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Coinage metal metallacycles involving a fluorinated 3,5-diarylpyrazolate

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Abstract.

Copper(I) and silver(I) pyrazolate complexes $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ and $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ have been synthesized using the fluorinated 3,5-(diaryl)pyrazole $3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2PzH$ and copper(I) oxide and silver(I) oxide, respectively. The gold(I) analog was obtained from a reaction between Au(THT)Cl and $[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]H/NaH$. The X-ray crystal structures show that the coinage metal complexes $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]M\}_3$ (M = Cu, Ag, Au) are trinuclear in the solid state. They feature, distorted nine-membered M_3N_6 metallacyclic cores. The M-N distances follow Cu < Au < Ag, which is the trend expected from covalent radii of the corresponding coinage metal ions. The $3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2PzH$ forms hydrogen bonded trimers in the solid state that are further organized by π-stacking between aryl rings. Solid samples of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]M\}_3$ display blue photoluminescence. The copper complex $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ is an excellent catalyst for mediating azide-alkyne cycloaddition chemistry.

Introduction.

Pyrazolate complexes of monovalent coinage metals (Cu(I), Ag(I), Au(I)) represent an important class of coordination compounds whose significance spans multiple areas of chemistry, including acid/base and host/guest chemistry, metallophilic d^{10}-d^{10} interactions, supramolecular assemblies, M-M bonded excimers and exciplexes, luminescence,[1-16] as well as catalysis.[13, 17-20] Trinuclear structures are the most common motif among homoleptic coinage metal pyrazolates while tetranuclear, hexanuclear and polymeric complexes are also known to a lesser degree.[1, 6, 20-24] For example, a search of Cambridge Structural Database (CSD)[25] for 3,5-diphenylpyrazolate ligand based copper, silver and gold complexes shows that $\{[3,5\text{-}(Ph)_2Pz]M\}_3$ (Figure 1, **1**, M = Cu, Ag, Au; X = H),[26, 27] $\{[4\text{-}Cl\text{-}3,5\text{-}(Ph)_2Pz]M\}_3$ (Figure 1, **1**, M = Cu, Ag, Au; X = Cl),[24, 28, 29] $\{[4\text{-}Br\text{-}3,5\text{-}(Ph)_2Pz]M\}_3$ (Figure 1, **1**, M = Ag, Au; X = Br),[30] $\{[4\text{-}I\text{-}3,5\text{-}(Ph)_2Pz]M\}_3$ (Figure 1, **1**, M = Ag, Au; X = I),[29] $\{[4\text{-}Me\text{-}3,5\text{-}(Ph)_2Pz]Ag\}_3$[29] are known and feature trinuclear structures. In addition, a few tetramers $\{[3,5\text{-}(Ph)_2Pz]Cu\}_4$,[20] $\{[4\text{-}Cl\text{-}3,5\text{-}(Ph)_2Pz]Cu\}_4$,[28] {[4-

(^{t}BuCO$_2$)-3,5-(Ph)$_2$Pz]Ag}$_4$,[31] and hexamers {[3,5-(Ph)$_2$Pz]Au}$_6$,[27] and {[4-(^{t}BuCO$_2$)-3,5-(Ph)$_2$Pz]Ag}$_6$[31] resulting from the same or similar pyrazolate ligands have also been observed, depending on the method of synthesis and crystallization.

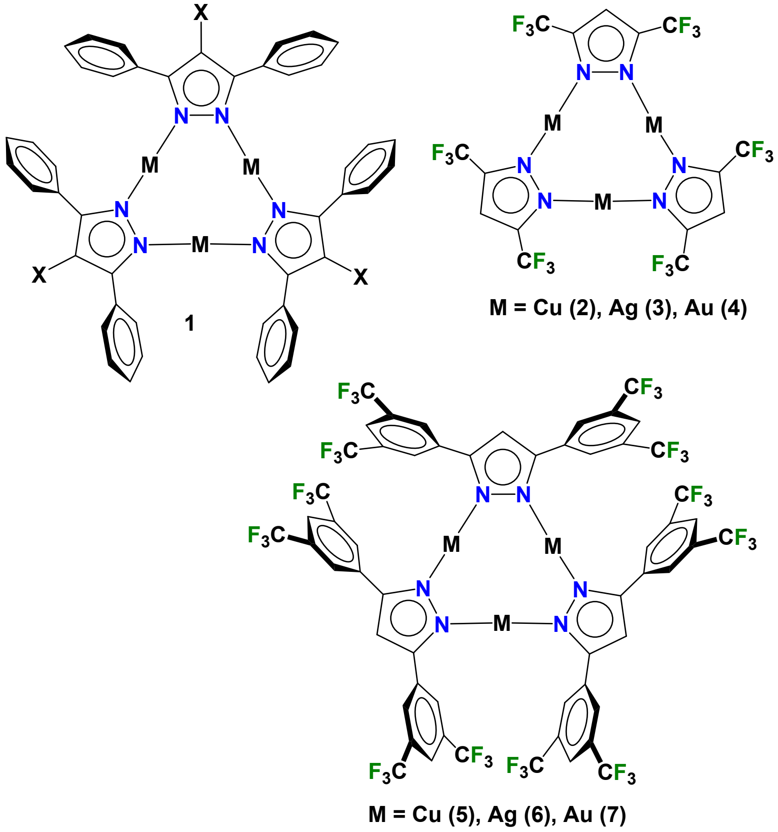


Figure 1. Several coinage metal complexes involving pyrazolate ligand support

An area of research activity in our laboratory concerns the chemistry of copper, silver and gold complexes of highly fluorinated pyrazolates.[7, 32-44] Several years ago, we reported a convenient synthetic route to copper(I) and silver(I) adducts {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ (**2**) and {[3,5-(CF$_3$)$_2$Pz]Ag}$_3$ (**3**) using [3,5-(CF$_3$)$_2$Pz]H and the corresponding metal(I) oxides (Figure 1).[7, 45] These trinuclear d^{10} pyrazolates and the related {[3,5-(CF$_3$)$_2$Pz]Au}$_3$ (**4**) show remarkable photophysical properties and donor-acceptor chemistry.[7, 32, 34, 36, 42, 46, 47] For example, the copper complex {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ exhibits bright phosphorescent emissions both in the solid state and in frozen solutions under UV excitation that can be easily fine- and coarse-tuned to multiple visible colors by varying the solvent, copper adduct concentration, temperature, and the excitation wavelength.[32, 34] These coinage metal complexes **2-4** serve as π-acids, and form adducts with π-bases like benzene, toluene, mesitylene and naphthalene as well as with C_{60} forming diverse supramolecular aggregates.[38, 39, 42, 46, 47] The silver complex $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ also serves as an excellent sensor for the detection of volatile aromatic hydrocarbons such as benzene and toluene.[36] In addition, the trinuclear $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ complex readily reacts with alkynes and CO forming dinuclear and tetranuclear species.[18, 41, 48] It is also an excellent catalyst for azide-alkyne Click-chemistry.[18] Various other groups have also investigated the interesting chemistry of $\{[3,5\text{-}(CF_3)_2Pz]M\}_3$ (**2-4**, M = Cu, Ag, Au).[1, 2, 10, 15, 49-51]

Structurally authenticated coinage metal pyrazolates such as $\{[3,5\text{-}(CF_3)_2Pz]M\}_3$ with fluoro alkyl substituents are noticeably less common,[25] and fluorinated aryl groups are barely explored compared to those featuring hydrocarbon substituents (e.g., Me, *i*-Pr, *t*-Bu, Ph) on the pyrazolate ligand backbone. Considering current interest in metal pyrazolates and in particular, the attractive features of the fluorinated analogs, we embarked on a project to develop fluorinated diarylpyrazolate ligands such as $[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]^-$ and investigate their chemistry. Here we report the synthesis of $3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2PzH$, and the isolation of coinage metal complexes $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]M\}_3$ (Figure 1, **5-7**; M = Cu, Ag, Au), as well as their X-ray crystal structural data and preliminary photophysical and catalytic properties.

Results and discussion.

The diketone 1,3-bis(3,5-bis(trifluoromethyl)phenyl)propane-1,3-dione was synthesized from a mixture of 3,5-bis(trifluoromethylbenzoate and 3,5-bis(trifluoromethyl)acetophenone under basic conditions using a modified literature method utilized in the synthesis of somewhat related 1,3-bis(4-methylphenyl)propane-1,3-dione.[52] It was isolated as a white solid in 87% yield. The ^1H NMR spectrum of 3,5-(3,5-

$(CF_3)_2PhCO)_2CH_2$ in $CDCl_3$ suggest the presence of enol form, 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one in solution. The pyrazole 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ was synthesized by a cyclocondensation reaction involving 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one and hydrazine monohydrate, and isolated as a colorless crystalline solid in 87% yield. The 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ is soluble in acetone and tetrahydrofuran at room temperature and in hot benzene and hot chloroform. It was characterized by several methods including X-ray crystallography. The ^1H NMR spectrum in $CDCl_3$ includes three peaks assignable to 3,5-$(CF_3)_2Ph$ protons (δ 8.18 and 7.87 ppm) and CH of the pyrazole (δ 7.11 ppm) ring. ^{19}F NMR spectrum displayed a singlet at δ -63.23 ppm.

The analysis of the crystals obtained from $CHCl_3$ by single crystal X-ray diffraction show that 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ forms hydrogen bonded trimers in the solid state (Figure 2) that are further organized by π-stacking between aryl rings (with centroid to centroid distances ranging from 3.70-3.87 Å). The trimeric form is unexpected considering the steric demands of the bulky aryl groups at the 3- and 5-positions, facing each other in a planar arrangement. The aggregate accommodates that encounter by twisting pyrazolyl planes and placing aryl groups above and below each other (Figure 2). The nitrogen atoms of the trimeric core forms a distorted chair configuration with N•••N distances (the distances between donor and acceptor nitrogen atoms of the hydrogen bond) of 2.85 Å. Solid state structures of NH-pyrazoles have indeed attracted interest as they show diverse structures ranging from dimers, trimers, tetramers, hexamers, and polymers (catemers) and due to the tautomerism.[53-55] They are also of interest because binary group 11 metal pyrazolates (in-which N-H is replaced by N-M; M = Cu, Ag, Au) also show some parallels as noted earlier. Among 1,3-diarylpyrazoles,[25] the dimeric form appears to be the most common (e.g., in 4-(CF_3)-3,5-$(Ph)_2PzH$,[56] 4-(NC)-3,5-$(Ph)_2PzH$,[57] 4-(Br)-3,5-$(Ph)_2PzH$,[53] 3-(4-$(CF_3)Ph$)-5-(Ph)PzH[58]) while examples of tetramers (e.g., 3,5-$(Ph)_2PzH$)[59] and polymers (e.g., 3,5-(4-Cl-Ph)$_2$PzH,[60] 3,5-(4-NC-Ph)$_2$PzH,[61]) are also known.

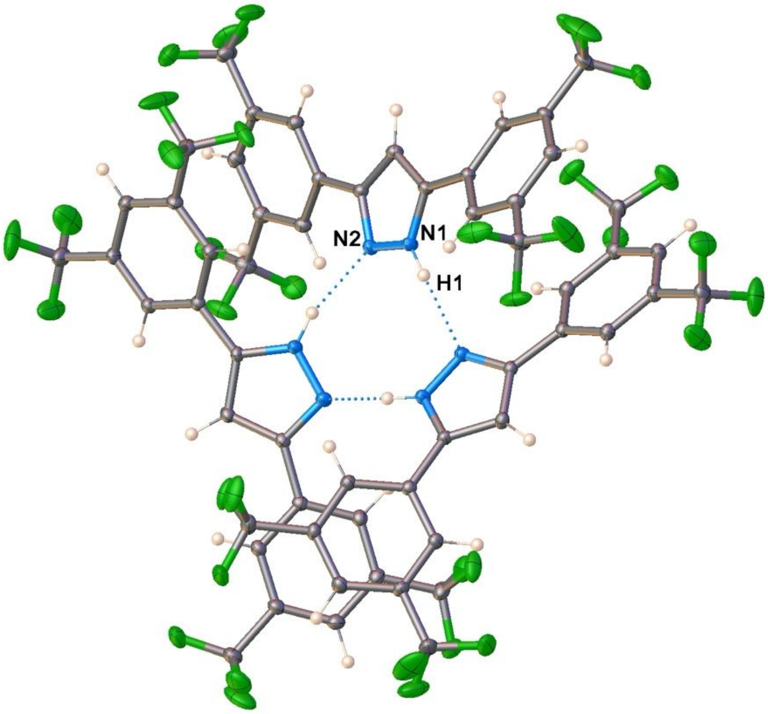


Figure 2. Molecular structure of 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ showing the trimers resulting from NH•••N hydrogen bonding

The trinuclear {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Cu\}_3$ (**5**) was synthesized by using copper(I) oxide and 3,5-(3,5-$(CF_3)_2Ph)_2PzH$ via a method similar to that reported for {[3,5-$(CF_3)_2Pz]Cu\}_3$.[45] However, unlike the 3,5-trifluoromethyl pyrazole analog, it was found that the formation of **5** did not take place when benzene was used as a solvent but works well when higher boiling toluene was used. The Cu(I) oxide/pyrazole mixture in toluene was refluxed under nitrogen overnight and filtered while maintaining the solution temperature above 90 ^{0}C to remove the excess metal oxide. It was found that if the solution was allowed to cool below 90 ^{0}C, the product began to precipitate. The hot-filtered clear solution was allowed to slowly come to room temperature to obtain colorless needles. ^{1}H NMR spectrum of these crystals in $CDCl_3$ showed an upfield shifted C*H* resonance of the pyrazolyl rings (δ 7.00 ppm) with respect to the starting material (δ 7.11 ppm), indicating the formation of the trinuclear complex {[3,5-(3,5-$(CF_3)_2Ph)_2Pz]Cu\}_3$. The ^{1}H NMR also indicated the inclusion of some toluene molecules in the crystalline copper complex. The trapped toluene can be removed by drying the crystals under vacuum at 90 ^{0}C for about 4 hours. It was found that the toluene-free crystals were much less soluble in solvents such as $CDCl_3$.

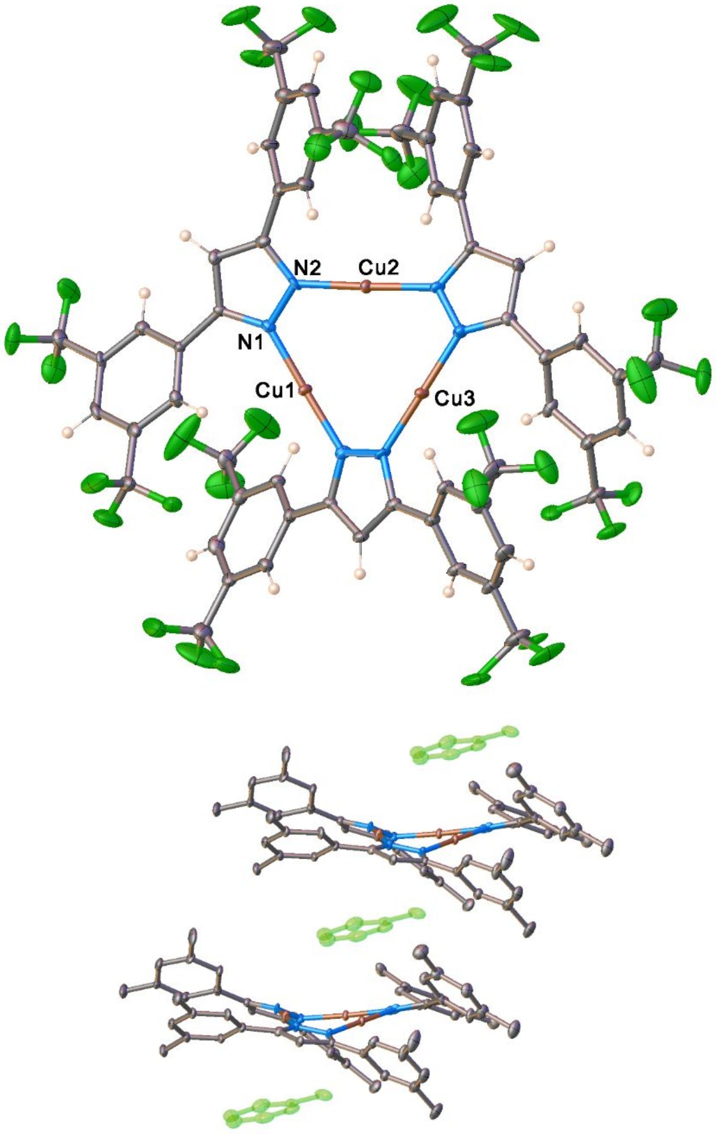


Figure 3. **Top:** Molecular structure of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ (toluene molecules in the crystal lattice have been omitted for clarity), and **Bottom:** A view showing intercalation of toluene molecules between $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ (hydrogen and fluorine atoms have been omitted for clarity)

Table 1. Selected bond distances (Å) and angles (°) of trinuclear copper(I), silver(I) and gold(I) complexes supported by pyrazolates with 3,5-diaryl groups on the pyrazolyl rings. M = Cu, Ag or Au

Metal pyrazolate	M-N	N-M-N	M•••M (intra-trimer)	M•••M (inter trimer)	Ref
$\{[3,5\text{-}(Ph)_2Pz]Cu\}_3$	2.041(7)-2.105(7)	169.2(3)-178.6(3)	3.280-3.406	over 5	[26]
$\{[4\text{-}Cl\text{-}3,5\text{-}(Ph)_2Pz]Cu\}_3$	1.849(2)-1.867(2)	173.22(9)-178.42(9)	3.140-3.251	4.704	[28]
$\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$	1.843(7)-1.869(7)	175.2(3)-178.1(3)	3.133-3.285	over 5	This work
$\{[3,5\text{-}(Ph)_2Pz]Ag\}_3$	2.073(4)-2.106(4)	171.17(17)-172.30(16)	3.357-3.525	2.979	[62]
$\{[4\text{-}Cl\text{-}3,5\text{-}(Ph)_2Pz]Ag\}_3$	2.082(10)-2.112(11)	175.6(4)-177.8(4)	3.469-3.549	over 5	[29]
$\{[4\text{-}Br\text{-}3,5\text{-}(Ph)_2Pz]Ag\}_3$	2.054(10)-2.132(10)	170.1(4)-178.4(4)	3.312-3.632	over 5	[30]
$\{[4\text{-}I\text{-}3,5\text{-}(Ph)_2Pz]Ag\}_3$	2.074(5)-2.093(5)	173.6(2)-174.8(2)	3.414-3.596	over 5	[29]
$\{[4\text{-}(Me)\text{-}3,5\text{-}(Ph)_2Pz]Ag\}_3$	2.059(3)-2.092(3)	169.85(14)-175.95(15)	3.342-3.573	3.937	[29]
$\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$	2.072(4)-2.088(5)	174.2(2)-177.1(2)	3.368-3.433	over 5	This work
$\{[3,5\text{-}(Ph)_2Pz]Au\}_3$	1.978(9)	179.6(3)	3.368	over 5	[27]
$\{[4\text{-}Cl\text{-}3,5\text{-}(Ph)_2Pz]Au\}_3$	1.997(7)-2.009(6)	178.2(3)-179.2(3)	3.340-3.386	4.387	[29]
$\{[4\text{-}Br\text{-}3,5\text{-}(Ph)_2Pz]Au\}_3$	1.998(6)-2.016(6)	178.1(2)-179.6(3)	3.348-3.379	4.442	[30]
$\{[4\text{-}I\text{-}3,5\text{-}(Ph)_2Pz]Au\}_3$	2.003(15)-2.045(13)	175.4(6)-178.0(6)	3.347-3.455	over 5	[29]
$\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$	1.996(3)-2.013(3)	176.66(14)-177.28(14)	3.288-3.369	over 5	This work

For comparison, the van der Waals contact distance of two metal atoms based on values suggested by Bondi[63] and Alvarez[64] are: for Cu•••Cu = 2.80 and 4.76 Å, Ag•••Ag = 3.44 and 5.06 Å, and Au•••Au = 3.32 and 4.64 Å, respectively.

The copper(I) complex $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ (**5**) was re-crystallized from toluene. The X-ray crystal structure of **5** shows that it crystallizes with 1.5 molecules of toluene in the asymmetric unit. One of these toluene molecules and $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ forms extended columns as illustrated in Figure 3, with closest Cu•••C(toluene) separations of 3.32 and 3.47 Å. These distances are slightly longer than sum of the Bondi's van der Waals radii of copper and carbon 1.40 + 1.70 = 3.10 Å.[63] However, more recent work from Alveraz[64] places van der Waals contact distance of copper and carbon at 4.15 Å implying noteworthy interactions between these moieties**.** This tendency of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ to intercalate arenes is similar to that observed with $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ (**2**).[38] The partially occupied (second) toluene molecule occupies the space between these columns. Selected bond distances and angles of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ are given in Table 1. It is a trinuclear species with a somewhat twisted Cu_3N_6 metallacyclic core.

The silver(I) complex $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ (**6**), was synthesized using a method similar to that used for $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ using the appropriate pyrazole $3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2PzH$ and silver(I) oxide.[45] Similarly to the copper analog, it was found that the higher boiling toluene (instead of benzene) is needed for the efficient reaction. The $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ was isolated as a white solid in moderate yield (51%). The ^1H NMR spectrum of the solid samples indicated the presence of some trapped toluene, which was removed by drying the solids under vacuum at 60 ^{0}C overnight. These solids were then recrystallized from dichloromethane/hexanes (4:1) at -20 ^{0}C to give colorless needle-like crystals. It is soluble in most common organic solvents such benzene, dichloromethane, acetonitrile, toluene, and tetrahydrofuran and in hot hexane.

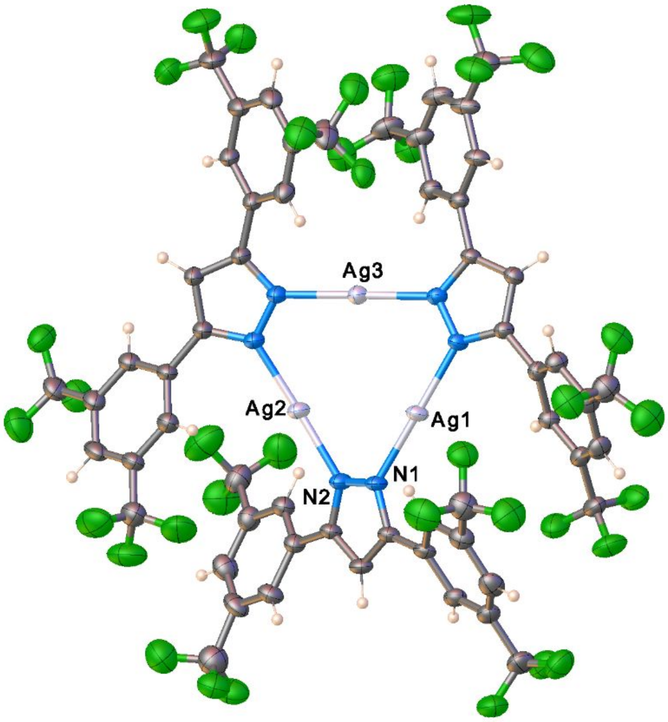


Figure 4. Molecular structure of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ (dichloromethane molecules in the crystal lattice have been omitted for clarity)

The silver(I) complex {[3,5-(3,5-$(CF_3)_2Ph)_2$Pz]Ag}$_3$ (**6**) crystallizes with molecules of dichloromethane the asymmetric unit. The molecular structure of {[3,5-(3,5-$(CF_3)_2Ph)_2$Pz]Ag}$_3$ (Figure 4) shows that it is a trinuclear species and forms a somewhat twisted Ag_3N_6 core to avoid unfavorable steric interactions of 3,5-aryl groups of the neighboring pyrazolates in **6**. There are no close inter-trimer Ag•••Ag contacts as seen with several trinuclear silver pyrazolates bearing alkyl substituents[24, 42, 65] and in some analogs with 3,5-diarylated pyrazolates (Table 1). The bulky aryl groups in {[3,5-(3,5-$(CF_3)_2Ph)_2$Pz]Ag}$_3$ likely hinder the close face-to-face approach of neighboring trimers from above and below the trimer-plane to form inter-trimer argentophilic contacts.

The synthesis of the trinuclear pyrazolate complex of gold(I), {[3,5-(3,5-$(CF_3)_2Ph)_2$Pz]Au}$_3$ (**7**) involved the reaction between [3,5-(3,5-$(CF_3)_2Ph)_2$Pz]Na (prepared from NaH and 3,5-(3,5-$(CF_3)_2Ph)_2$PzH) and Au(THT)Cl in THF. The product {[3,5-(3,5-$(CF_3)_2Ph)_2$Pz]Au}$_3$ was found to be light sensitive and generates the starting pyrazole ligand back upon prolonged exposure to light (~ 2 days). The molecular structure of the gold(I) complex {[3,5-(3,5-$(CF_3)_2Ph)_2$Pz]Au}$_3$ (**7**) is illustrated in Figure 4. It is also a trinuclear species similar to the lighter coinage metal adduct analogs **5** and **6**. It has a relatively less twisted (more planar) M_3N_6 core. For example, there are 3, 6, and 5 nitrogen or metal atoms with deviations over 0.2 Å (largest 0.26, 0.34 and 0.29 Å) from mean-plane of M_3N_6 core of the Au, Ag, and Cu adducts **7-5**, respectively. Table 1 summarizes selected bond distances and angles for {[3,5-(3,5-$(CF_3)_2Ph)_2$Pz]Au}$_3$ in addition to other related systems. The M-N distances of **5-7** follow the trend expected from covalent radii of the corresponding coinage metal ions,[7, 66] with longest and shortest M-N distances observed in the silver(I) and copper(I) complexes, respectively.

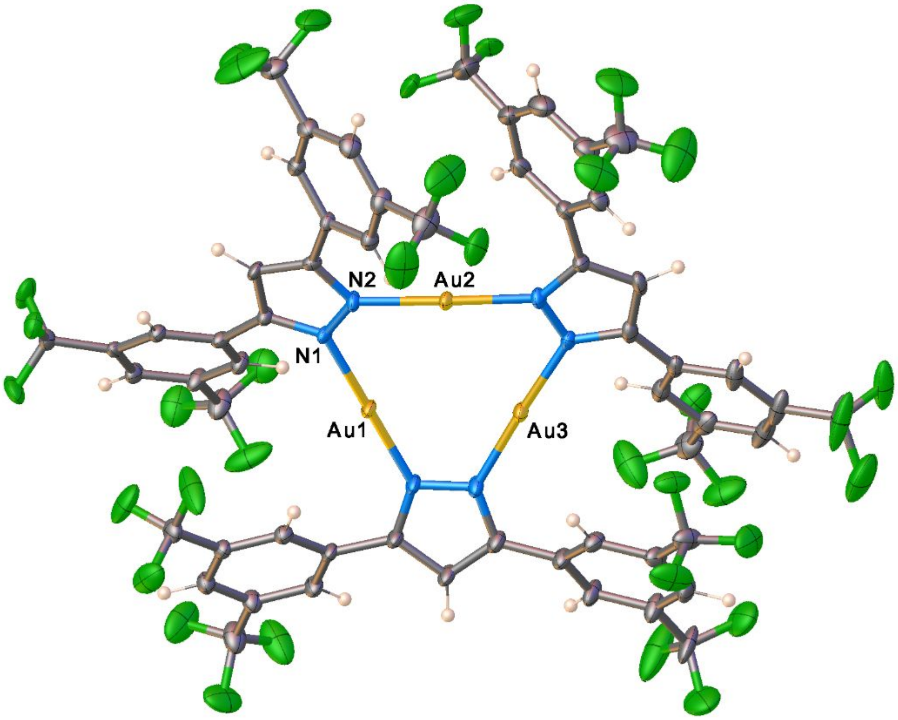


Figure 5. Molecular structure of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$ (**7**)

Photophysical properties: All three metal pyrazolates **5-7** exhibited blue luminescence upon exposure to UV radiation. The copper and silver analogs exhibited luminescence only at lower temperatures (e.g., 77 K), while the gold analog display luminescence at both at room temperature and lower temperatures. For example at 77 K, $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ (**5**) displayed a light blue luminescence under UV radiation with an excitation maximum at 315 nm and emission maximum at 460 nm, with a Stokes Shift of ~8200 cm^{-1} (Figure 6). The gold(I) complex, $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$ emitted bright blue light under UV light with an excitation maximum at 310 nm and emission maximum at 460 nm, with a Stokes shift of ~8500 cm^{-1}. (Figure 6). As noted above, these $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]M\}_3$ complexes do not show close inter-trimer metallophilic interactions in the solid state. The somewhat similar blue emissions observed in these three coinage metal complexes $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]M\}_3$ supported by 3,5-diaryl substituted pyrazolates (featuring extended aromatic systems) are likely a result of pyrazole ligand centered luminescence[58] that are sensitized via internal heavy atom effect. We have observed similar emissions in $\{[3\text{-}(CF_3),5\text{-}(Ph)Pz]Cu\}_3$.[34]

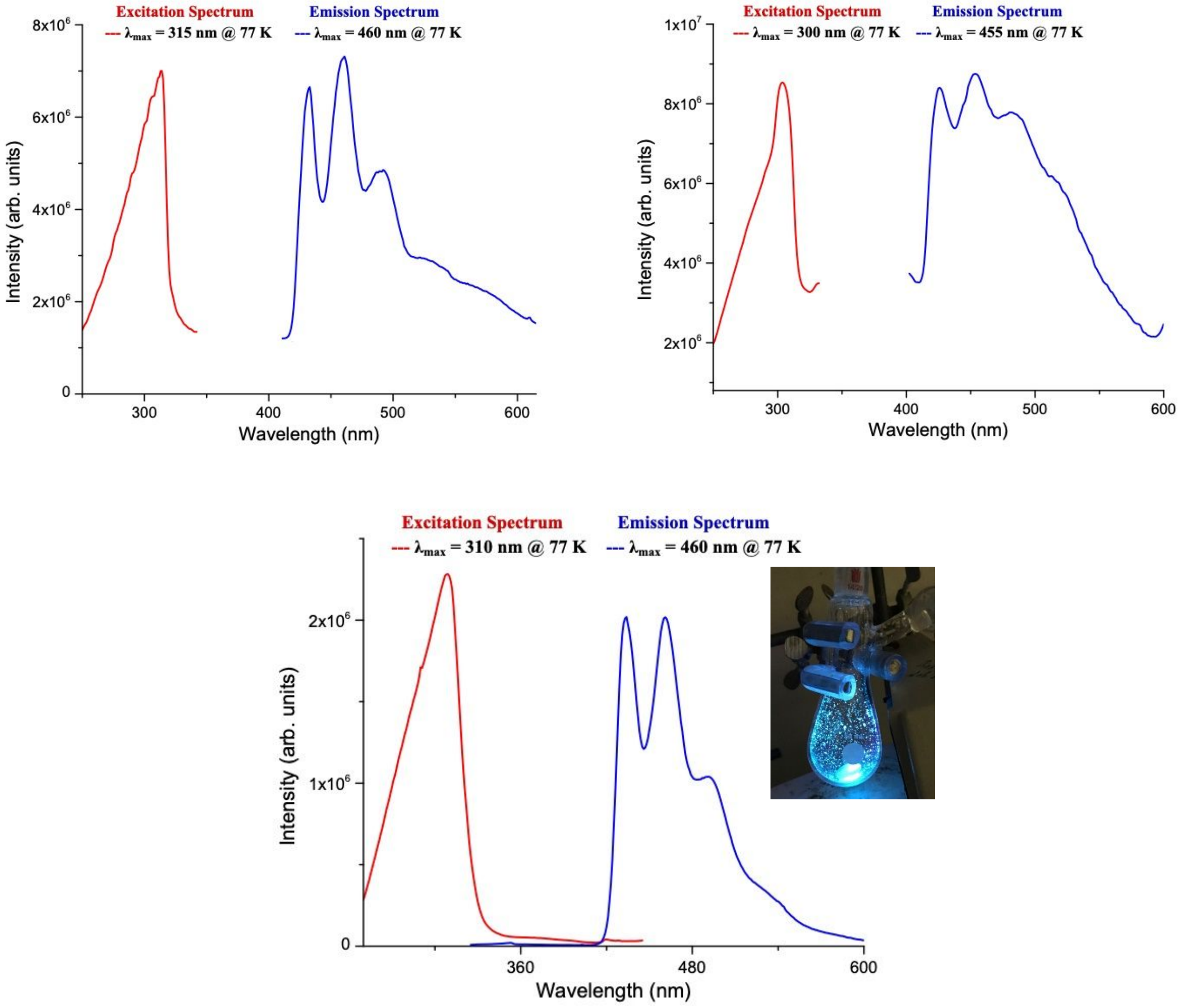
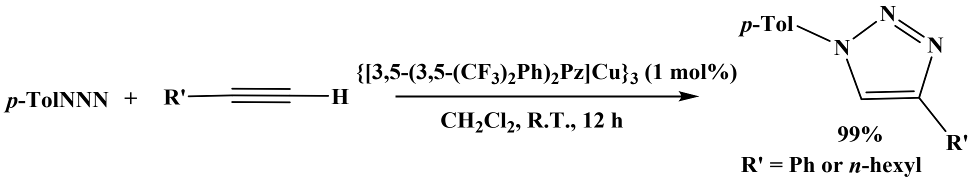


Figure 6. Emission and excitation spectra of crystalline solid samples of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ (top left) and $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ (top right) and $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$ (bottom) at 77 K. Bottom insert: a photo showing the emission color of the gold complex under UV exposure.

Catalysis: Copper catalyzed synthesis of 1,2,3-triazoles via the cycloaddition of azides to triple bonds of alkynes is a very important process involving copper and alkynes.[67-72] The standard catalytic system uses copper(II) salts such as copper sulfate pentahydrate in the presence of a reducing agent, such as sodium ascorbate.[68] Recently, we and others reported that $\{\mu\text{-}[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ is an excellent, stand-alone catalyst for the cycloaddition of azides to terminal alkynes.[18, 19] In an attempt to extend this work to other copper(I) pyrazolates, we probed the viability of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ as a catalyst in azide-cycloaddition of alkynes.



Scheme 1. The $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ catalyzed alkyne-azide cycloaddition of terminal alkynes and *p*-tolylazide

Indeed, $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$, is an excellent catalyst for azide-alkyne cycloaddition of *p*-tolylazide with 1-octyne or phenylacetylene (Scheme 1), leading to 1,2,3-triazoles in ≥ 99% conversion (Table 2), under mild conditions, without any additives, and in high isolated yields. The silver and gold analogs were inactive under similar conditions.

Table 2. Azide-alkyne cycloaddition chemistry. Reactions were performed at room temperature in CH_2Cl_2 using catalyst (1 mol%), alkyne (1.5 mmol), *p*-tolylazide (1.5 mmol)

Entry	Catalyst	Alkyne	Percent Conversion	Isolated Yield
1	$\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$	1-octyne	99 %	94 %
2	$\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$	1-octyne	0 %	N/A
3	$\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$	1-octyne	0 %	N/A
4	$\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$	phenylacetylene	100 %	97 %

Cyclopropanation of olefins is also an important reaction.[73, 74] Previous reports indicate that tetranuclear copper(I) pyrazolate complexes, $\{[3,5\text{-}(Ph)_2Pz]Cu\}_4$, $\{[3,5\text{-}(t\text{-}Bu)_2Pz]Cu\}_4$, and $\{[3,5\text{-}(sec\text{-}BuCO_2)_2Pz]Cu\}_4$ catalyze the cyclopropanation of alkenes in high *trans:cis* ratios and conversion yields.[75]

We also investigated the ability of the copper(I) complex $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ to catalyze the cyclopropanation of alkenes, but found the cyclopropane yields to be low. For example, 3 mol% of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ catalyzes the reaction of styrene (in excess) with ethyl diazoacetate (EDA) in dichloromethane (catalyst:EDA:styrene molar ratio of 1:33:100) to afford ethyl-2-phenylcyclopropane-1-carboxylate in 45% yield. The *trans*-diastereomer is found in moderately greater excess in the product mixture (similar to the previous report).[75] The $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ also catalyzes the same process affording slightly lower yield of the cyclopropane (37%) product. Although we did not optimize the reaction conditions, this preliminary work shows that trinuclear $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ and $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ are capable of mediating carbene transfer to olefins (see Supporting Information).

In summary, we have successfully synthesized a useful fluorinated pyrazole, $3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2PzH$ and utilized it in the preparation of homoleptic, copper(I), silver(I) and gold(I) complexes $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]M\}_3$ (**5-7**). X-ray crystal structures of the precursor pyrazole and $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]M\}_3$ are also reported. They all feature trimeric structures. These complexes **5-7** displayed solid state photoluminescence at lower temperature for the copper and silver, and both at lower and room temperature for the gold adduct. The $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ is an excellent catalyst for azide-alkyne cycloaddition chemistry. It can also mediate olefin cyclopropanations. We are currently expanding this work to other fluorinated aryl pyrazolates and applications.

Experimental section

General Procedures.

All preparations and manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk technique. Commercially available solvents were purified and dried by standard methods and degassed twice by freeze-pump-thaw method prior to use. Glassware was oven dried overnight at 150 °C. NMR spectra were acquired at 25 °C, on a JEOL Eclipse 500 spectrometer (^1H, 500.16 MHz; ^{13}C, 125.78 MHz and ^{19}F, 470.62 MHz), unless otherwise noted. ^{19}F NMR values were referenced to external

$CFCl_3$. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed using a Perkin-Elmer Model 2400 CHN analyzer. Au(THT)Cl and p-tolyl azide were prepared via a reported routes.[76, 77] Other reagents were obtained from commercial sources and used as received.

1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one:

Sodium hydride (60% in mineral oil, 0.468 g, 11.72 mmol) was washed with hexanes (5 mL) at room temperature under an atmosphere of nitrogen. Anhydrous THF (20 mL) was then added. In a separate flask, 3',5'-bis(trifluoromethyl)acetophenone (2.00 g, 7.80 mmol) was combined with methyl 3,5-bis(trifluoromethyl)benzoate (2.32 g, 8.58 mmol) and added to the sodium hydride solution, dropwise. The resultant mixture was heated at reflux for 36 hours. The mixture was cooled to room temperature and ice-cold 10% hydrochloric acid (40 mL) was added dropwise to the rapidly stirred mixture, forming a precipitate. Diethyl ether (25 mL) was added to dissolve the precipitate. The organic layer was isolated by extraction, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum to afford an off-white solid. This solid was recrystallized in acetone to afford the title compound as colorless needles (3.35 g, 87%). m.p. 173 °C. Anal. Calculated for $C_{19}H_8F_{12}O_2$: C, 45.99%; H, 1.62%; N, 0%. Found: C, 45.98%; H, 1.62%; N, 0%. ^1H NMR ($CDCl_3$, 500 MHz) δ: 16.59 (s, 1H, O*H*), 8.44 (s, 4H, ar C*H*), 8.11 (s, 2H, ar C*H*), 6.89 (s, 1H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 500 MHz) δ: 183.5 (s, *C*=O), 137.0 (s, ar *C*), 132.8 (q, $^2J_{CF} = 33.6$ Hz, *C*CF$_3$), 127.5 (s, ar *C*), 126.4 (m, $^3J_{CF} = 3.6$ Hz, ar *C*), 123.0 (q, $^1J_{CF} = 274$ Hz, *C*F$_3$), 94.0 (s, *C*H). ^{19}F NMR ($CDCl_3$, 500 MHz) δ: -63.11. We have also confirmed the identity of this molecule using X-ray crystallography but the data quality is not high enough for publication of the crystal structure. Crystal Data for $C_{19}H_8F_{12}O_2$ (M =496.25 g/mol): monoclinic, space group C2/c (no. 15), a = 24.913(6) Å, b = 8.3684(18) Å, c = 9.241(2) Å, β = 110.639(6)°, V = 1802.9(7) Å^3, Z = 4, T = 101.49 K, μ(MoKα) = 0.201 mm^{-1}, *Dcalc* = 1.828 g/cm^3.

3,5-(3,5-(CF$_3$)$_2$Ph)$_2$PzH: To a solution of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)-3-hydroxyprop-2-en-1-one (2.00 g, 4.04 mmol) in chloroform (40 mL), hydrazine monohydrate (303 mg, 6.06 mmol) was added, dropwise. The resulting yellow solution was refluxed overnight. Once cooled to room temperature 40 mL of H_2O was slowly added, precipitating the product. This solid was isolated by vacuum filtration, and dried under vacuum. The white solid was recrystallized from hot chloroform to give colorless cubic crystals (2.18 g, 87%). m.p. 188 °C. Anal. Calculated for $C_{19}H_8F_{12}N_2$: C, 46.36%; H, 1.64%; N, 5.69%. Found: C, 46.21%; H, 1.36%; N, 5.80%. ^{1}H NMR (CDCl$_3$, 500 MHz) 8.18 (s, 4H, ar C*H*), 7.87 (s, 2H, ar C*H*), 7.11 (s, 1H, Pz*H*), could not observe the NH resonance. ^{13}C{^{1}H} NMR (CDCl$_3$, 500 MHz) δ: 146.8 (s, Pz*C*), 132.7 (q, $^2J_{CF}$ = 33.6 Hz, *C*CF$_3$), 132.7 (s, ar *C*), 125.8 (s, ar *C*), 122.4 (m, ar *C*, $^3J_{CF}$ = 3.6 Hz), 123.2 (q, $^1J_{CF}$ = 274 Hz, *C*F$_3$), 102.3 (s, Pz*C*H). ^{19}F NMR (CDCl$_3$, 500 MHz) δ: -63.23 ppm.

{[3,5-(3,5-(CF$_3$)$_2$Ph)$_2$Pz]Cu}$_3$ (**5**): 3,5-(3,5-(CF$_3$)$_2$Ph)$_2$PzH (200 mg, 0.41 mmol) and Cu_2O (29 mg, 0.20 mmol) are combined in a flask and 15 mL dry toluene. The resulting mixture was refluxed overnight. The mixture was filtered while still hot to remove excess Cu_2O. The resulting clear solution was allowed to slowly come to room temperature, giving colorless needles. The crystalline solid was dried under reduced pressure to obtain **5** (130 mg, 57%). Anal. Calcd for $C_{57}H_{21}Cu_3F_{36}N_6$•0.3 toluene: C, 41.95%; H, 1.39%; N, 4.97%, Found: C, 42.29%; H, 1.33%; N, 5.88%. The crystals were dried under vacuum at 90 °C for 4 hours to remove toluene. ^{1}H NMR (CDCl$_3$, 500 MHz): 8.07 (s, 4H, ar C*H*); 7.65 (s, 2H, ar C*H*); 7.00 (s, 1H, Pz*H*). ^{19}F NMR (CDCl$_3$, 500 MHz): -63.47 ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 500 MHz) on sample containing some toluene: 153.2 (s, Pz*C*), 132.6 (q, $^2J_{CF}$ = 34.8 Hz, *C*CF$_3$), 126.3 (s, ar *C*), 125.9 (s, ar *C*), 123.1 (q, $^1J_{CF}$ = 274 Hz, *C*F$_3$), 122.2 (s, ar *C*), 104.5 (Pz*C*H), and toluene peaks present (toluene free product is not very soluble in CDCl$_3$). X-ray quality crystals were obtained by cooling a warm solution of **5** in toluene.

{[3,5-(3,5-(CF$_3$)$_2$Ph)$_2$Pz]Ag}$_3$ (**6**): 3,5-(3,5-(CF$_3$)$_2$Ph)$_2$PzH (500 mg, 1.01 mmol) and Ag_2O (118 mg, 0.51 mmol) were combined in a flask and 20 mL dry toluene was added. This solution was protected from light and refluxed overnight. After cooling to room temperature, the mixture was filtered through Celite to obtain a colorless solution. This solution was dried under reduced pressure to yield a white solid. Trapped toluene was removed by drying the solids under vacuum at 60 ^{0}C overnight. , 310 mg, 51% yield. Anal. Calcd for $C_{57}H_{21}Ag_3F_{36}N_6$: C, 38.09%; H, 1.18%; N, 4.68%, Found: C, 38.33%; H, 1.39%; N, 4.19%. ^{1}H NMR ($CDCl_3$, 500 MHz): 8.08 (s, 4H, ar C*H*); 7.77 (s, 2H, ar C*H*); 7.06 (s, 1H, Pz*H*). ^{19}F NMR ($CDCl_3$, 500 MHz): -63.52 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 500 MHz): 151.9 (br s, Pz*C*), 134.3 (s, ar *C*), 132.5 (q, $^2J_{CF}$ = 33.6 Hz, *C*CF_3), 126.0 (s, ar *C*), 123.0 (q, $^1J_{CF}$ = 272 Hz, *C*F_3), 122.1 (s, ar *C*), 103.2 (Pz*C*H). The product was recrystallized from dichloromethane: hexane (4:1) at -20 °C to give colorless needle-like crystals of **6**.

{[3,5-(3,5-(CF_3)$_2$Ph)$_2$Pz]Au}$_3$ (**7**): NaH (8.9 mg, 0.22 mmol, 60% in oil) was washed free from oil with dry hexanes (2 mL). In a separate flask, (3,5-(CF_3)$_2$Ph)$_2$PzH (100 mg, 0.20 mmol) was dissolved in 10 mL dry THF. This solution was then slowly added dropwise to the NaH solution, at 0 °C. The resulting mixture was allowed to stir for 1 hour. This sodium salt of pyrazolate was filtered to remove any excess NaH and then added to Au(THT)Cl (64 mg, 0.20 mmol) in 5 mL dry THF. The resulting solution was stirred for 6 hours at room temperature, protected from light by aluminum foil. The solution was filtered through Celite and the filtrate was pumped dried to obtain **7** as a white solid (82 mg, 57%). Anal. Calcd for $C_{57}H_{21}Au_3F_{36}N_6$: C, 33.16%; H, 1.03%; N, 4.07%, Found: C, 33.32%; H, 0.88%; N, 3.98%. ^{1}H NMR ($CDCl_3$, 500 MHz): 8.15 (s, 4H, ar C*H*); 7.72 (s, 2H, ar C*H*); 7.17 (s, 1H, Pz*H*). ^{19}F NMR ($CDCl_3$, 500 MHz): -63.59 ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 500 MHz): 151.6 (s, Pz*C*), 133.6 (s, ar *C*), 132.2 (q, $^2J_{CF}$ = 33.6 Hz, *C*CF_3), 127.2 (s, ar *C*), 122.8 (q, $^1J_{CF}$ = 274 Hz, *C*F_3), 122.4 (m, ar *C*), 106.3 (Pz*C*H). Solid samples of **7** was recrystallized from toluene to obtain X-ray quality crystals.

General procedure for Azide-Alkyne Cycloaddition:

The catalyst (0.015 mmol, 1 mol% based on *p*-tolylazide) was dissolved in CH_2Cl_2 (5 mL) under a nitrogen atmosphere at room temperature. The alkyne (1.5 mmol) was slowly added, followed by *p*-tolylazide (1.5 mmol). The mixture was stirred at room temperature overnight, under a nitrogen atmosphere. The crude mixture was analyzed using ^1H NMR, to check for the presence of the desired triazole.

General procedure for cyclopropanation:

The catalyst (0.023 mmol, 3 mol% based on ethyl diazoacetate, EDA) was dissolved in CH_2Cl_2 (10 mL) under a nitrogen atmosphere at room temperature. Styrene (2.25 mmol) was added, followed by slow addition over 10 hours of EDA (0.75 mmol). The mixture was stirred at room temperature overnight, under a nitrogen atmosphere, while EDA was added. After complete addition, the mixture was stirred for 1 day at room temperature. The crude mixture was analyzed using ^1H NMR, to check for the presence of cyclopropane. Percent yield and percentage of cis/trans isomers were calculated using ^1H NMR and an internal standard of dimethylformamide. The ^1H NMR also shows peaks corresponding to diethyl maleate and diethyl fumarate.

Photophysical properties.

The steady state photoluminescence of the three complexes (white microcrystiline powders packed into 5 mm quartz tubes) were recorded using the FluoroMax-3 spectrofluorometer (Horiba Jobin Yvon, France) with the DataMax software (Horiba, Japan). Excitation and Emission spectra were recorded in the range of 250–600 nm with a bandpass of 1 nm. The resulting spectra were corrected to the background intensity of the 150W Xe arc lamp. The 77 K photoluminescence data were collected by submerging the sample in liquid nitrogen using a Suprasil quartz liquid nitrogen dewar.

X-ray Structure Determinations. A suitable crystal covered with a layer of hydrocarbon/Paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low temperature nitrogen stream.

The X-ray intensity data were measured on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed using the Bruker Apex program suite. Absorption corrections were applied using SADABS. Initial atomic positions were located by direct methods using XT, and the structures of the compounds were refined by the least-squares method using SHELXL[78, 79] within Olex2[80] GUI. The $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Cu\}_3$ (**5**) crystallizes in Triclinic P-1 space group with 1.5 molecules of toluene. Compound $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ (**6**) crystallizes with 2 molecules of dichloromethane in the crystal lattice. Crystals tend to crack at low temperature and therefore data were collected at room temperature. One of the CH_2Cl_2 molecules show significant disorder and a quite a few fluorine atoms of CF_3 groups show positional disorder. The disordered CH_2Cl_2 was removed using MASK routine in Olex2. Positional disorder of fluorine atoms were managed by SHELX constraints. All these issues lower the structure quality somewhat and therefore metrical parameters of $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Ag\}_3$ should be treated with care. In $\{[3,5\text{-}(3,5\text{-}(CF_3)_2Ph)_2Pz]Au\}_3$ (**7**), a highly disordered solvent molecule was removed using the PLATON SQEEZE routine. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions and refined riding on corresponding carbons. X-ray structural figures were generated using Olex2. CCDC 2012029-2012032 files contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK). Additional details are provided in supporting information section.

Crystal Data for 3,5-(3,5-$(CF_3)_2Ph)_2PzH$, $C_{19}H_8F_{12}N_2$ (M =492.27 g/mol): trigonal, space group R-3 (no. 148), a = 17.7048(6) Å, c = 31.8231(11) Å, V = 8638.8(7) Å^3, Z = 18, T = 99.99 K, μ(MoKα) = 0.184 mm^{-1}, $Dcalc$ = 1.703 g/cm^3, 36951 reflections measured (5.466° $\leq 2\Theta \leq$ 59.264°), 5428 unique (R_{int} = 0.0228, R_{sigma} = 0.0144) which were used in all calculations. The final R_1 was 0.0332 (I > 2σ(I)) and wR_2 was 0.0900 (all data).

Crystal Data for{[3,5-(3,5-$(CF_3)_2$Ph$)_2$Pz]Cu$\}_3$•1.5(toluene), $C_{67.5}H_{33}Cu_3F_{36}N_6$ (M =1802.62 g/mol): triclinic, space group P-1 (no. 2), a = 8.4054(10) Å, b = 19.555(2) Å, c = 21.674(2) Å, α = 107.382(2)°, β = 91.600(2)°, γ = 98.226(2)°, V = 3355.4(7) Å^3, Z = 2, T = 100.01 K, μ(MoKα) = 1.091 mm^{-1}, $Dcalc$ = 1.784 g/cm^3, 30015 reflections measured (5.654° ≤ 2Θ ≤ 52°), 13114 unique (R_{int} = 0.0440, R_{sigma} = 0.0620) which were used in all calculations. The final R_1 was 0.0864 (I > 2σ(I)) and wR_2 was 0.2592 (all data).

Crystal Data for {[3,5-(3,5-$(CF_3)_2$Ph$)_2$Pz]Ag$\}_3$•CH_2Cl_2, $C_{58}H_{23}Ag_3Cl_2F_{36}N_6$ (M =1882.33 g/mol): triclinic, space group P-1 (no. 2), a = 8.6941(5) Å, b = 15.8573(8) Å, c = 26.1433(13) Å, α = 89.287(2)°, β = 85.728(2)°, γ = 87.428(2)°, V = 3590.5(3) Å^3, Z = 2, T = 299.06 K, μ(MoKα) = 1.019 mm^{-1}, $Dcalc$ = 1.741 g/cm^3, 37199 reflections measured (5.768° ≤ 2Θ ≤ 52.998°), 14836 unique (R_{int} = 0.0332, R_{sigma} = 0.0407) which were used in all calculations. The final R_1 was 0.0615 (I > 2σ(I)) and wR_2 was 0.1945 (all data).

Crystal Data for {[3,5-(3,5-$(CF_3)_2$Ph$)_2$Pz]Au$\}_3$, $C_{57}H_{21}Au_3F_{36}N_6$ (M =2064.70 g/mol): monoclinic, space group P2$_1$/c (no. 14), a = 8.3667(5) Å, b = 31.7232(19) Å, c = 25.7197(15) Å, β = 91.507(2)°, V = 6824.1(7) Å^3, Z = 4, T = 100.0 K, μ(MoKα) = 6.573 mm^{-1}, $Dcalc$ = 2.010 g/cm^3, 89629 reflections measured (5.694° ≤ 2Θ ≤ 60.054°), 19862 unique (R_{int} = 0.0345, R_{sigma} = 0.0273) which were used in all calculations. The final R_1 was 0.0317 (I > 2σ(I)) and wR_2 was 0.0702 (all data).

Supporting Information Available: X-ray crystallographic data, additional figures and details, spectroscopic data, summary of bond distances and angles.

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There are no conflicts of interest to report

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TOC

Photoluminescent, trinuclear, coinage metal pyrazolates have been isolated using a fluorinated diaryl-pyrazolate.