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Synthesis, Structural Characterization, Reactivity, and Catalytic Properties of Copper(I) Complexes with a Series of Tetradentate Tripodal Tris(pyrazolylmethyl)amine Ligands

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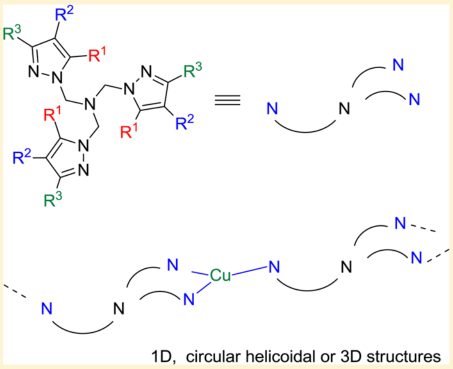
Supporting Information



ABSTRACT: Novel tris(pyrazolylmethyl)amine ligands Tpa^{Me3}, Tpa^{*,Br}, and Tpa^{Br3} have been synthesized and structurally characterized. The coordination chemistries of these three new tetradentate tripodal ligands and the already known Tpa and Tpa* have been explored using different copper(I) salts as starting materials. Cationic copper(I) complexes [Tpa^{x}Cu]PF$_6$ (**1–4**) have been isolated from the reaction of [Cu(NCMe)$_4$]PF$_6$ and 1 equiv of the ligand. Complexes **2** (Tpa^x = Tpa*) and **3** (Tpa^x = Tpa^{Me3}) have been characterized by X-ray studies. The former is a 1D helical coordination polymer, and the latter is a tetranuclear helicate. In both structures, the Tpa^x ligand adopts a $\mu^2{:}\kappa^2{:}\kappa^1$-coordination mode. However, in solution, all of the four complexes form fluxional species. When CuI is used as the copper(I) source, neutral compounds **5–8** have been obtained. Complexes **6–8** exhibit a 1:1 metal-to-ligand ratio, whereas **5** presents 2:1 stoichiometry. Its solid-state structure has been determined by X-ray diffraction, revealing its 3D polymeric nature. The polymer is composed by the assembly of [Tpa$_2$Cu$_4$I$_4$] units, in which Cu$_4$I$_4$ presents a step-stair structure. The Tpa ligands bridge the Cu$_4$I$_4$ clusters, adopting also a $\mu^2{:}\kappa^2{:}\kappa^1$-coordination mode. As observed for the cationic derivatives, the NMR spectra of **5–8** show the equivalence of the three pyrazolyl arms of the ligands in these complexes. The reactivities of cationic copper(I) derivatives **1–4** with PPh$_3$ and CO have been explored. In all cases, 1:1 adducts [Tpa^{x}CuL]PF$_6$ [L = PPh$_3$ (**9–11**), CO (**12–15**)] have been isolated. The crystal structure of [Tpa*Cu(PPh$_3$)]PF$_6$ (**9**) has been obtained, showing that the coordination geometry around copper(I) is trigonal-pyramidal with the apical position occupied by the tertiary amine N atom. The Tpa* ligand binds the Cu center to three of its four N atoms, with one pyrazolyl arm remaining uncoordinated. In solution, the carbonyl adducts **13–15** exist as a mixture of two isomers; the four- and five-coordinate species can be distinguished by means of their IR ν_{CO} stretching bands. Finally, the catalytic activities of complexes **1–4** have been demonstrated in carbene- and nitrene-transfer reactions.

■ INTRODUCTION

Copper(I) complexes containing polydentate nitrogen ligands[1] display a rich structural chemistry as a result of its d^{10} electronic configuration, which enables it to adopt a great variety of coordination numbers and geometries. This flexible coordination ability has allowed the assembly of complex supramolecular architectures[2] with interesting photoluminescent properties[3] and potential applications in material science.[4] In addition, copper(I) complexes with tripod nitrogen ligands have enjoyed considerable success in bioinorganic chemistry because they have been used as models for reaction centers in proteins such as those involved in oxygen activation.[5]

Another important field in which these coordination compounds have been largely applied is catalysis. Within this context, our research group has been investigating, for the last few decades, the catalytic properties of families of copper(I) complexes with tris(pyrazolyl)borate[6] (Tp^x) and tris(pyrazolyl)methane[7] (Tpm^x) ligands (Figure 1) in an array of

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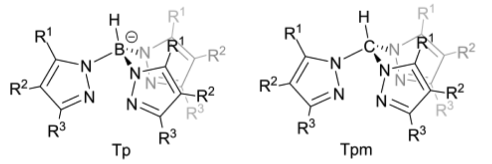
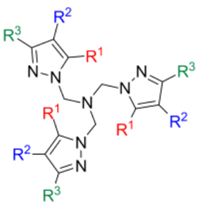


Figure 1. Ligands frequently used for our research group.

catalytic processes that span from carbene- and nitrene-transfer reactions,[8−10] oxidation reactions,[11] atom-transfer radical addition[12] and atom-transfer radical polymerization[13] reactions, Ullmann and Golberg type condensations,[14] and copper-catalyzed azide−alkyne cycloaddition (CuAAC) reactions.[15]

While exploring the activity of the precatalyst [Tpm^{*,Br}Cu(MeCN)]BF$_4$[16] in the reaction of *N*-carbonylazides and -alkynes, we discovered a novel transformation that led to the formation of 2,5-disubstituted oxazoles rather than the expected 1,4-disubstituted *N*-carbonyltriazoles.[17] In order to improve both the activity and selectivity of the catalyst, different Tpm^x ligands were tested with no success. At this point, we considered the preparation of a novel copper(I) precatalyst, focusing our attention on a family of tetradentate tripodal ligands, the tris(pyrazolylmethyl)amine (Tpa^x) ligands[18] (Chart 1) structurally related with tripod Tp^x and Tpm^x ligands. The choice of this type of ligand was dictated primarily by the need to keep a coordination environment similar to that found for the Tpm*Cu derivative but also by the acceleration effect exerted by tris(heterocyclemethyl)amine ligands in CuAAC reactions.[19] Furthermore, the electronic and steric properties of the ligand could be easily tuned by changing the nature of the substituents on the pyrazole rings. Unlike Tp^x and Tpm^x ligands, the coordination chemistry of Tpa^x ligands with transition metals has been much less explored.[20] However, some copper(II),[18c,21] and to a lesser extent copper(I),[18c,21a] coordination complexes are known, but only the crystal structures of two mononuclear Tpa-Cu^I species have been reported to date.[18c,21a]

Chart 1



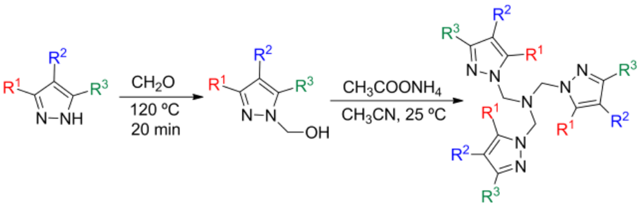
Tpa^x	R^1	R^2	R^3
Tpa	H	H	H
Tpa*	Me	H	Me
Tpa^{Me_3}	Me	Me	Me
Tpa^{*,Br}	Me	Br	Me
Tpa^{Br_3}	Br	Br	Br

We describe here the synthesis of a series of tris(pyrazolylmethyl)amine ligands (Chart 1) and the preparation and spectroscopic characterization of several cationic and neutral Tpa^x-Cu^I complexes. The solid-state crystal structures of some of these copper(I) derivatives have been determined, revealing their multinuclear nature. The reactivity of the new complexes toward CO and PPh$_3$ has also been studied. Finally, a survey on the catalytic activity of Tpa^x-Cu^I complexes in standard carbene- and nitrene-transfer reactions has been undertaken.

■ RESULTS AND DISCUSSION

Synthesis of Ligands. Tpa^x ligands were prepared in good yields by the same procedure as that described for the synthesis of Tpa[18b] and Tpa*[18c] derivatives (Scheme 1). For those containing a bromo substituent on the pyrazolyl ring, their synthesis required heating of the corresponding hydroxymethylpyrazolyl precursors with ammonium acetate at 70 °C for 3 (Tpa^{*,Br}) and 6 days (Tpa^{Br3}), respectively.

Scheme 1



The three new ligands were characterized by elemental analyses and NMR spectroscopy. Their ^{1}H NMR spectra in CD$_3$CN displayed a single resonance in the range of 4.85−5.50 ppm assigned to methylene protons, whereas the corresponding ^{13}C{^{1}H} NMR signals were found in the 63.1−68.2 ppm range. The structures of Tpa^{*,Br} and Tpa^{Br3} were also determined by X-ray crystallography (Figure 2a,b). In both structures, the geometry around the tertiary amine N atom is almost tetrahedral. The mean bond distances and angles are near identical in both ligands and in agreement with those reported for Tpa*[18c] and Tpa^{iPr2}.[18c] As noted from crystallographic data, substituents on the pyrazolyl ring do not exert much influence on the ligand structure.

$$\text{Tpa}^x + [\text{Cu(NCMe)}_4]\text{PF}_6 \xrightarrow[\text{rt}]{\text{MeOH}} [\text{Tpa}^x\text{Cu}]\text{PF}_6 \quad \begin{array}{l} \mathbf{1}, \text{Tpa}^x = \text{Tpa} \\ \mathbf{2}, \text{Tpa}^x = \text{Tpa*} \\ \mathbf{3}, \text{Tpa}^x = \text{Tpa}^{\text{Me3}} \\ \mathbf{4}, \text{Tpa}^x = \text{Tpa}^{*,\text{Br}} \end{array} \tag{1}$$

Synthesis of Complexes. Cationic copper complexes **1**−**4** were prepared following the procedure reported[18c] for the synthesis of [Tpa*Cu]PF$_6$ (**2**), i.e., by reacting [Cu(NCMe)$_4$]PF$_6$ with equimolar amounts of the Tpa^x ligands in methanol (MeOH) at room temperature (eq 1). All attempts to synthesize the Tpa^{Br3}-Cu^I derivative resulted in the unsuccessful recovery of only unreacted starting materials at the end of the reaction. This could be attributed to the poor donating properties of the Tpa^{Br3} ligand due to the presence of nine Br atoms in this ligand.

Complexes **1**−**4** precipitated from MeOH solutions and were isolated as white solids in high yields. They were only soluble in acetonitrile and dimethyl sulfoxide (DMSO) and could be exposed to air while in the solid state but not in solution. ^{1}H NMR spectra of **1**, **3**, and **4** in CD$_3$CN evidenced coordination of the ligands to the Cu ion, as inferred from the slight downfield shifts of the resonances of pyrazolyl rings with respect to those observed for the free ligands. Moreover, the observation of a unique set of signals for all three pyrazolyl arms of the Tpa^x ligands in their ^{1}H and ^{13}C{^{1}H} NMR spectra indicated the existence of a fluxional process in solution (see the Experimental Section). No other resonances were observed, in spite of the use of [Cu(NCMe)$_4$]PF$_6$ as the copper source. In good agreement with this, IR spectra of **1**, **3**, and **4** did not exhibit any absorption in the region due to $\nu_{C\equiv N}$ bands, and elemental analyses also supported this observation.

Fujisawa et al. proposed a tetradentate κ^4-coordination mode of the Tpa* ligand in **2** based on its analytical and spectroscopic features. Considering that such data matched those found for

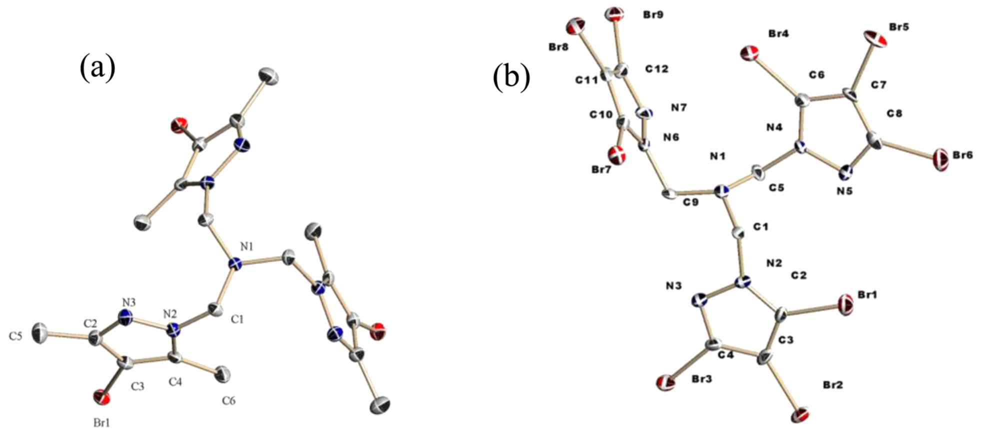


Figure 2. Molecular structures of Tpa^{*,Br} (a) and Tpa^{Br3} (b). Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for Tpa^{*,Br}: C1−N1, 1.446(5); N1−C1#1, 1.446(5); N1−C1#2, 1.446(5); C1−N1−C1#1, 113.2(3); C1−N1−C1#2, 113.2(3); C1#1−N1−C1#2, 113.2(3). Selected bond lengths (Å) and bond angles (deg) for Tpa^{Br3}: N1−C1, 1.421(8); N1−C5, 1.473(8); N1−C9, 1.449(7); C1−N1−C9, 116.9(5); C1−N1−C5, 115.9(5); C9−N1−C5, 113.2(5).

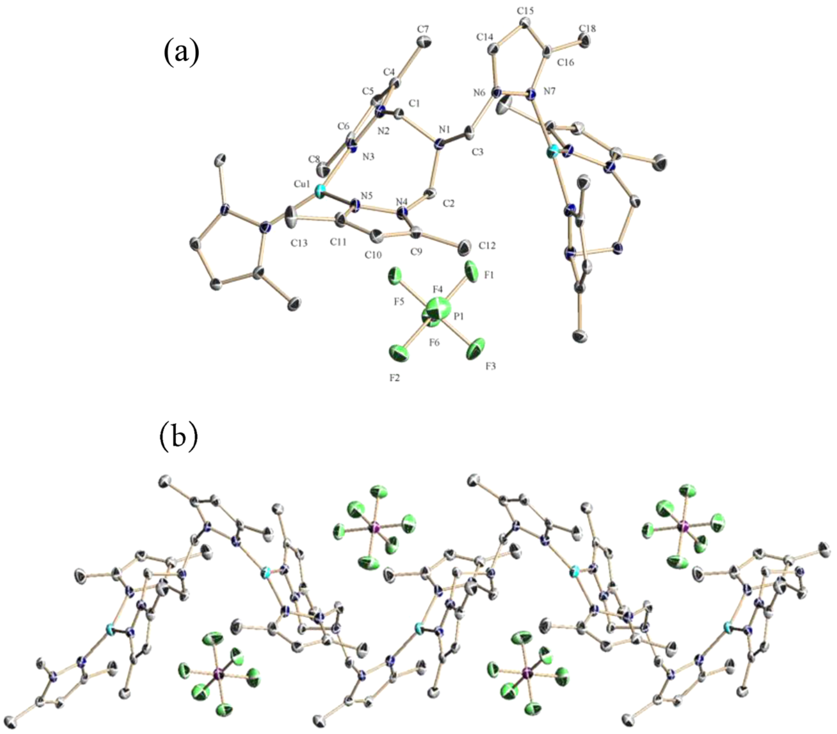


Figure 3. (a) ORTEP representation of the coordination environment around the Cu^{I} centers in **2**. H atoms have been omitted for clarity. Selected bond lenghts (Å) and angles (deg) for **2**: Cu1−N3, 1.989(3); Cu1−N5, 2.004(4); Cu1−N7#, 1.964(3); N7#−Cu1−N3, 128.11(15); N7#−Cu1−N5, 118.79(14); N3−Cu1−N5, 112.70(14). (b) Structure of the 1D helices in **2** that run along the *b* axes.

complexes **1**, **3**, and **4**, it was reasonable to suggest that Tpa^{x} ligands in these complexes coordinated the Cu^{I} ion in the same fashion. To further confirm this proposal, we decided to determine the solid-state structures of **1**−**4**. Unfortunately, only single crystals of **2** and **3** suitable for X-ray diffraction studies could be obtained so far. To our surprise, the two copper complexes were not mononuclear in nature but polynuclear copper(I) derivatives. The crystal structure of **2** (Figure 3) shows that this material is an infinite one-dimensional (1D) helical coordination polymer of composition $\{[\mathrm{Tpa}^*\mathrm{Cu}]\mathrm{PF}_6\}_\infty$.[2a,e,4c,22] Each Cu^{I} ion is coordinated to two pyrazole N atoms of one Tpa* ligand and a pyrazole N atom of another ligand, forming a distorted trigonal-planar CuN_3 arrangement, with the N−Cu−N angles varying from 112.7 to 128.1° (Figure 3). The Cu−N distances range from 1.964 to 2.004 Å (average 1.986 Å) and are similar to those reported for mononuclear Tpa-Cu^{I} species.[23] The apical amine N of each Tpa* ligand remains unbound, resulting in a μ^2:κ^2:κ^1-coordination mode for the Tpa* moiety. The coordination scheme described above affords 1D helical chains, with an equal amount of each enantiomer in the crystal. The Cu−Cu separation between metals linked by the same bridging Tpa* ligand is 6.840 Å excluding any interaction between the two metal ions.

The X-ray crystal structure of **3** (Figure 4) discloses the compound to be a tetramer with a tetranuclear circular helical architecture.[24] As in complex **2**, each Cu^{I} ion is coordinated to

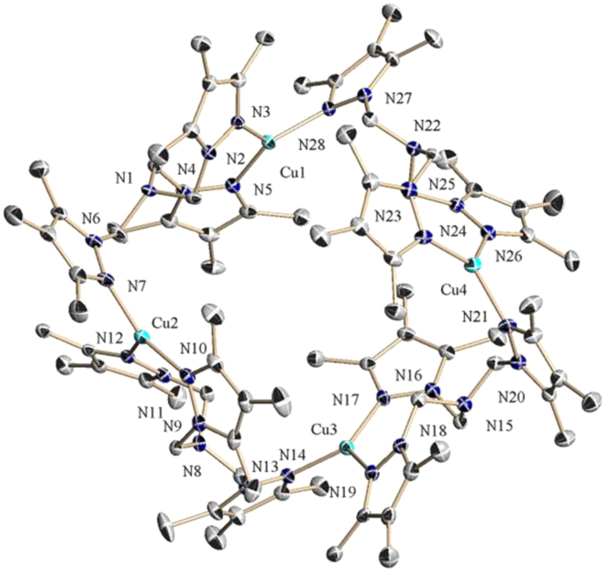


Figure 4. ORTEP drawing of **3**. H atoms have been omitted for clarity. Selected bond lenghts (Å) and angles (deg) for **3**: Cu1−N5, 1.965(5); Cu1−N3, 1.989(5); Cu1−N28, 1.968(5); Cu2−N7, 1.966(6); Cu2−N10, 1.960(6); Cu2−N12, 2.017(5); Cu3−N14, 1.963(5); Cu3−N17, 1.967(6); Cu3−N19, 2.007(6); Cu4−N21, 1.996(6); Cu4−N24, 1.958(6); Cu4−N26, 1.990(6); N5−Cu1−N28, 124.3(2); N5−Cu1−N3, 118.0(2); N28−Cu1−N3, 117.0(2); N10−Cu2−N7, 128.4(2); N10−Cu2−N12, 118.6(2); N7−Cu2−N12, 113.0(2); N14−Cu3−N17, 120.4(2); N14−Cu3−N19, 120.3(2); N17−Cu3−N19, 119.3(2); N24−Cu4−N21, 122.2; N24−Cu4−N26, 119.5(2); N26−Cu4−N21, 118.3(2).

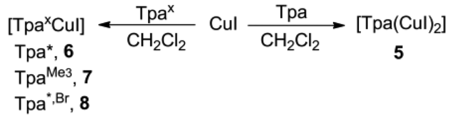
three pyrazole N atoms provided by two different Tpa^{Me3} units, adopting a distorted trigonal-planar geometry. The Tpa^{Me3} ligand exhibits coordination behavior identical with that observed for the Tpm* ligand in compound **2**. Cu−N bond lengths (average 1.979 Å) and bond angles (average 120.2°) and the intermetallic Cu−Cu separation (6.921−7.157 Å) are similar to those found for **2**. A hexafluoro phosphate anion resides inside the cavity formed by the Cu ions and the pyrazole rings, with the remaining anions being packed around the tetrameric units. The anion that occupies the cavity shows short contacts with the methyl and methylene protons of the Tpa^{Me3} ligands [see the Supporting Information (SI) for details]. A similar encapsulation of the anions has been described for other copper-containing coordination polymers.[25]

As shown above, the Tpa* and Tpa^{Me3} ligands do not bind the Cu^{I} center using the three pyrazole N atoms (κ^3-coordination mode) or their full denticity in a tetradentate fashion (κ^4-coordination mode). Conversely, they act as bridging ligands between two metal ions, chelating one of them through two of the pyrazolyl arms and using the third arm to bridge the other metal. As a result, each Cu center is in a three-coordinate distorted trigonal-planar environment. The lower coordination geometry displayed by the Cu^{I} ion in these crystal structures may reflect the difficulty of the Tpa* and Tpa^{Me3} ligands to fulfill the strong preference of this metal ion for tetrahedral coordination presumably because of steric constraints. In line with this, the bulky derivative tris[3-(4-methoxyphenyl)-5-methylpyrazolylmethyl]amine has been found to coordinate to Cu^{I} ions, adopting a κ^4-coordination mode.[21a] The steric bulk of the substitutent at the 3 position of the pyrazolyl rings in this particular ligand seems to reduce the strain, allowing bonding of the four N atoms to the metal ion.

However, the solid-state structures found for **2** and **3** were not maintained in solution, and NMR spectra of both polymer and tetranuclear compounds in CD_3CN at room temperature showed the equivalence of all three pyrazolyl arms of the ligands. The observed dynamic behavior could result from a fast equilibrium in solution between species with different nuclearities or from a fluxional process involving association or dissociation of the ligand in the polynuclear complexes. The insolubility of **2** and **3** prevented the study of the behavior of these compounds in other deuterated solvents and also performance of variable-temperature NMR experiments.

The coordination chemistry of the Tpa^{x} ligands was also explored using CuI as the copper(I) source. The reaction of CuI with 1 equiv of Tpa^{x} ligands in dichloromethane afforded colorless solutions, from which complexes **5**−**8** were obtained (Scheme 2) as white solids by precipitation (**5**) or by evaporation of the solvent (**6**−**8**). Elemental analysis obtained for **5** indicated a 2:1 copper/ligand ratio, whereas those obtained for **6**−**8** were in accordance with formulations as 1:1 adducts. Presumably, the steric hindrance of the substituent (methyl group) at the third position of the pyrazolyl groups in complexes **6**−**8** favored the formation of 1:1 adducts. A similar behavior has been observed in the reactions of CuI with the tris(pyrazolyl)methane ligands Tpm and Tpm*.[14]

Scheme 2



The most relevant information that could be inferred from ^{1}H and ^{13}C{^{1}H} NMR spectra of **5**−**8** in DMSO-d_6 or $CDCl_3$ solutions was the equivalence of all three pyrazolyl arms of the ligands in these molecules. In view of the different structural behavior found for derivatives **2** and **3** in solution and in the solid state and considering the well-known tendency of copper(I) halides with chelating ligands to form multinuclear systems with diverse structural complexity,[2d,26] it was not possible to propose a formulation for complexes **5**−**8** on the basis of their analytical and spectroscopic data. Efforts to grow crystals of X-ray quality were fruitless, leading in most cases to decomposition of the starting compounds except for **5**, whose solid-state structure could be resolved. X-ray structural analysis reveals a three-dimensional (3D) polymeric network constructed with {$(Tpa)_2Cu_4I_4$} units (Figure 5). Each [Cu_4I_4] core is formed by two planar rhomboid [Cu_2I_2] clusters constituted by two μ_2-I atoms linking two Cu^{I} atoms. They are connected through two Cu−I interactions [2.780(1) Å], giving rise to a “step stair” [Cu_4I_4] fragment (Figure 5). These fragments are cross-linked through bridging Tpa ligands, forming the infinite network. Each of the Tpa molecules acts as a tridentate ligand (μ^2:κ^2:κ^1-coordination mode) binding to two Cu atoms of different [Cu_4I_4] cores. Both Cu1 and Cu2 atoms can be considered in a four-coordinate distorted tetrahedral geometry; however, their coordination environments are different from each other. The Cu1 atoms binds to two I atoms (I1 and I2) and two pyrazole N atoms (N1 and N3) of the same Tpa ligand, while the Cu2 atoms coordinate to three I atoms (one I1 and two I2) and one N atom (N5) from a neighboring [$Cu_4I_4(Tpa)_2$] fragment. The Cu−N and Cu−I bond lengths are comparable to those found for similar steplike

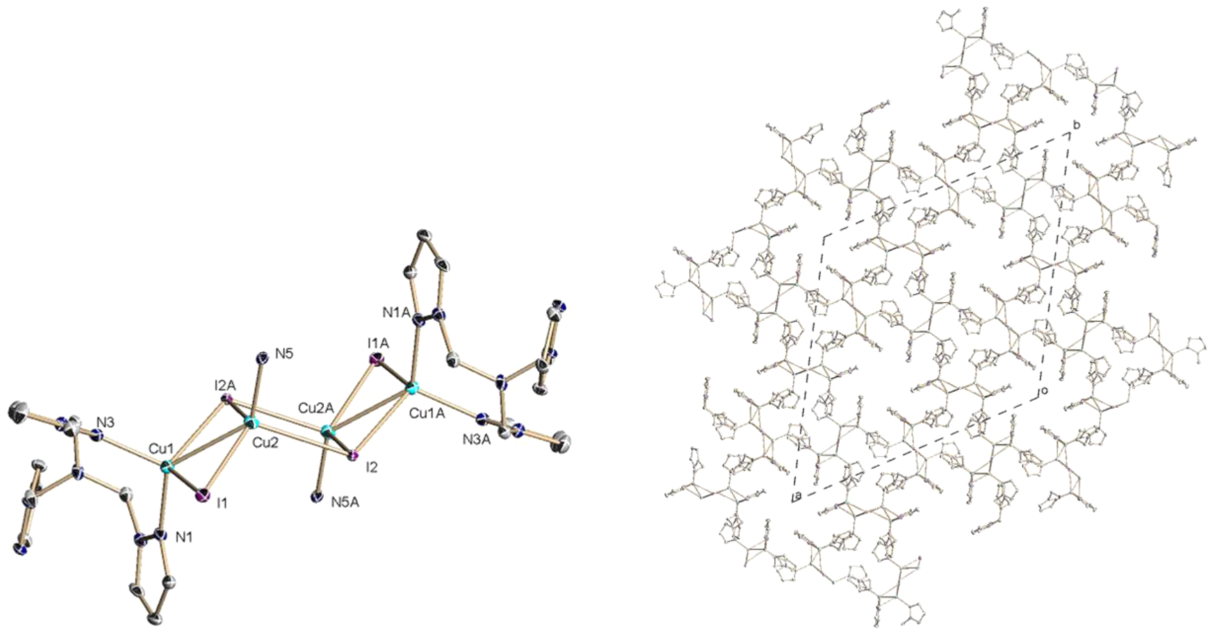


Figure 5. Left: ORTEP representation of the coordination environment around the Cu^I centers in **5**. H atoms have been omitted for clarity. Selected bond lenghts (Å) and angles (deg) for **9**: Cu1−N1, 2.033(2); Cu1−N3, 2.0272(19); Cu2−N5, 2.0419(19); Cu1−I1, 2.6401(3); Cu1−I2#1, 2.7110(3); Cu2−I1, 2.5901(3); Cu2−I2, 2.7799(3); Cu2−I2#1, 2.6407(3); Cu1−Cu2, 2.6971(4); N3−Cu1−N1, 110.02(7); N3−Cu1−I1, 106.96(5); N3−Cu1−I2#1, 109.19(6); N5−Cu2−I1, 112.50(6); N5−Cu2−I2#1, 112.62(5); N5−Cu2−I2, 101.11(5). Right: 3D network viewed along the *c* axis.

Cu_4I_4 units.[2j,4g,27] The Cu1···Cu2 separation of 2.6965(5) Å is shorter than the sum of the van der Waals radii for copper(I) (2.80 Å)[28] and lies within the range of distances reported for this interaction in other structurally characterized copper(I) iodide tetrameric cluster analogues.[27]

Examples of copper(I) halide coordination polymers based on stair-step Cu_4I_4 with chelating ligands as structural motifs are scarce, and those reported present mainly 1D[27a,27i,29] or two-dimensional (2D)[27a,30] structures. Few examples of 3D coordination polymers but containing as building blocks the tetranuclear cubane-like Cu_4I_4 clusters have recently been described and exhibit interesting photoluminiscent properties.[31] Hence, the structure of **5** represents a rare example of a 3D copper(I) coordination polymer made up of stair-step Cu_4I_4 tetramer units linked by a tetradentate tripod nitrogen ligand. Clearly, this structure is not maintained in solution, where the equivalence of the three pyrazolyl rings does not match with the solid-state structure. We have no additional information to propose the solution structure of **5**.

Reactivity Studies. The reactivity of cationic Tpa^x-Cu^I complexes **1−4** to PPh_3 and CO was also explored. Upon mixing of an equimolar amount of PPh_3 and the copper complexes in CH_2Cl_2, the phosphine derivatives **9−11** were obtained in high yields except in the case of the parent Tpa-Cu, **1**, for which no reaction was observed (eq 2).

$$[\mathrm{Tpa}^{x}\mathrm{PF}_6] + \mathrm{PPh}_3 \xrightarrow[\mathrm{rt}]{\mathrm{CH_2Cl_2}} \underset{\substack{\mathrm{Tpa}^{*},\ \mathbf{9} \\ \mathrm{Tpa}^{\mathrm{Me3}},\ \mathbf{10} \\ \mathrm{Tpa}^{*,\mathrm{Br}},\ \mathbf{11}}}{[\mathrm{Tpa}^{x}\mathrm{Cu(PPh)PF}_6]} \qquad (2)$$

The X-ray structure of **9** was determined, and as shown in Figure 6, it consists of a mononuclear phosphine adduct in which the Cu ion is in a four-coordinate CuN_3P environment bonded to two pyrazole N atoms, the tertiary amine N atom, and a P atom. The geometry around the metal center is distorted trigonal-pyramidal, with the tertiary amine N atom occupying the apical position. The bond to the amine N atom [2.355(3) Å] is longer than those to the pyrazole N atoms [2.014(3) and 2.015(3) Å], denoting a weak interaction with the Cu^I ion. The structure of this cationic copper(I) complex has been reported by Fujisawa et al. as a ClO_4 salt,[18c] and it is analogous to that described for the complex [(tmpa)Cu-(PPh_3)]PF_6, where tmpa is a tripodal tetradentate tris-(pyridylmethyl)amine ligand.[32]

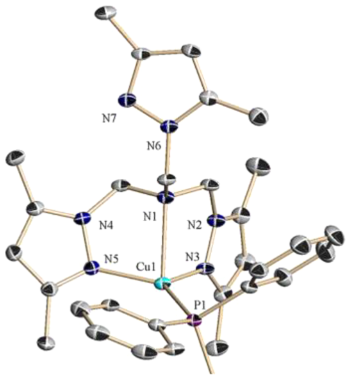
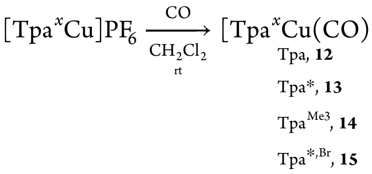


Figure 6. ORTEP representation of the molecular structure of **9**. H atoms have been omitted for clarity. Selected bond lenghts (Å) and angles (deg) for **9**: Cu1−N3, 2.014(3); Cu1−N5, 2.051(3); Cu1−P1, 2.1777(11); Cu1−N1, 2.355(3); N3−Cu1−N5, 112.51(14); N3−Cu1−P1, 119.51(11), N5−Cu1−P1, 127.64(11).

Despite the fact that the Tpa* ligand in the solid-state structure of **9** presented a tridentate κ^3-coordination mode with an uncoordinated pyrazolyl arm, room temperature ^1H and $^{13}C\{^1H\}$ NMR spectra of this derivative as well as those of the phosphine adducts **10** and **11** recorded in $CDCl_3$ displayed only one set of signals for the three pyrazolyl groups. This observation indicated once more the existence of a dynamic process in solution that averaged the chemical environment of the three arms of the ligand. This fluxional motion could imply association/dissociation of the pendant pyrazolyl arm with the formation of a five-coordinate species. A similar process has been invoked to explain the dynamic behavior in solution of the complex $[(tmpa)Cu(CNMe)]^+$ containing the structurally related tmpa ligand.[32,33]

When CO was bubbled into suspensions of complexes **1−4** in CH_2Cl_2 at room temperature, colorless solutions were obtained. After removal of the solvent, complexes **12−15** were isolated as white solids (eq 3). Elemental analyses agreed with a formulation as 1:1 CO adducts.



$$[Tpa^xCu]PF_6 \xrightarrow[CH_2Cl_2,\ rt]{CO} [Tpa^xCu(CO)]PF_6 \quad \begin{array}{l} Tpa,\ \mathbf{12} \\ Tpa^*,\ \mathbf{13} \\ Tpa^{Me3},\ \mathbf{14} \\ Tpa^{*,Br},\ \mathbf{15} \end{array} \qquad (3)$$

Additional evidence for the binding of CO to the Cu^I ion in **12−15** came from NMR and IR spectroscopy. In the $^{13}C\{^1H\}$ NMR spectra of **13−15** (CD_2Cl_2 at room temperature), the resonance of CO appeared at ca. 173 ppm. However, such a resonance was not observed in the $^{13}C\{^1H\}$ NMR spectrum of the CO adduct of the Tpa derivative **12**; actually, in spite of the observance of the CO ligand in the IR spectrum in solution, only the starting material was observed during the NMR experiment, even in the presence of a CO atmosphere, suggesting the lability of the coordinated CO ligand to the Cu^I ion in this complex. On the other hand, the room temperature ^1H NMR spectra of **13−15** were very similar to each other and, as in those described above, revealed the equivalence of the pyrazolyl groups in the coordinated ligands. In addition, resonances due to the ligands in **13** and **14** appeared to be slightly broad, a phenomenon that was even more pronounced in the spectrum of **15**. Karlin et al. have proposed the existence of an equilibrium in solution between four- and five-coordinate structures in compounds of the type $[(tmpa)Cu(CO)]^+$ on the basis of IR studies.[34] Considering that one pyrazolyl arm of the Tpa* ligand in the solid-state structure of $[TpaCu(PPh_3)]^+$ remained uncoordinated and that the complex exhibited fluxional behavior in solution, it was reasonable to propose that a similar equilibrium (Scheme 3) takes place in solutions of **12−15**. Further evidence for such equilibria came from IR studies in CH_2Cl_2 solutions. ν_{CO} stretching frequencies exhibited for **12−15** varied from 2073 to 2107 cm^{-1} (Table 1), values that fell in the normal range found for LCu^I-CO adducts (2040−2125 cm^{-1}).[34] A single IR band was observed for **12**, the Cu−CO adduct with the parent Tpa ligand (2087 cm^{-1}), whereas two CO bands were observed for the Tpa* derivative, **13**, at 2103 and 2076 cm^{-1}, with the less energetic one being predominant. These bands could be assigned to the ν_{CO} values of each of the two isomers. Because the carbonyl stretching frequencies decrease with increasing π-back-bonding electron donation from the metal center to the CO ligand, the highest ν_{CO} value should correspond to the four-coordinate isomer and the lowest to the five-coordinate one. The observation of only one CO stretching band in CH_2Cl_2 solutions of **12** suggests that only one carbonyl isomer was present in solution. Because the absence of substituents in the pyrazolyl rings makes the parent Tpa ligand the less bulky but also the less electron-donating of the whole series, it is reasonable to propose that the observed ν_{CO} band should correspond to the five-coordinate species. IR spectra of **14** and **15** also exhibited two bands. The presence of a methyl group at the 4 position of the pyrazolyl rings in **14** produced a slight shift of the ν_{CO} values to lower energy (2099 and 2073 cm^{-1}, with the less energetic band being the less intense), while a bromine substituent in **15** caused a shift of the bands to higher energy (2107 and 2083 cm^{-1}, with the less energetic being the most intense).

Scheme 3

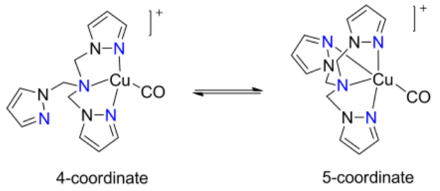


Table 1. Carbonyl Stretching Frequencies for $[Tpa^xCu(CO)]^+$ in CH_2Cl_2 Solutions

	12	13	14	15
ν_{CO} (cm^{-1})	2087	2103, 2076	2099, 2073	2107, 2083

The difficulty of growing crystals suitable for X-ray diffraction for any $[Tpa^xCu(CO)]^+$ adducts prevented one from gaining information about the coordination geometry of the Cu^I ion in the solid state.

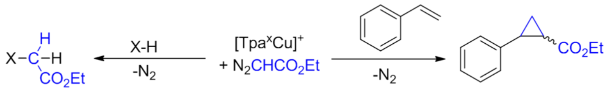
Catalytic Studies. A survey on the catalytic properties of cationic copper(I) complexes **1−4** in carbene- and nitrene-transfer reactions was carried out. Ethyl diazoacetate (EDA) was used as the carbene source, and the substrates tested in the presence of 5 mol % (with respect to EDA) of the copper precatalysts were styrene, aniline, ethanol, and cyclohexane (Table 2).

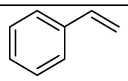
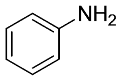
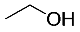
Cyclopropanation of styrene was achieved both by the addition of EDA in one portion and by slow addition (3 h, entry 1) with the aid of a syringe pump, with the conversions in the latter case always being slightly superior. Diastereoselectivity (cis/trans ratio) found in all of the reactions was almost the same, but the best performance in terms of the conversion toward the cyclopropane products were observed for complexes **2−4**. The cis/trans ratio corresponds to the very often observed diastereoselectivity with catalysts with low steric hindrance. Only in very few cases, with highly constrained metal centers, have selective transformations been reported.[9e]

Insertion of the CH_2CO_2Et fragment into the N−H and O−H bonds (entries 2 and 3) were also accomplished in very high yields with all of the catalysts employed. These results are comparable to those obtained with cationic $[Tpm^*Cu(NCMe)]BF_4$[9b] and neutral Tp^x-containing catalysts.[9e,35] However, the insertion reaction into the C−H bond of cyclohexane afforded very low conversions (less than 10%) of the expected product. Only when using a very electrophilic Cu center such as that found in the $Tp^{Br3}Cu(NCMe)$ complex, has functionalization of cyclohexane by carbene insertion been achieved in high yield (90%).[9c]

Next, the catalytic activities of **1−4** were tested in nitrene-transfer reactions using *N*-tosyliminobenzyliodinane (PhINTs) as the nitrene source. As shown in Table 3, all four copper precatalysts accomplished aziridination of styrene in very good yield, with the $Tpa^{*,Br}$-Cu derivative **4** having the best

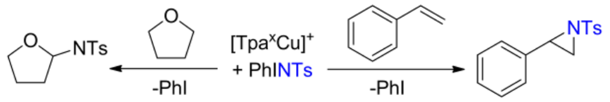
Table 2. Carbene-Transfer Reactions from EDA Using Complexes 1−4 as Catalysts

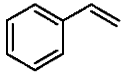


entry	substrate	catalyst	conversion[b]
1		1	82 (37:63)[c,d]
			88 (33:67)[c,e]
		2	82 (33:67)[c,d]
			95 (35:65)[c,e]
		3	80 (38:62)[c,d]
			94 (37:63)[c,e]
		4	81 (38:62)[c,d]
			96 (38:62)[c,e]
2	 NH_2	1	97[f]
		2	98[f]
		3	97[f]
		4	99[f]
3	 OH	1	94[f]
		2	98[f]
		3	97[f]
		4	99[f]

[a] Reaction conditions for cyclopropanation: styrene/EDA/catalyst (100:20:1) in dichloromethane (4 mL), for N−H insertion, aniline/EDA/catalyst (100:40:1) in dichloromethane (10 mL), and for O−H insertion, EDA/catalyst (40:1) in ethanol (5 mL). [b] Yield determined by NMR of the reaction mixture with an internal standard. Diethyl fumarate and maleate accounted for the remaining diazo compound. [c] In parentheses, the cis/trans ratio. [d] EDA added in one portion. [e] Slow addition of EDA for 3 h. [f] Slow addition of EDA for 12 h.

Table 3. Nitrene-Transfer Reactions Using Complexes 1−4 as Catalysts[a]



entry	substrate	catalyst	conversion[b]
1		1	85
		2	91
		3	88
		4	94
2		1	64
		2	64
		3	70
		4	84

[a] Reactions conditions for the aziridination: styrene/PhINTs/catalyst (100:20:1) and, for amination, PhINTs/catalyst (20:1) in THF (5 mL). [b] Yield determined by NMR of the reaction mixture with an internal standard. Tosylamine accounted for the remaining nitrene source.

performance (entry 1). As for insertion of the nitrene unit into the C−H bonds at the α position of the tetrahydrofuran (THF) molecule, the amination product was obtained in moderate yields, except for precatalyst **4**, for which 84% of conversion was obtained (entry 2). These results compare well with those found for Tp^{x}Cu complexes.[10c,36]

CONCLUSIONS

A family of tetradentate tripodal tris(pyrazolyl)methylamine ligands, Tpa^{x}, has been synthesized, and their cationic $[\mathrm{Tpa}^{x}\mathrm{Cu}]\mathrm{PF_6}$ complexes **1−4** and neutral derivatives $[\mathrm{Tpa_2Cu_4I_4}]$ (**5**) and $[\mathrm{Tpa}^{x}\mathrm{CuI}]$ (**6−8**) have been prepared and characterized. The solid-state structures of **2**, **3**, and **5** reveal their multinuclear nature: **2** is a helical 1D copper(I) coordination polymer, **3** has a tetranuclear helical structure, and **5** has a 3D network formed by stair-step $\mathrm{Cu_4I_4}$ building blocks. The latter is a rare example of a 3D copper(I) coordination polymer based on distorted stair-step $\mathrm{Cu_4I_4}$ clusters with tetradentate $\mathrm{N_4}$ ligands. In all three structurally characterized compounds, the Tpa^{x} ligands chelate through two of the three pyrazole N atoms to one $\mathrm{Cu^I}$ center and bridge another $\mathrm{Cu^I}$ ion through coordination of the third pyrazolyl arm. The reactivity of cationic complexes **1−4** toward $\mathrm{PPh_3}$ and CO has also been examined. The 1:1 adducts $[\mathrm{Tpa}^{x}\mathrm{Cu(PPh_3)}]\mathrm{PF_6}$ (**9−11**) and $[\mathrm{Tpa}^{x}\mathrm{Cu(CO)}]\mathrm{PF_6}$ (**12−15**) have been isolated. The X-ray structure of **9** shows its mononuclear nature as well as a coordination mode for the Tpa* ligand through two pyrazolyl arms and the tertiary amine N atom. Solution IR studies carried out with the CO adducts **13−15** suggest the existence of an equilibrium between four- and five-coordinated copper(I) species. NMR studies underline the dynamic behavior of all of these copper(I) complexes in solution because the ligand resonances are simpler than the solid-state structures would predict. Finally, the catalytic activity of cationic derivatives **1−4** have been demonstrated in carbene- and nitrene-transfer reactions, with results comparable to those of analogous Tp- and Tpm-$\mathrm{Cu^I}$ systems.

EXPERIMENTAL SECTION

General Methods. All reactions and manipulations were carried out under an oxygen-free nitrogen atmosphere with standard Schlenk techniques. Reagents were purchased from commercial suppliers and used without further purification. Solvents were dried and degassed before use. The ligands Tpa[18b] and Tpa*[18c] and the complex $[\mathrm{Tpa^*Cu}]\mathrm{PF_6}$[18c] were prepared according to the literature procedures. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. ^{1}H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. Elemental analyses were performed in Unidad de Análisis Elemental of the Universidad de Huelva.

General Procedure for the Synthesis of Tris(pyrazolylmethyl)amine Ligands $\mathrm{Tpa}^{\mathrm{Me3}}$, $\mathrm{Tpa}^{*,\mathrm{Br}}$, and $\mathrm{Tpa}^{\mathrm{Br3}}$. For $\mathrm{Tpa}^{\mathrm{Me3}}$, 1-(hydroxymethyl)-3,4,5-trimethylpyrazole (2.40 g, 17.1 mmol) and ammonium acetate (0.45 g, 5.82 mmol) were stirred in acetonitrile (50 mL) at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was washed with $\mathrm{Et_2O}$ to eliminate the unreacted starting material and dissolved in $\mathrm{CH_2Cl_2}$. The addition of $\mathrm{Et_2O}$ produced the precipitation of a white microcrystalline solid, which was dried under vacuum. Yield: 2.20 g (99%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 4.87 (s, 6H), 2.07 (s, 9H), 1.84 (s, 9H), 1.79 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$): δ 146.3, 136.7, 112.1, 62.4, 11.7, 8.3, 7.9. Anal. Calcd for $\mathrm{C_{21}H_{33}N_7}$: C, 65.07; H, 8.67; N, 25.56. Found: C, 65.07; H, 8.77; N, 25.24. For $\mathrm{Tpa}^{*,\mathrm{Br}}$, following the same procedure, the reaction mixture was heated at 70 °C for 3 days. Yield: 2.3 g (70%). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 5.01 (s, 6H), 2.19 (s, 9H), 1.96 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $\mathrm{CDCl_3}$): δ 146.8, 138.3, 95.5, 64.0, 12.5, 9.7. Anal. Calcd for $C_{18}H_{24}Br_3N_7$: C, 37.39; H, 4.18; N, 16.16. Found: C, 37.21; H, 4.25; N, 16.83. For Tpa^{Br3}, following the same procedure, the reaction mixture was heated at 70 °C for 6 days. Yield: 4.3 g (68%). ^1H NMR (400 MHz, DMSO-d_6): *δ* 5.50 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-d_6): *δ* 127.7, 116.6, 99.6, 68.2. Anal. Calcd for $C_{12}H_6Br_9N_7$: C, 14.90; H, 0.63; N, 10.14. Found: C, 14.32; H, 0.41; N, 10.01.

Synthesis of $[\text{Tpa}^x\text{Cu}]PF_6$ Complexes [Tpa^x = Tpa (1), Tpa^{Me3} (3), and $\text{Tpa}^{*,\text{Br}}$ (4)]. A solution of the corresponding Tpa^x ligand (0.3 mmol) in anhydrous MeOH (20 mL) was added to a stirred solution of $[\text{Cu(NCMe)}_4]PF_6$ (0.149 g, 0.4 mmol) in MeOH (20 mL). Precipitation of a white solid was observed. The reaction mixture was stirred for 2 h at room temperature, and the resulting suspension was filtered. The solid was washed with Et_2O and dried under vacuum. **1**. Yield: 0.12 g (87%). ^1H NMR (400 MHz, CD_3CN): *δ* 7.64 (d, 3H, *J* = 2.3 Hz), 7.56 (d, 3H, *J* = 1.7 Hz), 6.33 (t, 3H, *J* = 2.2 Hz), 5.23 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN): *δ* 141.2, 131.9, 107.2, 67.1. Anal. Calcd for $C_{12}H_{15}CuF_6N_7P$: C, 30.94; H, 3.25; N, 21.05. Found: C, 30.69; H, 3.18; N, 20.63. **3**. Yield: 0.13 g (70%). ^1H NMR (400 MHz, CD_3CN): *δ* 4.91 (s, 6H), 2.19 (s, 9H), 2.01 (s, 9H), 1.91 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN): *δ* 147.5, 137.7, 112.9, 61.2, 11.2, 8.5, 7.1. Anal. Calcd for $C_{21}H_{33}CuF_6N_7P{\cdot}0.5CH_2Cl_2$: C, 40.70; H, 5.40; N, 15.45. Found: C, 41.08; H, 5.30; N, 15.20. **4**. Yield: 0.59 g (70%). ^1H NMR (400 MHz, CD_3CN): *δ* 5.06 (s, 6H), 2.22 (s, 9H), 2.08 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3CN): *δ* 147.1, 139.1, 95.3, 63.0, 11.8, 9.5. Anal. Calcd for $C_{18}H_{24}Br_3CuF_6N_7P$: C, 27.48; H, 3.08; N, 12.46. Found: C, 27.39; H, 2.93; N, 12.03.

Synthesis of $[\text{Tpa}^x\text{CuI}]$ Complexes [Tpa^x = Tpa (5), Tpa* (6), Tpa^{Me3} (7), and $\text{Tpa}^{*,\text{Br}}$ (8)]. A stirred solution of CuI (0.057 g, 0.3 mmol) in acetonitrile (20 mL) was treated with a solution of the corresponding Tpa^x ligand (0.3 mmol) in acetonitrile (20 mL). Precipitation of a solid was immediately observed. The mixture was stirred for 5 h at room temperature, and the solid was separated by filtration, washed with dichloromethane to remove unreacted material and with diethyl ether, and then dried under vacuum. **5**. Yield: 0.38 g (99%). ^1H NMR (400 MHz, DMSO-d_6): *δ* 7.80 (s, 3H), 7.64 (s, 3H), 6.30 (s, 3H), 5.39 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-d_6): *δ* 141.3, 131.9, 106.3, 66.5. Anal. Calcd for $C_{24}H_{30}Cu_4I_4N_{14}$ $0.3Et_2O$: C, 23.39; H, 2.58; N, 15.07. Found: C, 23.55; H, 2.22; N, 15.54. **6**. Yield: 0.18 g (99%). ^1H NMR (400 MHz, $CDCl_3$): *δ* 5.88 (s, 3H), 4.96 (s, 6H), 2.39 (s, 9H), 2.09 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $CDCl_3$): *δ* 149.9, 140.1, 106.9, 61.2, 14.6, 10.8. Anal. Calcd for $C_{18}H_{27}CuIN_7 \cdot 0.25CH_2Cl_2$: C, 39.63; H, 5.01; N, 17.73. Found: C, 39.66; H, 5.06; N, 17.50. **7**. Yield: 0.17 g (99%). ^1H NMR (400 MHz, $CDCl_3$): *δ* 4.92 (s, 6H), 2.36 (s, 9H), 2.02 (s, 9H), 1.88 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $CDCl_3$): *δ* 148.9, 136.8, 113.3, 61.1, 13.1, 9.4, 7.9. Anal. Calcd for $C_{21}H_{33}CuIN_7{\cdot}0.5\ CH_2Cl_2$: C, 41.89; H, 5.56; N, 15.91. Found: C, 42.21; H, 5.48; N, 16.25. **8**. Yield: 0.23 g (99%). ^1H NMR (400 MHz, DMSO-d_6): *δ* 5.18 (s, 6H), 2.24 (s, 9H), 2.10 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO-d_6): *δ* 146.9, 139.0, 95.3, 63.7, 13.4, 10.2. Anal. Calcd for $C_{18}H_{24}Br_3CuIN_7{\cdot}0.5CH_2Cl_2$: C, 27.40; H, 3.11; N, 12.09. Found: C, 26.97; H, 2.92; N, 11.80.

Synthesis of $[\text{Tpa}^x\text{Cu(PPh}_3)]PF_6$ Complexes [Tpa^x = Tpa* (9), Tpa^{Me3} (10), and $\text{Tpa}^{*,\text{Br}}$ (11)]. A solution of PPh_3 (0.057 g, 0.217 mmol) in dichloromethane (15 mL) was treated with the corresponding $[\text{Tpa}^x\text{Cu}]PF_6$ complex (0.217 mmol). The reaction mixture was stirred for 3 h at room temperature, and the solvent was evaporated under reduced pressure. **9**. Yield: 0.18 g (99%) ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.49−7.43 (m, 9H), 7.28−7.25 (m, 6H), 5.92 (s, 3H), 4.71 (s, 6H), 2.21 (s, 9H), 2.11 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $CDCl_3$): *δ* 149.7, 141.9, 133.1, 131.9, 130.8, 129.3, 107.1, 61.2, 14.1, 10.8. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $CDCl_3$): *δ* 0.06 (s, *P*Ph$_3$). Anal. Calcd for $C_{36}H_{42}CuF_6N_7P_2{\cdot}0.33CH_2Cl_2$: C, 51.92; H, 5.12; N, 11.66. Found: C, 52.06; H, 4.96; N, 11.58. **10**. Yield: 0.18 g (99%). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.41−7.35 (m, 9H), 7.20−7.16 (m, 6H), 4.58 (s, 6H), 2.04 (s, 9H), 1.96 (s, 9H), 1.80 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $CDCl_3$): *δ* 148.4, 138.5, 133.1, 132.0, 130.9, 129.3, 113.5, 61.3, 12.6, 9.4, 7.9. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $CDCl_3$): *δ* 0.06 (s, *P*Ph$_3$). Anal. Calcd for $C_{39}H_{48}CuF_6N_7P_2{\cdot}0.5CH_2Cl_2$: C, 52.90; H, 5.51; N, 10.93. Found: C, 53.07; H, 5.46; N, 10.99. **11**. Yield: 0.23 g (99%). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.43 (br s, 9 H), 7.24 (br s, 6 H), 4.76 (br s, 6H), 2.22 (br s, 9H), 2.05 (br s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $CDCl_3$): *δ* 148.5, 140.4, 133.0, 131.2, 131.0, 129.5, 96.4, 62.1, 13.0, 10.2. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $CDCl_3$): *δ* 0.81 (s, *P*Ph$_3$). Anal. Calcd for $C_{36}H_{39}Br_3CuF_6N_7P_2{\cdot}0.5CH_2Cl_2$: C, 40.17; H, 3.69; N, 8.65. Found: C, 40.21; H, 3.74; N, 8.93.

Synthesis of $[\text{Tpa}^x\text{Cu(CO)}]PF_6$ Complexes [Tpa^x = Tpa (12), Tpa* (13), Tpa^{Me3} (14), and $\text{Tpa}^{*,\text{Br}}$ (15)]. Through a suspension of the corresponding $[\text{Tpa}^x\text{Cu}]PF_6$ complex (0.074 mmol) in CH_2Cl_2 (30 mL) was bubbled CO for 20 min, resulting in a colorless solution. The solvent was removed under vacuum, and the product was obtained as a white powder of analytical purity. **12**. IR (CH_2Cl_2 solution, cm^{-1}): 2087. **13**. ^1H NMR (400 MHz, CD_2Cl_2): *δ* 5.98 (s, 3H), 4.85 (s, 6H), 2.31 (s, 9H), 2.25 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): *δ* 172.9, 149.9, 141.7, 107.3, 60.7, 13.8, 10.4. Anal. Calcd for $C_{19}H_{27}CuF_6N_7OP{\cdot}0.14CH_2Cl_2$: C, 38.96; H, 4.60; N, 16.62. Found: C, 38.54; H, 4.87; N, 17.20. IR (CH_2Cl_2 solution, cm^{-1}): 2103, 2076. **14**. ^1H NMR (400 MHz, CD_2Cl_2): *δ* 4.86 (s, 6H), 2.22 (s, 9H), 2.15 (s, 9H), 1.91 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): *δ* 172.8, 148.6, 138.5, 113.8, 61.9, 12.1, 8.9, 7.5. Anal. Calcd for $C_{22}H_{33}CuF_6N_7OP$: C, 42.62; H, 5.36; N, 15.81. Found: C, 42.75; H, 5.28; N, 15.25. IR (CH_2Cl_2 solution, cm^{-1}): 2099, 2073. **15**. ^1H NMR (400 MHz, CD_2Cl_2): *δ* 4.92 (br s, 6H), 2.32 (br s, 9H), 2.30 (br s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_2Cl_2): *δ* 172.4, 149.2, 140.4, 96.6, 61.7, 12.8, 9.5. Anal. Calcd for $C_{19}H_{24}Br_3CuF_6N_7OP{\cdot}CH_2Cl_2$: C, 26.70; H, 2.91; N, 10.90. Found: C, 26.53; H, 3.06; N, 11.33. IR (CH_2Cl_2 solution, cm^{-1}): 2107, 2083.

Typical Procedure for Carbene-Transfer Reactions: Styrene Cyclopropanation. To a solution of the corresponding $[\text{Tpa}^x\text{Cu}]PF_6$ complex (0.0125 mmol) and styrene (1.25 mmol) in CH_2Cl_2 (5 mL) was added ethyl diazoacetate (EDA; 0.25 mmol) for 3 h with the aid of a syringe pump. The consumption of EDA was monitored by gas chromatography. Volatiles were removed under reduced pressure, and the crude reaction product was dissolved in $CDCl_3$. 9-Anthracenecarboxaldehyde was added as an internal standard, and conversions were determined by ^1H NMR. The results are summarized in Tables 2 and S1 in the SI.

Typical Procedure for Nitrene-Transfer Reactions: Styrene Aziridination. To a solution of the corresponding $[\text{Tpa}^x\text{Cu}]PF_6$ complex (0.0125 mmol) and styrene (1.25 mmol) in dichloromethane (5 mL) were added PhINTs in one portion (0.25 mmol). The mixture was stirred for 3 h at room temperature. The volatiles were removed under reduced pressure, and the crude reaction product was dissolved in $CDCl_3$. 9-Anthracenecarboxaldehyde was added as an internal standard, and conversions were determined by ^1H NMR. The results are summarized in Tables 3 and S4 in the SI.

X-ray Crystal Determination. Single crystals of **2**, **3**, **5**, and **9** coated with dry perfluoropolyether were mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173(2) K] to the goniometer head. Data collection[37] were carried out on a Bruker-Nonius X8 Kappa Apex II CCD area detector diffractometer using graphite-monochromatic radiation $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, by means of ω and φ scans with narrow frames. Data reduction was performed using *SAINT*[37] and corrected for Lorentz polarization effects and absorption by a multiscan method applied by *SADABS*.[38] The structures were solved by direct methods (*SIR-2002*)[39] and refined against all F^2 data by full-matrix least-squares techniques with *SHELXTL*.[40] All non-H atoms were refined with anisotropic displacement parameters. The H atoms were included from calculated positions and refined riding on their respective C atoms with isotropic displacement parameters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, analytical and spectroscopic data, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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