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FULL PAPER

Synthesis and crystal structure of gold(I) complexes with triazole and triphenylphosphine ligands: monomeric complex [Au(1,2,3-L)-(PPh_3)] and dimeric complex [Au(1,2,4-L)(PPh_3)]$_2$ (HL = triazole) through an Au–Au bond in the solid state

Kenji Nomiya,* Ryusuke Noguchi, Katsunori Ohsawa and Kazuhiro Tsuda

Department of Materials Science, Faculty of Science, Kanagawa University, Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan. E-mail: nomiya@info.kanagawa-u.ac.jp

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Two novel gold(I)–triphenylphosphine complexes with nitrogen-containing heterocycles, [Au(1,2,3-L)(PPh_3)] **1** and [Au(1,2,4-L)(PPh_3)]$_2$·$x$$H_2O$ (x = 0.5–1.0) **2** (HL = triazole) were synthesized from stoichiometric reactions of a precursor complex [AuCl(PPh_3)] with HL in acetone in the presence of NaOH, and isolated as colorless needles and cubic crystals, respectively. The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction. Complexes **1** and **2** were also fully characterized by complete elemental analyses, TG/DTA and FT-IR in the solid state and by solution NMR (^{31}P, ^{1}H and ^{13}C) spectroscopies and solution molecular-weight measurements. Complex **1** consisted of a monomeric 2-coordinate AuNP core both in the solid state and in solution, while, in contrast, **2** comprised a dimeric $(AuNP)_2$ core through an Au–Au bond in the solid state, but a monomeric AuNP core in solution. Within the two gold(I) complexes composed of very closely related nitrogen-containing heterocycles and a common bulky PPh_3 ligand, it was found that aggregation through the Au···Au interaction in **2** was overruled in **1**. The molecular structures of **1** and **2** were also compared with those of the corresponding silver(I) analogs, [Ag(1,2,3-L)(PPh_3)$_2$]$_n$ **3** and [Ag(1,2,4-L)(PPh_3)$_2$]$_n$ **4**, the molecular structures of which have been recently determined as helical polymers in the solid state.

Over the past 30 years, interest has increased in the coordination chemistry of silver(I) and gold(I) complexes with biological or medicinal activities.[1–7] The molecular design and structural determination of such silver(I) and gold(I) complexes with common ligands are an intriguing aspect of bioinorganic chemistry, inorganic syntheses and metal-based drugs. For example, the thiosulfato complexes of silver(I) and gold(I), $[Ag(S_2O_3)_2]^{3-}$ (STS) with anti-ethylene activity[8] and $[Au(S_2O_3)_2]^{3-}$ (Sanocrisin) with anti-arthritic activity,[1,9] are a classical, but prototypic case; the former has 4-coordinate silver(I) with tetrahedral geometry caused by a bridging thiosulfate ligand,[10] while the latter has been established as a 2-coordinate linear structure with an AuS_2 core.[9c] Recently, we have realized a combination of several silver(I) and gold(I) complexes with common thiol ligands, such as $\{Na[Ag(Htma)]\cdot 0.5H_2O\}_n$ (n = 24–34; H_3tma = thiomalic acid)[11a] and gold thiomalate, $\{Na_2[Au(tma)]\cdot 1.75H_2O\}_n$ (n = 3–10),[3,9a,12a] and of $\{Na[Ag(tsa)]\cdot H_2O\}_n$ (n = 21–27; H_2tsa = thiosalicylic acid)[13] and $Na_3[Au(tsa)_2]\cdot 5H_2O$.[14] These oligomeric silver(I) complexes have displayed effective antimicrobial activities against selected bacteria, yeast and mold,[11a,13] whereas the corresponding gold(I) complexes have shown effective anti-arthritic activities.[15] Structure determination with X-ray analysis of these complexes has been unsuccessful because most of them were hard to crystallize,[3,9a,11b] the exception being gold thiomalate, $\{Na_2Cs[Au_2(Htma)(tma)]\}_n$, the crystal structure of which was very recently solved.[12k] On the other hand, tertiary phosphine ligands have been utilized in order to limit polymerization of the [Au(SR)] unit (HSR = thiol ligand).[16] Thus, we have also substantiated another combination of silver(I) and gold(I) complexes consisting of a thiol or N-containing heterocyclic ligand with an auxiliary ligand (PPh_3) such as in [Ag(Htsa)(PPh_3)$_3$] and [Au(Htsa)(PPh_3)],[17] and [Ag(im)(PPh_3)$_3$] (Him = imidazole) and [Au(im)(PPh_3)].[18,19]

Recent advances in gold chemistry have highlighted the flexible metal–metal bonding modes exhibited by this element.[20] Particular attention has been paid to compounds which contain weak intermolecular metal–metal interactions with gold–gold separations typically in the range 2.5–3.5 Å, which are less than 3.60 Å, twice the van der Waals radii for gold.[21,22] Schmidbaur *et al.* have suggested that steric effects play a decisive role, since the weak forces associated with the Au···Au contacts are easily overruled by steric repulsion and other factors such as packing forces. In solution, it is the solvation by solvent molecules which overrules the aggregation through Au···Au contacts.[23]

The affinity of gold for the nitrogen atom, in comparison with sulfur and phosphorus atoms, is very low indeed, and most compounds with gold–nitrogen bonds are of limited stability.[23] Nevertheless, a number of neutral or ionic gold(I) complexes with nitrogen centers in the presence of the auxiliary P-donor ligands have been prepared, *e.g.*, as neutral complexes such as [Au(pyrmd)(PPh_3)] (Hpyrmd = 5-fluoro-1-(tetrahydrofuran-2-yl)-(1*H*,3*H*-pyrimidine-2,4-dione),[24] [Au(im-2-R)(PPh_3)] (R = H, Me, *i*-Pr, Ph),[25] and [Au(pz)(PPh_3)] (Hpz = pyrazole),[26] and as ionic species such as $[Au(Him)(PPh_3)]^+[Z]^-$ (HZ = picric acid),[27a] $[Au(NMe_3)(PPh_3)]ClO_4$,[28] $[Au(qncd)(PPh_3)]BF_4$ (qncd = quinuclidine),[29] $[Au(Q)(PPh_3)]ClO_4$ [Q = 2,6-dimethylpyridine, naphthyridine, 2-(2-pyridyl)benzimidazole].[30] However, in gold(I) complexes with N-donor ligands, Au···Au interactions are scarce and only a few examples have been recently found such as in $[Au(NH_2Bu^t)(PMe_3)]BF_4$ and $[\{Au(PMe_3)\}_2NH(CH_2Ph)]BF_4$,[23] and $[\{Au(PPh_3)\}_4(\mu\text{-bbzim})](ClO_4)_2$ (H_2bbzim = 2,2′-bibenzimidazole).[31]

On the other hand, examples of the corresponding neutral silver(I) complexes with an $AgN(PPh_3)$ unit have been recently reported, *e.g.*, such as $[Ag_2(pz)_2(PPh_3)_2]$ and $[Ag_2(pz)_2(PPh_3)_3]$.[32a] Very recently, we have isolated two other neutral silver(I) complexes with a 4-coordinate $Ag(N)_2(PPh_3)_2$ core using 1,2,3-triazole and 1,2,4-triazole ligands, *i.e.*, [Ag(1,2,3-L)-

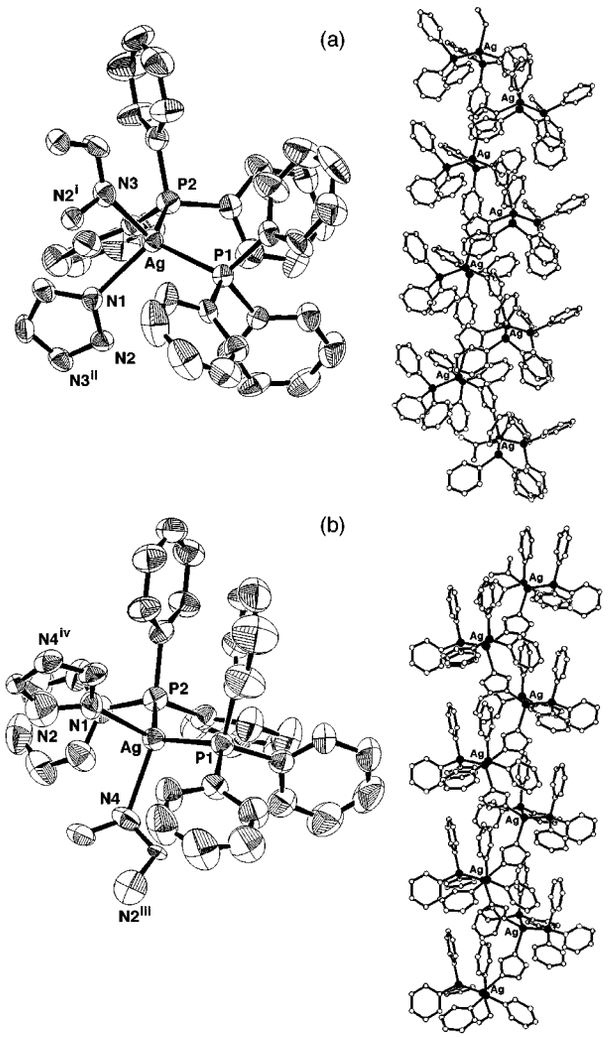

Fig. 1 (a) Molecular structure of the local coordination around each silver(I) center of $[Ag(1,2,3\text{-}L)(PPh_3)_2]_n$ **3** with 50% probability ellipsoids (symmetry operations; i; $x, -y, z - 0.5$, ii; $x, -y, z + 0.5$) and its helical polymer structure. (b) Molecular structure of the local coordination around each silver(I) center of $[Ag(1,2,4\text{-}L)(PPh_3)_2]_n$ **4** with 50% probability ellipsoids (symmetry operations iii; $1.5 - x, y - 0.5, 0.5 - z$, iv; $1.5 - x, y + 0.5, 0.5 - z$) and its helical polymer structure.[33] In both polymeric structures, black circles represent silver atoms, and small and large gray circles represent nitrogen and phosphorus atoms, respectively.

$(PPh_3)_2]_n$ **3** and $[Ag(1,2,4\text{-}L)(PPh_3)_2]_n$ **4** (HL = triazole), as crystals and characterized them both to be helical polymers in the solid state by single-crystal X-ray diffraction (Fig. 1).[33]

In a separate account, the development of crystalline Au^I compounds with a 2-coordinate AuSP core stems from the discovery of auranofin [(tetraacetylthioglucose)(triethylphosphine)gold(I)],[4] which has been used in chemotherapy as an effective anti-arthritic agent for oral administration, although the mechanism of the action is not established yet. We have also been interested in the anti-arthritic activity of the crystalline nitrogen-centered gold(I) complexes described here.

Thus, in the present work, we have aimed at (i) preparing the neutral gold(I) complexes $[Au(1,2,3\text{-}L)(PPh_3)]$ **1** and $[Au(1,2,4\text{-}L)(PPh_3)]_2 \cdot xH_2O$ ($x = 0.5$–1.0) **2** with two nitrogen-containing heterocyclic ligands, 1,2,3- and 1,2,4-triazole, in the presence of an auxiliary P-donor ligand, (ii) determining by their crystal structure analysis whether an Au···Au interaction occurs in them, (iii) comparing their molecular structures with those of the silver(I) analogs **3** and **4** and (iv) elucidating the solution behavior of **1** and **2**.

Herein we report full details of the synthesis and isolation of **1** as colorless needle crystals and **2** as colorless cubic crystals. The compositional characterization of **1** and **2** in the solid state has been achieved by complete elemental analyses, FT-IR, thermogravimetric and differential thermal analyses (TG/DTA) and the structural characterization with single-crystal X-ray crystallography. The Au···Au interaction found in **2** in the solid state is a rare example. Also reported are the characterization of **1** and **2** by solution NMR (^{31}P, ^1H and ^{13}C) spectroscopies and solution molecular-weight measurements.

Results and discussion

Compositional characterization

Two gold(I) complexes with triazole (HL) and triphenylphosphine ligands, **1** and **2**, were synthesized by stoichiometric reactions in acetone of the precursor complex $[AuCl(PPh_3)]$ with HL in the presence of NaOH, and isolated in 51.0% (0.29 g) and 53.6% (0.29 g) yields, respectively, as colorless crystals soluble in most organic solvents, by a vapor diffusion method with benzene/hexane as the internal/external solvents.

Complete elemental analyses of **1** and **2** for C, H, N, P and Au, for the samples dried overnight at room temperature under 10^{-3}–10^{-4} Torr, showed that their compositions had molar ratios of $Au^I : L : PPh_3 = 1 : 1 : 1$. Their TG/DTA measurements done under atmospheric conditions confirmed the absence of any solvated molecules for **1** because no weight loss was observed below the decomposition temperature 198 °C and the presence of 0.5–1.0 hydrated water for **2** because 1.31% weight loss was observed below the decomposition temperature 195 °C.

IR measurements confirm the presence of coordinated PPh_3 molecules in **1** as typical vibrational bands at 1479, 1435, 748, 711, 691, 547 and 504 cm^{-1} and at 1487, 1436, 747, 712, 694, 544 and 500 cm^{-1} in **2**. In both complexes, the IR measurements also show that L coordinates to the gold(I) atom as a triazolate anion, but not as a neutral triazole, because multiple vibrational bands due to N–H stretchings observed in free HL in the 3100–2600 cm^{-1} region disappear. Thus, molecular formulae of **1** and **2** in the solid state can then be represented as having a general formula of $[AuL(PPh_3)]_n$.

From single-crystal X-ray analysis, described later, the gold(I) compounds **1** and **2** are a monomer and dimer in the solid state, respectively, which is in contrast with the silver(I) analogs **3** and **4** which are helical polymers in the solid state (Fig. 1).[33]

On the other hand, molecular weight measurements in acetone solution revealed that both **1** and **2** were present as a monomeric species in solution. Probably these complexes are also monomeric in CH_2Cl_2 solution, because their solution ^{31}P NMR spectra are virtually identical.

Molecular structures

Single crystals suitable for single-crystal X-ray analysis were obtained for **1** and **2**. The molecular structures of **1** and **2** with the atom numbering scheme are depicted in Figs. 2 and 3, respectively. Selected bond distances and angles with their estimated standard deviations are listed in Table 1.

The neutral complex **1** is a monomer consisting of an $AuL(PPh_3)$ core coordinated by a triazolate anion, in which the geometry around the gold(I) atom is described as almost linear coordination, the P–Au–N angle being 178.7(5)°. Among the three nitrogen atoms of 1,2,3-triazolate, the N(2) and N(3) atoms do not participate in the coordination. In Table 2, bond distances and angles of the previously reported neutral and ionic gold(I) complexes are listed. The bond distance Au–N [1.98(2) Å] in **1** is slightly shorter, but the distance Au–P

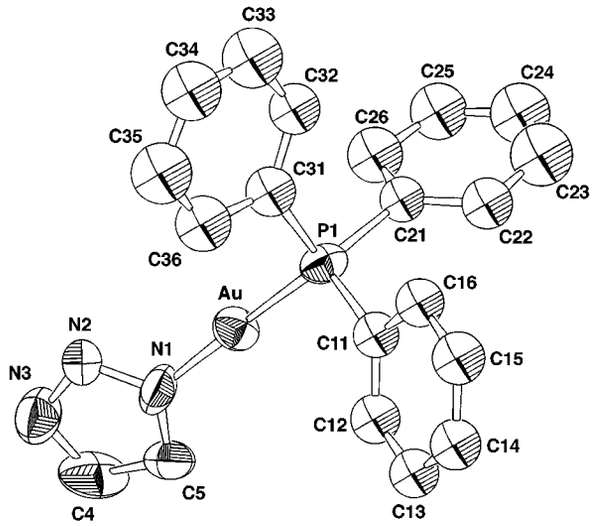

Fig. 2 Molecular structure of [Au(1,2,3-L)(PPh_3)] **1** with 50% probability ellipsoids.

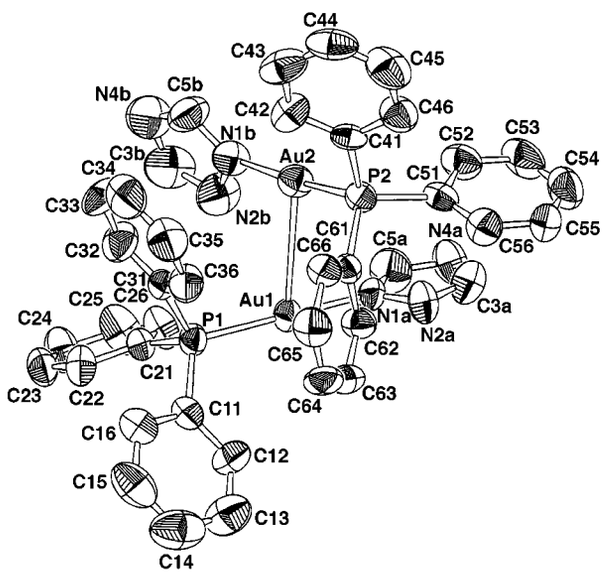

Fig. 3 Molecular structure of [Au(1,2,4-L)(PPh_3)]$_2$ **2** with 50% probability ellipsoids.

[2.229(5) Å] in **1** is similar to those in the reported neutral complexes; [Au(L^1)(PPh_3)] (HL^1 = 1-methylthymine) [Au–N and Au–P, 2.20(1) and 2.240(5) Å, respectively],[36n] [Au(L^2)(PPh_3)] (HL^2 = 6-methylpyridone) [2.077(9) and 2.236(3) Å],[27b] [Au(pyrmd)(PPh_3)] [2.042(24) and 2.235(7) Å],[24] [Au(L^3)(PPh_3)] (HL^3 = 3,7-dihydro-1,3-dimethyl-1*H*-purine-2,6-dione) [2.047(6) and 2.231(2) Å][35] and [Au(L^4)(PPh_3)] (HL^4 = 7-azaindole) [2.033(5) and 2.233(1) Å].[34]

The most interesting feature in **2** is the presence of an intramolecular Au(1)–Au(2) distance of 3.1971(6) Å, which is significantly less than twice the van der Waals radii for gold, 3.60 Å, indicating a weak intramolecular interaction between the two AuL(PPh_3) cores. This complex with one water of hydration in the crystals has an isolated dimeric unit without any intermolecular interaction. In this dimeric complex **2**, the N(2) and N(4) atoms of 1,2,4-triazolate similarly do not participate in the coordination to the gold(I). The two Au–N distances [Au(1)–N(1a) 2.026(7), Au(2)–N(1b) 2.037(7) Å] and the two Au–P distances [Au(1)–P(1) 2.243(2), Au(2)–P(2) 2.238(2) Å] are comparable with those of **1**. The geometry around each gold(I) atom was also described as almost linear coordination, the P(1)–Au(1)–N(1a) and P(2)–Au(2)–N(1b) angles being 177.1(2) and 172.7(3)°, respectively. In the very closely related

Table 1 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

1		**2**	
Au–P1	2.229(5)	Au1–Au2	3.1971(6)
Au–N1	1.98(2)	Au1–P1	2.243(2)
P1–C11	1.80(2)	Au2–P2	2.238(2)
P1–C21	1.83(2)	Au1–N1a	2.026(7)
P1–C31	1.82(3)	Au2–N1b	2.037(7)
N1–N2	1.31(2)	P1–C11	1.826(9)
N2–N3	1.33(2)	P1–C21	1.807(8)
N1–C5	1.36(3)	P1–C31	1.795(9)
N3–C4	1.35(4)	P2–C41	1.831(9)
		P2–C51	1.803(9)
		P2–C61	1.826(8)
		N1a–N2a	1.364(9)
		N1a–C5a	1.32(1)
		N4a–C3a	1.31(1)
		N4a–C5a	1.32(1)
		N1b–N2b	1.367(10)
		N1b–C5b	1.34(1)
		N2b–C3b	1.33(1)
		N4b–C3b	1.32(1)
		N4b–C5b	1.30(1)
P1–Au–N1	178.7(5)	P1–Au1–N1a	177.1(2)
Au–P1–C11	111.9(8)	P2–Au2–N1b	172.7(3)
Au–P1–C21	114.2(7)	Au1–Au2–P2	101.06(6)
Au–P1–C31	112.6(9)	Au2–Au1–P1	98.21(6)
Au–N1–N2	121(1)	Au1–Au2–N1b	85.0(2)
Au–N1–C5	130(1)	Au2–Au1–N1a	83.7(2)
N1–N2–N3	111(1)	Au1–N1a–N2a	121.6(6)
C11–P1–C21	108(1)	Au1–N1a–C5a	132.4(8)
C11–P1–C31	103(1)	Au2–N1b–N2b	122.7(7)
C21–P1–C31	104(1)	Au2–N1b–C5b	130.1(8)
N2–N1–C5	107(2)	Au1–P1–C11	114.8(3)
N2–N3–C4	104(2)	Au1–P1–C21	110.2(3)
		Au1–P1–C31	113.1(3)
		Au2–P2–C41	108.7(3)
		Au2–P2–C51	117.0(3)
		Au2–P2–C61	113.3(3)

complex **1**, there exists neither an intermolecular nor intramolecular gold(I)–gold(I) interaction. The AuNP core with the gold(I)–gold(I) interaction is not very common as listed in Table 3; the only precedents are the ionic complexes, [Au(NH_2Bu^t)(PMe_3)]$^+BF_4^-$ with the Au–Au distance of 3.047(1) Å and [{Au(PMe_3)}$_2$NH(CH_2Ph)]$^+BF_4^-$ with 3.171(1) and 3.143(1) Å, Table 3.[23] Thus, the gold(I)–gold(I) interaction within the neutral N–Au–P complex found in **2** is a very rare case.

The pairing of gold(I) atoms either intra- or intermolecularly and the formation of polymers *via* metal–metal interactions are well-established phenomena in gold(I) coordination chemistry.[21a] As to the gold(I)–gold(I) interaction, it has been suggested that neither is there a correlation between the nature of the gold(I)–gold(I) interaction, *i.e.*, intramolecular *vs.* intermolecular, and the Au–Au distance. Recently it has been suggested, however, that the steric effects play a decisive role in the formation of gold(I)–gold(I) contacts.[23]

In the present complexes **1** and **2** with a common bulky PPh_3 ligand, the difference between their ligands is only in the position of one nitrogen atom, *i.e.*, N(3) or N(4), within the triazolate ring. The difference in basicity of their nitrogen atoms should not be very large, because both nitrogen atoms can coordinate to silver(I) atoms as recently found in the corresponding silver(I) analogs **3** and **4**, where the triazolate ligands bridge two silver(I) atoms to form helical polymer structures. In **2**, one triazolate ring (N1b–C5b) nearly overlaps with one (C31–C36) of phenyl rings in the PPh_3 group with a separation in the range of 3.4–4.0 Å, suggesting the possibility of stabilization by a stacking interaction between them. However, since this complex is not symmetrical, the stacking of the other triazolate ring (N1a–C5a) is not observed. Thus, the features observed in **1** and **2** are in contrast to those of [Au(NH_2Bu^t)(PMe_3)]$^+BF_4^-$ and [Au(NH_2Bu^t)($PMePh_2$)]$^+BF_4^-$ with and

Table 2 Comparison of Au–N and Au–P distances (Å) and P–Au–N angle (°) for structures containing AuNP core

	Au–N	Au–P	P–Au–N	Ref.
$[Au(NMe_3)(PPh_3)]ClO_4$	2.108(7)	2.231(2)	179.3(2)	28
$[Au(qncd)(PPh_3)]BF_4$	2.11(1)	2.240(4)	173.0(3)	29
$[Au(dmpy)(PPh_3)]ClO_4$	2.091(3)	2.233(4)	178.8(3)	30
$[Au(napy)(PPh_3)]ClO_4$	2.093(13)	2.230(4)	174.3(4)	30
$[Au(pbzim)(PPh_3)]ClO_4$	2.075(4)	2.238(1)	172.4(1)	30
$[\{Au(PPh_3)\}_4(\mu\text{-bbzim})](ClO_4)_2$	2.03(2)	2.236(6)	172.3(5)	31
	2.05(1)	2.233(5)	173.9(5)	
	2.06(1)	2.239(5)	171.2(4)	
	2.06(2)	2.233(5)	174.7(5)	
$[Au(NH_2Bu^t)(PMe_3)]BF_4$	2.13(1)	2.236(4)	175.7(4)	23
	2.11(1)	2.235(3)	174.8(3)	
$[Au(NH_2Bu^t)(PPh_2Me)]BF_4$	2.105(8)	2.235(3)	176.4(2)	23
$[\{Au(PMe_3)\}_2NH(CH_2Ph)]BF_4$	2.071(8)	2.246(3)		23
	2.073(8)	2.248(3)		
$[Au(L^1)(PPh_3)]$	2.20(1)	2.240(5)	178.7(4)	36(*n*)
$[Au(L^2)(PPh_3)]$	2.077(9)	2.236(3)	173.4(3)	27(*b*)
$[Au(pyrmd)(PPh_3)]$	2.042(24)	2.235(7)	174.5(6)	24
$[Au(L^4)(PPh_3)]$	2.033(5)	2.233(1)	176.6(2)	34
$[Au(L^3)(PPh_3)]$	2.047(6)	2.231(2)	176.1(2)	35
$[\{Au(PPh_3)\}_2(\mu\text{-bbzim})]$	2.053(9)	2.228(3)	176.9(3)	31
[Au(1,2,3-L)(PPh_3)] **1**	1.98(2)	2.229(5)	178.7(5)	*a*
$[Au(1,2,4\text{-L})(PPh_3)]_2$ **2**	2.026(7)	2.243(2)	177.1(2)	*a*
	2.037(7)	2.238(2)	172.7(3)	

dmpy = 2,6-dimethylpyridine; napy = 1,8-naphthyridine; pbzim = 2-(2-pyridyl)benzimidazole. *a* This work.

without the gold(I)–gold(I) interaction, respectively, because it has been considered that steric effects of the bulky Bu^t and $PMePh_2$ groups prevent the intimate approach required for metal–metal contact in the $[Au(NH_2Bu^t)(PMePh_2)]^+BF_4^-$ complex.[23]

Solution NMR (^{31}P, ^1H and ^{13}C)

The ^{31}P NMR spectra (Fig. 4a, 4c) measured at room temperature in CD_2Cl_2 of **1** and **2** show only one resonance at δ 31.1 and 31.5, respectively, the chemical shifts of which are in the region usually observed for the PPh_3 ligands coordinated to gold(I) and can be compared with those of related compounds: [Au(im)(PPh_3)] at δ 32.46 and [AuCl(PPh_3)] at δ 33.40.[18,37] These resonances are observed at much lower field than those of PPh_3 coordinated to a silver(I) atom, *e.g.*, **3** at δ 6.48,[33] **4** at δ 4.84,[33] [Ag(im)$(PPh_3)_3$] at δ 3.71,[18] $[Ag_2(pz)_2(PPh_3)_2]$ at δ 9.87 and $[Ag_2(pz)_2(PPh_3)_3]$ at δ 6.13.[32a]

The low-temperature ^{31}P NMR measurements showed that (i) the single peak in **1** in CD_2Cl_2 observed at δ 31.1 at room temperature was split into two peaks at δ 30.6 and 30.0 with an intensity ratio of 2:1 at −90 °C (Fig. 4b), and (ii) the original single-line spectrum was recovered at room temperature from the low-temperature splitting ^{31}P NMR spectrum. On the other hand, the single peak in **2** in CD_2Cl_2 at δ 31.5 at room temperature was observed as a single peak at δ 30.5 at −90 °C (Fig. 4d). Both complexes should be present as a monomer in solution, because of their solution molecular weight measurements. Thus, the low-temperature ^{31}P NMR measurements indicate that, in solution at room temperature, the coordination of nitrogen atoms on the triazolate ligand to the gold(I) atom exchange dynamically; in **1** all three nitrogen atoms [N(1), N(2) and N(3)] participate in coordination at room temperature, while in **2** only two nitrogen atoms [N(1) and N(2)] do, but N(4) does not.

The ^1H and ^{13}C NMR spectra of **1** and **2** measured at room temperature in CD_2Cl_2 exhibit only one resonance for the coordinating triazolate anion, respectively, also as a result of dynamic exchange. However, in response to the low-temperature ^{31}P NMR spectra, the single ^1H NMR peak at δ 7.80 at room temperature for the 1,2,3-triazolate ligand of **1** is changed to the splitting peaks at δ 7.75 and 7.82 at −90 °C.

The solution NMR (^{31}P, ^{109}Ag, ^1H and ^{13}C) spectra at room temperature of the corresponding silver(I) complexes **3** and **4** have been also interpreted as averaged signals resulting from the rapid dynamic exchange among several unequivalent ^{109}Ag

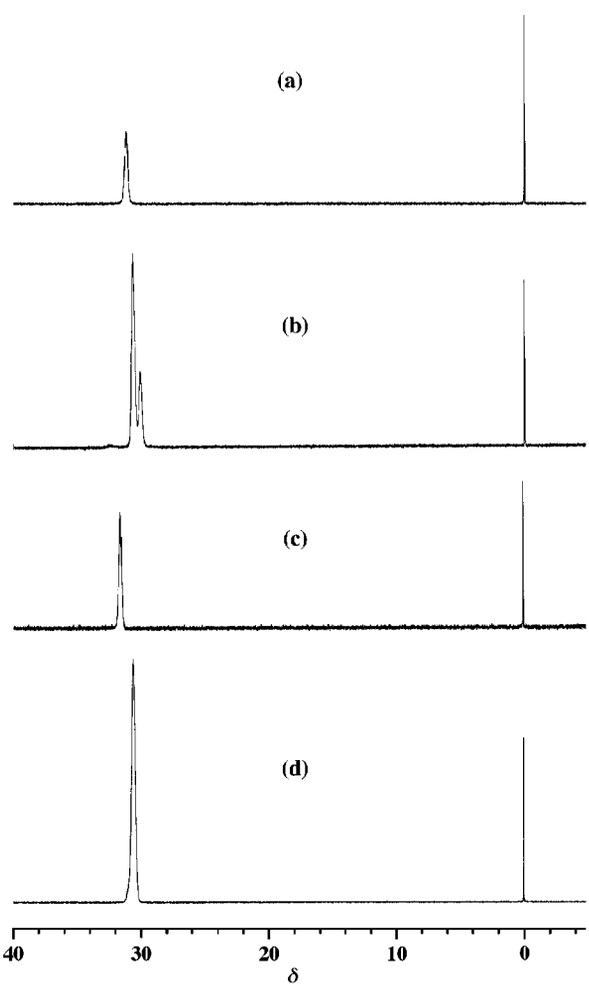

Fig. 4 ^{31}P-{^1H} NMR spectra measured in CD_2Cl_2 of [Au(1,2,3-L)(PPh_3)] **1** (a) at room temperature and (b) at −90 °C, and of $[Au(1,2,4\text{-L})(PPh_3)]_2$ **2** (c) at room temperature and (d) at −90 °C.

Table 3 Comparison of Au–Au interactions and distances (Å) for structures containing AuYP core (Y = Cl, SR and N)[a]

Entry	Complexes	Au–Au	Ref.
Intramolecular Au–Au interactions			
1	$[Au_2(Cl)_2(dppm)]$	3.351(2)	36(*c*)
2	$[Au_2(Cl)_2\{[(Ph_2P)_2C]PMe_3\}]$	3.000(1)	36(*b*)
3	$[Au_2(Cl)_2\{1,1'$-bis(diphenylphosphino)-1,1′-bicyclopropyl$\}]$	3.085(1)	36(*d*)
4	$[Au_2(Cl)_2(Ph_2PCHCHPPh_2)]$	3.05(1)	36(*e*)
5	$[Au_2(SCH_2CH_2PEt_2)_2]$	3.104	36(*f*)
6	$[Au_2(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_2]$	3.096(2)	22
7	$[Au_3(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)_3]$	2.9624(12) 3.1966(14)	22
8	$[Au_2\{S_2CN(C_2H_4OMe)_2\}_2]$	2.7902(6)	20
9	$[Au_4(\mu\text{-}S_2C_6H_3CH_3)_2(PEt_3)_2]$	3.104(6) 3.058(3) 3.116(6) 3.017(3)	36(*o*)
10	$[Au_4Ag(CH_2SiMe_3)_4(\mu\text{-dppm})_2]SO_3CF_3$	3.2170(9) 3.2773(12)	36(*q*)
11	$[\{Au(PPh_3)\}_4(\mu\text{-bbzim})](ClO_4)_2$	3.157(1) 3.222(1)	31
12	$[\{Au(PMe_3)\}_2NH(CH_2Ph)]BF_4$	3.171(1)	23
13	$[Au(1,2,4\text{-L})(PPh_3)]_2$ **2**	3.1971(6)	[b]
Intermolecular Au–Au interactions			
14	$[Au(Cl)\{2,4,6\text{-}(Bu^t)_3C_6H_2Ph_2\}]_2$	3.440(1)	36(*g*)
15	$[Au_2(Cl)_2(dppe)]_2$	3.189(1)	36(*h*)
16	$[Au_2(Cl)_2(dppe)]_2$	3.187(1) 3.221(1)	36(*i*)
17	$[Au_2(Cl)_2\{Ph_2P(CH_2)_2AsPh_2\}]_2$	3.21	36(*j*)
18	$[Au_2(Cl)_2\{Ph_2PCH_2As(Ph)CH_2PPh_2\}]_2$	3.141(1)	36(*a*)
19	$[Au_2(1,3\text{-}S_2C_6H_4)(PPh_3)_2]$	3.0834(8)	22
20	$[Au_2\{S_2CN(C_2H_4OMe)_2\}_2]$	3.1572(7)	20
21	[AuSPh(*o*-OMe)(TPA)]	3.263(2) 3.341(2)	36(*p*)
22	$[AuSPh(3,5\text{-}Cl_2)(TPA)]$	3.0468(10)	36(*p*)
23	$[Au(NH_2Bu^t)(PMe_3)]BF_4$	3.047(1)	23
24	$[\{Au(PMe_3)\}_2NH(CH_2Ph)]BF_4$	3.143(1)	23
25	$[Au(NH{=}CMe_2)_2]CF_3SO_3$	3.1663(5) 3.1705(5)	36(*r*)
26	$[Au(C{\equiv}CSiMe_3)(CNBu^t)]$	3.1244(10)	36(*r*)
27	$[AuCl(Ph_2C{=}NH)]$	3.3633(5)	36(*s*)
28	$\{[Au(Ph_2C{=}NH)_2][AuCl_2]\}_2$	3.1944(5)	36(*s*)
Polymers			
29	$[Au_2(Cl)_2(Ph_2PCHCHPPh_2)]_n$	3.043(1)	36(*k*)
30	$[Au_2(Cl)_2\{Ph_2PCH_2C(CH_2)CH_2PPh_2\}]_n$	3.294	36(*l*)
31	$[Au_2(Cl)_2(dppp)]_n$	3.316	36(*m*)
32	$[Au_2(p\text{-tc})_2(dppb)]_n$	3.094(1)	21(*a*)
33	$[Au_2(p\text{-tc})_2(dpppn)]_n$	3.200(1)	21(*a*)

dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; dpppn = 1,5-bis(diphenylphosphino)pentane; *p*-tc = *p*-thiocresol; TPA = 1,3,5-triaza-7-phosphaadamantanetriylphosphine; SPh(*o*-OMe) and $SPh(3,5\text{-}Cl_2)$ are benzenethiolate ligands with substituent groups as indicated. [a] This table is made by supplementing many additional data to the table previously reported by Narayanaswamy *et al.*[21a] [b] This work.

species containing ionic species such as $[Ag(PPh_3)_4]^+L^-$ and $[Ag(PPh_3)_2]^+L^-$.[33]

Conclusion

Using nitrogen-containing heterocycles, 1,2,3-triazole and 1,2,4-triazole (HL), in the presence of PPh_3, two novel neutral complexes $[Au(1,2,3\text{-L})(PPh_3)]$ **1** and $[Au(1,2,4\text{-L})(PPh_3)]_2 \cdot xH_2O$ (x = 0.5–1.0) **2** were isolated as colorless crystals in good yields and their crystal structures determined by single-crystal X-ray diffraction. Two heterocyclic ligands in these complexes act as anionic monodentate ligands. Complex **1** consisted of a monomeric 2-coordinate AuNP core in the solid state, while **2** comprised of a dimeric $(AuNP)_2$ core through an Au–Au bond in the solid state. The Au···Au interaction found in **2** in the solid state is rare. These features were in contrast to the fact that the two corresponding silver(I) analogs $[Ag(1,2,3\text{-L})(PPh_3)_2]_n$ **3** and $[Ag(1,2,4\text{-L})(PPh_3)_2]_n$**4** are helical polymers constituted by bridging triazolate ligands in the solid state. On the other hand, **1** and **2** in solution were present as a monomeric species. Their solution (^{31}P, ^1H and ^{13}C) NMR spectra measured at room temperature were interpreted based on the presence of an equilibrium due to the rapid dynamic exchange on the NMR timescale, the presence of which was evidenced from low-temperature ^{31}P NMR measurements. The title complexes are also of interest as a possible new type of metal-based drug; studies of their biological activities are planned.

Experimental

Materials

The following were used as received: 1,2,4-triazole, $NaAuCl_4 \cdot 2H_2O$, NaOH, triphenylphosphine, dichloromethane, ethanol, methanol, diethyl ether, hexane, light petroleum (bp: 30–60 °C), acetone, benzene (all from Wako); 1,2,3-triazole (Aldrich); CD_2Cl_2, acetone-d_6 (Isotec). $[AuCl(PPh_3)]$ was prepared according to the literature.[37] Benzene should be used in a fume hood as it is toxic.

Instrumentation/analytical procedures

Elemental analyses after overnight drying under 10^{-3}–10^{-4} Torr were carried out by Mikroanalytishes Labor Pascher (Remagen, Germany). Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out using a Rigaku TG 8101D and TAS 300 data processing system. TG/DTA measurements were run under air with a temperature ramp of 1 °C min^{-1} between 20 and 500 °C. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer in KBr disks at room temperature.

Molecular weight measurements in acetone solutions based on the vaporimetric method using a vapor pressure osmometer were done by Mikroanalytishes Labor Pascher (Remagen, Germany) and evaluated for 11.285 mg of the complex **1** dissolved in 0.9367 g of acetone and for 11.309 mg of the complex **2** dissolved in 0.8301 g of acetone.

^{1}H NMR (399.65 MHz), ^{13}C-{^{1}H} NMR (100.40 MHz) and ^{31}P-{^{1}H} NMR (161.70 MHz) spectra in solution were recorded at 22 °C in 5 mm outer diameter tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data processing system. ^{1}H and ^{13}C-{^{1}H} NMR spectra of the complexes were measured in CD_2Cl_2 solution with reference to internal $SiMe_4$. Chemical shifts are reported on the δ scale and resonances downfield of $SiMe_4$ (δ 0) are recorded as positive. ^{31}P-{^{1}H} NMR (161.70 Hz) spectra were measured in CD_2Cl_2 or acetone-d_6 solution with reference to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts are reported as negative for resonances upfield of H_3PO_4 (δ 0).

Preparations

[Au(1,2,3-L)(PPh$_3$)] 1. 0.495 g (1.00 mmol) of [AuCl(PPh$_3$)] and 0.072 g (1.04 mmol) of 1,2,3-HL were dissolved in 100 mL acetone. To the solution 1.0 mL of 1.0 M NaOH aqueous solution (1.00 mmol) was added. During 1 h stirring, white powder of NaCl was produced and it was filtered off using a folded filter paper (Whatman No. 2). The obtained colorless clear filtrate was evaporated to dryness at 50 °C with a rotary-evaporator. The residue was dissolved in 30 mL benzene. The clear filtrate obtained through a folded filter paper (Whatman No. 2) was added dropwise to 200 mL hexane. White precipitates formed, which were collected on a membrane filter (JG 0.2 μm), washed twice with 20 mL light petroleum and dried thoroughly by suction.

Crystallization was performed by vapor diffusion method. The obtained white powder was redissolved in 15 mL benzene and the solution was filtered through a folded filter paper (Whatman No. 2). The colorless filtrate was placed in an internal small vial and hexane used as an external solvent within a screw-capped vial for the vapor diffusion. After 6 h at room temperature, colorless needle crystals began to form. After a few days, the crystals were collected on a membrane filter (JG 0.2 μm), washed twice with 100 mL light petroleum, and dried *in vacuo* for 2 h. Yield was 0.29 g (51.0%). Relatively light- and thermally-stable, colorless needle crystals obtained as compound **1** were soluble in methanol, ethanol, acetone, dichloromethane, chloroform, benzene and DMSO, but insoluble in diethyl ether, light petroleum, hexane and water.

For the sample dried overnight at room temperature under 10^{-3}–10^{-4} Torr: Found: C, 45.33; H, 3.22; N, 7.92; P, 5.80; Au, 37.40, total 99.67%. Calc. for $C_{20}H_{17}N_3PAu$ or [Au(1,2,3-L)(PPh$_3$)]: C, 45.56; H, 3.25; N, 7.97; P, 5.87; Au, 37.35%. TG/DTA data under atmospheric conditions: no weight loss was observed below the decomposition temperature; decomposition began around 198 °C with an endothermic peak at 198 °C and exothermic peaks at 212 and 258 °C. Molecular weight measurement: 512 in acetone; calc. 527.3 for [Au(1,2,3-L)(PPh$_3$)]. Some prominent IR bands in the 1700–400 cm^{-1} region (KBr disk): 1479m, 1435vs, 1400w, 1309w, 1226w, 1184w, 1101s, 1070w, 1043s, 998m, 795m, 748s, 711s, 691vs, 547vs, 504vs cm^{-1}. ^{1}H NMR measured in CD_2Cl_2 with reference to internal $SiMe_4$ at room temperature: δ 7.50 (15H, m, aryl protons), 7.80 (2H, s, H4 + H5 of L). ^{1}H NMR in CD_2Cl_2 at −90 °C: δ 7.52, 7.61 (15H, m, aryl), 7.82, 7.75 (2H, s, H4 + H5 of L). ^{13}C NMR measured in CD_2Cl_2 with reference to internal $SiMe_4$ at room temperature: δ 131.51 (C4 + C5 of L), 128.79 (d, J_{CP} 64.3, phenyl), 129.74 (d, J_{CP} 11.0, phenyl), 132.53 (s, phenyl), 134.67 (d, J_{CP} 13.1 Hz, phenyl). ^{31}P NMR measured at room temperature with reference to an external 25% aqueous H_3PO_4 in a sealed capillary: δ 31.1 in CD_2Cl_2 and δ 32.1 in acetone-d_6. ^{31}P NMR measured in CD_2Cl_2 at −90 °C by a substitution method: δ 30.6, 30.0.

[Au(1,2,4-L)(PPh$_3$)]$_2$·xH$_2$O (x = 0.5–1.0) 2. Compound **2** was isolated in a similar manner to the work-up described above using 0.040 g (1.00 mmol) of solid NaOH, 0.069 g (1.00 mmol) of 1,2,4-HL in 10 mL methanol and 0.495 g (1.00 mmol) of [AuCl(PPh$_3$)] suspended in 20 mL methanol, instead of 1.0 M aqueous NaOH, 1,2,3-HL and 100 mL acetone as the initial solvent. Yield was 0.29 g (53.6% with respect to one hydrated species). Relatively light- and thermally-stable, colorless cubic crystals were soluble in methanol, ethanol, acetone, dichloromethane, chloroform, benzene and DMSO, but insoluble in diethyl ether, light petroleum, hexane and water.

For the sample dried overnight at room temperature under 10^{-3}–10^{-4} Torr: Found: C, 45.24; H, 3.05; N, 7.90; P, 5.80; Au, 37.20, total 99.19%. Calc. for $C_{20}H_{17}N_3PAu$ or [Au(1,2,4-L)(PPh$_3$)] as a monomer unit: C, 45.56; H, 3.25; N, 7.97; P, 5.87; Au, 37.35%. TG/DTA data under atmospheric conditions: 1.31% weight loss was observed below the decomposition temperature; calc. 0.85% for x = 0.5 and 1.68% for 1.0 in [Au(1,2,4-L)(PPh$_3$)]·xH$_2$O; decomposition began around 195 °C with an endothermic peak at 195 °C and exothermic peaks at 324 and 470 °C. Molecular weight measurement: 545 in acetone; calc. 527.3 for [Au(1,2,4-L)(PPh$_3$)] as a monomer unit. Some prominent IR bands in the 1700–400 cm^{-1} region (KBr disk): 1487s, 1436s, 1375w, 1284w, 1255m, 1192m, 1154m, 1101s, 1082m, 1027w, 997m, 964w, 867m, 854m, 747s, 712m, 694vs, 544vs, 500s cm^{-1}. ^{1}H NMR measured in CD_2Cl_2 with reference to internal $SiMe_4$ at room temperature: δ 7.50 (15H, m, aryl protons), 8.05 (2H, s, H3 + H5 of L), 2.15 (H_2O). ^{13}C NMR measured in CD_2Cl_2 with reference to internal $SiMe_4$ at room temperature: δ 150.79 (C3 + C5 of L), 128.80 (d, J_{CP} 62.3, phenyl), 129.77 (d, J_{CP} 13.1, phenyl), 132.53 (s, phenyl), 134.66 (d, J_{CP} 15.1 Hz, phenyl). ^{31}P NMR measured at room temperature with reference to an external 25% aqueous H_3PO_4 in a sealed capillary: δ 31.5 in CD_2Cl_2 and δ 32.4 in acetone-d_6. ^{31}P NMR measured in CD_2Cl_2 at −90 °C by a substitution method: δ 30.5.

X-Ray crystallography

Compounds **1** and **2** formed colorless needle crystals and colorless cubic crystals, respectively, by vapor diffusion of the benzene–hexane system. During a few days standing of the solutions at room temperature, crystals of sufficient quality for single-crystal X-ray diffraction studies were grown.

Each single-crystal of **1** and **2** was mounted on glass fiber and transferred to a Rigaku AFC5S diffractometer. Cell contents and orientation matrix of **1** and **2** were obtained from the least-squares refinement of 18 and 25 reflections, respectively. The reflection data were collected using ω–2θ scan with graphite-monochromated Mo-Kα radiation at room temperature. The intensities of three standard reflections which were measured after every 150 reflections remained constant throughout data collection. The data were corrected for Lorentz and polarization effects and empirical absorption corrections based on ψ scans were applied to the data. For the overall averaged transmission curve, the transmission factors of **1** and **2** were in the range of 0.49–1.00 and 0.65–1.00, respectively. The structures were solved by direct methods followed by subsequent differ-

Table 4 Summary of crystal data

	[Au(1,2,3-L)(PPh_3)]	[Au(1,2,4-L)(PPh_3)]$_2$·H_2O
Formula	$C_{20}H_{17}N_3PAu$	$C_{40}H_{36}N_6P_2Au_2O$
M	527.31	1072.64
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P2_1/c$ (no. 14)
a/Å	12.689(4)	13.575(3)
b/Å	13.660(7)	11.623(3)
c/Å	10.93(1)	24.739(2)
β/°		101.35(1)
V/Å^3	1894(1)	3827(1)
F(000)	1008	2056
Z	4	4
D_c/g cm^{-1}	1.849	1.861
Crystal size/mm	0.3 × 0.2 × 0.2	0.3 × 0.3 × 0.3
No. of reflections used for unit cell dimension	18	25
(2θ range/°)	(20.1–25.9)	(26.6–29.1)
Radiation (λ/Å)	Mo–Kα (0.71069)	Mo-Kα (0.71069)
Scan mode	ω–2θ	ω–2θ
Scan width/°	1.26 + 0.30 tan θ	0.73 + 0.30 tan θ
Scan speed/min^{-1}	4	8
2θ Range/°	6–55	6–55
μ/cm^{-1}	78.85	78.08
Total reflections	2492	9602
Unique reflections	2492	9225
Observed reflections	1561 [$I > 2.00\sigma(I)$]	4609 [$I > 2.00\sigma(I)$]
R,R'	0.052, 0.055	0.037, 0.028
Goodness of fit	1.46	1.31

$R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $R' = [\Sigma(w[|F_o| - |F_c|]^2/[\Sigma w(|F_o|)^2]]^{\frac{1}{2}}$, with $w = 4F_o^2/[\sigma^2(F_o^2)]$.

ence Fourier calculation and refined by a full-matrix least-squares procedure using TEXSAN package.[38] All non-hydrogen atoms, except carbon atoms in the phenyl group of **1**, were refined anisotropically, and all hydrogen atoms and the phenyl carbon atoms of **1** isotropically.

A summary of crystal data, data collection, and refinement for **1** and **2** is given in Table 4.

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38 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX 1985 and 1992.

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