au bond is overly simplistic. Moreover, the structure of **2** can be regarded as a “snapshot” of a transmetalation process of an aryl group which, given the nature of the CNC ligand, cannot progress further. The use of combined metallic systems as cooperative catalysts in synthetic processes where transmetalation is one of the key steps is a field of growing interest, and complex **2** can be viewed as a structural model of some proposed intermediates in these processes. We are in the way to prepare new Pt–M complexes with other acceptor metals such as Ag(I) and Cu(I) in order to study the influence of these variations on the $[\text{Pt-R}] \rightarrow [\text{M}]$ bonding system.

Theoretical calculations will be carried out in order to gain insight into the nature of the metallic interactions and the influence of the acceptor fragments.

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1.- Experimental section.

1.1.- General procedures and materials. A literature method was followed to prepare the starting material [Pt(CNC)(dmsu)] (CNC = 2,6-diphenylpyridinate).^[1] Solvents were dried by using a MBraun SPS-800 System. Other chemicals were obtained from commercial sources and used as received. Elemental analyses were carried out by using a Perkin-Elmer 2400 CHNS/O Series II microanalyzer. IR spectra were recorded by using a Perkin-Elmer Spectrum 100 FT-IR spectrometer (attenuated total reflectance device in the range 250-4000 cm^{-1}). Mass spectra were registered by using a Microflex matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) Bruker or an Autoflex III MALDI-TOF Bruker instruments. Unless otherwise stated, ^1H , ^{13}C , ^{31}P , and ^{195}Pt NMR spectra were recorded on a Bruker AV-400 spectrometer operating at 400.132 (^1H), 100.624 (^{13}C), 161.923 (^{31}P), and 85.679 MHz (^{195}Pt), and the spectroscopic measurements were carried out at room temperature. Chemical shifts of the measured nuclei (δ , in ppm) are given with respect to the standard references: SiMe_4 (^1H and ^{13}C), 85% H_3PO_4 (^{31}P), and Na_2PtCl_6 in D_2O (^{195}Pt). Coupling constants (J) are given in Hertz. The signal attributions and coupling constant assessment was made on the basis of a multinuclear NMR analysis of each compound including monodimensional spectra, ^1H COSY, ^1H - ^{13}C HMQC, ^1H - ^{13}C HMBC and ^{13}C APT. The NMR spectral assignments for the [Pt(CNC)] fragment in complexes **1** and **2** follow the numbering shown in Scheme 1.

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

1.2.- Preparation of [Pt(CNC)(PPh₃)] (1**)** A variation of the method reported in the literature^[2] is used to prepare this complex: To a solution of [Pt(CNC)(dmsu)] (0.200 g, 0.40 mmol) in dichloromethane (20 mL) at room temperature, PPh_3 (0.125 g, 0.48 mmol) was added. After 4 hours of stirring the solution was evaporated to dryness. The yellow precipitate

which appeared was decanted, washed with methanol (5 mL) and *n*-hexane (10 mL) and finally air dried (Yield: 0.245 g, 90 %). Anal. Found: C, 61.43; H, 3.39 N 2.18. Calcd for $C_{35}H_{26}NPt$: C, 61.22; H, 3.82; N, 2.04. IR (cm^{-1}): 1597 (m, $\nu(N-C)$), 1575 (w, $\nu(N-C)$), 1563 (w, $\nu(N-C)$), 1544 (w, $\nu(N-C)$), 1099 (m, $\nu(P-C)$), 693 (s, $\nu(P-C)$), 541 (vs, $\nu(P-C)$), 507 (vs, $\nu(P-C)$). 1H NMR (CD_2Cl_2): δ = 7.84 (6H, m, *o*-Ph(PPh_3)), 7.68 (1H, t, $^3J_{H7-H6}$ = 7.9, H7), 7.48-7.36 (13H, overlapped signals: H5 and H6 in [Pt(CNC)] fragment, *m*-Ph(PPh_3), and *p*-Ph(PPh_3)), 6.90 (2H, ddd, $^3J_{H4-H5}$ = 7.6, $^3J_{H4-H3}$ = 7.4, $^4J_{H4-H2}$ = 1.0, H4), 6.83 (2H, ddd, $^3J_{H3-H4}$ = 7.4, $^3J_{H3-H2}$ = 7.4, $^4J_{H3-H5}$ = 1.4, H3), 6.23 (2H, dd, $^3J_{H2-H3}$ = 7.4, $^4J_{H2-H4}$ = 1.0, $^3J_{Pt-H2}$ = 33.6, H2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 167.0 (s, $^2J_{C-Pt}$ = 35.6, C8), 166.4 (s, $^1J_{C-Pt}$ = 754.7, C1), 151.5 (s, C9), 141.0 (s, C7), 139.2 (s, $^2J_{C-Pt}$ = 55.4, C2), 135.8 (d, $^2J_{C-P}$ = 11.5, $^3J_{C-Pt}$ = 40.8, *o*-C- PPh_3), 131.1 (s, C-*p*- PPh_3), 130.0 (s, $^3J_{C-Pt}$ = 33.0, C3), 128.7 (d, $^3J_{C-P}$ = 10.6, C-*m*- PPh_3), 124.3 (s, $^3J_{C-Pt}$ = 25.8, C5), 124.0 (s, C4), 115.4 (s, $^3J_{C-Pt}$ = 27.1, C6). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 28.5 (s, $^1J_{P-Pt}$ = 4102). ^{31}P NMR (121.5 MHz, CD_2Cl_2 , 193K): δ = 23.1 (s, $^1J_{P-Pt}$ = 4037). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ = -4316 (d, $^1J_{Pt-P}$ = 4102). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2 , 193K): δ = -4336 (d, $^1J_{Pt-P}$ = 4037). MS-MALDI+ DIT: m/z = 687 $[Pt(C_{17}H_{11}N)(C_{18}H_{15}P)+H]^+$.

1.3.- Preparation of the complex [(CNC)(PPh_3)PtAu(PPh_3)](ClO_4) (2) The synthesis was carried out under a strict argon atmosphere. To a solution of $[AuCl(PPh_3)]$ (0.076 g, 0.15 mmol) in tetrahydrofuran (20 mL) at $-40^\circ C$, $AgClO_4$ (0.032 g, 0.15 mmol) was added. After 75 minutes of stirring in the absence of light the suspension was filtered. To the collected solution, complex $[Pt(CNC)(PPh_3)]$ (0.100 g, 0.15 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 $C_{53}H_{41}AuClN_2O_4P_2Pt$: C, 51.12; H, 3.32; N, 1.12. IR (cm^{-1}): 1598 (w, $\nu(N-C)$), 1580 (vw, $\nu(N-C)$), 1563 (vw, $\nu(N-C)$), 1096 (s, $\nu(P-C)$), 1078 (s, $\nu(ClO_4^-)$), 689 (s, $\nu(P-C)$), 619 (m, $\nu(ClO_4^-)$), 536 (vs, $\nu(P-C)$), 513 (vs, $\nu(P-C)$), 498 (vs, $\nu(P-C)$). 1H NMR (CD_2Cl_2): δ = 7.92 (1H, t, $^3J_{H7-H6}$ = 8.0, H7), 7.72 (2H, dd, $^3J_{H5-H4}$ = 7.6, $^4J_{H5-H3}$ = 1.3, H5), 7.70-7.67 (6H, m, $^3J_{Ho-Hm}$ = 8.3, $^4J_{Ho-Hp}$ = 1.2, *o*-Ph of ligand PPh_3 (Pt)), 7.62 (2H, d, $^3J_{H6-H7}$ = 8.0, 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, $^3J_{Hm-Ho}$ = 8.3, $^3J_{Hm-Hp}$ = 2.7, *m*-Ph(PPh_3)(Au)), 7.26 (2H, ddd, $^3J_{H4-H5}$ = 7.6, $^3J_{H4-H3}$ = 7.6, $^4J_{H4-H2}$ = 1.0, H4), 7.21 (6H, td, $^3J_{Hm-Ho}$ = 8.3, $^3J_{Hm-Hp}$ = 2.5, *m*-Ph(PPh_3)(Pt)), 7.11-7.08 (6H, m, td, $^3J_{Ho-Hm}$ = 8.3, $^4J_{Ho-Hp}$ = 1.2, *o*-Ph(PPh_3)(Au)), 6.84 (2H, ddd, $^3J_{H3-H4}$ = $^3J_{H3-H2}$ = 7.6, $^4J_{H3-H5}$ = 1.3, H3),

6.08 (2H, dd, $^3J_{\text{H2-H3}} = 7.6$, $^4J_{\text{H2-H4}} = 1.0$, $^3J_{\text{H2-Pt}} = 25.9$ Hz, H2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 164.4$ (s, C8), 154.2 (s, C9), 146.1 (s, $^1J_{\text{C-Pt}} = 654.2$, C1), 143.0 (s, C7), 142.1 (s, C2), 136.1 (d, $^1J_{\text{C-P}} = 11.5$, $^3J_{\text{C-Pt}} = 25.4$, *o*-C-PPh₃(Pt)), 134.1 (d, $^1J_{\text{C-P}} = 13.9$, *o*-C-PPh₃(Au)), 132.8-132.4 (d, $^4J_{\text{C-P}} = 2.1$, d, $^4J_{\text{C-P}} = 1.6$, *p*-C-PPh₃(Au) and *p*-C-PPh₃(Pt)), 130.5 (s, $^3J_{\text{C-Pt}} = 33.2$, C3), 129.9 (d, overlapped signals of *m*-C-PPh₃(Au) and C5), 129.3 (d, $^1J_{\text{C-P}} = 11.1$, *m*-C-PPh₃(Pt)), 125.9 (s, $^4J_{\text{C-Pt}} = 22.9$ Hz, C4), 117.6 (d, $^4J_{\text{C-P(Pt)}} = 3.1$, C6). ^{31}P NMR (121.5 MHz, CD_2Cl_2): $\delta = 34.6$ (s, $^2J_{\text{P(Au)-Pt}} = 254$), 22.5 (s, $^1J_{\text{P-Pt}} = 3680$). ^{31}P NMR (121.5 MHz, CD_2Cl_2 , 193K): $\delta = 35.8$ (s, $^2J_{\text{P(Au)-Pt}} = 242$), 22.1 (s, $^1J_{\text{P-Pt}} = 3660$). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = -4017$ (dd, $^1J_{\text{Pt-P}} = 3680$, $^2J_{\text{Pt-P(Au)}} = 254$). $^{195}\text{Pt}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 193K): $\delta = -4060$ (dd, $^1J_{\text{Pt-P}} = 3660$, $^2J_{\text{Pt-P(Au)}} = 242$). MS-MALDI+ DCTB: $m/z = 1145$ [(C₁₇H₁₁N)(PPh₃)PtAu(C₁₈H₁₅P)]⁺.

1.4.- Figures S1 and S2: $^{31}\text{P}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of complex 2.

Figure S1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of [(CNC)(PPh₃)PtAu(PPh₃)](ClO₄) (**2**) in CD_2Cl_2 at different temperatures.

Figure S2. $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of complex $[(\text{CNC})(\text{PPh}_3)\text{PtAu}(\text{PPh}_3)](\text{ClO}_4)$ (**2**) in CD_2Cl_2 at different temperatures.

2.- X-ray structure determinations.

2.1. Experimental procedures and refinement. Crystal data and other details of the structure analyses are presented in Table S3. 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 Me₂CO. Crystals were mounted at the end of quartz fibres. The radiation used in all cases was graphite monochromated MoK α (λ = 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.^[3] The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on F^2 with SHELXL-97.^[4] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} values of their attached parent atoms. Full-matrix least-squares refinement of these models against F^2 converged to final residual indices given in Table S3. CCDC 1452239 and 1452240 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Table S1. Selected bond lengths (Å) and angles (°) for [Pt(CNC)(PPh₃)] (**1**)

Pt–N	2.0191(17)	Pt–C(12)	2.071(2)
Pt–C(1)	2.072(2)	Pt–P	2.2093(5)
N–Pt–C(12)	80.27(8)	N–Pt–C(1)	80.22(8)
C(12)–Pt–C(1)	159.89(9)	N–Pt–P	175.97(5)
C(12)–Pt–P	102.15(6)	C(1)–Pt–P	97.61(6)

Table S2. Selected bond lengths (Å) and angles (°) for [(CNC)(PPh₃)PtAu(PPh₃)](ClO₄) (**2**)

Pt–N	2.036(3)	Pt–C(13)	2.063(3)
Pt–C(7)	2.158(3)	Pt–P(1)	2.2433(9)
Pt–Au	2.7222(2)	Au–C(7)	2.225(3)
Au–P(2)	2.2422(9)		
N–Pt–C(13)	80.04(12)	N–Pt–C(7)	78.95(12)
C(13)–Pt–C(7)	156.30(14)	N–Pt–P(1)	173.92(8)
C(13)–Pt–P(1)	96.20(10)	C(7)–Pt–P(1)	105.59(9)
C(7)–Au–P(2)	153.25(8)	P(2)–Au–Pt	152.38(2)

Figure S3. View of the molecular structure of the complex [Pt(CNC)(PPh₃)] (**1**).

Table S3. Crystal data and structure refinement for complexes [Pt(CNC)(PPh₃)] (**1**) and [(CNC)(PPh₃)PtAu(PPh₃)](ClO₄) (**2**).

	1	2
Formula	C ₃₅ H ₂₆ NPPt	C ₅₃ H ₄₁ AuClNO ₄ P ₂ Pt
M_t	686.63	1245.31
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pna2_1$
$a/\text{\AA}$	13.9578(2)	16.6765(2)
$b/\text{\AA}$	9.4227(1)	13.1713(1)
$c/\text{\AA}$	20.5692(3)	20.8357(2)
$\beta/^\circ$	95.682(1)	90
$V/\text{\AA}^3$	2691.97(6)	4576.59(8)
Z	4	4
$D_c/\text{g cm}^{-3}$	1.694	1.807
T/K	100(1)	100(1)
μ/mm^{-1}	5.297	6.431
$F(000)$	1344	2408
2θ range/ $^\circ$	8.6-57.6	8.8-57.6
Collected reflections	29972	26496
Unique reflections	6494	10324
R_{int}	0.0214	0.0249
$R_1, wR_2^a (I > 2\sigma(I))$	0.0178, 0.0468	0.0191, 0.0415
R_1, wR_2^a (all data)	0.0192, 0.0474	0.0202, 0.0420
GOF (F^2) ^b	1.026	1.060
Abs. struct. par.	-	-0.006(3)

^a $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$. $wR_2 = [\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}$. ^b Goodness-of-fit = $[\sum w (F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

3.- DFT calculations.

3.1. Computational details.

Geometry optimizations without symmetry constraints were carried out with the Gaussian 09^[5] suite of programs using the BP86^[6] functional in conjunction with the D3 dispersion correction suggested by Grimme and co-workers.^[7] Platinum and gold atoms were described using the scalar-relativistic Stuttgart-Dresden SDD effective core potentials and their associated double- ζ basis sets,^[8] complemented with a set of polarization functions.^[9] The 6-31G(d) basis set was used for C, H, N and P atoms. This level is denoted BP86-D3/6-31G(d)&SDD+f(Pt, Au). Stationary points were characterized by calculating the Hessian matrix analytically to confirm that all species are minima on the potential energy surface.

Wiberg Bond Indices and donor-acceptor interactions have been computed using the natural bond orbital (NBO) method.^[10] The energies associated with these two-electron interactions have been computed according to the following equation:

$$\Delta E_{\phi\phi^*}^{(2)} = -n_{\phi} \frac{\langle \phi^* | \hat{F} | \phi \rangle^2}{\varepsilon_{\phi^*} - \varepsilon_{\phi}}$$

where $\hat{F}$ is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled Natural Bond Orbitals having ε_{ϕ} and ε_{ϕ^*} energies, respectively; n_{ϕ} stands for the occupation number of the filled orbital.

The orbital interactions in the model complex **2** have been investigated with the EDA-NOCV method,^[11] which combines the energy decomposition analysis (EDA)^[12] with the natural orbitals for chemical valence (NOCV).^[13] The EDA-NOCV method makes it possible to partition the total orbital interactions into pairwise contributions of the orbital interactions. Details of the method can be found in the literature.^[14]

The EDA-NOCV calculations were carried out using the BP86-D3/6-31G(d)&SDD+f(Pt, Au) optimized geometries with the program package ADF 2013.01^[15] using the same functional (BP86-D3) in conjunction with a triple- ζ -quality basis set using uncontracted Slater-type orbitals (STOs) augmented by two sets of polarization function with a frozen-core approximation for the core electrons.^[16] An auxiliary set of s, p, d, f, and g STOs were used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.^[17] Scalar relativistic effects were incorporated by applying the zeroth-order

regular approximation (ZORA).^[18] This level of theory is denoted BP86-D3/TZ2P+//BP86-D3/6-31G(d)&SDD+f(Pt, Au).

3.2. DFT modelling of the dynamic exchange process.

To gain more insight into the dynamic exchange process involving complex **2**, we have performed relaxed scans of this species at different C–Pt–Au angles starting from its equilibrium geometry ($\theta = 50.6^\circ$). The results obtained at the BP86-D3/6-31G(d)&SDD+f(Pt, Au) level are summarized graphically in Figure S3. According to our results, the exchange process reaches its maximum at $\theta = 90^\circ$ (the corresponding species lies 8.9 kcal/mol above the global minimum). Interestingly, the structure having $\theta = 90^\circ$ exhibits equivalent Pt–C bond distances (2.096 Å), which nicely agrees with the NMR data discussed in the main text.

Figure S4 Fully relaxed scans (BP86-D3/6-31G(d)&SDD+f(Pt, Au) level) for the dynamic process of complex **2** performed at different C–Pt–Au angles.

3.3. Cartesian coordinates and electronic energy of the DFT optimized structure of complex 2.

Cartesian coordinates (in Å) and total energy (in a. u., ZPVE included) of complex **2** (BP86-D3/6-31G(d)&SDD+f(Pt, Au) level).

2: E= -2703.291529

Pt	1.459045000	-0.948684000	-0.267104000
Au	-1.142540000	-0.285429000	-0.940651000
P	2.079237000	1.234792000	-0.169729000
P	-2.832286000	0.373059000	0.456067000
N	0.856196000	-2.914128000	-0.204510000
C	0.181511000	-3.454576000	-1.258916000
C	-0.360898000	-4.745595000	-1.140726000
H	-0.925922000	-5.180982000	-1.968757000
C	-0.177141000	-5.450344000	0.058942000
H	-0.603316000	-6.452533000	0.171675000
C	0.555706000	-4.884556000	1.110958000
H	0.717487000	-5.442532000	2.036593000
C	1.090336000	-3.590511000	0.960375000
C	0.148509000	-2.578850000	-2.447209000
C	0.392022000	-1.164883000	-2.239718000
C	0.508300000	-0.363295000	-3.407665000
H	0.686393000	0.708898000	-3.304164000
C	0.379682000	-0.905621000	-4.698529000
H	0.474847000	-0.252990000	-5.573309000
C	0.123634000	-2.274872000	-4.865790000
H	0.023975000	-2.700911000	-5.869701000
C	0.015926000	-3.110391000	-3.740878000
H	-0.127700000	-4.187564000	-3.882208000
C	1.934820000	-2.841430000	1.900848000
C	2.380746000	-1.542752000	1.465735000
C	3.279921000	-0.862018000	2.310244000
H	3.676770000	0.113449000	2.012857000
C	3.685177000	-1.399262000	3.545361000
H	4.384084000	-0.836678000	4.174840000
C	3.203382000	-2.646764000	3.974085000
H	3.515796000	-3.062390000	4.937567000
C	2.335645000	-3.370127000	3.145639000
H	1.982822000	-4.356941000	3.467103000
C	3.907607000	1.416616000	-0.152037000
C	4.659023000	0.451046000	-0.858417000
H	4.142952000	-0.384006000	-1.348114000
C	6.057179000	0.549955000	-0.908517000
H	6.635659000	-0.201366000	-1.456457000
C	6.712070000	1.600293000	-0.243004000
H	7.804609000	1.670421000	-0.273033000
C	5.967238000	2.554959000	0.469445000
H	6.477140000	3.368457000	0.996500000
C	4.566886000	2.469422000	0.513898000
H	3.994270000	3.210012000	1.081234000
C	1.522652000	2.289276000	-1.571075000
C	2.373873000	2.576285000	-2.656587000
H	3.419031000	2.249845000	-2.637285000
C	1.877126000	3.274196000	-3.771168000
H	2.543785000	3.493185000	-4.612063000
C	0.535233000	3.688931000	-3.808522000
H	0.152637000	4.228054000	-4.681768000

C	-0.311313000	3.422314000	-2.717496000
H	-1.355154000	3.754316000	-2.722730000
C	0.180468000	2.729042000	-1.603204000
H	-0.483902000	2.547423000	-0.752841000
C	1.418487000	2.140678000	1.290274000
C	0.916587000	1.437453000	2.404098000
H	0.888369000	0.346664000	2.398239000
C	0.438081000	2.136520000	3.524066000
H	0.035166000	1.573266000	4.370828000
C	0.456615000	3.540555000	3.542737000
H	0.082278000	4.084362000	4.416704000
C	0.947501000	4.248789000	2.431191000
H	0.961498000	5.344187000	2.437251000
C	1.417168000	3.555093000	1.305967000
H	1.768206000	4.114015000	0.431846000
C	-2.358751000	-0.028816000	2.184796000
C	-1.422540000	-1.062149000	2.409353000
H	-0.967995000	-1.583371000	1.559154000
C	-1.033441000	-1.391270000	3.715900000
H	-0.277294000	-2.168537000	3.871266000
C	-1.590452000	-0.702831000	4.807589000
H	-1.288014000	-0.958679000	5.828797000
C	-2.525627000	0.324758000	4.589663000
H	-2.952647000	0.868580000	5.439065000
C	-2.903316000	0.670885000	3.282894000
H	-3.601481000	1.498838000	3.116837000
C	-4.446826000	-0.423858000	0.119854000
C	-5.458142000	-0.470789000	1.102915000
H	-5.271068000	-0.076421000	2.107302000
C	-6.702193000	-1.039936000	0.796231000
H	-7.484048000	-1.080170000	1.561978000
C	-6.944494000	-1.559225000	-0.487821000
H	-7.917901000	-2.003048000	-0.722144000
C	-5.939087000	-1.515935000	-1.467415000
H	-6.124170000	-1.925570000	-2.466055000
C	-4.688970000	-0.953392000	-1.165637000
H	-3.895095000	-0.926738000	-1.922480000
C	-3.126679000	2.181094000	0.403468000
C	-2.214847000	3.047299000	1.045845000
H	-1.415091000	2.641380000	1.673125000
C	-2.335795000	4.434192000	0.879619000
H	-1.622158000	5.094919000	1.382145000
C	-3.357450000	4.963869000	0.073029000
H	-3.448301000	6.047593000	-0.056418000
C	-4.267517000	4.101818000	-0.562638000
H	-5.071492000	4.511367000	-1.183504000
C	-4.155579000	2.711654000	-0.401830000
H	-4.865827000	2.041844000	-0.899117000

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