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# Au(III) and Pt(II) Complexes of a Novel and Versatile 1,4-Disubstituted 1,2,3-Triazole-Based Ligand Possessing Diverse Secondary and Tertiary Coordinating Groups

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S Supporting Information

ABSTRACT: A novel 1.4-disubstituted 1.2.3-triazole-based ligand, 2-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)propane-1,3diamine (ptpd), which possesses pyridyl and diamino secondary and tertiary coordinating groups was synthesized in excellent yield. The reactivity of 2-(1-phenyl-1H-1,2,3triazol-4-yl)pyridine (ptp), di-tert-butyl (2-azidopropane-1,3diyl)dicarbamate (Boc<sub>2</sub>-ptpd), and ptpd·3HCl was investigated with Au(III) and Pt(II) precursors. Analysis including X-ray crystal structures of [Au(III)Cl<sub>3</sub>(ptp)] (1), [Au(III)Cl<sub>2</sub>- $(ptpd)][Au(I)Cl_2][OH]{[NaAuCl_4 \cdot 2H_2O]}n$  (3), and [Pt- $(II)Cl_2(ptpdH_2)][PtCl_4]$  (4) revealed that ptpd (i) serves as



a monodentate ligand for Au(III) coordinating to the metal center via the pyridine nitrogen only, (ii) preferentially coordinates Au(III) via the bidentate diamino group over the monodentate pyridine group, (iii) can coordinate Pt(II) in a bidentate fashion via the pyridyl nitrogen and the triazole N-3, and (iv) can bridge two Pt(II) centers through bidentate chelation at the diamino group and bidentate chelation via the pyridyl nitrogen and the triazole N-3. ptpd represents a versatile ligand template for the development of mixed metal complexes.

# INTRODUCTION

There has been much recent interest in the development of novel triazole-based ligands to construct a diverse range of fascinating coordination complexes<sup>1-6</sup> including supramolecular cage structures,<sup>7,8</sup> cylinders,<sup>9-11</sup> and polymers,<sup>12</sup> for example. Triazoles represent unique building blocks, and in turn triazole coordination chemistry is strongly associated with a variety of applications including drug development, catalysis, metal ion sensing, and imaging.<sup>1</sup>

1,4-Disubstituted 1,2,3-triazole-based ligands are largely synthesized by the well-known copper catalyzed 1,3-dipolar cycloaddition reaction between azides and terminal alkynes (Figure 1).<sup>2</sup> The 1,2,3-triazole heterocyclic ring readily coordinates metal centers and through a variety of modes, N-2, N-3, and C-5 coordination for instance (Figure 1). Furthermore, selective alkylation (e.g., methylation) of 1,2,3triazoles generates the corresponding 1,2,3-triazolylidenes, which can be metalated to give the corresponding 1,2,3triazolylidene coordination complexes (Figure 1).<sup>1</sup>

Triazoles are ideally suited to build countless multidentate ligand systems given the high synthetic flexibility associated with click chemistry.<sup>1,2</sup> Secondary coordination groups can be introduced at the 1- and/or 4-positions to supplement the inherent coordinating ability of the triazole group. For example 1,2,3-triazoles have been typically tethered to nitrogen



Figure 1. Copper catalyzed azide alkyne cycloaddition (top) and coordination modes associated with 1,4-disubstituted 1,2,3-triazoles ligands (bottom).

containing heterocycles such as pyridine, pyrimidine, and pyrazine rings, and coordination complexes of numerous metal centers have been reported (Figure 2).<sup>5,13–17</sup>

In addition to the "regular" or common coordination via the N-3 of 1,4-disubstituted 1,2,3-triazoles, N-2 coordination is observed in the case of "inverse" triazoles, which are essentially

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**Figure 2.** Representative examples of 2-pyridyl 1,2,3-triazoles Pd(II), Pt(II), Ru(II), and Re(I) coordination complexes.<sup>15,10,14,16</sup>

generated by switching the "R" groups associated with the original azide and alkyne (Figure 2).

Inverse 1,2,3-triazole ligands such as 2-(4-phenyl-1H-1,2,3-triazole-1-yl)pyridine have also been developed and their Pd(II), Pt(II), Re(I), and Ru(II) complexes synthesized (Figure 3).<sup>18</sup>



**Figure 3.** General structures of inverse 1,4-disubstituted 2-pyridyl 1,2,3-triazole ligands and representative examples of their Pd(II), Pt(II), Re(I), and Ru(II) complexes.<sup>18</sup>

Novel ligand design and synthesis is fundamental to coordination chemistry and the development of coordination complexes with applications in drug development,<sup>17,19</sup> catalysis,<sup>5</sup> and photophysics, for example.<sup>20–22</sup> We describe the synthesis and characterization of a novel polydentate 1,4-disubstituted 1,2,3-triazole based-ligand, 2-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)propane-1,3-diamine (ptpd) and its corresponding Au(III) and Pt(II) complexes.

# RESULTS AND DISCUSSION

**Synthesis of 1,4-Disubstituted 1,2,3-triazole Ligands.** The 1,4-disubstituted 1,2,3-triazole ligands were synthesized via the classic copper(I) catalyzed click reaction (1,3-diploar cycloaddition) between an azide and terminal alkyne.

2-(1-Phenyl-1*H*-1,2,3-triazol-4-yl)pyridine (ptp) was synthesized as previously reported<sup>13</sup> upon reaction of 2-ethynyl pyridine and phenyl azide in the presence of  $CuSO_4$  and sodium ascorbate (Figure 4), and analysis fully concurred with reported values.<sup>13</sup>

Reaction of 2-ethynylpyridine and di-tert-butyl (2-azidopropane-1,3-divl)dicarbamate in the presence of  $CuSO_4$  and sodium ascorbate afforded di-tert-butyl (2-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)propane-1,3-diyl)dicarbamate (Boc<sub>2</sub>ptpd) in excellent yield. Standard Boc (Boc = tert-butyloxycarbonyl) deprotection of Boc<sub>2</sub>-ptpd with HCl gave ptpd·3HCl (Figure 4), which was characterized by elemental analysis, <sup>1</sup>H, <sup>13</sup>C NMR, and IR spectroscopy, and mass spectrometry. In the <sup>1</sup>H NMR spectrum of ptpd·3HCl in  $D_2O_2$ , the triazole proton serves as an important diagnostic signal and is found as a singlet downfield at 9.12 ppm. Three signals associated with the pyridyl protons are observed between 8.01 and 8.78 ppm and integrated for four in total as required. The diaminopropane methine proton and methylene protons are found at 5.55 and 3.81 ppm, respectively. The <sup>13</sup>C NMR spectrum exhibits the required nine signals and the triazole C5 carbon found at 127.3 ppm as determined by C-H COSY (Figure S7, Supporting Information (SI)). ESI-MS in the positive mode (Figure S8, SI) was used to identify product ion fragments associated with ptpd + H (219.1 amu) and ptp + Na (241.1 amu). Furthermore, ptpd features as a ligand in X-ray crystal structures described below.

Synthesis of Gold(III) Complexes. ptp was synthesized to serve as a model ligand to investigate the reactivity of Na[Au(III)Cl<sub>4</sub>] with the 2-pyridyl 1,2,3-triazole moiety of the ptpd ligand, which also possesses the additional diaminopropane group. Reaction of Na[Au(III)Cl<sub>4</sub>] with ptp in methanol afforded [Au(III)Cl<sub>3</sub>(ptp)] (1) in good yield (80%) (Figure 5). The Au(III) complex was characterized by elemental analysis, <sup>1</sup>H NMR, mass spectrometry, and X-ray crystallography. Elemental analysis is consistent with one ptp ligand and three chlorine atoms per Au(III) center. In the <sup>1</sup>H NMR spectrum in acetone- $d_6$ , the triazole is the furthest downfield signal as a singlet at 9.63 ppm. Six signals associated with the pyridyl and phenyl protons are observed between 9.31 and 7.62 ppm and integrate for nine in total as required. ESI-MS in the positive mode (Figure S11, SI) enables identification of product ion fragments only and those associated with ptpd + H (223.1 amu) and  $AuCl_3 + H$  (303.2 amu). Single crystals suitable for X-ray diffraction were isolated from slow evaporation of 1 in acetone.

The solid state structure of 1 is shown in Figures 6 and 7. The square planar Au(III) is coordinated to the pyridine nitrogen with Au–N = 2.072(3) Å (Figure 6). A long-range interaction with the triazole nitrogen is observed, N…Au = 2.853(4) Å (Figure 7), similar to that seen in [Au(III)-Cl<sub>3</sub>Rbipy] (R = (1-phenyl)ethyl, N…Au = 2.758 Å).<sup>23</sup> There is also a twist between the pyridine and triazole rings of 23.427(12)° to accommodate this interaction, slightly shallower than that of ca. 28.4° in [Au(III)Cl<sub>3</sub>Rbipy]. The coordination sphere of the Au(III) center is completed as a symmetry generated dimer with long Au–Cl intermolecular

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Figure 4. Copper catalyzed synthesis of the 1,4-disubstituted 1,2,3-triazole ligands ptp (top) and ptpd·3HCl (bottom).



Figure 5. Synthesis of  $[AuCl_3(ptp)]$  (1, top), synthesis of  $[AuCl_2(pbt)]Cl$  featuring the proposed bidentate pyridyl triazole coordination (middle),<sup>37</sup> and synthesis of  $[AuCl_3(Boc_2-ptpd)]$  (2, bottom).



Figure 6. Molecular structure of  $[Au(III)Cl_3(ptp)]$  (1) with selected atom labeling. Atomic displacement shown at 50% probability.

contacts of 3.6911(17) Å, and the dimer is stabilized by a weak bifurcated C-H…Cl interaction ( $d_{C...Cl} = 3.642(5)$  Å, 3.466(5) Å) (Figure 7). This type of dimerization has been seen



**Figure** 7. Symmetry generated dimer of  $[Au(III)Cl_3(ptp)]$  (1) (symmetry generation = 1 - x, 1 - y, 2 - z). Au–Cl intermolecular contacts are 3.6911(17) Å, and the dimer is stabilized by a weak bifurcated C–H···Cl interaction ( $d_{C..Cl}$  = 3.466(5) Å, 3.642(5) Å). Octahedral coordination geometry for Au(III). Selected atoms labeled and displacement shown at 50% probability.

previously in the literature<sup>24-33</sup> with a median Au…Cl distance of 3.65 Å. The coordination geometry around the Au(III) center is a distorted octahedron.

While there are multiple reports in the literature of Au(I) 1,2,3-triazoylidene complexes,<sup>34–36</sup> to the best of our knowledge, there is only one report in the literature describing Au(III) coordination to a triazole N-2 or N-3. Yang et al. reported the synthesis of a Au(III) complex of 1-(pyridin-2yl)-1H-benzo[d][1,2,3]triazole (pbt) as a catalyst for the synthesis of  $E-\alpha$ -haloenones.<sup>37</sup> The complex, which features an inverse triazole with respect to the pyridine, was formulated as [AuCl<sub>2</sub>pbt)]Cl as per elemental analysis, and in turn, the pbt ligand is proposed to act as a bidentate chelating ligand via the pyridine nitrogen and triazole N-2 (Figure 5). It is possible, given the crystal structure described herewithin, that the Au(III) center in the proposed [AuCl<sub>2</sub>(pbt)]Cl is coordinated to three chlorido ligands and not two and if so should be reformulated as [AuCl<sub>3</sub>(pbt)].

Having established that Au(III) readily coordinates to ptp but via the 2-pyridyl group only, we investigated the reactivity of Au(III) with the Boc<sub>2</sub>-ptpd, where the diamino group is not free to coordinate to Au(III). Reaction of Na[Au(III)Cl<sub>4</sub>] with  $Boc_2$ -ptpd in methanol afforded  $[Au(III)Cl_3(Boc_2-ptpd)]$  (2) in excellent yield (91%) (Figure 5). Elemental analysis is consistent with one Boc2-ptpd ligand and three chlorido ligands per Au(III) center. In the <sup>1</sup>H NMR spectrum in acetone- $d_{6i}$  the triazole is the furthest downfield signal as a singlet at 8.98 ppm. Four signals associated with the pyridyl protons are observed between 8.94 and 7.93 ppm and integrate for four in total as required. The diaminopropane methine proton and methylene protons are found at 5.00 and 3.63 ppm, respectively. A singlet integrating for 18 is found at 1.34 ppm accounting for the tert-butyl (tBu) protons associated with the two Boc protecting group. ESI-MS in the positive mode (Figure S14, SI) enables identification of product ion fragments relating to AuCl<sub>2</sub>(Boc<sub>2</sub>-ptpd) (685.1 amu), AuCl<sub>2</sub>- $(Boc_2-ptpd) - tBu$  (629.1 amu), and AuCl<sub>2</sub> $(Boc_2-ptpd) - tBu$ 2*t*Bu (573.1 amu). In the IR spectrum, the carbamate  $\nu$ (C= O) is evident at 1667  $\text{cm}^{-1}$ .

The X-ray crystal structure previously described for 1 fully supports the proposition that ptpd serves as a monodentate ligand in 2, binding Au(III) by the pyridine nitrogen only.

Having established that Au(III) readily reacted with both ptp and Boc<sub>2</sub>-ptpd, we investigated the reactivity of Au(III) with our novel and fully deprotected multidentate ligand, ptpd, which possesses a pyridyl and a diamino group in addition to the 1,2,3-triazole. Na[Au(III)Cl<sub>4</sub>] was reacted with ptpd, post neutralization of ptpd-3HCl with base, in water to rapidly give a yellow solid (3), which is essentially insoluble in laboratory solvents, deuterated or not.

ESI-MS in the positive mode (Figure S16, SI) enables identification of product ion fragments relating to  $AuCl_2(ptpd)$  at 485.1 amu.

Fortunately, single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from the filtrate at rt. As expected, ptpd preferentially coordinates Au(III) via the bidentate diamino group over the monodentate pyridine group (Figure 8). There are relatively few examples of  $[Au(III)Cl_2]^+$ coordinated by diamine groups in the literature. Three ethane



**Figure 8.** Hydrogen bonded hydroxide/AuCl<sub>2</sub> (50% occupied each) charge balanced complex in **3.** The  $[Au(III)Cl_2(ptpd)][Au(I)Cl_2]-[OH]$  complex also has a { $[NaAuCl_4:2H_2O]$ }*n* site sharing with the hydroxide at a lower occupancy. See Figure S28B. Selected labeling and atomic displacement shown at 50% probability.

diamine coordinated examples have been reported with chloride and nitrate counterions.<sup>38–40</sup> Several cyclohexane diamine chloride complexes are also known.<sup>41,42</sup> In these complexes, Au-N distances are 2.02836(8)-2.05900(11) Å. The structure of 3 (Figure 8) features the ligand ptpd with an Au(III)Cl2+ group coordinated by the bidentate diamino group. The Au–N distances (2.037(5) and 2.053(5) Å) are slightly longer than in previous examples but shorter than that seen in 1. The Au(III) $Cl_2N_2$  moiety is planar. The counterions are the linear  $[Au(I)Cl_2]^-$  anion and hydroxide (O1), which are half-occupied. The coordination sphere of the Au(III) center is completed by a chloride from the linear  $[Au(I)Cl_2]^$ anion (Cl3...Au1 = 3.2383(16) Å) and a chloride from the neighboring [Au(III)Cl<sub>2</sub>(ptpd)]<sup>+</sup> cation (Cl1, symmetry generation = x, 3/4 - y, -1/2 + z; Cl1…Au1 = 3.5236(14) Å) forming a distorted elongated octahedron, as seen in 1 for the Au(III) center (Figure 7). These cations pack tail to tail (pyridyl to pyridyl) and form a  $\pi$  stacked assembly (see Figures S26-S28, SI). In the extended structure, the hydroxide anion is hydrogen bound to a water molecule and this forms a hydrogen bonded scaffold tying the [Au(III)Cl<sub>2</sub>(ptpd)][Au- $(I)Cl_2$  chains together along the bc plane (see Figure S26). The partially occupied  $[NaAuCl_4 \cdot 2H_2O]n$  (with disordered chlorides in three locations) also form chains which run parallel to the *b*-axis and separate pairs of anion bridged cations of 3 (see Figure S27).

There are many reports in the literature in relation to the reduction of Au(III) centers on reaction with nucleophiles in aqueous solution,  $^{43-45}$  including pyridine.  $^{46}$  Specifically Durović et al. reported that reaction of  $[AuCl_4]^-$  with equimolar amounts of pyridine gave the substitution product, whereas, in the presence of excess pyridine, a second step involved reduction of Au(III) to Au(I).  $^{46}$ 

Retrospective examination of the elemental analysis determined for the bulk solid, post elucidation of the X-ray crystal structure of the minor crystalline product isolated from the filtrate, revealed that the analysis of the bulk solid was consistent with the formula,  $Na_{0.5}[Au(III)Cl_2(ptpd)][Au(I)-Cl_2][Au(III)Cl_4]_{0.5}$  (3).

**Synthesis of Pt(II) Complexes.** As highlighted above, ptp was synthesized to serve as a model ligand to investigate the reactivity of the 2-pyridyl 1,2,3-triazole moiety of the ptpd ligand, which also possesses the additional diaminopropane group. A Pt(II) ptp complex and its X-ray crystals structure was previously reported by Schweinfurth et al. (Figure 6).<sup>14</sup> The structure clearly highlights the propensity of the 2-pyridyl 1,2,3-triazole moiety to act as a bidentate ligand for Pt(II) centers (Figure 7).

To demonstrate that the 2-pyridyl 1,2,3-triazole moiety in our novel multidentate ptpd ligand could also effectively bind to Pt(II) centers,  $K_2[PtCl_4]$  was reacted with ptpd·3HCl in acetic acid under reflux for 4 days to give  $[Pt(II)Cl_2(ptpdH_2)]$ - $[PtCl_4]$  (4, Figure 9) in excellent yield (91%). In selecting acetic acid as a solvent, the diamino group was "protected" and less likely to coordinate Pt(II) as the amines are protonated in an acidic solvent.

Elemental analysis is consistent with one  $ptpdH_2$  ligand and six chlorine atoms per two Pt(II) centers. In the <sup>1</sup>H NMR spectrum in acetone- $d_6$ , the triazole is the furthest downfield signal as a singlet at 8.98 ppm. Four poorly resolved signals associated with the pyridyl protons are observed between 8.66, 8.11, 7.99, and 7.43 ppm and integrate for four in total as required. The six ammonium protons are observed as a



Figure 9. Structures of  $[PtCl_2(ptp)]$  (top left)<sup>14</sup> and  $[PtCl_2(ptpdH_2)][PtCl_4]$  (4, top right) and proposed structure for  $[Pt_3Cl_4(ptpd)_2]Cl_2$  (5, bottom).

multiplet at 8.40 ppm. The methane and methylene protons are found at 5.40 and 3.42 ppm, respectively. ESI-MS in the positive mode (Figure S19, SI) enables identification of product ion fragments relating to  $PtCl_2ptpd + 2Na$  (532.4) and  $PtCl_2ptpd + H$  (484.6). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from the filtrate at rt.

The major conformation of 4 is shown in Figure 10 (see Figure S29 for further information on disorder). In 4, the metal chloride is coordinated to the pyridyl and triazole nitrogen atoms with Pt–N distances of 2.001(10), 2.16(3), and 1.994(10), 1.84(2) Å, respectively. Pt–Cl distances are 2.284(3) and 2.290(3) Å for both complexes. The metal ligand moiety is essentially planar in both unique molecules in



**Figure 10.** Asymmetric unit of 4 showing the one conformation of disordered ligand moiety (coordinated to Pt2) as well as anion (Pt3) with occupancy ca. 50%. Solvents have been omitted and residual unresolved solvent was also removed using SQUEEZE (approximately SMeOH, 6H<sub>2</sub>O per unit cell). Displacement shown at 50% probability and only metal and halogen atoms labeled for clarity. Dotted lines indicate hydrogen bonding.

the structure. There are few congeners with substituents on the triazole (pridyl,<sup>47</sup> phenyl,<sup>14</sup> hexyl<sup>48</sup>) reported in the literature. In these few examples, pyridyl N–Pt distances range from 2.02850(13)–2.04760(13) Å, triazole N–Pt 1.98608(9)–2.01150(12) Å, and Pt–Cl 2.27786(14)–2.29160(14) Å. Also in these complexes, the metal ligand moiety is essentially planar. In 4, however, the [Pt(II)Cl<sub>2</sub>(ptpdH<sub>2</sub>)]<sup>2+</sup> groups stack parallel to the *b*-axis in an ABCDA motif with a separation of ca. 3.4 Å. The Pt atoms do not line directly over each other but are offset with a  $d_{\text{Pt--Pt}}$  of 3.30783(14) and 3.58774(16) Å. The anions [PtCl<sub>4</sub>]<sup>2–</sup> surround the stacks along the (001) plane.

Given that Pt(II) readily reacts with both ptp and  $ptpdH_2$ , we investigated the reactivity of Pt(II) with our novel and fully deprotected multidentate ligand, ptpd, which possesses a pyridyl and a diamino group in addition to the 1,2,3-triazole.  $K_2[PtCl_4]$  was reacted with ptpd in a 2:1 ratio, over 3 days at rt in water, to give the proposed  $[Pt(II)_3Cl_4(ptdp)_2]Cl_2$  (5). Elemental analysis is consistent with two ptpd ligands and six chlorine atoms per three Pt(II) centers.

Given **5** is essentially insoluble in common laboratory solvents, NMR spectroscopic characterization was not successfully undertaken. HRMS helped identify the product ion fragment associated with PtCl(ptpd) (449.027) and PtCl<sub>2</sub>(ptpd) + H (485.034) and significantly Pt<sub>2</sub>(ptpd)<sub>2</sub>Cl<sub>3</sub> (933.100), Pt<sub>2</sub>(ptpd)<sub>2</sub>Cl<sub>4</sub> + H (969.065), and Pt<sub>3</sub>(ptpd)<sub>2</sub>Cl<sub>5</sub> (1198.993, Figures S21-23, SI). Though bis(diamino) complexes are more closely associated with Pd(II) centers, Pt(II) bis(diamino) complexes are well represented in the literature,<sup>49,50</sup> including Pt complexes of 1,3-diaminopropane.<sup>51</sup> In addition, bis(ethylenediamino)platinum(II) chloride is commercially available. In turn, we tentatively suggest that our novel ligand ptpd in **5** bridges two Pt(II) centers as per the proposed coordination compound in Figure 9.

# CONCLUSION

The synthesis and characterization of a novel polydentate 1,4disubstituted 1,2,3-triazole-based ligand, 2-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)propane-1,3-diamine (ptpd), is described. X-ray structural characterization of  $[Au(III)Cl_3(ptp)]$  (1),  $[Au(III)Cl_2(ptpd)][Au(I)Cl_2][OH]{[NaAuCl_4·2H_2O]}n$  (3), and  $[Pt(II)Cl_2(ptpdH_2)][PtCl_4]$  (4) and characterization of  $[Au(III)Cl_3(Boc_2-ptpd)]$  (2) and  $[Pt(II)_3Cl_4(ptdp)_2]Cl_2$  (5) support the proposition that ptpd is an interesting multidentate ligand that can bind metal centers through a variety of coordination modes including bidentate coordination through the diamino group, bidentate through the triazole N-3 and pyridyl nitrogen, and monodentate through the pyridyl nitrogen. Ultimately, ptpd is a versatile and ideal ligand template for the development of mixed metal complexes of Pt and Au and Pt/Au and other transition metals.

# EXPERIMENTAL SECTION

**Materials and Instrumentation.** 2-Ethynylpyridine,  $CuSO_4$ .  $SH_2O$ , sodium ascorbate, and deuterated solvents were purchased from Sigma-Aldrich and used without further purification. 2-(1- Phenyl-1*H*-1,2,3-triazol-4-yl)pyridine (ptp)<sup>14</sup> and di-*tert*-butyl (2 azidopropane-1,3-diyl)dicarbamate<sup>20</sup> were synthesized as previously reported. *Caution!* Please note azide containing compounds are potentially explosive and should be handled and stored with extreme care. Infrared spectroscopy measurements were obtained using a Nicolet iS10 FT-IR (Thermo Fisher Scientific, Waltham, MA, USA). The infrared spectra were recorded from 400 to 4000 wavenumbers (cm<sup>-1</sup>) and analyzed using OMNIC software (ver. 9.6, Thermo Fisher

#### Table 1. Crystallographic Data for Au(III) and Pt(II) Triazole Complexes 1, 3, 4

	1	3	4
empirical formula	$C_{13}H_{10}AuCl_3N_4$	$C_{20}H_{36,60}Au_{3.80}C_{19,21}N_{12}Na_{0.80}O_{4.40}$	$C_{10.25}H_{17}Cl_6N_6O_{0.25}Pt_2$
formula weight	525.57	1608.97	831.18
temperature (K)	100(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073
instrument	ECO	ECO	ECO
crystal system	triclinic	monoclinic	triclinic
space group	$P\overline{1}$	$P2_{1}/c$	$P\overline{1}$
a (Å)	6.960(3)	15.2675(6)	12.4400(6)
b (Å)	9.060(4)	18.9896(7)	13.3881(6)
c (Å)	12.468(6)	7.1416(3)	15.1617(7)
$\alpha$ (deg)	88.87(3)	90	76.6984(17)
$\beta$ (deg)	76.044(16)	99.1035(11)	68.0193(18)
γ (deg)	86.372(11)	90	89.2239(19)
volume (Å <sup>3</sup> )	761.5(6)	2044.44(14)	2271.40(19)
Z	2	2	4
ho (calc. Mg/m <sup>3</sup> )	1.472	2.614	2.431
$\mu \ (\mathrm{mm}^{-1})$	2.292	14.250	13.018
F(000)	492	1483	1522
crystal size (mm <sup>3</sup> )	$0.28\times0.24\times0.16$	$0.18 \times 0.08 \times 0.08$	$0.13\times0.03\times0.03$
heta range for data collection (deg)	2.806-28.414	2.908-26.468	2.269-26.560
reflns collected	11304	40737	36729
independent reflns	3795 [R(int) = 0.0462]	4212 [R(int) = 0.0293]	9231 $[R(int) = 0.0891]$
max and min transmission	0.7457 and 0.3481	0.0276 and 0.0080	0.7454 and 0.4504
data/restraints/parameters	3795/0/190	4212/965/232	9231/604/648
goodness-of-fit on $F^2$	1.067	1.106	1.030
final R indices $[I > 2\sigma(I)]$	R1 = 0.0260, wR2 = 0.0550	R1 = 0.0258, wR2 = 0.0657	R1 = 0.0495, wR2 = 0.0980
R indices (all data)	R1 = 0.0337, wR2 = 0.0579	R1 = 0.0297, wR2 = 0.0673	R1 = 0.0928, wR2 = 0.1131
largest diff. peak and hole $(e \cdot Å^{-3})$	1.195 and -2.065	1.233 and -0.853	1.977 and -2.523
CCDC No.	1855200	1855201	1855202

Sceintific). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer. The spectra were analyzed using MestReNova software. The residual undeuterated solvent signals were used as internal references.<sup>52</sup> Mass spectrometry experiments were performed on an Advion Expression Compact Mass Spectrometer where 10  $\mu$ L of the samples was injected in 300  $\mu$ L of methanol:isopropyl-alcohol:water:formic acid (80:10:10:1 v/v). The mass spectrometry data were acquired in both positive and negative ion modes, and the spectra were analyzed using the Advion Mass Express software program. High Res MS mass spectra were acquired using a Bruker Compact spectrometer in positive mode. The instrument was calibrated using Tune Mix-L solution, (Agilent Technologies). Samples were infused by syringe pump and masses were recorded over the range 30-2000 m/z. Operating conditions were as follows: end-plate offset 500 V, capillary 4500 V, nebulizer 0.4 bar, dry gas 4.0 L/min, and dry temperature 180 °C. MicroTof control 4.1 and Data Analysis 4.4 were used to carry out the analysis. Elemental analysis (C, H, N, and Cl) was performed at the Microanalytical Laboratory, School of Chemistry and Chemical Biology, University College Dublin, Ireland.

**Synthesis.** Di-tert-butyl (2-(4-(Pyridin-2-yl)-1H-1,2,3-triazol-1-yl)propane-1,3-diyl)dicarbamate (Boc<sub>2</sub>-ptpd). 2-Ethynylpyridine (392  $\mu$ L, 3.879 mmol) and di-tert-butyl (2-azidopropane-1,3-diyl)-dicarbamate (1.223 g, 3.879 mmol) were dissolved in 3:2 MeOH:H<sub>2</sub>O (100 mL). CuSO<sub>4</sub>·SH<sub>2</sub>O (48 mg, 0.192 mmol) and sodium ascorbate (1.1 g, 5.552 mmol) in water (10 mL) was added, and the reaction was stirred for 2 h at rt. The reaction was quenched with saturated ammonium chloride (50 mL) and extracted into DCM (2 × 75 mL). The organic layer was washed with brine (60 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude product was subject to column chromatography on silica using 10:1 DCM:EtOAc to yield Boc<sub>2</sub>-ptpd as a greenish yellow solid (Trz = triazole). 1.597 g, 98%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.60 (s, 1H, TrzH), 8.24–8.11 (m, 2H, PyrH), 7.78 (t, J = 7.6 Hz, 1H, PyrH),

7.25–7.22 (m, 1H, PyrH), 5.29 (d, J = 6.7 Hz, 2H, NH), 4.78–4.71 (m, 1H, CH), 3.86–3.54 (m, 4H, CH<sub>2</sub>), 1.43 (d, J = 6.4 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ : 156.50, 147.78, 130.38, 129.05, 128.47, 125.79, 120.34, 80.26, 60.46, 41.41, 28.45 ppm. MS (ESI+) m/z: ([M + H]<sup>+</sup>) 419.3.

2-(4-(*Pyridin-2-yl*)-1*H*-1,2,3-*triazol*-1-*yl*)*propane*-1,3-*diamine Trihydrochloride* (*ptpd*·3*HCl*). 6 M HCl (8 mL) was added to Boc<sub>2</sub>-ptpd (550 mg, 1.314 mmol) dissolved in EtOAc (8 mL), giving a dark green/black solution which was stirred at rt for 3 h. The white solid precipitate was filtered under vacuum to yield ptpd·3HCl (402 mg, 93%). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 9.12 (s, 1H, TrzH), 8.78 (d, *J* = 5.7 Hz, 1H, PyrH), 8.64 (t, *J* = 7.9 Hz, 1H, PyrH), 8.42 (d, *J* = 8.1 Hz, 1H, PyrH), 8.01 (t, *J* = 6.7 Hz, 1H, PyrH), 5.55 (td, *J* = 9.6, 4.7 Hz, 1H, CH), 3.81 (ddd, *J* = 17.8, 14.1, 6.8 Hz, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O)  $\delta$ : 147.3, 142.0, 141.7, 140.6, 127.3, 126.3, 124.7, 57.5, 40.8 ppm. MS (ESI+) *m*/*z*: ([ptpd + H]<sup>+</sup>) 219.1, ([ptpd + Na]<sup>+</sup>) 241.1. FT-IR  $\nu_{max}$  (cm<sup>-1</sup>): 3066, 2854, 2009, 1610, 1496, 1219, 1093.

[Au(III)Cl<sub>3</sub>(ptp)] (1). Na[AuCl<sub>4</sub>]·2H<sub>2</sub>O (90 mg, 0.23 mmol) and ptp (50 mg, 0.23 mmol) were dissolved in MeOH (10 mL) and stirred at rt for 18 h. The solid precipitate was collected by vacuum filtration, washed with cold MeOH and dried to yield 1 as a yellow solid. 100 mg, 80%; <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)  $\delta$ : 9.63 (s, 1H, TrzH), 9.31 (d, <sup>3</sup>*J* = 5.8 Hz, 1H, ArH), 8.49 (d, *J* = 3.8 Hz, 2H, ArH), 8.05 (dd, <sup>3</sup>*J* = 5.8 Hz, <sup>4</sup>*J* = 3.8 Hz, 2H, ArH), 7.96 (dd, <sup>3</sup>*J* = 9.4, <sup>4</sup>*J* = 5.8 Hz, 1H, ArH), 7.4–7.67 (m, 2H, ArH), 7.62 (dd, <sup>3</sup>*J* = 10.6, <sup>4</sup>*J* = 4.3 Hz, 1H, ArH) ppm. MS (ESI+) *m*/*z*: ptp 223.1, AuCl<sub>3</sub>+H 303.2; EA calc. % for C<sub>13</sub>H<sub>10</sub>AuCl<sub>3</sub>N<sub>4</sub>·0.5CH<sub>3</sub>OH requires C, 29.94; H, 2.23; N, 10.35; Cl, 19.69, found C, 29.84 H, 1.81 N, 10.35 Cl, 19.31%. FT-IR  $\nu_{max}$  (cm<sup>-1</sup>): 3101, 2088, 1604, 1593, 1571, 1556, 1503, 1474, 1468, 1447, 1424, 1238, 1170, 1107, 1040.

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of  $[Au(III)Cl_3(ptp)]$  in acetone.

 $[Au(III)Cl_3(Boc_2-ptpd)]$  (2). Na[AuCl\_4].2H<sub>2</sub>O (95 mg, 0.24 mmol) and Boc\_2-ptpd (100 mg, 0.24 mmol) were dissolved in MeOH (10

mL) and stirred at rt for 18 h. The addition of water (10 mL) induced precipitation of a yellow solid, which was collected by vacuum filtration, washed with cold water, and dried to yield **3**. 158 mg, 91%; <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>)  $\delta$ : 8.98 (s, 1H, TrzH), 8.94 (d, <sup>3</sup>*J* = 5.3 Hz, 1H, ArH), 8.58 (t, *J* = 7.7 Hz, 1H, ArH), 8.47 (d, *J* = 8.0 Hz, 1H, ArH), 7.93 (t, *J* = 6.3 Hz, 1H, ArH), 5.10–5.00 (m, 1H, CH), 3.77–3.63 (m, 4H, CH<sub>2</sub>), 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>) ppm. MS (ESI+) *m/z*: AuCl<sub>2</sub>(Boc<sub>2</sub>-ptpd) 685.1, AuCl<sub>2</sub>(Boc<sub>2</sub>-ptpd) – *t*Bu 629.1, AuCl<sub>2</sub>(Boc<sub>2</sub>-ptpd) – 2*t*Bu 573.1; EA calc. % for C<sub>20</sub>H<sub>30</sub>AuCl<sub>3</sub>-N<sub>6</sub>O<sub>4</sub>.1.25CH<sub>3</sub>OH requires C, 33.50; H, 4.63; N, 11.03; Cl, 13.96, found C, 33.34 H, 4.02 N, 10.91 Cl, 13.64%. FT-IR  $\nu_{max}$  (cm<sup>-1</sup>): 3333, 3133, 2976, 1687 ( $\nu$ C=O), 1606.

 $Na_{0.5}[Au(III)Cl_2(ptpd)][Au(II)Cl_2][Au(III)Cl_4]_{0.5}$  (3). Na[AuCl<sub>4</sub>]·2H<sub>2</sub>O (200 mg, 0.502 mmol) dissolved in water (8 mL) was added to a solution of ptpd·3HCl (82 mg, 0.251 mmol) and NaOH (30 mg, 0.75 mmol) in water (3 mL) and stirred at rt for 24 h. The solid, which precipitated instantly, was collected by vacuum filtration, washed with water and Et<sub>2</sub>O to yield **2** as a pale yellow-brown solid. 108 mg, 46%; MS (ESI+) m/z: AuCl<sub>2</sub>(ptpd) 485.1. EA calc. % for C<sub>10</sub>H<sub>14</sub>Au<sub>2.5</sub>Cl<sub>6</sub>-N<sub>6</sub>Na<sub>0.5</sub> requires C, 12.85; H, 1.51; N, 8.99; Cl, 22.75, found C, 13.25; H, 1.44; N, 8.99; Cl, 22.64%. FT-IR  $\nu_{max}$  (cm<sup>-1</sup>): 3095, 2948, 2354, 1605, 1569, 1471, 1446.

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from the filtrate.

[Pt(II)Cl<sub>2</sub>( $\bar{p}$ tpdH<sub>2</sub>)][PtCl<sub>4</sub>] (4). K<sub>2</sub>PtCl<sub>4</sub> (104 mg, 0.251 mmol) and ptpd·3HCl (82 mg, 0.251 mmol) were dissolved in acetic acid (6.5 mL) and refluxed at 115 °C for 4 days. The solution was cooled to rt, and the precipitated solid was vacuum filtered, washed with water, MeOH, EtOH, and Et<sub>2</sub>O to yield 4 as a pale brown solid; 50 mg, 47%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 8.88 (s, 1H), 8.66 (s, 1H), 8.40 (m, *J* = 47.6 Hz, 6H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.99 (t, *J* = 7.5 Hz, 1H), 7.43 (s, 1H), 5.40 (s, 1H), 3.55−3.42 (m, 4H) ppm. MS (ESI+) *m*/*z*: PtCl<sub>2</sub>ptpd + 2Na 532.4, PtCl<sub>2</sub>ptpd + H 484.6. EA calc. % C<sub>10</sub>H<sub>16</sub>Cl<sub>6</sub>N<sub>6</sub>Pt<sub>2</sub>·0.5CH<sub>3</sub>COOH requires C, 15.49; H, 2.13; N, 9.85; found C, 15.52; H, 1.87; N, 9.69%. FT-IR  $\nu_{max}$  (cm<sup>−1</sup>): 3093, 2981, 2360, 1587, 1493, 1466, 1382, 1281, 1250, 1131, 1099.

Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from the filtrate.

 $[Pt(II]_3Cl_4(ptdp)_2]Cl_2$  (5). K<sub>2</sub>PtCl<sub>4</sub> (300 mg, 0.72 mmol) dissolved in water (5 mL) was added to a solution of ptpd·3HCl (118 mg, 0.36 mmol) and KOH (43 mg, 0.11 mmol) in water (5 mL). The solution was stirred at rt for 3 days, and a pale yellow solid was collected by vacuum filtration, washed with water, ethanol, and diethyl ether, and dried to give 5. 193 mg, 65%; MS (ESI+) m/z: PtCl(ptpd) 449.027, PtCl<sub>2</sub>(ptpd) + H 485.034, Pt<sub>2</sub>(ptpd)<sub>2</sub>Cl<sub>3</sub> 933.100, Pt<sub>2</sub>(ptpd)<sub>2</sub>Cl<sub>4</sub> + H 969.065, and Pt<sub>3</sub>(ptpd)<sub>2</sub>Cl<sub>5</sub> 1198.993. EA calc. % C<sub>20</sub>H<sub>28</sub>Cl<sub>6</sub>N<sub>12</sub>Pt<sub>3</sub> requires C, 19.46; H, 2.29; N, 13.62; Cl, 17.23, found C, 19.37; H, 2.30; N, 13.36; Cl, 16.98%. FT-IR  $\nu_{max}$  (cm<sup>-1</sup>): 3516, 3194, 3105, 2980, 2889, 2360, 1614, 1602, 1578, 1470, 1410.

X-ray Crystallography. X-ray structural analyses for all samples were performed on a Bruker D8 Quest ECO at 100(2) K with an Oxford Cryostream cryostat, with samples mounted on a MiTeGen microloop using Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ; see Table 1). Bruker APEX<sup>53</sup> software was used to collect and reduce data and determine the space group. Absorption corrections were applied using SADABS.<sup>54</sup> Structures were solved with the XT structure solution program<sup>55</sup> using Intrinsic Phasing and refined with the XL refinement package<sup>56</sup> using Least Squares minimization in Olex2.<sup>57</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters.

In the structure of 3, in the asymmetric unit, the counterions  $AuCl_2$ and  $OH^-$  are only 50% occupied. The  $OH^-$  occupies the same space as the Na (40% occupied) in the charge neutral  $[Na(H_2O)_2AuCl_4]_n$ which is only partially occupied. This moiety was modeled with restraints (DFIX, SADI, SIMU, ISOR) and constraints (EADP O2, O3 and Cl4;Cl5; Cl6;Cl7; Cl8; Cl9) with the Cl atoms in three separate locations (43, 32, and 5% occupancy, refined to a total of 80% using SUMP). The hydroxide is coordinated to a water molecule at 50% occupancy, and the Na is also coordinated to two water molecules at 40% and 80% occupancy. Hydrogen atoms were added to the water molecules to align as best as possible to hydrogen bonding receptors.

In the structure of 4, one ligand was disordered in two locations ca. 50% and modeled with restraints (SADI, SIMU, ISOR). One  $PtCl_4$  moiety was also modeled in two positions at 50% occupancy with one restraint (SIMU).

The half-occupied methanol molecule was modeled with restraints (ISOR). The remaining disordered solvent in the void (H<sub>2</sub>O/MeOH) was removed using SQUEEZE<sup>S8</sup> (155 electrons in a 330 Å<sup>3</sup> solvent accessible void, approximately 5MeOH, 6H<sub>2</sub>O per unit cell).

Crystallographic data, CCDC 1855200–1855202, can be obtained free of charge from the Cambridge Crystallographic Data Centre.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01994.

Selected NMR, mass, and IR spectra, crystal structure diagrams (PDF)

# **Accession Codes**

CCDC 1855200–1855202 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

# Notes

The authors declare no competing financial interest.

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