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Transfer of the Chelating Ligands in the Systems $[LAuCl_2]^+$–$[PdCl_4]^{2-}$: Synthesis and Structure of the Salt $(NH_4)_{0.20}[(Bipy)AuCl_2]_{1.04}[(Bipy)PdCl_2]_{0.96}[AuCl_4]_{0.76}[PdCl_4]_{0.24}$

N. S. Akhmadullina[a, *], **A. V. Churakov**[b], **O. N. Shishilov**[c], **and Yu. F. Kargin**[a]

[a] *Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences,*
Leninskii pr. 49, Moscow, 119991 Russia
[b] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia*
[c] *Lomonosov State University of Fine Chemical Technologies, Moscow, Russia*
**e-mail: nakhmadullina@mail.ru*

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Abstract—The formation of binary complex salts containing gold(III) in the cation and palladium(II) in the anion in the systems $[(Bipy)AuCl_2]^+$–$[PdCl_4]^{2-}$ occurs by transfer of the N,N-electron-donating chelating ligand bipyridine and the chloride ligands between the gold-containing cation and the palladium-containing anion. The resulting neutral salt $[(Bipy)PdCl_2]$ crystallizes together with the anion $[AuCl_4]^-$ from acetonitrile–water (1 : 1–1 : 2, v/v) to give the complex salt $(NH_4^+)_{0.20}[(Bipy)AuCl_2^+]_{1.04}[(Bipy)PdCl_2]_{0.96}[AuCl_4^-]_{0.76}PdCl_4^{2-}]_{0.24}$ with a total Au : Pd ratio of 3 : 2. The ammonium cation is formed from acetonitrile upon its hydrolysis most likely catalyzed by Pd complexes. Quantum-chemical calculations were performed to study the transfer of the chelating ligand theoretically.

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INTRODUCTION

Mixed Au–Pd complexes are of interest as precursors to homo- and heterogeneous heterometallic catalysts [1]. Both these metals possess pronounced catalytic properties [2, 3], and their possible synergism in mixed systems is important in basic and applied aspects. Keeping the proper metal ratio constant (provided that metals are distributed uniformly) is a special problem. This problem has been successfully solved for palladium systems with many 3*d* [4], rare-earth [5], and even alkaline metals [6]. Attempted preparation of similar Pd–Au complexes has failed. The documented clusters Pd–Au [7] and Au–Pd [8] are accessible in low yields through a sophisticated (and nonselective) synthetic approach and hence cannot be used widely.

A facile and promising route to relatively simple Au–Pd-containing complexes and materials with a given Au : Pd ratio involves the synthesis of complex salts in which the cation comprises one metal and the anion comprises the other [9]. We employed the $[PdCl_4]^{2-}$ anion as a palladium(II) source because it can easily be prepared and is stable [10]. Gold(III) was part of the complex cation $[LAuCl_2]^+$, where L is an N,N-electron-donating chelating ligand for stabilization of relatively unstable Au(III) compounds. Since the cation is singly charged and the anion is doubly charged, the ratio of the reactants should be 2 : 1 and the same Au : Pd ratio should be expected in the reaction products. However, we found that a reaction of $K_2[PdCl_4]$ with $[(Bipy)AuCl_2]Cl$ in aqueous systems does not follow an ordinary metathesis pattern. During this reaction, the bipyridine (N,N-electron-donating) and chloride ligands are transferred between the ions $[PdCl_4]^{2-}$ and $[(Bipy)AuCl_2]^+$ to give $[(Bipy)PdCl_2]$ and $[AuCl_4]^-$, and acetonitrile undergoes hydrolysis to ammonium (NH_4^+) cations. The recrystallized product can be formulated as $(NH_4)_{0.20}[(Bipy)AuCl_2]_{1.04}[(Bipy)PdCl_2]_{0.96}[AuCl_4]_{0.76}[PdCl_4]_{0.24}$ (**I**). In complex **I**, the formal oxidation state of gold is +3 and that of palladium is +2 (Au : Pd = 3 : 2).

EXPERIMENTAL

Elemental analyses for C, H, and N were carried out on a CHNS-OEA 1108 analyzer (Carlo Erba). Analyses for gold and palladium were performed on an Optima 5200 ICP-AES spectrometer (PerkinElmer). NMR spectra were recorded on an AVANCE II spectrometer (Bruker). 2,2'-Bipyridine (Fluka), NaOH, $PdCl_2$, $HAuCl_4 \cdot 3H_2O$, and organic solvents (all reagent grade) were used as purchased. The complex salts $K_2[PdCl_4]$ and $[(Bipy)AuCl_2]Cl$ were prepared as described in [11] and [12], respectively.

Synthesis of salt I. A solution of $[(Bipy)AuCl_2]Cl$ (92 mg, 0.2 mmol) in water (10 mL) was added to a solution of K_2PdCl_4 (33 mg) in water (5 mL). The resulting mixture was stirred in the dark at room temperature for 4 h. The yellow precipitate that formed was filtered off and recrystallized from acetonitrile–water (1 : 1–1 : 2, v/v). The yield of salt **I** was 80 mg (65% with respect to gold), yellow needle-like crystals.

For $C_{20}H_{16.8}N_{4.2}Cl_8Au_{1.8}Pd_{1.2}$

anal. calcd., %: C, 22.21; H, 1.55; N, 5.44; Au, 32.77; Pd, 11.80.

Found, %: C, 21.87; H, 1.24; N, 5.28; Au, 31.23; Pd, 12.45.

X-ray diffraction study of salt I was carried out on a Bruker SMART APEX II automated diffractometer at 120 K (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω scan mode). The crystals ($C_{20}H_{16.8}N_{4.2}Cl_8Au_{1.8}Pd_{1.2}$, $M = 1081.80$) are monoclinic, space group $C2/m$, $a = 24.888(12)$, $b = 6.805(3)$, $c = 9.034(4)$ Å, $\beta = 110.943(6)°$, $V = 1428.8(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.514$ g/cm^3, $\mu(MoK_\alpha) = 10.733$ mm^{-1}, $F(000) = 999$. The intensities of 4977 reflections (1840 unique reflections, $R_{int} = 0.0509$) were measured for $1.75° < \theta < 28.00°$ ($-32 \le h \le 28$, $8 \le k \le 8$, $-11 \le l \le 11$). An absorption correction was applied by measuring the intensities of equivalent reflections [13]. The structure was solved by the direct methods and refined anisotropically for all non-hydrogen atoms by the full-matrix least-squares method on F^2 (SHELXTL [14]). All hydrogen atoms were located geometrically and refined using a riding model. The crystal was a pseudomerohedral twin with the twinning matrix 1 0 2 0 –1 0 0 0 –1 and a domain ratio of 0.72 : 0.28. The refinement revealed that the metal centers are shared by gold and palladium in both the anion and the cation. Independent refinement of the occupancies of these positions gave Au : Pd = 0.52 : 0.48 for the bipyridine complex and Au : Pd = 0.76 : 0.24 for the anion. With these occupancy ratios, the crystal has an uncompensated negative charge. The structure has a cavity with a volume appropriate to a non-hydrogen atom for which our calculations give a noticeable residual electron density peak in the crystallographic center of inversion. This peak was identified as a partially occupied ammonium cation, which serves to compensate for the excess charge. The final R factors are $R_1 = 0.0718$ for 1545 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.1909$ for all reflections. The number of parameters refined was 86, GOOF = 1.401, $\Delta\rho_{min/max} = -3.018/5.312$, e Å^3.

Structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 965721; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

An NMR experiment was carried out for a one-tenth scale model of the synthesis. The salt $[(Bipy)AuCl_2]Cl$ (9.2 mg) was dissolved in D_2O (1 mL), and a ^1H NMR spectrum of the resulting solution was recorded. ^1H NMR, δ: 8.04–8.11 (m, 2H); 8.35 (d, 1H); 8.64–8.70 (m, 4H); 9.48 (d, 1H). Then a solution of K_2PdCl_4 (3.3 mg) in D_2O (0.5 mL) was added to the NMR tube, with immediate recording of a ^1H NMR spectrum. ^1H NMR, δ: 8.10 (t, 2H); 8.63–8.72 (m, 4H); 9.47 (d, 2H).

Quantum-chemical calculations of the ligand transfer in the systems $[(Bipy)AuCl_2]^+$–$[PdCl_4]^{2-}$ and the isomerization $[(Bipy)AuCl_2]Cl$–$(Bipy)AuCl_3$. Full optimization of the geometries of all complexes in the ground state was performed using the density functional theory (DFT) approach with the hybrid exchange-correlation functional B3LYP [15–17] and the second-order Moeller–Plesset perturbation theory (MP2) with the GAMESS UK program package [18]. The calculations involved the Hay–Wadt double-zeta basis set lanl2dz [19–22] and the hybrid basis set combining the basis set lanl2dz with the effective core potential (ECP) for heavy atoms (Pd and Au) [23, 24] and the split-valence basis set 6-31G* (for neutral molecules) or 6-31G+* (for ions) for light atoms [25–27]. The geometries of all the complexes were optimized in the gas phase. The frequencies of the normal modes were calculated to check for an energy minimum on the potential energy surface.

RESULTS AND DISCUSSION

Salt metathesis is widely used to obtain binary complex salts. We studied the following metathesis reaction in aqueous systems:

$$K_2[PdCl_4] + 2[(Bipy)AuCl_2]Cl \rightarrow [(Bipy)AuCl_2]_2[PdCl_4] + 2KCl.$$

The reaction product was recrystallized from acetonitrile–water (1 : 1–1 : 2, v/v) to give bright yellow crystals. X-ray diffraction from the crystals showed that the composition and structure of the product differ substantially from the expected ones.

In structure **I**, both metal centers are shared by gold and palladium with Au : Pd = 0.52 : 0.48 (bipyridine complex) and 0.76 : 0.24 (anion). The bipyridine complex lies in the plane m, while the anion MCl_4 and the ammonium cation are at points where the axes 2 meet the same plane m (Fig. 1). Fundamentally, this disorder is possible because the geometrical parameters of the complexes $[(Bipy)AuCl_2^+]$ and $[(Bipy)PdCl_2]$, like those of the anions $AuCl_4^-$, $[PdCl_4^{2-}]$, are close (Table 1). For instance, a survey of the Cambridge Crystallographic Data Collection (version 5.32; May, 2013 [28]) shows that the average Au–Cl and Pd–Cl bond lengths in the square planar anions MCl_4 (M = Au and Pd) are 2.278

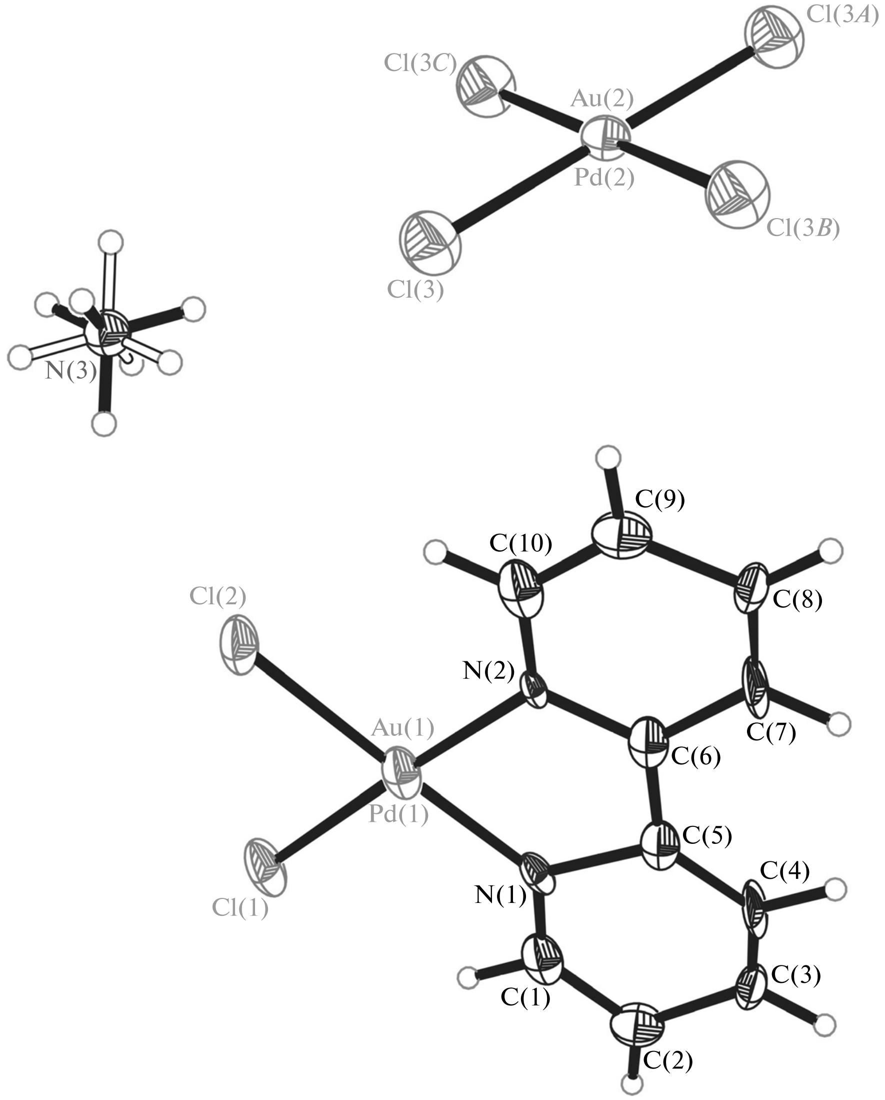


Fig. 1. Structural units in the crystal of complex **I**.

(178 entries, 749 bond lengths) and 2.278 Å (103 entries, 388 bond lengths), respectively.

Note that the Au : Pd ratio found for the metal centers may be erroneous because the crystal under discussion proved to be a pseudomerohedral twin (see Experimental); the occupancy and domain ratios (BASF) show an appreciable correlation upon the least-squares refinement.

Table 1. Selected bond lengths *d* and bond angles ω in structure **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
M(1)–N(1)	1.94(2)	M(1)–Cl(1)	2.279(6)	M(2)–Cl(3)	2.265(5)
M(1)–N(2)	1.997(16)	M(1)–Cl(2)	2.303(7)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(1)M(1)N(2)	83.6(8)	Cl(1)M(1)Cl(2)	88.1(3)	Cl(3)M(2)Cl(3)	89.2(3)
N(1)M(1)Cl(1)	93.9(6)	N(2)M(1)Cl(2)	94.3(6)	Cl(3)M(2)Cl(3)	90.8(3)
N(1)M(1)Cl(2)	177.9(6)	N(2)M(1)Cl(1)	177.6(6)	Cl(3)M(2)Cl(3)	180

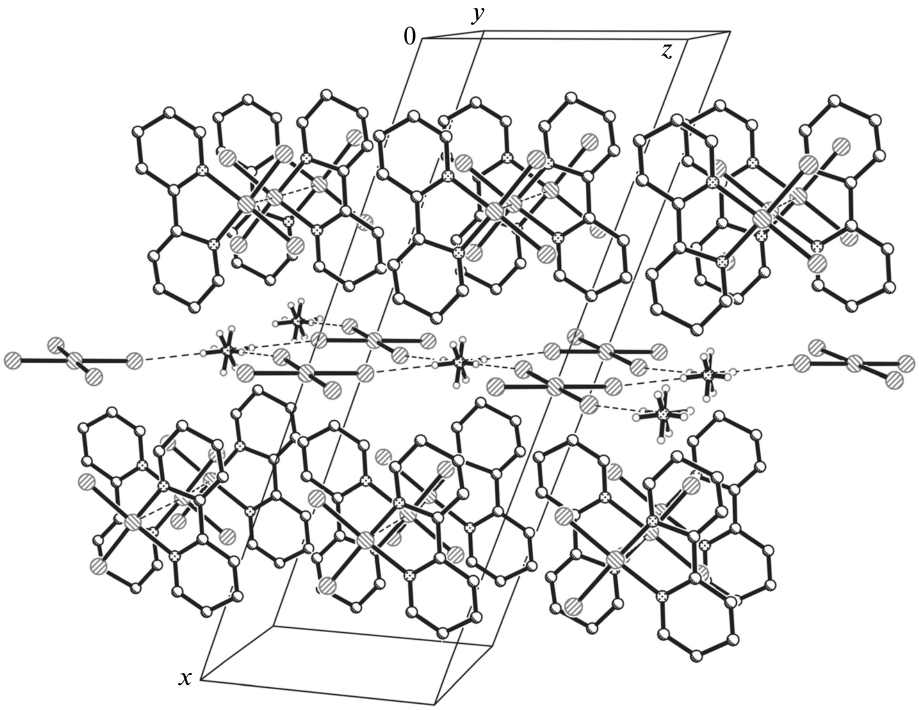


Fig. 2. Crystal packing of complex **I**.

In the crystal, the layers of the complexes $[(Bipy)MCl_2]$ alternate with the layers consisting of the anions MCl_4 and disordered ammonium cations (Fig. 2). The length of the hydrogen bond N···Cl is 3.442(5) Å. Interestingly, the bipyridine layers are stacked in such a way that the planes of adjacent complexes are strictly parallel, with an interplanar spacing of 3.302(2) Å. The stacks show intermolecular M···M interactions characteristic of square planar gold and palladium complexes (M···M, 3.427 Å).

The absence of potassium from salt **I** and the ratio Au : Pd = 3 : 2 were confirmed by data from inductively coupled plasma atomic emission spectroscopy. Therefore, this formally simple metathesis reaction is accompanied by ligand transfer between the complex ions, including the transfer of the N,N-electron-donating chelating ligand bipyridine, which is transferred from the Au atom to the Pd atom. Earlier, we have already observed the transfer of phenanthroline in gold complexes according to the scheme [29]:

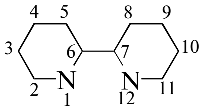
$$2[(Phen)AuCl_2]Cl \rightarrow [(Phen)AuCl_2][AuCl_4].$$

Quantum-chemical calculations showed that this pathway is thermodynamically allowed and most favorable in the systems $[(Phen)AuCl_2]^+$–Cl^-–RCO_2^- under consideration ($R = CF_3$, CH_3, and CMe_3). Here we carried out a further theoretical study of the transfer of chelating ligands between the complex anions of gold and palladium.

First we calculated the geometries of the complex cation $[(Bipy)AuCl_2]^+$ and the neutral molecule $(Bipy)PdCl_2$ using different methods. This was done to choose the most suitable method for subsequent estimation of their thermodynamic parameters. The methods included the Hartree–Fock, DFT, and MP2 approaches with the Hay–Wadt double-zeta basis set lanl2dz and the hybrid basis set combining the basis set lanl2dz/ECP for heavy atoms (Pd and Au) and the split-valence basis set 6-31G* (for neutral molecules) and 6-31G+* (for ions) for light atoms. The results obtained are given in Table 2.

First of all, it should be noted that the geometry of the bipyridine ligand in the crystal structure is strongly distorted, which cannot be simulated by none of the methods used in the calculations for the gas phase. All the methods overestimate most C–C bond lengths in the bipyridine molecule and most metal–ligand distances. The C(4)–C(5) and especially C(8)–C(9) bond lengths are highly overestimated. However, these bonds in the crystal structure under discussion are substantially shorter than those in other metal complexes with bipyridine. Therefore, this overestimation can be attributed to the packing effect. In contrast, the C(3)–C(4), C(5)–C(6), C(9)–C(10), and C(12)–C(7) bond lengths are underestimated. The best fit to the geometries of the complexes is provided by the Hartree–Fock and B3LYP/lanl2dz approximations. The Hartree–Fock method is slightly superior in describing the coordination environment of the metal atom in the complex gold cation, while the DFT approach

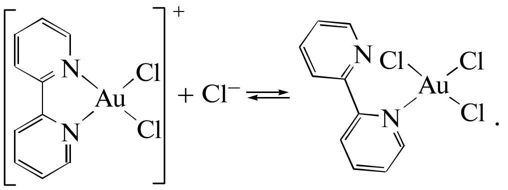
Table 2. X-ray diffraction data and the results of quantum-chemical calculations for the cation $[(Bipy)AuCl_2]^+$ and the neutral molecule $(Bipy)PdCl_2$

Bond length	X-ray diffraction	$[(Bipy)AuCl_2]^+$					$(Bipy)PdCl_2$		
		HF/lanl2dz	B3LYP/lanl2dz	MP2/lanl2dz	B3LYP/hybrid	MP2/hybrid	HF/lanl2dz	B3LYP/lanl2dz	MP2/lanl2dz
1–2	1.324	1.341	1.356	1.377	1.35	1.367	1.337	1.356	1.375
2–3	1.326	1.391	1.403	1.418	1.396	1.406	1.394	1.404	1.42
3–4	1.417	1.388	1.405	1.424	1.397	1.411	1.388	1.406	1.424
4–5	1.294	1.4	1.407	1.421	1.4	1.409	1.396	1.404	1.42
5–6	1.424	1.382	1.403	1.423	1.397	1.412	1.389	1.407	1.424
6–1	1.335	1.361	1.377	1.394	1.372	1.385	1.351	1.374	1.391
6–7	1.444	1.482	1.478	1.493	1.472	1.48	1.486	1.478	1.494
7–8	1.309	1.382	1.403	1.423	1.397	1.412	1.389	1.407	1.424
8–9	1.174	1.4	1.407	1.421	1.4	1.409	1.396	1.405	1.42
9–10	1.496	1.388	1.405	1.424	1.397	1.411	1.389	1.406	1.424
10–11	1.369	1.391	1.403	1.418	1.396	1.406	1.394	1.404	1.42
11–12	1.287	1.341	1.356	1.377	1.35	1.367	1.337	1.356	1.375
12-7	1.480	1.361	1.377	1.394	1.372	1.385	1.351	1.374	1.391
M–N(1)	1.935	2.068	2.088	2.105	2.091	2.097	2.116	2.07	2.087
M–N(2)	1.997	2.068	2.088	2.105	2.091	2.097	2.116	2.07	2.087
M–Cl(1)	2.279	2.349	2.381	2.388	2.378	2.392	2.385	2.372	2.353
M–Cl(2)	2.303	2.349	2.381	2.388	2.378	2.392	2.385	2.372	2.353

(B3LYP/lanl2dz) provides much better results for the neutral palladium complex. For this reason, we used the latter method in subsequent calculations.

It was somewhat surprising that the calculations at the MP2 level for both the ligand Bipy and the coordination environment of gold and palladium describe their geometries less accurately. Earlier, the opposite effect has been noted for osmium complexes [30]. In addition, less accurate results were also obtained with the hybrid basis set for both the palladium and gold complexes, although the basis set 6-31G* for light atoms is augmented (for gold complexes) with a diffuse function usually improving the description of charged species like the cation $[(Bipy)AuCl_2]^+$.

In the next step, we calculated the isomers of the complex $(Bipy)AuCl_3$. This complex is traditionally thought of as the cation–anion compound $[(Bipy)AuCl_2]Cl$, which is confirmed by easy replacement of one chloride ion in metathesis reactions (e.g., with $NaBF_4$ [31]). At the same time, complexes with 6,6'-disubstituted bipyridines and 2,9-disubstituted 1,10-phenanthrolines are known to exist as neutral compounds in which the chelating ligand is coordinated only through one N atom, while the second electron-donating atom is linked with the Au atom only by a weak intramolecular interaction [32]. We assumed that the complex with unsubstituted bipyridine can exist, at least in solution, in a similar form:



The calculated the Gibbs energy change in the above reaction at 298.150 K by the DFT method (B3LYP) and at the MP2 level using the double-zeta basis set lanl2dz and the aforementioned hybrid basis set. The results obtained are given in Table 3. Since all the calculations give a high (in absolute value) negative ΔG, the equilibrium of this reaction is shifted toward the formation of the complex with three coordinated Cl atoms. This was taken into account when calculating the thermodynamic parameters of the bipyridine transfer (Table 4). The calculations were performed in the context of DFT (B3LYP/lanl2dz) and the perturbation theory (MP2/lanl2dz). Note that calculations with the hybrid basis set fail to optimize the geometry

Table 3. Gibbs energy changes calculated for the reaction $[(Bipy)AuCl_2]^+ + Cl^- \rightarrow (Bipy)AuCl_3$

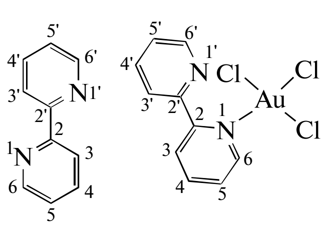
Method	$[(Bipy)AuCl_2]^+ + Cl^- \rightarrow (Bipy)AuCl_3$			ΔG, kcal/mol
	Gibbs energy G, au			
B3LYP/lanl2dz	−660.356338	−5.013656	−675.546648	−110.85
MP2/lanl2dz	−656.962397	−14.793424	−671.933816	−111.692
B3LYP/hybrid	−1550.78678	−460.28975	−2011.21355	−85.9832
MP2/hybrid	−1546.50757	−459.68617	−2006.2483	−34.2383

Table 4. Gibbs energy changes calculated for the reaction $[(Bipy)AuCl_2]^+ + Cl^- \rightarrow (Bipy)AuCl_3$

Method	$(Bipy)AuCl_3 + [PdCl_4]^{2-} \rightarrow (Bipy)PdCl_2 + [AuCl_4]^- + Cl^-$					ΔG, kcal/mol
	Gibbs energy G, au					
B3LYP/lanl2dz	−675.546648	−186.775361	−651.94235	−195.475999	−15.013656	−69.0231
MP2/lanl2dz	−671.933816	−185.161687	−648.61652	−193.783233	−14.793424	−61.2886

of the complex $(Bipy)PdCl_2$ and always give from three to six imaginary frequencies (depending on the basis set used for light atoms) for the complex anion $[PdCl_4]^{2-}$; we tried all possible combinations for the basis sets 6-31 and 6-311 with one and two diffuse and polarization functions.

Our calculations demonstrated that this transfer is feasible and thermodynamically allowed. This process is kinetically facilitated by the ligand Bipy changing its coordination from bidentate to monodentate in the starting gold complex. Our assumptions about the mechanism of this transfer were confirmed by data from NMR spectroscopy. The spectrum of the starting gold complex $[(Bipy)AuCl_2]Cl$ in D_2O shows a set of four signals with a ratio of 1 : 4 : 2 : 1 in the range characteristic of aromatic signals. The assignment of the signals for the ligand Bipy in the ^1H NMR spectrum is shown below:



Protons	Bipy	$(Bipy)AuCl_3$
3,3'; 4,4'	8.05	8.64–8.70
5,5'	7.54	8.04–8.10
6,6'	8.56	9.48(6), 8.35(6)'

We assigned the signals by analyzing the NMR spectra of bipyridine and its metal complexes in aqueous solutions [33]. The spectrum of bipyridine in water, in contrast to its solutions in organic solvents, is known to consist of three rather than four signals because the signals for the C(3,3')H and C(4,4')H protons overlap to give a multiplet at δ 8.05; the signal for the C(5,5')H protons is shifted upfield (δ 7.54) and that for the C(6,6')H protons is shifted downfield (δ 8.56). The spectrum of the complex $[(Bipy)AuCl_2]Cl$ shows a signal at δ 8.64–8.70 (C(3,3')H and C(4,4')H), a signal at δ 8.04–8.10 (C(5,5')H), and two signals at δ 9.48 and 8.35 (C(6,6')H). The splitting of the latter signal into two can be explained by the fact that the formally cation–anion complex $[(Bipy)AuCl_2]Cl$ can actually exist as $[(Bipy)AuCl_3]$ (see Scheme above). In this case, one of the C(6,6')H protons is in the coordinated pyridine moiety, while the other is in the formally uncoordinated one. Addition of a solution of K_2PdCl_4 results in immediate precipitation. The signals in the ^1H NMR spectrum become much less intense and fewer: the spectrum consists of three signals with a ratio of 2 : 4 : 2, which is typical of symmetric metal complexes with bipyridine of the type $(Bipy)ML_2$. Apparently, these changes are due to the reaction

$$2(Bipy)AuCl_3 + [PdCl_4]^{2-}$$
$$= (Bipy)PdCl_2 + [AuCl_4]^- + [(Bipy)AuCl_2]^+ + 2Cl^-.$$

Presumably, it is the precipitate of the cation–anion complex $[(Bipy)AuCl_2]^+\{[AuCl_4]^-\}_x\{[PdCl_4]^{2-}\}_{0.5-0.5x}$ that forms first, while the solution mainly contains $(Bipy)PdCl_2$ (so its signals appear in the spectrum). Then the cations $[(Bipy)AuCl_2]^+$ are partly replaced by isostructural $(Bipy)PdCl_2$ molecules. The K^+ cations that compensate for the positive charge are in turn replaced by ammonium cations upon recrystallization from acetonitrile–water. The ammonium cations are formed by hydrolysis of acetonitrile:

$$CH_3CN + H_2O \rightarrow CH_3COO^-NH_4^+.$$

It is known that palladium complexes present in the system studied can promote hydrolytic transformations of nitriles [34].

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