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Two Triazole-Based Phosphine Ligands Prepared via Temperature-Mediated Li/H Exchange: Cu^{I} and Au^{I} Complexes and Structural Studies

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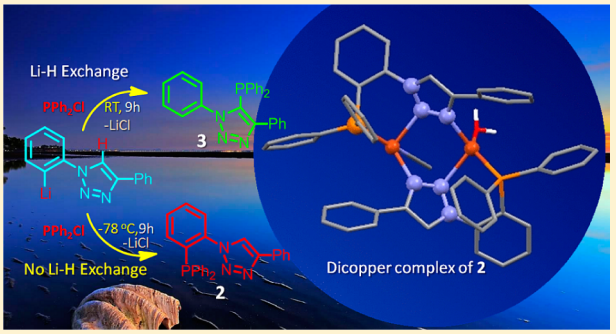
Supporting Information

ABSTRACT: The kinetically favored triazole-based phosphine 1-(2-(diphenylphosphino)phenyl)-4-phenyl-1*H*-1,2,3-triazole (**2**, L_1) and its thermodynamically preferred isomer, 5-(diphenylphosphino)-1,4-diphenyl-1*H*-1,2,3-triazole (**3**, L_2), were obtained by the temperature-controlled lithiation of 2-bromotriazole followed by the reaction with chlorodiphenylphosphine. The structures of phosphines **2** and **3** were determined by X-ray diffraction. Upon reaction with late transition-metal derivatives (Cu^{I}, Ag^{I}, and Au^{I}), phosphines **2** and **3** form complexes with monodentate (Cu^{I}, Ag^{I}, and Au^{I}; κ^{1}-*P*), chelate (Cu^{I}; κ^{2}-*P*,*N*), bridged bidentate (Cu^{I}; μ^{2}-*P*,*N*), and tridentate (Cu^{I}; μ^{2},κ^{2}-*P*,*N*,*N*) modes of coordination. Reactions with copper(I) halides produced mono-, di-, and tetranuclear complexes, whereas the reaction of **2** with $[Cu(NCCH_3)_4]BF_4$ yielded the binuclear complex $[Cu_2(CH_3CN)_2\{o\text{-}Ph_2P(C_6H_4)\{1,2,3\text{-}N_3C(Ph)C(H)\}\text{-}\mu\text{-}(\kappa\text{-}P,\kappa\text{-}N),\kappa\text{-}N\}_2](BF_4)_2$ (**10**) with the ligand acting as a six-electron donor involving phosphorus and two triazole nitrogen atoms. The copper complexes of **2** and **3** containing rhomboid Cu_2X_2 units, $[(Cu)_2(\mu\text{-}X)_2\{o\text{-}Ph_2P(C_6H_4)\{1,2,3\text{-}N_3C(Ph)C(H)\}\text{-}\kappa\text{-}P\}_2]$ (**4**, X = Cl; **5**, X = Br), on treatment with 1,10-phenanthroline and 2,2′-bipyridine gave mixed-ligand complexes of the type $[(CuX)(N\cap N\text{-}\kappa^{2}\text{-}N,N)\{o\text{-}Ph_2P(C_6H_4)\{1,2,3\text{-}N_3C(Ph)C(H)\}\text{-}\kappa\text{-}P\}]$ (N∩N = 1,10-phen and 2,2′-bipy; X = Cl, Br, and I).



INTRODUCTION

The design and synthesis of triazole-based ligand systems have drawn considerable attention in the last few decades owing to their novelty in organometallic chemistry and catalytic applications.[1−4] The copper-catalyzed version of the Huisgen 1,3-dipolar cycloaddition reaction reported by Sharpless and Meldal is a versatile click reaction for coupling azides with alkynes.[5−7] This is also a convenient method to incorporate triazole functionalities into phosphine systems or vice versa. Although triazole itself is a good ligand,[8,9] it is anticipated that incorporating phosphine moieties on the ring atoms or into the exocyclic groups would give interesting ambidentate properties, which can be exploited in catalytic reactions. For example, triazole-based phosphines such as ClickPhos $[Ph\{1,2,3\text{-}N_3C(PPh_2)C(Ph)\}]$,[10,11] ClicFerrophos $[1\text{-}PPh_2Fc\text{-}2\text{−}CH(Me)\{1,2,3\text{-}N_3C(PPh_2)C(Ph)\}]$,[12,13] ClickPhine $[Ph\{1,2,3\text{-}N_3C(CH_2PPh_2)C(Ph)\}]$,[14] and bisphosphines of the type $[R_2PCH_2\{1,2,3\text{-}N_3C(CH_2PR_2)C(H)\}]$ (R = Ph, Cy, ^{t}Bu, ^{i}Pr)[15,16] have been employed in various catalytic reactions. As an extension of our interest[17] and the interest of others[18] to get more insight into the triazole-based phosphines, we sought to examine the compatibility of triazoles with phosphorus moieties. This paper describes a very simple and efficient synthetic route to prepare two structural isomers differing in the positions of phosphorus moieties, 1-(2-(diphenylphosphino)phenyl)-4-phenyl-1*H*-1,2,3-triazole (**2**) and 5-(diphenylphosphino)-1,4-diphenyl-1*H*-1,2,3-triazole[19] (**3**), by temperature-mediated Li/H exchange reaction of 2-bromophenyl triazole (**1**). Also, copper(I) and gold(I) complexes of these two new ligands and the X-ray structures of several complexes including the ligands are described herein.

RESULTS AND DISCUSSION

Synthesis of 1-(2-(Diphenylphosphino)phenyl)-4-phenyl-1*H*-1,2,3-triazole (2) and 5-(Diphenylphosphino)-1,4-diphenyl-1*H*-1,2,3-triazole (3). The reaction of 2-bromophenyl azide with phenylacetylene in the presence of copper sulfate and sodium ascorbate under Sharpless conditions yielded 1-(2-bromophenyl)-4-phenyl-1*H*-1,2,3-triazole $[o\text{-}Br(C_6H_4)\text{-}1,2,3\text{-}N_3]$ (**1**) as a white crystalline solid in good yield. The ^{1}H NMR spectrum of **1** showed a singlet at 8.17 ppm corresponding to the triazolic proton. The reaction of **1** with ^{n}BuLi at −78 °C followed by the addition of 1 equiv of PPh_2Cl at −78 °C resulted in the formation of the kinetically stable phosphine derivative, $[o\text{-}Ph_2PC_6H_4\{1,2,3\text{-}N_3C(Ph)C\text{-}$

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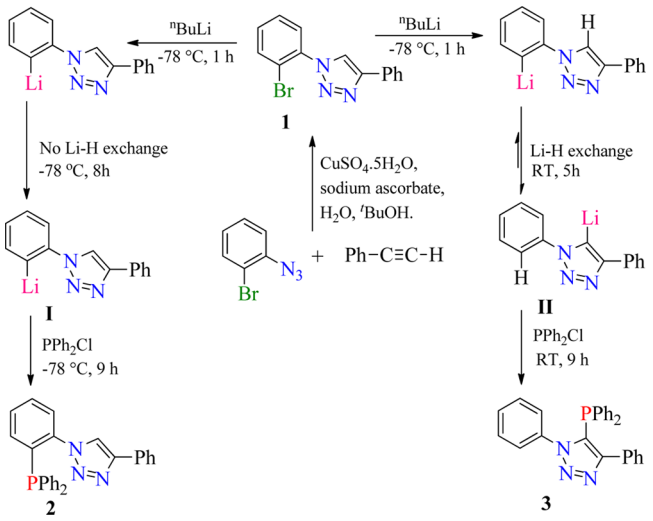
Inorg. Chem. XXXX, XXX, XXX−XXX

(H)}] (**2**). However, the successive treatment of 2-bromophenyl-triazole with ^{n}BuLi at −78 °C and 1 equiv of PPh_2Cl at room temperature yielded 5-(diphenylphosphino)-1,4-diphenyl-1*H*-1,2,3-triazole, [C_6H_5{1,2,3-$N_3C(Ph)C$-(PPh_2)}] (**3**) as a white crystalline solid as shown in Scheme 1. The lithiation of 2-bromophenyl-triazole using ^{n}BuLi gave

Scheme 1. Probable Pathways for the Formation of Phosphines 2 and 3



the kinetically favored intermediate **I** at low temperature, whereas the same reaction at room temperature resulted in the formation of thermodynamically more stable intermediate **II**. Subsequent reactions of **I** and **II** with chlorodiphenylphosphine produced new triazole-based phosphines **2** and **3**. The reaction of phenyltriazole [C_6H_4{1,2,3-$N_3C(Ph)CH$}] with ^{n}BuLi at −78 °C followed by the addition of chlorodiphenylphosphine also resulted in the formation **3** in 75% yield. The temperature-controlled lithiation of 2-bromophenyl-triazole (**1**) provides a novel methodology for the synthesis of very useful products by considering different electrophiles at the phenylic and triazolic positions of **1**. Recently, Baumann and co-workers reported[20] the one-pot synthesis of a structural isomer of **3**, namely, 4-(diphenylphosphino)-1,5-diphenyl-1*H*-1,2,3-triazole, and its di-, tri-, and tetrameric copper complexes. The $^{31}P\{^{1}H\}$ NMR spectra of **2** and **3** consist of single resonances at −15.5 and −30.2 ppm, respectively. The ^{1}H NMR spectrum of **2** showed a sharp singlet at 7.73 ppm for the triazolic proton, whereas the same was not observed in the case of **3**.

To gain some insight into the nature of isomerization process, variable-temperature (VT) ^{7}Li and ^{31}P NMR studies of **I** in diethyl ether (external locking) and phosphine **2** (in deuterated dimethyl sulfoxide (DMSO-d_6)) were performed. The dynamic NMR investigation revealed the initial formation of lithiated product **I** at low temperature showing a singlet ($\delta_{^{7}Li}$) at 1.87 ppm. When the solution was warmed, a second singlet started appearing at 1.23 ppm, the intensity of which gradually increased, whereas the intensity of the former decreased proportionately, and at 25 °C it vanished completely (Figure 1) indicating the complete isomerization of product **I** into product **II**. The VT ^{31}P NMR of phosphine **2** in DMSO-d_6 did not show any isomerization leading to the formation of phosphine **3**. The singlet ($\delta_{^{31}P}$ −15.5) observed at room temperature did not change even at 100 °C ruling out any possibility of isomerization of **2** to **3** (see Supporting Information Figure S38). Similar results were obtained in the VT cross polarization magic-angle spinning ^{31}P NMR of phosphines **2** and **3** as well. Density functional theory calculations also supported these observations (Figure 2). The initially formed lithiated product **I** at low temperature is a kinetically favored high-energy species, which, when warmed, isomerizes to thermodynamically favored low-energy species **II**.

Both the phosphines **2** and **3** were characterized by single-crystal X-ray analysis (see Figures 3). Single crystals of **2** were obtained from diethyl ether solution at 0 °C, and those of **3** were obtained from an ethanol solution of **3** stored at 0 °C for 24 h.

The asymmetric unit consists of two molecules of **2** with different orientations. In one molecule, the pyramidal geometry around the phosphorus atom (C1−P1−C7 = 104.45(11)°,

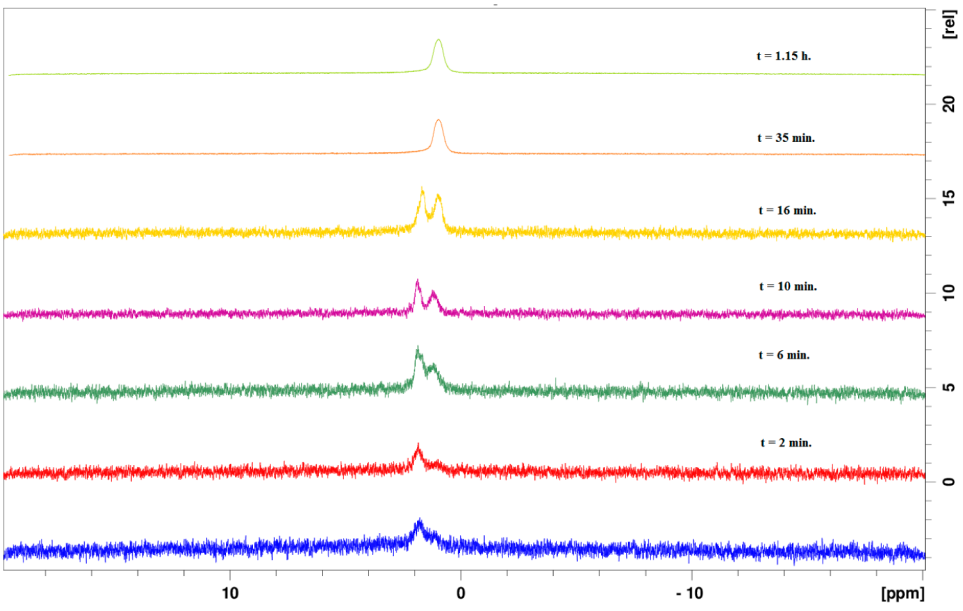


Figure 1. Time-dependent ^{7}Li NMR spectra for the reaction of **1** with *n*-butyl lithium in diethyl ether at 25 °C.

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Inorg. Chem. XXXX, XXX, XXX−XXX

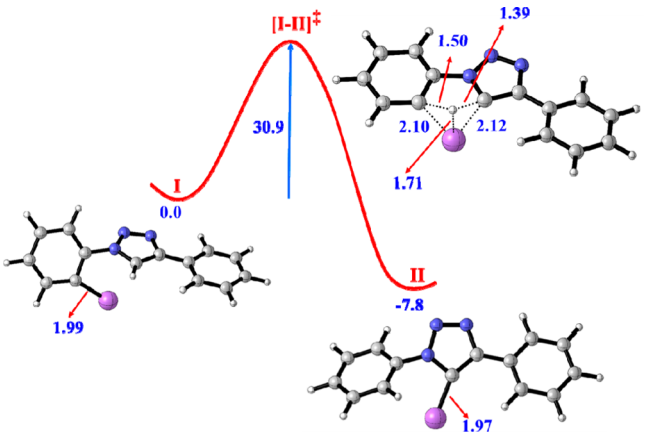

Figure 2. Lithium−hydrogen exchange transition state. Relative ΔG (in kcal/mol) and bond lengths (in Å).

C1−P1−C13 = 99.55(10)°, C7−P1−C13 = 101.43(10)°) is significantly more distorted than that of the second molecule (C39−P2−C27 = 102.15(10)°, C33−P2−C27 = 102.28(11)°, C33−P2−C39 = 102.15(10)°). However, the P−C bond distances are nearly the same in both the molecules; that is, P1−C13 = 1.850(2) Å, and P2−C39 = 1.845(2) Å. The two phenyl rings on the phosphorus atoms are almost orthogonal to each other as can be seen from their torsion angles (P1−C1−C6−C5 = 177.77(9)°, P1−C7−C8−C9 = −176.76(18)°, P2−C27−C28−C29 = −179.6(2)°, and P2−C33−C38−C37 = 176.8(18)°). The triazole ring is nearly planar with an N4−N5−N6 bond angle of 107.1(2)°. The interesting aspect in the molecular structure of **2** is the presence of intra- and intermolecular hydrogen bonding. In the case of phosphine **3**, one of the phenyl rings on the phosphorus atom is perpendicular to the central triazole ring, whereas the other phenyl ring shows a weak intramolecular aromatic $\pi-\pi$ interaction with the phenyl group bonded to the nitrogen atom of the triazole moiety. The $\pi-\pi$ interaction has an interplanar distance of 3.596 Å, which lies within the range of $\pi-\pi$ interactions (3.58−4.29 Å) reported in the literature.[21] As a consequence, the P1−C15 [1.8223(17) Å] bond distance is elongated when compared to P1−C21 [1.8204(17) Å]. The C7−P1−C15 bond angle is 102.31(7)°, whereas the C7−P1−C21 angle is found to be 103.21(7)°.

Copper(I) and Gold(I) Complexes. The newly prepared phosphine, 1-(2-(diphenylphosphino)phenyl)-4-phenyl-1*H*-1,2,3-triazole **2** and its structural isomer **3** are potential tridentate ligands, and it would be interesting to explore their coordination behavior with various transition-metal precursors, in particular, with group 11 metals due to their remarkable ability to adopt a variety of structural motifs and also to accept soft to not-so-soft donor atoms. The possible coordinating modes for the ligands **2** and **3** are depicted in Chart 1. Although simple κ^1-coordination via phosphorus atom is the most common and preferred mode for both the ligands **2** and **3**, ligand **2** with proper orientation of the triazole side arm can show chelating (II) as well as chelating-cum-bridging (III) modes to perform as a tridentate ligand, which is so far not observed with triazole-based derivatives. Other possible coordinating modes (IV, VI, and VII) depicted in Chart 1 are less likely; however, they are not ruled out, as appropriate metal precursors and certain orientations of the triazole arm might facilitate these coordination modes as well.

Reaction between CuX (X = Cl, Br, and I) and [*o*-$Ph_2P(C_6H_4)$\{1,2,3-$N_3C(Ph)C(H)$\}] (**2**) in 1:1 ratio produced binuclear complexes [$(Cu)_2(\mu$-X$)_2$\{*o*-$Ph_2P(C_6H_4)$\{1,2,3-N_3C-$(Ph)C(H)$\}-κ-*P*$\}_2$] (**4**, X = Cl; **5**, X = Br; **6**, X = I) and the tetranuclear octahedron-type complex [$(Cu)_4(\mu$-I$)_4$\{*o*-Ph_2P-(C_6H_4)\{1,2,3-$N_3C(Ph)C(H)$\}-$\mu(\kappa$-*P*,κ-*N*$)\}_2$] (**6a**) as shown in Scheme 2. Recently, a similar type of tetranuclear complex containing aminobis(phosphonite) ligands has been reported.[22] The ^{31}P NMR spectra of complexes **4**−**6** show single resonances at −7.4, −8.3, and −10.9 ppm, respectively. The ^{1}H NMR spectra of **4**−**6** consists of singlets at 8.93, 8.66, and 8.63 ppm corresponding to the triazolic protons.

Treatment of complexes **4**−**6** with 1,10-phenanthroline in 1:1 molar ratio afforded mixed ligand complexes [(CuX)(1,10-phen-κ^2-*N*,*N*)\{*o*-$Ph_2P(C_6H_4)$\{1,2,3-$N_3C(Ph)C(H)$\}-κ-*P*\}] (X = **7**, Cl; **8**, X = Br; **9**, X = I) as bright orange crystalline solids in good yield (Scheme 2). Complexes **7**−**9** are partially soluble in acetonitrile and dimethyl sulfoxide. The ^{31}P NMR spectra of complexes **7**−**9** show single peaks at −6.9, −6.4, and −5.0 ppm, respectively. The ^{1}H NMR spectra of these complexes show single broad resonances in the range of 8.85−8.91 ppm for the triazolic proton. The structure of **7** (Figure 4) was confirmed by single-crystal X-ray analysis.

The asymmetric unit consists of one molecule of **7** and two molecules of dichloromethane as solvent of crystallization. The copper atom displays distorted tetrahedral geometry with internal angles in the range of 79.98(13)−136.77(9)°. The Cu1−P1 and Cu1−Cl1 bond distances are 2.1923(11) and

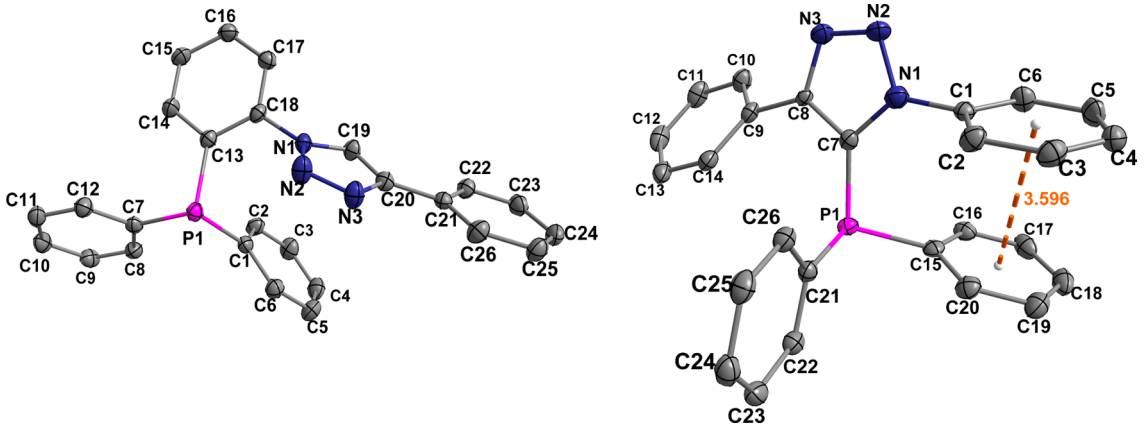

Figure 3. Molecular structures of **2** and **3**. All hydrogen atoms were omitted for clarity.

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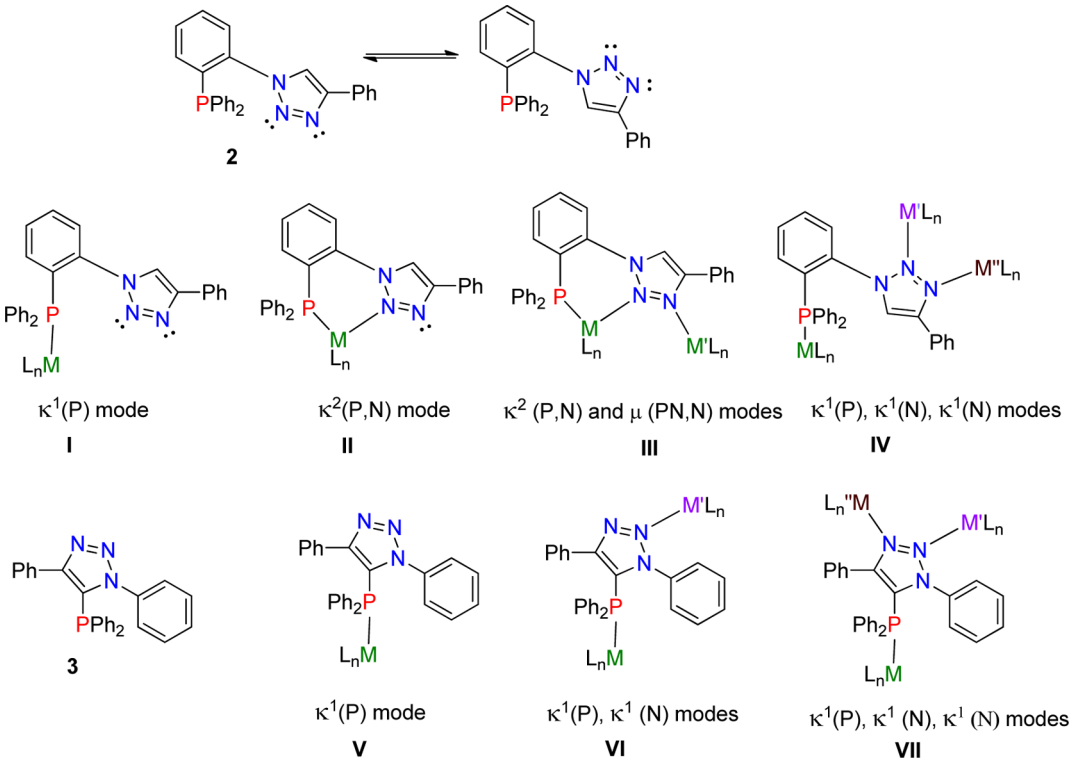
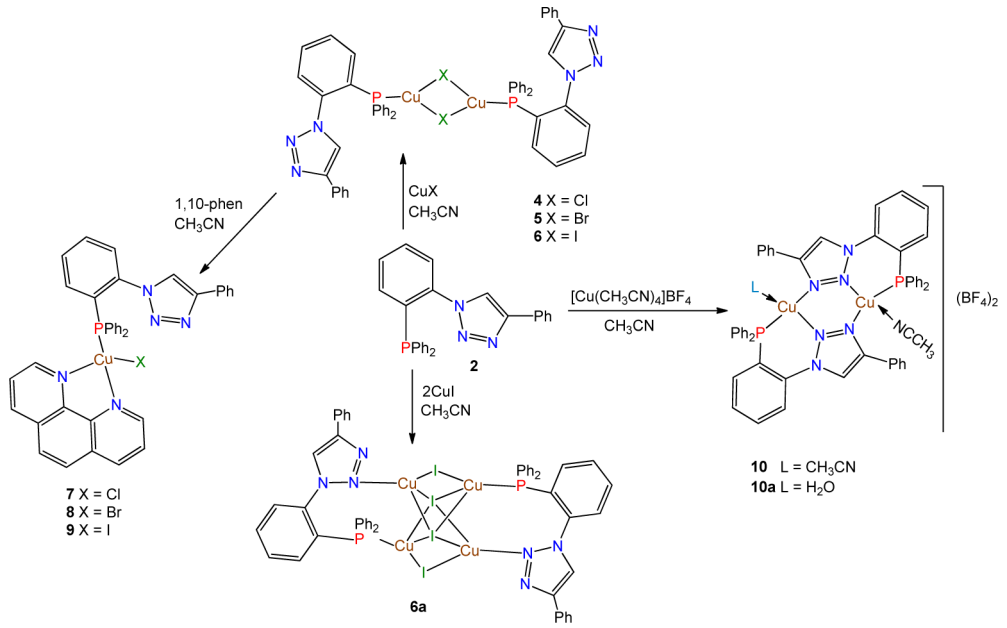
Inorg. Chem. XXXX, XXX, XXX−XXX

Chart 1. Possible Coordination Modes for Phosphines 2 and 3



Scheme 2. Copper(I) Complexes of 2



2.2871(10) Å, respectively. The triazole ring nitrogens are disposed away from the copper center, whereas the center triazolic carbon is closer to copper atom giving a stable configuration. The Cu−N distances (Cu1−N2 = 2.062(3) and Cu1−N1 = 2.142(3) Å) are comparable to the same observed in similar complexes reported in the literature.[23]

The reaction of **2** with 1 equiv of $[Cu(CH_3CN)_4]BF_4$ in acetonitrile yielded a binuclear complex $[Cu_2(CH_3CN)_2\{o\text{-}Ph_2P(C_6H_4)\{1,2,3\text{-}N_3C(Ph)C(H)\}\text{-}\mu\text{-}(\kappa\text{-}P,\kappa\text{-}N),\kappa\text{-}N\}_2](BF_4)_2$ (**10**) with the ligand exhibiting chelating as well as bridging modes of coordination as shown in Scheme 2. The ^{31}P NMR spectrum of **10** shows singlet at −9.1 ppm. The ^1H NMR spectrum consists of a sharp singlet at 2.06 ppm for coordinated acetonitrile and at 8.20 ppm for the triazolic protons. Complex **10** on recrystallization gave water-coordinated complex $[Cu_2(CH_3CN)(H_2O)\{o\text{-}Ph_2P(C_6H_4)\{1,2,3\text{-}N_3C(Ph)C(H)\}\text{-}\mu\text{-}(\kappa\text{-}P,\kappa\text{-}N),\kappa\text{-}N\}_2](BF_4)_2$ (**10a**) due to the presence of adventitious water, where one of the coordinated acetonitriles was replaced by a water molecule. The IR spectrum of **10** showed υ_{CN} at 2282 cm^{-1}, which is shifted to a higher wavenumber relative to free acetonitrile (2250 cm^{-1}) indicating an increased N≡C bond strength because of metal

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Inorg. Chem. XXXX, XXX, XXX−XXX

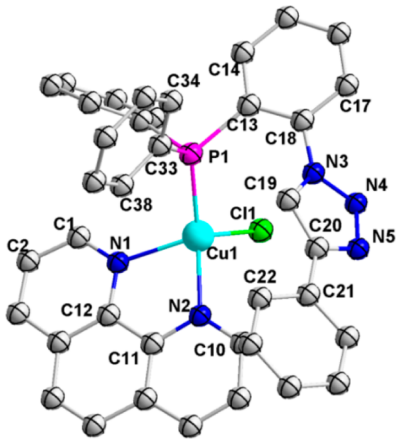

Figure 4. Molecular structure of **7**. All hydrogen atoms were omitted for clarity.

coordination.[24] The molecular structure of **10a** (Figure 5) was confirmed by single-crystal X-ray analysis.

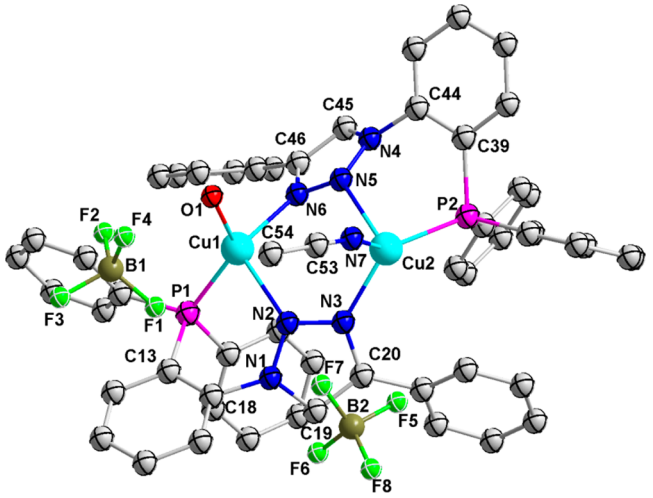

Figure 5. Molecular structure of **10a**. All hydrogen atoms were omitted for clarity.

The molecular structure reveals that the two copper centers are bridged by two molecules of ligand **2** forming a dimeric unit. Both the metal ions are tetrahedrally ligated by one phosphorus atom and two nitrogen atoms of each ligand and the fourth site by a solvent molecule. The N6−Cu1−O1 (95.33(9)°), O1−Cu1−P1 (127.99(7)°), O1−Cu1−N2 (105.60(9)°), P1−Cu1−N6 (130.28(7)°), and N2−Cu1−N6 (105.44(8)°) bond angles obviously indicate the distortion in the tetrahedral geometry, which is true for the second copper center also. The bite angles P1−Cu1−N2 (87.00(6)°) and P2−Cu2−N5 (89.65(6)°) are slightly different from each other. Both the copper atoms and bridging ligands are in a twisted boat conformation. The torsion angles Cu2−N5−N6−Cu1 (45.79°) and Cu2−N3−N2−Cu1 (50.85°) indicate that both the copper centers are slightly twisted from planarity. The Cu1−N2 and Cu2−N5 distances are 2.304(2) and 2.224(2) Å, respectively, which are quite different, whereas the Cu1−N6 (2.017(2) Å) and Cu2−N3 (2.017(2) Å) distances are the same. The Cu1−O1 and Cu2−N7 bond distances are 2.059(2) and 1.991(3) Å, respectively. The orientation of the triazole rings are slightly displaced from both the copper planes. The nonbonding Cu1···Cu2 distance is 3.667 Å. Weak hydrogen bonding, specifically, O1−H1A···F8 (2.957(5) Å, 161.6°), O1−H1B···F2 (2.788(3) Å, 148.6°), C2−H2···F2 (3.553(4) Å, 162.4°), C17−H17···F6 (3.285(4) Å, 153.1°), C43−H43···F5(3.199(4) Å, 147.6°), and C55−H55A···F7 (3.271(4) Å, 132.3°) were also observed. This is the first example of a crystallographically characterized cationic dicopper complex containing a triazolic phosphine acting as a tridentate ligand. The structure is similar to the recently reported silver complex of a pyridine-appended triazole, $[Ag(NO_3)\{(C_5H_5N)CH_2\text{-}\{1,2,3\text{-}N_3C(Ph)\}\text{-}\kappa\text{-}N,\kappa\text{-}N,\kappa\text{-}N\}]_2$.[9]

Copper Derivatives of $[C_6H_5\{1,2,3\text{-}N_3C(Ph)C(PPh_2)\}]$ (3). The reaction of **3** with 1 equiv of CuX (X = Cl, Br, and I) in acetonitrile yielded binuclear tricoordinated complexes $[Cu(\mu\text{-}X)_2Cu\{C_6H_5\{1,2,3\text{-}N_3C(Ph)C(PPh_2)\}\text{-}\kappa\text{-}P\}_2]$ (**11**, X = Cl; **12**, X = Br; **13**, X = I) with the ligand showing the monodentate coordination mode. Complexes **11**−**13** are colorless, air-stable solids and soluble in most organic solvents.

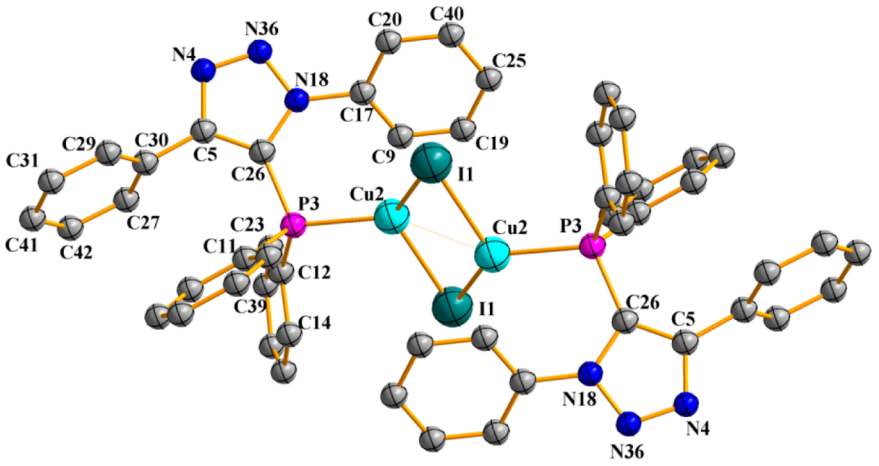

Figure 6. Molecular structure of **13**. All hydrogen atoms were omitted for clarity.

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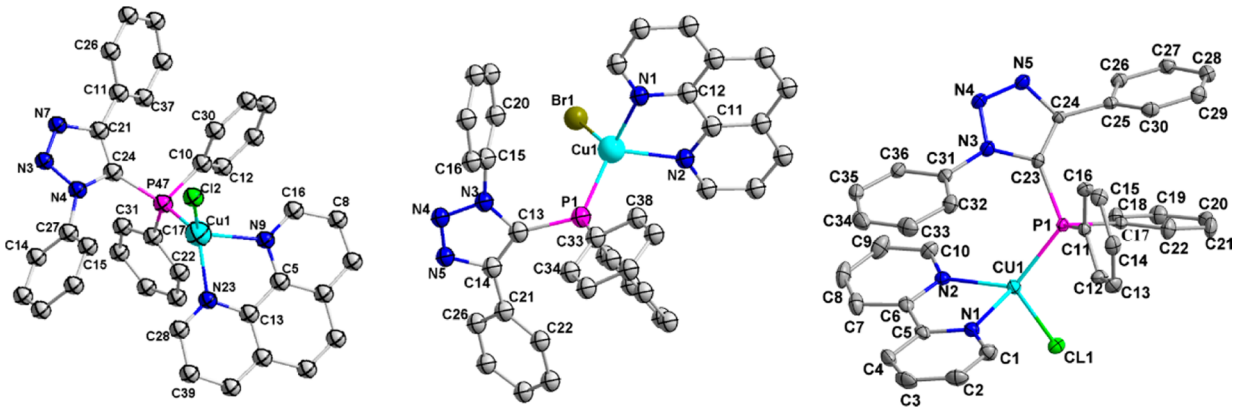


Figure 7. Molecular structures of **14**, **15**, and **17**. All hydrogen atoms were omitted for clarity.

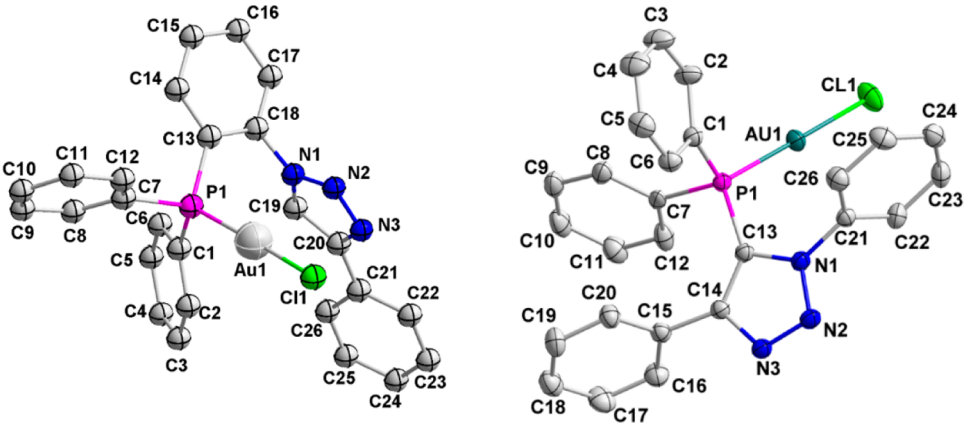
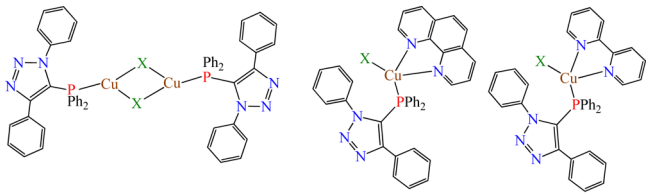


Figure 8. Molecular structures of **20** and **21**. All hydrogen atoms were omitted for clarity.



The ^{31}P NMR spectra of **11**–**13** show broad single resonances at −19.2, −23.3, and −28.1 ppm, respectively, which are considerably deshielded compared to that of the free ligand. The compositions and molecular structures of **11**–**13** were confirmed by microanalytical, ^{1}H NMR, and mass spectral data. The structure of **13** was confirmed by X-ray analysis.

Because of the presence of halo-bridged rhombic Cu_2X_2 units, the dimeric complexes **11**–**13** readily react with 2,2′-bipyridine and 1,10-phenanthroline to give monomeric complexes [(CuX)(1,10-phen-κ^2-*N*,*N*){C_6H_5{1,2,3-N_3C(Ph)C(PPh$_2$)}-κ-*P*}] (**14**, X = Cl; **15**, X = Br; **16**, X = I) and [(CuX)(2,2′-bipy-κ^2-*N*,*N*){C_6H_5{1,2,3-N_3C(Ph)C(PPh$_2$)}-κ-*P*}] (**17**, X = Cl; **18**, X = Br; **19**, X = I) as bright orange or yellow crystalline compounds. These complexes are moderately stable toward air and soluble in acetonitrile, dichloromethane, and dimethyl sulfoxide. The ^{31}P NMR spectra of complexes **14**–**19** show single resonances in the range from −16.7 to −24.3 ppm. The compositions of **14**–**19** were verified by ^{1}H NMR, mass spectrometry, microanalysis, and, in the cases of **13**–**15** and **17**, by single-crystal X-ray analysis.

The molecular structure of complex **13** (Figure 6) consists of Cu_2I_2 cores with each of the copper(I) centers being tricoordinated by one phosphorus atom and two bridging iodides. The molecule has crystallographically imposed centrosymmetry with two triazole moieties adopting the *anti*-conformation with respect to the copper centers. The [PCu(μ-I)$_2$CuP] unit is almost planar. Several trigonal planar binuclear copper complexes of this type containing monophosphines have been well-characterized.[20] The Cu2–P3 bond length (2.2328(9) Å) in complex **13** is comparable with that in [(Cu)$_2$(μ-I)$_2${(C_6H_5{1,2,3-N_3C(PPh$_2$)C(Ph)}}$_2$][24] (Cu–P = 2.2118(9) Å). The Cu···Cu distance of 2.568 Å indicates the possible metal–metal interaction between the two copper atoms having some positive or attractive interaction between the closed-shell d^{10} metal ions.[25] The Cu2–I1–Cu2, I1–Cu2–I1_a, I1–Cu2–P3, C26–P3–Cu2, and N4–N36–N18 bond angles are 59.41(1)°, 120.59(2)°, 124.24(2)°, 110.96(9)°, and 108.1(2)°, respectively. These angles obviously indicate a distortion of the copper coordination sphere.

The complexes **14**, **15**, and **17** (Figure 7) are isostructural. In these complexes the copper atoms are in a distorted tetrahedral geometry. The Cu–P distances are 2.2000(11), 2.1979(5), and 2.1874(5) Å for **14**, **15**, and **17**, respectively. There is π–π stacking in the case of **14** between 1,10-phenanthroline ring of two independent molecules with an interplanar distance of 3.337(5) Å. In complexes **14** and **15** the Cu1–N9, Cu1–N23, Cu1–N1, and Cu1–N2 distances are 2.147(3), 2.079(3), 2.0715(15), and 2.1403(14) Å, respectively. Considerable difference was observed between the two Cu–N atom distances

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Table 1. Crystallographic Information for Compounds 2, 3, 7, and 10a

	2	3	7	10a
formula	$C_{26}H_{20}N_3P$	$C_{26}H_{20}N_3P$	$C_{40}H_{32}Cl_5CuN_5P$	$C_{55}H_{47}B_2Cl_2Cu_2F_8N_7OP_2$
FW	405.42	4−5.40	854.46	1255.53
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	7.4106(4)	13.2112(14)	10.1064(5)	10.2654(7)
b, Å	15.1870(7)	11.1621(9)	13.1454(7)	12.6027(9)
c, Å	19.4567(9)	14.5906(14)	15.2293(8)	22.9535(16)
α, deg	72.029(1)	90	100.385(3)	100.6880(10)
β, deg	87.871(1)	108.833(11)	107.129(2)	92.7270(11)
γ, deg	86.280(1)	90	90.703(3)	107.2020(10)
V, Å^3	2078.19(18)	2036.4(4)	1897.23(17)	2277.8(3)
Z	4	4	2	2
ρ_{calc} g cm^{-3}	1.296	1.299	1.496	1.505
μ(Mo Kα)	0.150	0.153	4.747	0.996
F(000)	848	848	872	1276
crystal size, mm	0.10 × 0.12 × 0.16	02.x02 × 0.16	0.040 × 0.160 × 0.160	0.050 × 0.080 × 0.230
T, (K)	150(2)	100	102(2)	150(2)
2θ range, deg	1.1−28.3	2.42−31.384	3.09−68.41	1.78−28.71
total reflns	17837	12861	44874	25873
No. of indep reflns	13 685 [R_{int} = 0.0359]	3580 [R_{int} = 0.0720]	6748 [R(int) = 0.0583]	13 923 [R(int) = 0.0423]
R	0.0534	0.0411	0.0546	0.0514
wR_2	0.1463	0.1060	0.1472	0.1278
S	1.03	1.036	1.100	1.106

Table 2. Crystallographic Information for Compounds 13−15, 17, 20, and 21

	13	14	15	17	20	21
formula	$C_{26}H_{20}CuIN_3P$	$C_{38}H_{28}ClCuN_5P$	$C_{28}H_{28}BrCuN_5P$	$C_{36}H_{28}ClCuN_5P$	$C_{26}H_{20}AuClN_3P$	$C_{26}H_{20}AuClN_3P$
FW	595.86	684.61	608.97	660.59	637.84	637.84
crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.842(3)	10.053(3)	10.1081(10)	10.6311(5)	9.5590(5)	10.3148(5)
b, Å	14.101(4)	10.133(3)	10.2599(10)	11.0562(5)	9.9126(7)	10.3840(5)
c, Å	16.584(6)	15.978(5)	16.0076(15)	14.9648(7)	13.4010(7)	11.6306(6)
α, deg	90	82.510(12)	82.7180(13)	110.0360(6)	99.547(2)	78.009(2)
β, deg	95.314(7)	74.233(9)	73.6460(13)	90.8080(7)	95.713(2)	75.910(2)
γ, deg	90	81.596(11)	81.9780(13)	114.1740(7)	112.4390(10)	76.813(2)
V, Å^3	2291.7(12)	1542.5(8)	1570.7(3)	1482.92(12)	1138.79(12)	1161.02(10)
Z	4	2	2	2	2	2
ρ_{calc} (g cm^{-3})	1.727	1.474	1.288	1.479	1.860	1.825
μ(Mo Kα), mm^{-1}	2.390	0.884	2.041	0.917	6.666	6.539
F(000)	1176	704	620	680	616	616
crystal size, mm	0.20 × 0.20 × 0.20	0.26 × 0.10 × 0.26	0.140 × 0.240 × 0.260	0.080 × 0.120 × 0.190	0.050 × 0.160 × 0.180	0.150 × 0.160 × 0.170
T, (K)	100	100	150(2)	150(2)	150(2)	150(2)
2θ range, deg	2.9−25.0	3.10−25.0	2.01−29.17	2.12−29.24	1.57−32.03	1.83−33.14
total no. of reflns	16 534	11 628	28 849	27 361	48 372	41 604
no. of indep. reflns	3965 [R_{int} = 0.0302]	5296 [R_{int} = 0.0499]	8084 [R_{int} = 0.0326]	7662 [R(int) = 0.0419]	7887 [R_{int} = 0.0423]	8767 [R_{int} = 0.0411]
R	0.0232	0.0412	0.0293	0.0363	0.0182	0.0247
wR_2, S	0.0557, 1.080	0.1073, 1.01	0.0760, 1.04	0.0874, 1.030	0.0454, 1.068	0.0581, 1.055

of the 1,10-phenanthroline, whereas in complex **17**, the differences between the Cu−N bonds [Cu1−N1= 2.0879(15) Å, Cu1−N2 = 2.0678(16) Å] is marginal (0.0201 Å).

The gold complexes [AuCl{*o*-$Ph_2P(C_6H_4)$}{1,2,3-$N_3C(Ph)$-C(H)}-κ-*P*}] (**20**) and [AuCl{C_6H_5{1,2,3-$N_3C(Ph)C(PPh_2)$}-κ-*P*}] (**21**) were obtained by reacting ligands **2** and **3** with $AuCl(SMe_2)$ in 1:1 molar ratios in dichloromethane at room temperature. The ^{31}P NMR spectra of **20** and **21** consist of singlets at 27.8 and 12.3 ppm, respectively. In the ^{1}H NMR spectrum of **20**, the peak corresponding to the triazolic proton appeared as a singlet at 8.18 ppm. The electrospray ionization (ESI) mass spectrum of **20** showed a peak at 660.07 $[M + Na]^+$ as the base peak. The high-resolution mass spectrometry (HRMS) data for **21** consist of a molecular ion peak at m/z 638.0803 $[M + H]^+$. The molecular structures of **20** and **21** (Figure 8) were determined by single-crystal X-ray diffraction studies.

In complex **20**, two adjacent molecules are arranged in an *anti*-parallel manner, and hence there is no intermolecular gold−gold interaction, as the Au···Au separations are 5.017 and

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Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 2 and 3

bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
compound 2				compound 3			
P2−C39	1.845(2)	C39−P2−C33	102.15(10)	P1−C7	1.8146(17)	C7−P1−C21	103.21(7)
P2−C33	1.831(2)	C33−P2−C27	102.28(11)	P1−C21	1.8204(17)	C7−P1−C15	102.31(7)
P2−C27	1.829(2)	C39−C44−N4	121.1(2)	N3−N2	1.303(2)	N2−N3−C8	108.24(13)
N4−N5	1.350(3)	C44−N4−N5	121.33(17)	N3−C8	1.356(2)	N3−N2−N1	108.27(14)
N5−N6	1.314(3)	N4−N5−N6	107.1(2)	N2−N1	1.354(2)	N3−C8−C9	120.78(14)
N4−C45	1.349(3)	N4−C45−C46	105.35(19)	C8−C9	1.448(2)	N3−C8−C7	110.05(14)
C45−C46	1.372(3)	C46−N6−N5	109.4(2)	C8−C7	1.373(2)	C8−C7−P1	123.54(13)
C46−N6	1.365(3)	P2−C39−C44	122.55(17)	C7−N1	1.372(2)	N2−N1−C1	118.77(14)
N4−C44	1.437(3)	C33−P2−C39	102.15(10)	C1−N1	1.447(2)	C7−N1−C1	131.03(14)
C39−C44	1.407(3)	C44−C39−C40	116.0(2)				

5.511 Å.[26] The Au−Cl (2.2912(5) Å) and Au−P (2.2334(4) Å) bond lengths are comparable to those in $(PhO)_3PAuCl$ (Au−Cl = 2.273(5) Å, Au−P = 2.192(5) Å).[27] The geometry around gold is almost linear with Cl−Au−P bond angle of 175.891(16)°, which is similar to the same found in $(PhO)_3PAuCl$ (Cl−Au−P = 178.5(2)°). The two phenyl rings on phosphorus centers are perpendicular to each other with torsion angles P1−C1−C2−C3 (179.94(16)°) and P1−C7−C12−C11 (−176.44(14)°). The triazole ring nitrogens are away from the P1−C13−C18−N1 (−2.4(2)°) plane with the torsion angle C18−N1−N2−N3 being −179.57(16)°. In complex **20**, the Au−Cl (2.2912(5) Å) and Au−P (2.2334(4) Å) bond distances are similar to those found in $(PhO)_3PAuCl$ (Au−Cl = 2.273(5) Å, Au−P = 2.192(5) Å).[27] The Cl−Au−P bond angle of 175.891(16)° is slightly less than that found in $[Ph_3PAuCl]$[28] (Cl−Au−P = 179.63°).

CONCLUSIONS

Two new triazole-based phosphines have been reported. At low temperature, a kinetically controlled reaction prevails, whereas at room temperature (25 °C), the chemical equilibrium can assert itself via Li/H exchange, which leads to the isolation of thermodynamically more stable isomer. We anticipate that these kinetically versus thermodynamically controlled intermediates can act as potential synthons to generate useful organic products by using different electrophiles. Both the phosphines show interesting coordination properties. The phosphine with an exocyclic triazole (**2**) shows κ-P, κ^2-*P,N*-chelation as well as *μ*-(κ-*N*,κ-*N*)-bridging coordination modes to act as mono-, di-, or tridentate ligand. Tridentate coordination is rarely seen among triazole-based ligands. Reaction of **2** with $[Cu(NCCH_3)_4][BF_4]_2$ yielded a dicopper complex with ligand exhibiting rare tridentate mode of coordination. Phosphine with an endocyclic triazole (**3**) prefers monodentate (κ-P) coordination mode, although it can show bridging (*μ*-(κ-*N*,κ-P)) coordination mode; but with bulky arms on both the sides, it can be a very valuable ligand to stabilize the low-valent platinum metals. By choosing appropriate metal reagents and reaction conditions, both mono and chelating bidentate modes of coordination were achieved. It is anticipated that the synthetic flexibility found in the present system would be of enormous assistance in ever-growing field of click chelates, especially in connection with their potential catalytic and biological activities. Further metal chemistry and catalytic reactions with these systems are under active investigation in our laboratory.

EXPERIMENTAL SECTION

General Procedures. All manipulations were performed using standard vacuum-line and Schlenk techniques under a nitrogen atmosphere. All the solvents were purified by conventional procedures and distilled prior to use. The compounds CuX (X = Cl, Br),[29] $[Cu(CH_3CN)_4]BF_4$,[30] $AuCl(SMe_2)$,[31] and 2-bromophenylazide[32] were prepared according to the published procedures. Other chemicals were obtained from commercial sources and purified prior to use.

Instrumental Methods. The NMR spectra were recorded at the following frequencies: 400 MHz (^{1}H), 100 MHz (^{13}C), and 162 MHz (^{31}P) (*δ* in ppm) using either Varian VXR 400, Bruker AV 400, or Bruker AV 500 spectrometers. The spectra were recorded in $CDCl_3$ (or DMSO-d_6)) solutions with $CDCl_3$ (or DMSO-d_6) as an internal lock; tetramethylsilane and 85% H_3PO_4 were used as external standards for ^{1}H and ^{31}P{^{1}H} NMR, respectively. Positive shifts lie downfield to the standard in all of the cases. Infrared spectra were recorded on a Nicolet Impact 400 FTIR instrument in KBr disk or mineral oil mull. The microanalyses were performed using a Carlo Erba Model 1112 and flash EA 1112 series elemental analyzer. Mass spectra were recorded using Waters Q-TOF micro (YA-105), maXis impact, and 410 Prostar Binary LC. The melting points of all compounds were determined on a Veego melting point apparatus and are uncorrected. Low-temperature experiments were performed using a Julabo model FT 902.

*Synthesis of 2-Bromophenyltriazole [o-Br(C_6H_4){1,2,3-N_3C(Ph)C(H)}] (**1**).* 2-Bromophenylazide (1.97 g, 10.3 mmol) and phenylacetylene (0.930 g, 9.1 mmol) were suspended in a 1:1 mixture of water and tertiary butyl alcohol. Sodium ascorbate (3.6 mmol, freshly prepared solution in water) was added followed by $CuSO_4{\cdot}5H_2O$ (1.6 mmol, freshly prepared solution in water), and the reaction mixture was stirred for 24 h at room temperature. The product obtained was extracted with diethyl ether. The combined ether extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a yellow crystalline solid. Yield: 86% (2.4 g). mp 97−99 °C. HRMS (ESI): *m*/*z* Calcd for $C_{14}H_{10}N_3Br$ ($[M + H]^+$): 300.0136, 302.0116; found: 300.0161, 302.0081. IR: 1587, 1497, 1479 cm^{-1}. ^{13}C NMR ($CDCl_3$): *δ* 118.5, 120.4, 125.8, 128.1, 128.4, 128.5, 128.9, 129.7, 130.1, 131.2, 133.9, 136.5. ^{1}H NMR ($CDCl_3$): *δ* 7.26−7.49 (m, Ph, 5H), 7.50−7.94 (m, PhBr, 4H) 8.17 (s, CH, 1H). Anal. Calcd for $C_{14}H_{10}N_3Br$: C, 56.02; H, 3.35; N, 13.99. Found: C, 56.36; H, 3.23; N, 13.73%.

*Synthesis of [o-$Ph_2P(C_6H_4)$]{1,2,3-N_3C(Ph)C(H)}] (**2**).* To a Schlenk flask charged with 2-bromophenyltriazole **1** (2.11 g, 7.02 mmol) in diethyl ether (70 mL) was added dropwise a hexane solution of ^{n}BuLi (4.83 mL, 7.73 mmol, 1.6 M solution in hexane) at −78 °C, and the mixture was stirred for 8 h at −78 °C. A solution of PPh_2Cl (1.55 g, 1.28 mL, 7.02 mmol) in diethyl either (15 mL) was added into the mixture at −78 °C, followed by warming to room temperature, and stirring was continued for a further period of 9 h. The solution was filtered through a diatomaceous earth bed to remove LiCl. The dark yellow solution was concentrated under reduced pressure, and the residue obtained was washed with 4 × 4 mL of petroleum ether and dissolved in 30 mL of diethyl ether and stored at −15 °C to give **2** as

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Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 7, 10a, and 13

bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
compound 7				compound 10a				compound 13			
Cu1−N2	2.062(3)	N2−Cu1−N1	79.98(13)	Cu1−N6	2.017(2)	N6−Cu1−O1	95.33(9)	Cu2−I1	2.5704(9)	Cu2−I1−Cu2_a	59.41(1)
Cu1−N1	2.142(3)	N2−Cu1−P1	136.77(9)	Cu1−P1	2.1772(8)	O1−Cu1−P1	127.99(7)	Cu2_a−I1	2. 6110(9)	I1−Cu2−P3	124.24(2)
Cu1−P1	2.1923(11)	N1−Cu1−P1	108.20(9)	Cu2−N7	1.991(3)	N6−Cu1−P1	130.28(7)	Cu2−P3	2.2328(9)	I1−Cu2−I1_a	120.59(2)
Cu1−Cl1	2.2871(10)	N2−Cu1−Cl1	106.53(9)	Cu2−P2	2.1802(7)	N6−Cu1−N2	105.44(8)	P3−C11	1.821(3)	I1_a−Cu2−P3	109.21(2)
P1−C27	1.830(4)	N1−Cu1−Cl1	115.96(9)	P1−C1	1.815(3)	N2−N1−C18	122.6(2)	P3−C12	1.820(3)	N36−N4−C5	108.6(2)
P1−C33	1.833(4)	P1−Cu1−Cl1	107.09(4)	P1−C13	1.838(3)	N2−N3−C20	109.8(2)	P3−C26	1.809(3)	N36−N18−C17	120.6(2)
P1−C13	1.840(4)	C27−P1−C33	102.83(17)	N1−N2	1.353(2)	C2−C1−P1	116.2(2)	N4−N36	1.309(3)	N4−N36−N18	108.1(2)
N1−C1	1.319(5)	C27−P1−C13	102.15(17)	N1−C18	1.448(3)	C1−C2−C3	119.7(3)	N4−C5	1.352(4)	Cu2−P3−C11	113.31(9)
N3−N4	1.350(5)	N4−N3−C18	120.0(3)	N3−C20	1.362(3)	C6−C1−P1	123.7(2)	N18−N36	1.364(4)	Cu2−P3−C12	113.69(8)
N4−N5	1.312(5)	N4−N5−N3	107.1(3)	N2−N3	1.319(3)	C2−C1−P1	116.2(2)				

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 14, 15, and 17

bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
compound 14				compound 15				compound 17			
Cu1−Cl2	2.2794(11)	N9−Cu1−N23	79.46(11)	Br1−Cu1	2.3995(3)	N1−Cu1−N2	79.62(6)	Cu1−N2	2.0678(16)	N2−Cu1−N1	79.44(6)
Cu1−P47	2.2000(11)	P47−Cu1−N23	126.62(8)	Cu1−N1	2.0715(15)	N1−Cu1−P1	126.88(4)	Cu1−N1	2.0879(15)	N2−Cu1−P1	124.64(5)
Cu1−N9	2.147(3)	Cu1−P47−C10	101.38(11)	Cu1−N2	2.1403(14)	N2−Cu1−P1	109.30(4)	Cu1−P1	2.1874(5)	N1−Cu1−P1	122.35(5)
Cu1−N23	2.079(3)	Cu1−P47−C17	117.82(10)	Cu1−P1	2.1979(5)	N1−Cu1−Br1	111.50(4)	Cu1−Cl1	2.3161(5)	N2−Cu1−Cl1	107.94(4)
P47−C17	1.823(3)	C10−P47−C17	103.53(15)	P1−C33	1.8198(16)	N2−Cu1−Br1	107.89(4)	P1−C11	1.8253(18)	Cl1−P1−C17	104.26(8)
P47−C10	1.824(4)	C10−P47−C24	103.70(14)	P1−C13	1.8322(16)	P1−Cu1−Br1	114.416(1)	P1−C17	1.8270(18)	Cl1−P1−C23	104.45(8)
P47−C24	1.831(3)	C17−P47−C24	103.70(14)	N1−C12	1.361(2)	C33−P1−Cu1	117.65(6)	P1−C23	1.8315(18)	C17−P1−Cu1	111.27(6)
N3−N4	1.354(4)	N4−N3−N7	107.5(3)	N3−N4	1.349(2)	C13−P1−Cu1	123.34(4)	N1−C1	1.339(2)	C23−P1−Cu1	117.64(6)
N3−N7	1.307(4)	N3−N4−C24	111.4(3)	N4−N5	1.302(2)	C1−N1−Cu1	128.59(12)	N3−N4	1.356(2)	N5−N4−N3	108.17(15)
				N5−C14	1.366(2)	N3−N4−N5	107.52(14)	N4−N5	1.309(2)	N4−N5−C24	108.70(15)

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Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds 20 and 21

bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
compound 20				compound 21			
Au1−P1	2.2334(4)	C13−P1−Au1	114.27(5)	Au1−P1	2.2294(6)	P1−Au1−Cl1	179.23(3)
Au1−Cl1	2.2912(5)	P1−Au1−Cl1	175.891(16)	Au1−Cl1	2.2811(6)	C13−P1−C7	105.13(10)
P1−C1	1.8067(17)	N3−N2−N1	107.09(14)	P1−C13	1.801(2)	C13−P1−Au1	111.64(7)
P1−C7	1.8101(17)	C19−N1−N2	110.64(15)	P1−C1	1.803(2)	C7−P1−Au1	111.93(8)
P1−C13	1.8304(17)	N2−N1−C18	119.22 (14)	P1−C7	1.832(3)	N2−N1−C21	119.81(18)
N1−C19	1.352(2)	N2−N3−C20	109.31(15)	N1−N2	1.344(3)	N3−N2−N1	107.43(18)
N1−N2	1.353(2)	C2−C1−P1	119.44(13)	N1−C13	1.370(3)	C1−P1−C7	105.14(14)
N1−C18	1.438(2)	C1−C2−C3	119.64(18)	N1−C21	1.438(3)	C1−P1−Au1	114.91(8)
N3−C20	1.363(2)	C6−C1−P1	120.85(13)	N2−N3	1.313(3)	N2−N1−C13	111.10(18)
N2−N3	1.313(2)	C2−C1−C6	119.69(16)	N3−C14	1.362(3)	C13−P1−C1	107.40(10)

analytically pure colorless needles. Yield: 61.7% (1.76 g). mp 137−139 °C. IR: 2412, 1964, 1879, 1807, 1642, 1476, 1445 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 122.4, 126.0, 126.8, 128.4, 128.9, 129.5, 130.0, 130.2, 132.3, 134.1, 134.3, 134.7, 134.8, 135.5, 141.1, 147.3. ^1H NMR ($CDCl_3$): δ 7.05−7.76 (m, ArH, 19H), 7.73 (s, triazolicH, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −15.5 ppm (s). HRMS (ESI): *m/z* Calcd for $NaC_{26}H_{20}N_3P$ ($[M + Na]^+$): 428.1292; Found: 428.1286. Anal. Calcd for $C_{26}H_{20}N_3P$: C, 77.01; H, 4.97; N, 10.36; Found: C, 76.90; H, 4.89; N, 10.08%.

*Synthesis of [C_6H_5\{1,2,3-$N_3C(Ph)C(PPh_2)$\}] (**3**). (Method A).* To a Schlenk flask charged with 2-bromophenyltriazole (**1**) (2.2 g, 7.3 mmol) in diethyl ether (70 mL) at −78 °C was added dropwise a hexane solution of ^{n}BuLi (5.01 mL, 8.03 mmol, 1.6 M solution in hexane). The mixture was allowed to warm to room temperature and was stirred for 5 h. Again the solution was cooled to −78 °C, and PPh_2Cl (1.61 g, 1.33 mL, 7.3 mmol) was added dropwise through a cannula. The resulting mixture was slowly warmed to room temperature and stirred for 9 h, and LiCl was filtered off. The solvent was removed under reduced pressure, and the yellow oily residue obtained was washed with petroleum ether, dissolved in minimum amount ethanol, and stored at −15 °C to get analytically pure product of **3** as white crystalline solid. Yield: 62% (1.8 g).

Method B. To a solution of 1,4-diphenyl-1*H*-1,2,3-triazole[33] (1 g, 4.52 mmol) in diethyl ether (30 mL) at −78 °C ^{n}BuLi (3.1 mL, 1.6 M in hexane, 4.972 mmol) was added dropwise over 15 min. The reaction mixture was allowed to attain room temperature and was stirred for 6 h. The reaction mixture was cooled to −78 °C, and a solution of PPh_2Cl (0.997 g, 4.52 mmol) in diethyl ether (10 mL) was added dropwise over 20 min. The resulting mixture was stirred for 9 h at room temperature and then filtered through diatomaceous earth to remove LiCl. All the volatiles were removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 95:5) to obtain compound **1** as a white solid (1.37 g, 75%).

mp 152−154 °C. IR: 2342, 1964, 1876, 1596, 1498, 1468, 1434 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 120.4, 125.8, 126.3, 127.9, 128.5, 128.8, 129.0, 129.4, 129.7, 130.7, 132.3, 132.3, 132.5, 132.6, 137.2, 154.3. ^1H NMR ($CDCl_3$): δ 7.14−7.52 (m, ArH, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −30.2(s) ppm. HRMS (ESI): *m/z* Calcd for $C_{26}H_{21}N_3P$ ($[M + H]^+$): 406.1473; Found: 406.1478. Anal. Calcd for $C_{26}H_{20}N_3P$: C, 77.02; H, 4.97; N, 10.36. Found: C, 76.64; H, 4.83; N, 9.91%.

*Synthesis of [Cu_2(μ-Cl)$_2$\{o-$Ph_2P(C_6H_4)$\{1,2,3-$N_3C(Ph)C(H)$\}-κ-P\}$_2$] (**4**).* A solution of **2** (0.020 g, 0.049 mmol) in CH_3CN (5 mL) was added dropwise to a solution of CuCl (0.0049 g, 0.049 mmol) in CH_3CN (3 mL), and the mixture was stirred for 20 h at room temperature. The solvent was removed under vacuum, washed with 4 × 3 mL of petroleum ether, and dried in vacuo to give analytically pure product of **4** as a white solid. Yield: 72% (0.036 g). mp 147−149 °C (dec). ^1H NMR ($CDCl_3$): δ 7.10−7.80 (m, Ar, 38H), 8.93 (br, s, triazolicH, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −7.4(s) ppm. Anal. Calcd for $C_{52}H_{40}Cl_2Cu_2N_6P_2$: C, 61.91; H, 4.00; N, 8.33. Found: C, 62.23; H, 3.60; N, 8.23%.

*Synthesis of [(Cu)$_2$(μ-Br)$_2$\{o-$Ph_2P(C_6H_4)$\{1,2,3-$N_3C(Ph)C(H)$\}-κ-P\}$_2$] (**5**).* Compound **5** was synthesized by a procedure similar to **4** using CuBr (0.0070 g, 0.0493 mmol) and **2** (0.020 g, 0.0493 mmol). The analytically pure product **5** was obtained as a colorless powder. Yield: 68% (0.037g). mp: 154 °C. ^1H NMR (DMSO-d_6): δ 7.09−8.03 (m, Ar, 38H) 8.66 (br, s, triazolicH, 2H). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −8.3 (s) ppm. HRMS (ESI): *m/z* Calcd for $C_{52}H_{40}Cu_2N_6P_2Br_2$ ($[M-Br]^+$): 1015.056; Found: 1017.0544. Anal. Calcd for $C_{52}H_{40}Br_2Cu_2N_6P_2$: C, 56.87; H, 3.67; N, 7.66. Found: C, 56.75; H, 3.47; N, 7.87%.

*Synthesis of [Cu_2(μ-I)$_2$\{o-$Ph_2P(C_6H_4)$\{1,2,3-$N_3C(Ph)C(H)$\}-κ-P\}$_2$] (**6**).* Compound **6** was synthesized by a procedure similar to **5** using CuI (0.0188 g, 0.0986 mmol) and **2** (0.040 g, 0.0986 mmol). The analytically pure product **6** was obtained as a pale yellow powder. Yield: 81% (0.048 g). mp 246 °C (dec). ^1H NMR (DMSO-d_6): δ 7.30−7.7 (m, Ar, 38H), 8.87 (s, triazolicH, 2H). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −10.75 (s) ppm. HRMS (ESI): *m/z* Calcd for $C_{52}H_{40}Cu_2I_2N_6P_2$ ($[M-I]^+$): 1065.0410; Found: 1063.0421. Anal. Calcd for $C_{52}H_{40}Cu_2I_2N_6P_2$: C, 52.40; H, 3.38; N, 7.05. Found: C, 52.65; H, 3.47; N, 7.41%.

*Synthesis of [Cu_4(μ-I)$_4$\{o-$Ph_2P(C_6H_4)$\{1,2,3-$N_3C(Ph)C(H)$\}-κ^2-P,N\}$_2$] (**6a**).* Compound **6a** was synthesized by a procedure similar to **5** using CuI (0.0093 g, 0.0493 mmol) and **2** (0.020 g, 0.0493 mmol). The analytically pure product **6** was obtained as a pale yellow powder. Yield: 71% (0.055 g). mp 256−258 °C. ^1H NMR (DMSO-d_6): δ 7.10−7.98 (m, Ar, 38H), 8.63 (s, triazolicH, 2H). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −10.9 (s) ppm. Anal. Calcd for $C_{52}H_{40}Cu_4I_4N_6P_2 \cdot CH_2Cl_2$: C, 38.40; H, 2.56; N, 5.07. Found: C, 38.96; H, 2.01; N, 5.03%.

*Synthesis of [(CuCl)(1,10-phen-κ^2-N,N)\{o-$Ph_2P(C_6H_4)$\{$N_3C(Ph)C(H)$\}-κ-P\}] (**7**).* A solution of **2** (0.020 g, 0.049 mmol) in CH_3CN (5 mL) was added dropwise to a solution of CuCl (0.0049 g, 0.049 mmol) dissolved in CH_3CN (3 mL), and the mixture was stirred for 10 h at room temperature. Then 1,10-phenanthroline (0.0073 g, 0.0493 mmol) in CH_3CN (5 mL) was added, and the solution was stirred for a further period of 1 h. The solvent was removed under vacuum; the residue was washed with petroleum ether and dried in vacuo to give analytically pure product of **7** as orange solid. The X-ray quality crystals were obtained by recrystallizing it from a mixture of CH_2Cl_2/petroleum ether at room temperature. Yield: 83% (0.028g). mp 138 °C (dec). ^1H NMR ($CDCl_3$): δ 7.26−8.63 (m, ArH, 27H), 8.91 (br, s, triazolicH, 1H), 5.5 (CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.9 (s) ppm. Anal. Calcd For $C_{38}H_{28}ClCuN_5P \cdot CH_2Cl_2$: C, 60.85; H, 3.95; N, 9.10. Found: C, 60.63; H, 4.36; N, 9.17%.

*Synthesis of [CuBr(1,10-phen-κ^2-N,N)\{o-$Ph_2P(C_6H_4)$\{$N_3C(Ph)C(H)$\}-κ-P\}] (**8**).* To a solution of **5** (0.054 g, 0.0493 mmol) in CH_3CN (7 mL) was added dropwise 1,10-phenanthroline (0.0073 g, 0.0493 mmol) also in CH_3CN (4 mL). The mixture was stirred for 3 h at room temperature. The solvent was removed under vacuum; the residue was washed with petroleum ether and dried under vacuo to give analytically pure product of **8** as orange solid. Yield: 75% (0.027 g). mp 148−151 °C. ^1H NMR ($CDCl_3$): δ 7.23−8.61 (m, ArH, 27H), 8.85 (br, s, triazolicH, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.4 (s) ppm.

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Inorg. Chem. XXXX, XXX, XXX−XXX

HRMS (ESI): m/z Calcd for $C_{38}H_{28}CuN_5PBr$ ($[M\text{-}Br]^+$): 648.1373; Found: 648.1374. Anal. Calcd for $C_{38}H_{28}BrCuN_5P$: C, 62.59; H, 3.87; N, 9.60. Found: C, 62.83; H, 3.57; N, 9.29%.

*Synthesis of [CuI(1,10-phen-κ²-N,N){o-Ph₂P(C₆H₄){1,2,3-N₃C(Ph)-C(H)}-κ-P}] (**9**).* To a solution of **6** (0.077 g, 0.0493 mmol) in CH_3CN (7 mL) was added 1,10-phenanthroline (0.0073 g, 0.0493 mmol). The mixture was stirred for 3 h at room temperature. The solvent was removed under vacuum, and the residue was washed with petroleum ether and dried in vacuo to give analytically pure product of **9** as an orange solid. Yield: 74% (0.028 g). mp 243 °C (dec). ^{1}H NMR (DMSO-d_6): δ 7.12−8.06 (m, Ar, 27H), 8.90 (br, s, triazolicH, 1H). $^{31}P\{^1H\}$ NMR (DMSO-d_6): −5.00 (s) ppm. HRMS (ESI): m/z Calcd for $C_{38}H_{28}CuN_5PI$ ($[M\text{-}I]^+$): 648.1373; Found: 648.1376. Anal. Calcd for $C_{38}H_{28}ICuN_5P$: C, 58.81; H, 3.64; N, 9.02. Found: C, 58.55; H, 3.47; N, 8.66%.

*Synthesis of [Cu₂(CH₃CN)₂{o-Ph₂P(C₆H₄){1,2,3-N₃C(Ph)C(H)}-κ³-P,N,N}₂](BF₄)₂ (**10**).* A solution of **2** (0.015 g, 0.037 mmol) in CH_3CN (5 mL) was added dropwise to a solution of $[\{Cu(CH_3CN)_4\}BF_4]$ (0.0116 g, 0.037 mmol) dissolved in CH_3CN (3 mL), and the mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure, and the residue was washed with 4 × 3 mL of petroleum ether and dried in vacuo to give analytically pure product of **10** as a white solid. X-ray quality crystals (**10a**) were obtained by recrystallizing it from a mixture of CH_2Cl_2/petroleum ether, where one coordinated acetonitrile molecule was replaced by one water molecule. Yield: 65% (0.0286 g). mp 153−155 °C. IR(υ_{CN}) (KBr disk): 2282(s), 1485 (vs), 1435 (vs), 1360(s), 1310(s), 1282(m), 1222(s), 1185(w), 1068(w), 907(s), 840(w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.06 (s, CH_3CN, 6H), 6.81−7.83 (m, Ar, 38H), 8.20 (s, triazolicH, 2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −9.1 (s) ppm. Anal. Calcd for $C_{56}H_{46}N_8P_2Cu_2B_2F_8$: C, 56.35; H, 3.88; N, 9.39. Found: C, 56.75; H, 3.55; N, 9.23%. Anal. Calcd for $C_{54}H_{43}N_7P_2Cu_2OB_2F_8{\cdot}CH_2Cl_2$ (**10a**): C, 52.70; H, 3.62; N, 7.82. Found: C, 52.62; H, 3.43; N, 8.22%.

*Synthesis of [Cu₂(μ-Cl)₂{C₆H₅{1,2,3-N₃C(Ph)C(PPh₂)}-κ-P}₂] (**11**).* To a solution of **3** (0.030 g, 0.074 mmol) in CH_3CN (8 mL) was added CuCl (0.0073 g, 0.074 mmol) dissolved in CH_3CN (2 mL). The mixture was stirred for 6 h at room temperature. The solvent was removed under reduced pressure to afford the product as a colorless solid. Yield: 74% (0.055 g). mp 156−158 °C. ^{1}H NMR ($CDCl_3$): δ 6.90−7.57 (m, ArH, 40H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −19.2 ppm (s, br). Anal. Calcd for $C_{52}H_{40}N_6P_2Cu_2Cl_2$: C, 61.89; H, 3.99; N, 8.33. Found: C, 61.53; H, 3.54; N, 8.48%.

*Synthesis of [Cu₂(μ-Br)₂{C₆H₅{1,2,3-N₃C(Ph)C(PPh₂)}-κ-P}₂] (**12**).* To a solution of **3** (0.030 g, 0.074 mmol) in CH_3CN (8 mL) was added CuBr (0.0106 g, 0.074 mmol) dissolved in CH_3CN (2 mL), and the mixture was stirred for 6 h at room temperature. The solvent was removed under reduced pressure, and the residue was washed with petroleum ether to afford the product as a colorless solid. Yield: 71% (0.058 g). mp 138−141 °C. ^{1}H NMR ($CDCl_3$): δ 7.00−7.57 (m, ArH, 40H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.3 (s) ppm. Anal. Calcd for $C_{52}H_{40}N_6P_2Cu_2Br_2$: C, 56.89; H, 3.67; N, 7.65. Found: C, 57.13; H, 3.60; N, 7.46%.

*Synthesis of [Cu₂(μ-I)₂{C₆H₅{1,2,3-N₃C(Ph)C(PPh₂)}-κ-P}₂] (**13**).* To a solution of **3** (0.030 g, 0.074 mmol) in 5 mL CH_3CN was added CuI (0.0141 g, 0.074 mmol) dissolved in CH_3CN (3 mL). The mixture was stirred for 6 h at room temperature. The solvent was removed under reduced pressure, and the residue was washed with petroleum ether to afford the product as a colorless solid. The X-ray quality crystals were obtained by recrystallizing it from a mixture of CH_2Cl_2/petroleum ether at room temperature. Yield: 68% (0.060 g). mp > 230 °C. ^{1}H NMR ($CDCl_3$): δ 6.96−7.56 (m, Ar, 40H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −28.1 (s) ppm. Anal. Calcd for $C_{52}H_{40}N_6P_2Cu_2I_2$: C, 52.41; H, 3.38; N, 7.05. Found: C, 52.65; H, 3.16; N, 6.83%.

*Synthesis of [CuCl(1,10-phen-κ²-N,N){C₆H₅{1,2,3-N₃C(Ph)C-(PPh₂)}-κ-P}] (**14**).* To a solution of **11** (0.0373 g, 0.037 mmol) in acetonitrile (10 mL), was added 1,10 phenantroline (0.0073 g, 0.037 mmol) in the same solvent. The reaction mixture was stirred at room temperature for 2 h. The resulting orange solution was concentrated and kept at room temperature to give bright orange, X-ray quality crystals of **14**. Yield: 68% (0.017 g). mp 239−241 °C (dec). ^{1}H NMR ($CDCl_3$): δ 6.84−7.54 (m, Ar, 28 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −23.8 ppm. Anal. Calcd for $C_{38}H_{28}N_5PCuCl$: C, 66.66; H, 4.12; N, 10.23. Found: C, 66.41; H, 3.83; N, 9.81%.

*Synthesis of [CuBr(1,10-phen-κ²-N,N){C₆H₅{1,2,3-N₃C(Ph)C-(PPh₂)}-κ-P}₂] (**15**).* To a solution of **12** (0.0405 g, 0.037 mmol) in acetonitrile (10 mL) was added 1,10 phenanthroline (0.0073 g, 0.037 mmol) in the same solvent. The reaction mixture was stirred at room temperature for 2 h. The resulting orange solution was concentrated and kept at room temperature to give bright orange, X-ray quality crystals of **15**. Yield: 85% (0.023 g). mp 223−225 °C (dec). ^{1}H NMR ($CDCl_3$): δ 6.77−7.52 (m, ArH, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −22.4 ppm. HRMS (ES): m/z Calcd for $C_{38}H_{28}N_5PCu$ ($[M\text{-}Br]^+$): 648.1378; found: 648.14. Anal. Calcd for $C_{38}H_{28}N_5PCuBr$: C, 62.60; H, 3.87; N, 9.61. Found: C, 62.31; H, 3.50; N, 9.53%.

*Synthesis of [CuI(1,10-phen-κ²-N,N){C₆H₅{1,2,3-N₃C(Ph)C(PPh₂)}-κ-P}] (**16**).* A solution of **3** (0.0168 g, 0.041 mmol) in CH_3CN (5 mL) was added dropwise to a solution of CuI (0.0079 g, 0.041 mmol) dissolved in CH_3CN (3 mL), and the mixture was stirred for 6 h at room temperature. Then 1,10-phenanthroline (0.0082 g, 0.041 mmol) was added to the same solution, and stirring was continued for 2 h. The solvent was removed under vacuum, and the residue was washed with petroleum ether and dried in vacuo to give analytically pure product of **16** as a bright orange solid. Yield: 84% (0.027 g). mp 218−220 °C. ^{1}H NMR ($CDCl_3$): δ 6.78−8.75 (m, Ar, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.7 ppm. Anal. Calcd for $C_{38}H_{28}N_5PCuI$: C, 58.81; H, 3.64; N, 9.02. Found: C, 58.78; H, 3.33; N, 8.80%.

*Synthesis of [CuCl(2,2′-bipy-κ²-N,N){C₆H₅{1,2,3-N₃C(Ph)C(PPh₂)}-κ-P}] (**17**).* To a solution of **11** (0.0373 g, 0.037 mmol) in acetonitrile (10 mL), was added 2,2′-bipyridine (0.0058 g, 0.037 mmol) in the same solvent. The reaction mixture was stirred at room temperature for 2 h. The resulting yellow solution was concentrated and kept at room temperature to give pure, bright yellow, X- ray quality crystals. Yield: 75% (0.018 g). mp 197 °C (dec). ^{1}H NMR ($CDCl_3$): δ 6.96−7.48 (m, Ar, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −24.3 (s) ppm. Anal. Calcd for $C_{36}H_{28}N_5PCuCl$: C, 65.45; H, 4.27; N, 10.60. Found: C, 65.23; H, 3.96; N, 10.39.

*Synthesis of [CuBr(2,2′-bipy-κ²⁻N,N){C₆H₅{1,2,3-N₃C(Ph)C(PPh₂)}-κ-P}] (**18**).* To a solution of **12** (0.0405 g, 0.037 mmol) in acetonitrile (10 mL) was added 2,2′-bipyridine (0.0058 g, 0.037 mmol) in the same solvent. The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to afford the product as a bright yellow colored compound. Yield: 73% (0.019 g). mp 215 °C (dec). ^{1}H NMR (DMSO-d_6): δ 7.00−7.38 (m, Ar, 28H). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −22.7 ppm. HRMS (ESI): m/z Calcd for $C_{36}H_{28}CuN_5P$ ($[M\text{-}Br]^+$): 624.1370; found: 624.1373. Anal. Calcd for $C_{36}H_{28}N_5PCuBr$: C, 61.33; H, 4.00; N, 9.93. Found: C, 61.21; H, 3.75; N, 9.83%.

*Synthesis of [CuI(2,2′-bipy-κ²-N,N){C₆H₅{1,2,3-N₃C(Ph)C(PPh₂)}-κ-P}] (**19**).* A solution of **3** (0.030 g, 0.074 mmol) in CH_3CN (5 mL) was added dropwise to a solution of CuI (0.014 g, 0.074 mmol) dissolved in CH_3CN (3 mL), and the mixture was stirred for 4 h at room temperature. Then 2,2′-bipyridine (0.0115 g, 0.074 mmol) was added in the same solvent, and stirring was continued for 2 h. The solvent was removed under vacuum, and the residue was washed with petroleum ether and dried in vacuo to give analytically pure product of **19** as a bright yellow solid. Yield: 81% (0.045 g). mp 213-216 °C (dec). ^{1}H NMR (DMSO-d_6): δ 7.03−7.55 (m, Ar, 28H). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −24.2 (s). Anal. Calcd for $C_{36}H_{28}N_5PCuI$: C, 57.49; H, 3.75; N, 9.31. Found: C, 57.60; H, 3.45; N, 9.16%.

*Synthesis of [AuCl{o-Ph₂P(C₆H₄){1,2,3-N₃C(Ph)C(H)}-κ-P}] (**20**).* A solution of **2** (0.0150 g, 0.037 mmol) in CH_2Cl_2 (5 mL) was added in $AuCl(SMe_2)$ (0.0105 g, 0.037 mmol) dissolved in CH_2Cl_2 (3 mL). The mixture was stirred for 15 h at room temperature. The solvent was removed under vacuum; the residue was washed with petroleum ether and dried in vacuo to give analytically pure product **20** as a colorless powder. The X-ray quality crystals were obtained by recrystallizing it from a mixture of CH_2Cl_2/petroleum ether at room temperature. Yield: 85% (0.020 g). mp 130−132 °C. ^{1}H NMR ($CDCl_3$): δ 7.21−7.81 (m, Ar, 19H), 8.18 (s, triazolicH, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ

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27.8 (s) ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{20}N_3PAuCl$ ($[M + Na]^+$): 660.0646; Found: 660.0656. Anal. Calcd for $C_{26}H_{20}N_3PAuCl$: C, 48.95; H, 3.16; N, 6.59. Found: C, 48.83; H, 3.04; N, 6.50%.

*Synthesis of [AuCl{C_6H_5-1,2,3-$N_3C(Ph)C(PPh_2)$}-κ-P)] (**21**).* To a solution of **3** (0.030 g, 0.074 mmol) in CH_2Cl_2 (5 mL) was added $AuCl(SMe_2)$ (0.0218 g, 0.074 mmol) also in CH_2Cl_2 (5 mL), and the mixture was stirred for 4 h at room temperature. The solvent was removed under reduced pressure to afford the product as a colorless compound. The X-ray quality crystals were obtained by recrystallizing it from a mixture of CH_2Cl_2/petroleum ether at room temperature. Yield: 68% (0.032 g). mp > 230 °C (dec). ^{1}H NMR ($CDCl_3$): δ 7.06−7.55 (m, Ar, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 12.3 (s) ppm. HRMS (ESI): m/z Calcd for $C_{26}H_{21}N_3PAuCl$ ($[M + H]^+$): 638.0827; Found: 638.0803. Anal. Calcd for $C_{26}H_{20}N_3PAuCl$: C, 48.95; H, 3.16; N, 6.59. Found: C, 48.89; H, 3.41; N, 6.79%.

X-ray Crystallography. A crystal of each of the compounds in the present work suitable for X-ray crystal analysis was mounted on a Cryoloop with a drop of mineral oil and placed in the cold nitrogen stream on the Bruker APEX CCD or D8 Venture (for **9**) diffractometer. Full spheres of data were collected using a combination of three sets of 606 scans in ω (0.3° per scan) at φ = 0°, 120°, and 240° or three sets of 400 frames, each of width 0.5° in ω, collected at φ = 0.00°, 90.00°, and 180.00° and two sets of 800 frames, each of width 0.45° in φ, collected at ω = −30.00 and 210.00 (a hemisphere for **9**) under the control of the APEX2 program suite.[34] The crystals of **2**, **8a**, and **9** proved to be twinned (CELL_NOW).[35] The raw data were reduced to F^2 values using the SAINT+ software,[36] and a global refinement of unit cell parameters using ca. 7662−9746 reflections chosen from the full data sets was performed. In the case of the twinned crystals, two-component reflection files were generated in this step. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS[37] or TWINABS[38]). All the crystal structures were solved by direct method and refined by full-matrix least-squares procedures using the SHELXTL program package.[39,40] Hydrogen atoms attached to carbon were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. In the case of **2**, the full, two-component reflection file was used for the final refinement, while for **8a** and **9**, superior refinement was achieved with the single-component reflection file extracted from the twinned data by TWINABS. The details of X-ray structural determinations are given in Tables 1 and 2, and bond lengths and bond angles are given in Tables 3−6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01094.

NMR spectra of compounds **1** to **21**, computational studies for Li−H exchange (PDF)

Crystallogrpahic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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Inorg. Chem. XXXX, XXX, XXX−XXX