Scientia Iranica C (2016) 23(3), 1089–1094

SCIENTIA
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Sharif University of Technology
Scientia Iranica
Transactions C: Chemistry and Chemical Engineering
www.scientiairanica.com

Synthesis of a new T-shaped heterobinuclear Pt^0-Au^I complex $[(t\text{-}Bu_3P)_2PtAu(PPh_3)]BF_4$ from trinuclear gold cluster complex $[(PPh_3)Au]_3(\mu\text{-}O)BF_4$

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Received 28 July 2015; received in revised form 7 November 2015; accepted 16 January 2016

KEYWORDS
Synthesis;
Metal;
Complex;
Platinum;
Gold;
Cluster;
Binuclear.

Abstract. The heterobinuclear platinum(0)-gold(I) complex $[(t\text{-}Bu_3P)_2PtAu(PPh_3)]BF_4$, **5**, was synthesized by the reaction of trinuclear cluster complex $\{[(PPh_3)Au]_3(\mu\text{-}O)\}BF_4$, **4**, with one equiv of $[(t\text{-}Bu_3P)_2Pt]$ at room temperature. The heterobinuclear complex **5** was characterized using multinuclear NMR spectroscopy and elemental micro-analysis and was further identified by single crystal X-ray structure determination. Crystal structure of **5** shows a T-shaped geometry with an unsupported short distance Pt-Au dative bond.

1. Introduction

Metal-metal bonding occupies a prominent position in inorganic chemistry and the study of compounds containing the metal-metal interactions has been the subject of significant interest because of their potential applications in many fields, such as material chemistry [1] and the optoelectronic devices [2]. It is now well recognized that metal centers in some complexes or fragments can act as a nucleophile or Lewis base [3]. These Lewis bases can donate electrons to other metal complexes or fragments with the appropriate empty orbitals and form metal-metal dative bonds. Metal-metal dative bonds play an important role in the synthesis of the multinuclear metal complexes. The multinuclear metal complexes constructed via these bonding interactions display fascinating and unique chemical and physical properties that were not observed for their monomeric components [4]. The electron-rich platinum complexes can expand opportunities for the formation of metal-metal dative bonds. Examples of the use of the platinum(II) complexes in the synthesis of the cluster complexes containing Pt-M dative bonds have been reported in the literature. Cyclometalating platinum(II) complexes have also been successfully used as building blocks for the design of the heteropolynuclear complexes [Pt(II)-M(I); M = Ag, Au, Cu and Tl] [5]. The formation of these donor-acceptor Pt-M bonds has been shown to cause a significant change in the absorption and emission properties of the heteropolynuclear product complexes in comparison with those observed in the starting cyclometalated complexes. However, the research carried out in this area has mainly been focused on the platinum(II) complexes and only limited attention has been given to synthesis of the multinuclear complexes containing platinum(0) as Lewis base. For example, a series of 16e- platinum(0) complexes with general formula $[PtL_3Tl]X$ ($L = PPh_3$, PPh_2Py;

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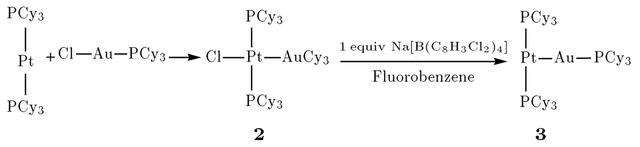


Scheme 1. Reaction of the gold complex AuCl(PCy_3) with [Pt(PCy_3)$_2$].

X = NO_3, AcO) have been prepared from mono or binuclear platinum(0) precursor complexes containing bridging ligands and $TlPF_6$ [6]. Also, we have recently reported the preparation of a tetranuclear linear cluster complex, [(t-Bu_3P)$_2$PtTl$_2$Pt(t-Bu_3P)$_2$](PF_6)$_2$, **1**, from reaction of the platinum(0) complex [Pt(t-Bu_3P)$_2$] with 1 equiv TlPF6 that shows an intense red emission originated from a platinum to thallium-thallium charge transfer state [7]. The cluster complex **1** has an asymmetric unit comprised of half of the cluster cation containing a very short Pt-Tl dative bond and a hexafluorophosphate counterion. Two asymmetric units [(t-Bu)$_3$P)$_2$PtTl] are linked together by one strong Tl^I-Tl^I thallous interaction. However, oxidative-addition of the Au-Cl bond in the gold complex AuCl(PCy_3) [Cy = cyclohexyl] to [Pt(PCy_3)$_2$] gives the corresponding platinum(II) complex trans-[Cl(Cy_3P)$_2$PtAu(PCy_3)], **2**, as shown in Scheme 1. The abstraction of the halide from **2** by addition one equivalent of Na[B($C_8H_3Cl_2$)$_4$] in a polar solvent, like fluorobenzene, yields the T-shaped complex [(Cy_3P)$_2$PtAu(PCy_3)][B($C_8H_3Cl_2$)$_4$], **3** [8].

These examples show that platinum(0) complexes can act as the basic center and are also able to form interesting Pt-M dative bonds. Continuing our interest in the synthesis of the bi and multiheteronuclear complexes, herein, we describe the preparation and crystal structure analysis of the new T-shaped heterobinuclear Pt^0-Au^I complex [(t-Bu_3P)$_2$Pt-Au(PPh_3)]BF_4, **5**, directly from reaction of the trinuclear cluster {[(PPh_3)Au]$_3$(μ-O)}BF_4, **4**, with the two-coordinated platinum(0) complex [(t-Bu_3P)$_2$Pt]. The heterobinuclear complex **5** shows an unsupported short Pt^0-Au^I dative bond.

2. Results and discussions

As summarized in Scheme 2, the reaction of the trinuclear cluster complex {[(PPh_3)Au]$_3$(μ-O)}BF_4, **4**, with 1 equiv of [(t-Bu_3P)$_2$Pt] at room temperature in acetone, gave the heterobinuclear complex [(t-Bu_3P)$_2$PtAu(PPh_3)]BF_4, **5**, in good yield by replacement of the bridging oxo ligand with the platinum(0) center. Complex **5** is a yellow solid that is stable in acetone solutions for several hours and fully characterized by multinuclear NMR spectroscopy and elemental microanalysis, which will be described in the Experimental Section.

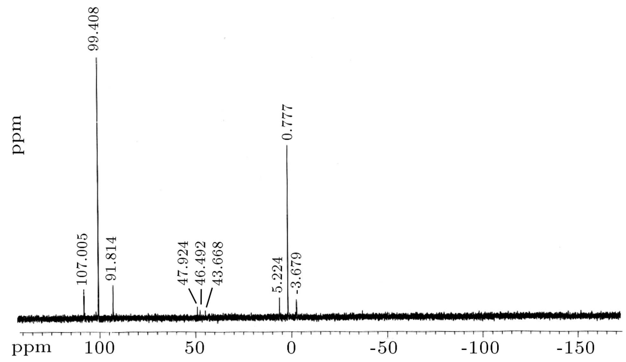
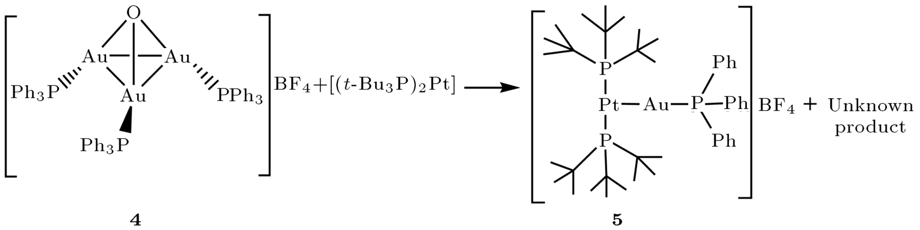


Figure 1. ^{31}P NMR spectrum (202 MHz) of **5** in $CDCl_3$.

The ^{31}P NMR spectrum of complex **5** (Figure 1) shows two singlet resonances at $\delta = 99.5$ and 0.7 ppm with coupling constants $J_{PtP} = 3079$ and 1781 Hz, respectively. The observed singlet resonance at $\delta = 99.5$ ppm with larger coupling constant ($^1J_{PtP} = 3079$ Hz) was assigned to the P atom of the tri-tert-butylphosphine ligand connected to the Pt center and the signal observed at $\delta = 0.7$ ppm with smaller coupling constant ($^1J_{PtP} = 1781$ Hz) was assigned to the P atom of the triphenylphosphine ligand connected to Au center. Consistently, the ^{195}Pt NMR spectrum of complex **5** (Figure 2) showed a triplet of doublets signal at $\delta = -3169$ ppm. The platinum signal appeared as a triplet due to coupling with two phosphorus atoms of the tri-tert-butylphosphine ligands that further splitted to a doublet with the phosphorous atom of the triphenylphosphine ligand. Finally, ^1H NMR spectrum of **5** shows two sets of signals around δ 7.5 and 1.6 ppm with relative intensity 1:3.6 due to protons of the phenyl and tert-butyl groups, respectively.

Yellow crystals of the complex **5** were obtained by the slow diffusion of ether into an acetone solution of **5** in a refrigerator for several days. The heterobinuclear Pt-Au complex **5** crystallizes in the



Scheme 2. Reaction of the cluster complex [(PPh_3) Au]$_3$(μ-O)BF4, 4, with [($^tBu_3P$)$_2$PT].

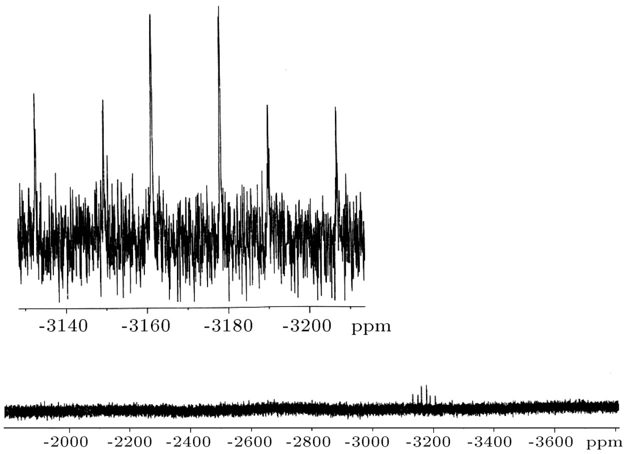


Figure 2. ^{195}Pt NMR spectrum (107 MHz) of **5** in $CDCl_3$.

monoclinic system, in the space group *P*21/*c*. The asymmetric unit of complex **5** comprises two binuclear cation complexes containing two Pt-Au dative bonds and two tetrafluoroborate anions as counterion. A view of the molecular structure of **5** is depicted in Figure 3, and the selected bond lengths and angles are listed in Table 1. Indeed, the Pt-Au distance of 2.54 Å is shorter than the sum of the covalent radii of the two elements (2.72 Å), indicating a strong Pt-Au dative bond. This distance is shorter than those found in previously reported non T-shaped platinum(0)-gold(I) complexes [9] and in the reported range for T-shaped platinum(0)-gold(I) complex **3** (2.569 Å) [8]. The $[(t\text{-Bu})_3P)_2PtAu]$ unit displays a slightly distorted T-shaped geometry around the Pt atom (P-Pt-P angle 172.5°) with the Au-Pt vector roughly perpendicular to the P-Pt-P axis (tilted by 3° with respect to the normal line of the P-Pt-P axis). The $[PtAu(PPh_3)]$ unit displays a slightly distorted linear geometry around the Au center (P-Au-Pt angle 172°) and the Au-P distance is 2.25 Å.

Table 1. Selected bond lengths (Å) and angles (deg) for complex **5**.

Au2 P21	2.2522(7)	P11 Au1 Pt1	172.201(19)
Au2 Pt2	2.53988(16)	P12 Pt1 P13	172.51(3)
Pt2 P22	2.3169(7)	P12 Pt1 Au1	92.808(18)
Pt2 P23	2.3214(7)	P13 Pt1 Au1	94.550(19)
Au1 P11	2.2546(7)	P21 Au2 Pt2	172.877(19)
Au1 Pt1	2.5433(17)	P22 Pt2 P23	172.64(3)
Pt1 P12	2.3195(7)	P22 Pt2 Au2	92.950(19)
Pt1 P13	2.3200(7)	P23 Pt2 Au2	93.987(19)

The crystal packing of **5** (Figure 4) shows that the molecules are stacked in an extended structure through hydrogen bondings between fluorine atom of the BF_4 counterions and the aromatic hydrogen atoms of the phenyl groups. Electron Spray Ionization Mass spectrometry (ESI-Mass) analysis of **5** was performed using methanol as the carrier and CH_2Cl_2 as solvent

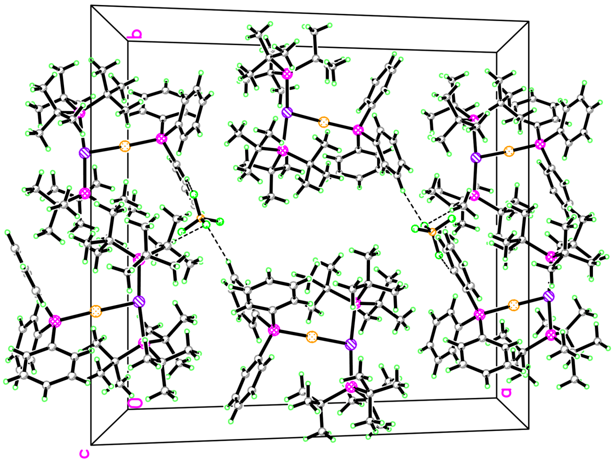


Figure 4. Packing diagram of **5** showing H-bonding interactions between F and hydrogen atoms of aromatic groups.

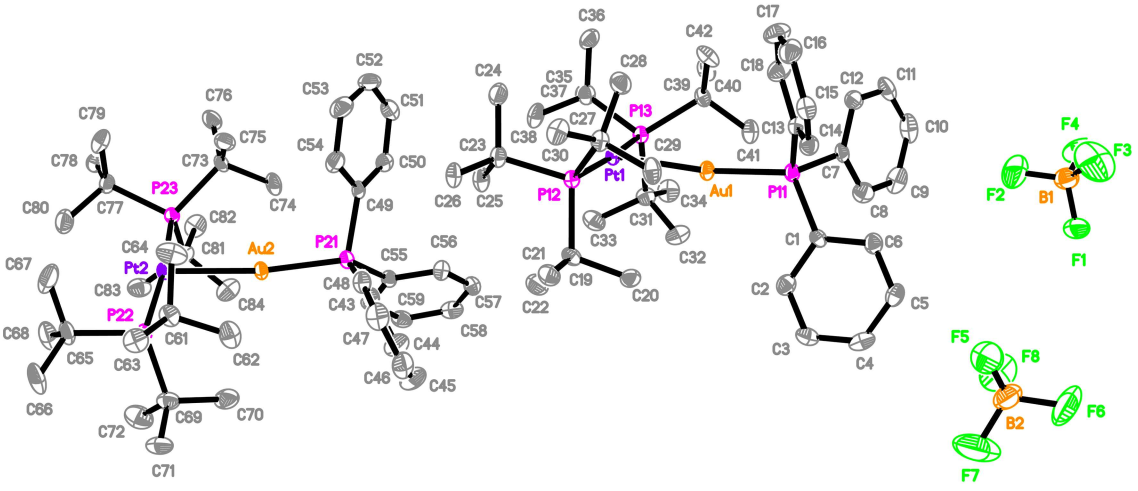


Figure 3. ORTEP plot of **5**; hydrogen atoms are omitted for clarity.

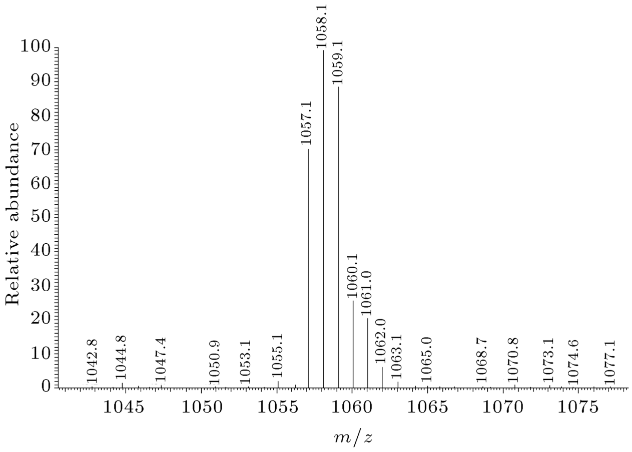


Figure 5. Positive ion mode ESI-mass spectrum of **5**.

(Figure 5). Analysis in positive-ion mode revealed an intense signal at m/z 1058 due to $[(t\text{-Bu}_3\text{P})_2\text{Pt-Au(PPh}_3)]^+$, indicating that **5** is stable in the gas phase. Simulated mass spectrum shows a similar pattern with experimental data.

3. Experimental

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance DRX 500-MHz spectrometer. The operating frequencies and references, respectively, are shown in parentheses as follows: ^{1}H (500 MHz, tetramethylsilane, SiMe_4), ^{31}P (202 MHz, 85% H_3PO_4), and ^{195}Pt (107 MHz, aqueous Na_2PtCl_4). The chemical shifts and coupling constants are in parts per million and hertz, respectively. Electrospray ion mass spectra (ESI-MS) were recorded using a Hewlett-Packard Series 1100 spectrometer or recorded using a HP-5989B spectrometer using methanol-water as the mobile phase. $[(t\text{-Bu}_3\text{P})_2\text{Pt}]$, PPh_3, and NaBF_4 were purchased from commercial sources, and $\text{AuCl(SMe}_2)$ and $\text{AuCl(PPh}_3)$ were prepared as described previously [10,11]. Crystal data and refinement parameters for **5** are given in Table 2.

3.1. $\{[(\text{PPh}_3)\text{Au}]_3(\mu\text{-O})\}\text{BF}_4$, 4

The trinuclear complex **4** was prepared by literature method [12] and same as the following procedures.

Table 2. Crystal data and structure refinement parameters of complex **5**.

Empirical formula	C42 H69 Au B F4 P3 Pt
Formula weight	1145.75
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	$a = 23.6319(4)$ Å
	$b = 21.6862(3)$ Å $\beta = 108.490(2)^\circ$
	$c = 18.4307(3)$ Å
Volume	8957.9(2) Å^3
Z	8
Density (calculated)	1.699 mg/m^3
Absorption coefficient	6.543 mm^{-1}
F(000)	4512
Crystal size	$0.09 \times 0.11 \times 0.15$ mm^3
θ range for data collection	4.18 to 30.00°
Index ranges	$-30 <= h <= 33$,
	$-30 <= k <= 28$,
	$-25 <= l <= 25$
Reflections collected	68246
Independent reflections	25961[R(int) = 0.0321]
Completeness to $\theta = 30.00^\circ$	99.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	25961/0/973
Goodness-of-fit on F^2	0.777
Final R indices [I>2 sigma(I)]	R1 = 0.0226, wR2 = 0.0332
R indices (all data)	R1 = 0.0461, wR2 = 0.0345
Largest diff. peak and hole	1.134 and -0.744 e.Å^{-3}

A solution of $AgBF_4$ (33.6 mg, 0.173 mmol) in methanol (1 mL) was added to $AuCl(PPh_3)$ (83.5 mg, 0.l69 mmol). The resulting AgCl precipitate was filtered off. A solution of KOH (10.8 mg, 0.299 mmol) and $NaBF_4$ (84.0 mg, 0.765 mmol) in methanol (20 mL) was added to the filtrate. After 1 h of stirring, the solvent was removed in vacuo. The resulting residue was extracted with CH_2C1_2 (3×20 mL). The combined CH_2C1_2 extracts were filtered, and ether (large excess) was added to precipitate the white product. ^{31}P NMR (202 MHz in $CDCl_3$), δ ppm 26 (s).

3.2. $[(t\text{-}Bu_3P)_2PtAu(PPh_3)]BF_4$, 5

To a solution of complex **4** (100 mg, 0.067 mmol) in acetone (20 mL) at room temperature under an argon atmosphere was added 1 equiv of $[(t\text{-}Bu_3P)_2Pt]$ (40 mg, 0.067 mmol). The mixture was stirred at this condition for 1.5 h in the dark, and then, the solvent was removed under reduced pressure. The residue was washed with ether (2×3 mL), and the product was dried under vacuum.

Yield: 70%. NMR data in $CDCl_3$: ^1H, δ (ppm) 7.5-8 (protons of the phenyl rings, 15 H), 1.6 (protons of the tert-butyl groups, 54 H); ^{31}P, δ (ppm) 99.5 (s, P connected to Pt center, $^1J_{PtP} = 3079$ Hz), 0.7 (s, P connected to Au center, $^1J_{PtP} = 1781$ Hz); ^{195}Pt, δ (ppm) -3169 (d of t). Anal. Calcd for $C_{42}H_{69}AuBF_4P_3Pt$: C, 44; H, 6. Found: C, 44.2; H, 6.4.

3.3. Crystal structure determinations

X-ray intensity data was collected on the Oxford Diffraction Xcalibur CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at a temperature of 150(2) K. The data reduction, including the analytical numerical absorption correction [13a], was performed using the *CrysAlis* software package [13b]. The structures were solved by direct methods (*SHELXS97*) and refined by full-matrix least squares (*SHELXL97*) on F^2 [14]. The non-H atoms were refined anisotropically. All of the H atoms were positioned geometrically and refined with the riding model approximation, with $U_{\text{iso}}(H)=1.2$ or $1.5U_{\text{eq}}(C)$. All calculations were carried out using *PLATON* [15]. For molecular graphics, the program *SHELXTL* was used [14]. The X-ray structural data was deposited at the Cambridge Crystallographic Data Centre and the corresponding CCDC number is 1435233.

Acknowledgment

We thank the Iran National Science Foundation (Grant No. 93016839), Sharif University of Technology Research Council (Grant No. G930615), for financial support. We thank the Ministry of Science, Education, and Sports of the Republic of Croatia and Prof. D. Matković-Ćalogovic for the X-ray diffraction facility.

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Biographies

Sirous Jamali is an Assistant Professor in Chemistry Department at Sharif University of Technology. He obtained his PhD degree from Chemistry Department of Shiraz University, in 2002, in the group of Prof. M. Rashidi. His current research interests focus on synthesis and characterization of new inorganic and organometallic compound and study of chemical and optical properties of them.

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Dalibor Milić is a postdoctoral researcher in the Biomolecular Research Lab of Biology and Chemistry Department, Paul Scherrer Institut. He received his PhD degree in Biomolecule Crystallography under the supervision of Prof. D. Matković-Čalogović in the Department of Chemistry, Division of General and Inorganic Chemistry, Zagreb, Croatia. His research focuses on structure and conformational dynamics of G protein-coupled receptors.