

Heterobimetallic Complexes

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Unusual Metal–Metal Bonding in a Dinuclear Pt–Au Complex: Snapshot of a Transmetalation Process

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Abstract: The dinuclear Pt–Au complex $[(\text{CNC})(\text{PPh}_3)\text{PtAu}(\text{PPh}_3)](\text{ClO}_4)$ (**2**) ($\text{CNC} = 2,6\text{-diphenylpyridinate}$) was 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 occurrence of unusual fluxional behavior involving the $[\text{Pt}^{\text{II}}]$ and $[\text{Au}^{\text{I}}]$ metal fragments. The $[\text{Pt}^{\text{II}}] \cdots [\text{Au}^{\text{I}}]$ 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 transition metals (d^8 , d^{10} , $d^{10}s^2$) is attracting considerable attention. 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] The interest in these systems has increased lately because species containing such 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 the 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 evidence for intermediates of this kind has been provided, and the nature and properties of these intermediates remains unexplored so far. Indeed, in the context of bimetallic catalysis, Casares, Espinet et al. 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 Pt^{II} (d^8) is the donor center par excellence,^[1,4,9,14–18] whereas Ag^{I} (d^{10}) is by far the most representative acceptor.^[19,20] In contrast, very few examples of $\text{Pt}^{\text{II}} \rightarrow \text{Au}^{\text{I}}$ (d^{10}) interactions 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. Herein we report the synthesis and characterization of a rare heterobimetallic Pt–Au complex with an unusual metal–metal bonding mode and a surprising dynamic behavior in solution. Such a 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**) was prepared by replacing the dimethyl sulfoxide ligand in $[\text{Pt}(\text{CNC})(\text{dms})]^{[29]}$ with PPh_3 . The crystal structure of **1** was determined by X-ray diffraction and shows the expected square-planar coordination around the platinum center (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°C led to the formation of $[(\text{CNC})(\text{PPh}_3)\text{PtAu}(\text{PPh}_3)](\text{ClO}_4)$ (**2**), which was obtained as an orange solid after workup (see experimental details in the Supporting Information).

The crystal structure of **2** was determined by X-ray diffraction (see the Supporting Information for details). A drawing of its complex cation is shown in Figure 1 along with a selection of relevant bond distances and angles. 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 PPh_3 ligand. This distance is among the shortest reported for $\text{Pt}^{\text{II}}\text{–Au}^{\text{I}}$ bonds,^[30] and is only comparable to those of the hydride-bridged complexes $[(\text{PR}_3)(\text{C}_6\text{X}_5)(\mu\text{-H})\text{PtAu}(\text{PPh}_3)]^+$ ($\text{R} = \text{PEt}_3$, $\text{X} = \text{F}$, 2.714(1) Å;^[21] $\text{R} = \text{PPh}_3$, $\text{X} = \text{Cl}$, 2.792(1) Å).^[23] Moreover, a striking feature of **2** is the interaction between the Au center and the *ipso* carbon atom 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 distance, which is 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,

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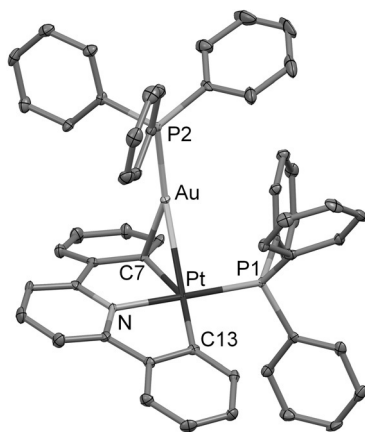


Figure 1. Molecular structure of the cation of complex **2**. Selected bond distances [Å] and angles [°]: Pt–Au 2.7222(2), Pt–C7 2.158(3), Pt–C13 2.063(3), Pt–N 2.036(3), Pt–P 2.2433(9), Au–C7 2.225(3); Pt–Au–P2 152.38(2), C7–Au–P2 153.25(8).

whereas the rest of the CNC ligand remains coplanar with the square-planar environment of the Pt center, the C7 ring deviates remarkably 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 the traditional model of square-planar $\text{Pt}^{\text{II}} \rightarrow \text{M}$ 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 is bent $152.38(2)^\circ$, with the result that the Au atom leans towards C7 (Au–Pt–C7 angle: $52.7(1)^\circ$). This kind of situation, although reported previously,^[9,15] remained unstudied until now.^[33]

The bonding situation of complex **2** was analyzed by means of density functional theory (DFT) calculations at the BP86-D3/6-31G(d)&SDD+f(Pt, Au) level by use of the methods atoms in molecules (AIM), natural bond orbital (NBO) analysis, and energy decomposition analysis (EDA-NOCV; 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 heterobimetallacycle. The

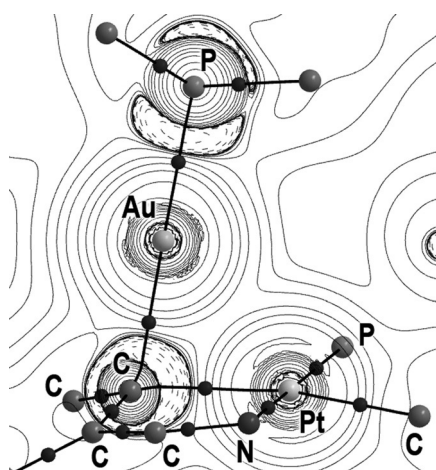


Figure 2. Contour-line diagram $\nabla^2\rho(r)$ for the cation of complex **2** in the Au–C–Pt plane (solid lines connecting nuclei: bond paths; black small spheres: bond critical points).

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. However, no bond path (or BCP) linking the Pt and Au metal centers was found in the topological analysis of the electron density. The NBO Wiberg bond indices 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 finding, a remarkable two-electron delocalization from a doubly occupied d(Pt) atomic orbital to a vacant p(Au) atomic orbital was located by applying the second-order perturbation theory (SOPT) of the NBO method (associated SOPT energy, $\Delta E^{(2)}$: -61.4 kcal mol $^{-1}$). This result indicates that the [PtCNC]→Au interaction is dative in nature.

Further quantitative information on the nature of the [PtCNC]...[Au]⁺ interaction in complex **2** could be gained by means of the EDA-NOCV method. The interaction shows prevalent ionic character, according to the contribution of the electrostatic term (ΔE_{elstat} , 52 % of the total attractive interactions; Table 1). This result is not surprising if we take

Table 1: EDA-NOCV values (kcal mol⁻¹) 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 ($\Delta E_{\text{elstat}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}}$).

into account that the [PtCNC] moiety and the positively charged [Au]⁺ cation were used as fragments in the bonding analysis. However, the covalent character is also very significant, as the orbital term (ΔE_{orb}) contributes 34% to the total attractive interactions. Furthermore, interactions due to dispersion forces (measured by the ΔE_{disp} term) are not negligible, as they contribute 14% to the total interaction energy.

The ΔE_{orb} term could 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**, in which the charge flow takes place in the direction from dark gray to light gray. 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 ($\Delta E(\rho 1) = -44.6 \text{ kcal mol}^{-1}$) 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 $[\text{Au}]^+ \rightarrow [\text{PtCNC}]$ back-donation is also found within this analysis, although this interaction is significantly lower ($\Delta E(\rho 2) = -11.4 \text{ kcal mol}^{-1}$, 13 % of ΔE_{orb}). This result supports the existence of a Pt–Au interaction, although weaker than

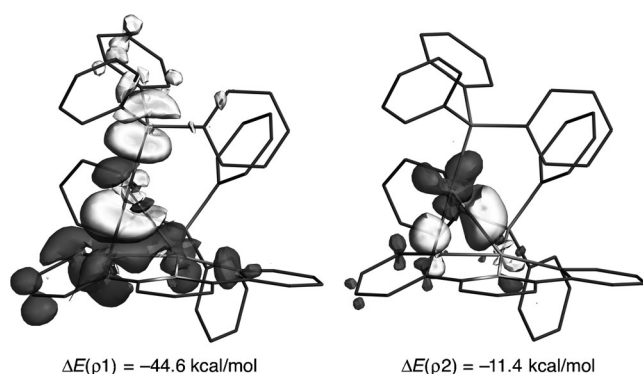


Figure 3. EDA-NOCV computed main deformation densities ($\Delta\rho$) for complex **2**. Charge flows from dark gray to light gray.

the Au–C interaction, which agrees nicely 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 readily broken and participate in rapid association–dissociation equilibria.^[34] Nevertheless, a remarkable feature of complex **2** is the persistence of the Pt–Au bond in solution. In agreement with the existence of a Pt–Au bond, the room-temperature ^{31}P NMR spectrum of **2** shows two signals corresponding to the two phosphorus atoms of the PPh_3 ligands, both of which show ^{195}Pt – ^{31}P coupling (Figure 4a). The signal corresponding to the P atom bonded

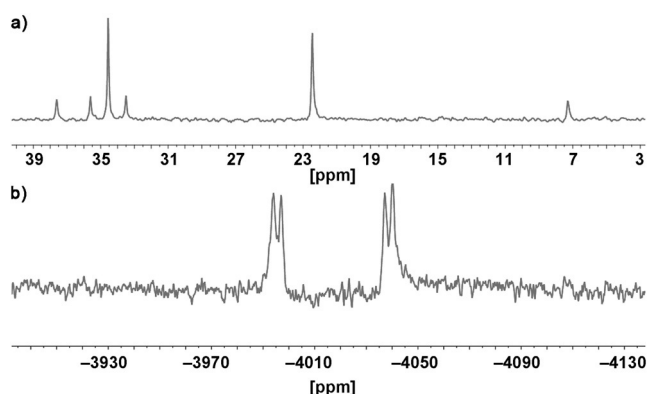


Figure 4. Room-temperature a) $^{31}\text{P}\{^1\text{H}\}$ and b) $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectra of a solution of **2** in CD_2Cl_2 .

to Pt appears as a singlet at 22.5 ppm with Pt satellites ($^1J_{\text{P-Pt}} = 3680$ Hz), whereas that 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 room-temperature ^{195}Pt NMR spectrum of **2** shows a doublet of doublets centered at -4017 ppm, with coupling constants of 3680 ($^1J_{\text{Pt-P}}$) and 254 Hz ($^2J_{\text{Pt-P}}$; Figure 4b). Thus, the presence of remote Pt–Au–P coupling, revealed by the $^2J_{\text{Pt-P}}$ constant, provides evidence for the persistence of the Pt–Au interaction in solutions of **2** in $[\text{D}_2]\text{dichloromethane}$. Moreover, 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 in electron density around the Pt center upon coordination to M^+ .^[15,16,32]

A striking feature of the NMR spectroscopic behavior of **2** in solution is that, despite the persistence of the Pt–Au bond, the phenylene rings are equivalent in both their ^1H and ^{13}C NMR spectra at room temperature. Thus, for example, only one signal corresponding to the CH_{ortho} atoms of the phenylene rings is observed, namely, a doublet at 6.07 ppm. The structure of **2** in solution therefore contrasts sharply with the solid-state structure and is proof of an unusual dynamic behavior that deserves further study. We collected a series of variable-temperature (VT) ^1H NMR spectra of **2** in solution (Figure 5). Interestingly, the 5–9 ppm region of the spectrum

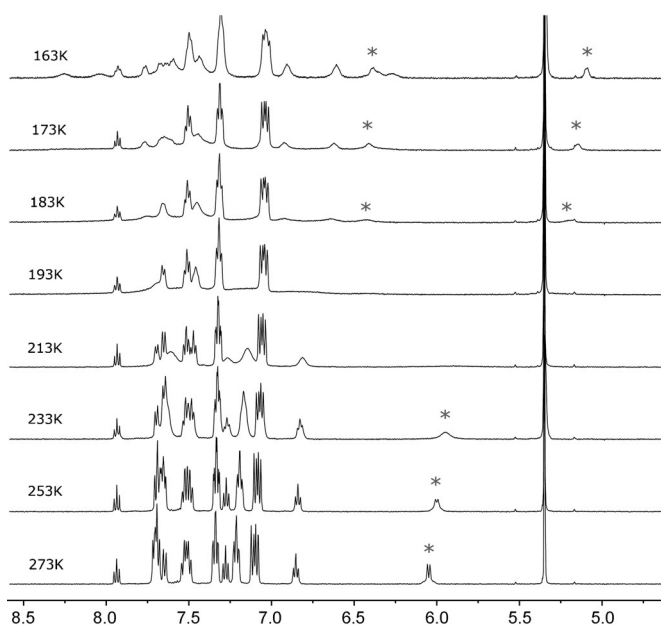
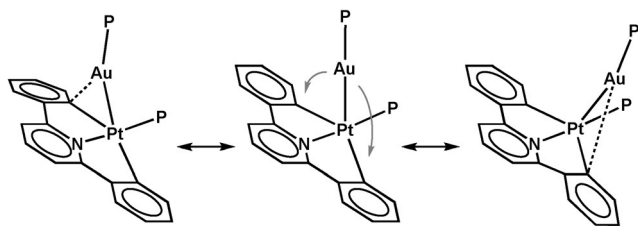


Figure 5. VT ^1H NMR spectra (recorded at 163–273 K) of a solution of **2** in CD_2Cl_2 .

at 163 K shows a more complex pattern than that recorded at room temperature, as a result of the decoalescence of several signals. Most notably, the doublet at 6.07 ppm is split into two broad peaks centered at 6.43 and 5.16 ppm. The coalescence temperature for this process is 203 K. According to the Gutowski equation, the estimation of $\Delta\delta$ and T_{coal} values (650 Hz and 203 K, respectively) affords an approximate activation free energy, $\Delta G^\ddagger$, of 8.8 kcal mol $^{-1}$ for this dynamic process, which can be described as a “metronome-like” exchange process (see Scheme 1), in which the Pt–Au bond anchors the two metallic fragments.^[35] DFT modeling of this process supported this proposal and enabled an activation barrier of 8.9 kcal mol $^{-1}$ to be estimated (see the Supporting Information).

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 that exist in the dinuclear system. The formation of



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

2 formally results from an electrophilic attack on a Pt–R bond of a Pt^{II} square-planar system, which can proceed by either attack on the metal center or on the platinum-bonded carbon atom of the R group. Thus, the well-known isolobal relationship between the [Au(PPh₃)]⁺ fragment and a proton^[36] suggests that **2** can alternatively be viewed as a model for a frozen intermediate of the protonation of a Pt^{II}–R species,^[37] a relevant process in connection with the functionalization of hydrocarbons by Pt complexes.^[38]

In conclusion, we have reported herein a novel heterobimetallic complex that exhibits a peculiar bonding situation involving Pt–Au and Au–C bonds. DFT calculations showed that these 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 the transmetalation of an aryl group, which, given the nature of the CNC ligand, can not progress further. The use of combined metallic systems as cooperative catalysts in synthetic processes in which 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 currently investigating the preparation of new Pt–M complexes with other acceptor metals, such as Ag^I and Cu^I, to study the influence of these variations on the [Pt–R]→[M] bonding system. Theoretical calculations will be carried out to gain insight into the nature of the metallic interactions and the influence of the acceptor fragments.

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Keywords: DFT calculations · donor–acceptor systems · fluxionality · heterobimetallic complexes · metal–metal bonds

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