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Copper(I) Complexes with Trispyrazolylmethane Ligands: Synthesis, Characterization, and Catalytic Activity in Cross-Coupling Reactions

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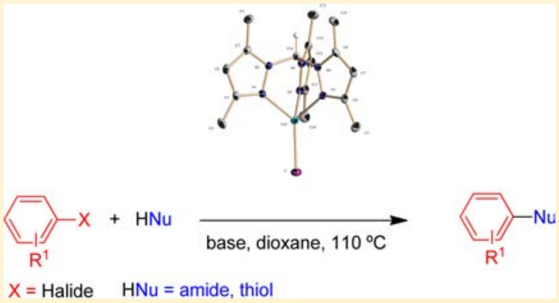
Supporting Information

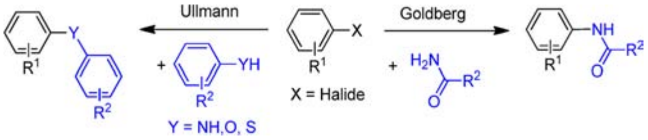
ABSTRACT: Three novel Cu(I) complexes bearing tris(pyrazolyl)methane ligands, Tpm^x, have been prepared from reactions of equimolar amounts of CuI and the ligands Tpm, (HC(pz)$_3$), Tpm*, (HC(3,5-Me$_2$-pz)$_3$), and Tpm^{Ms}, (HC(3-Ms-pz)$_3$). X-ray diffraction studies have shown that the Tpm and Tpm^{Ms} derivatives exhibit a 2:1 Cu:ligand ratio, whereas the Tpm* complex is a mononuclear species in nature. The latter has been employed as a precatalyst in the arylation of amides and aromatic thiols with good activity. The synthesis of a Tpm*Cu(I)-phthalimidate, a feasible intermediate in this catalytic process, has also been performed. Low temperature ^{1}H NMR studies in CDCl$_3$ have indicated that this complex exists in solution as a mixture of two, neutral and ionic forms. Conductivity measurements have reinforced this proposal, the ionic form predominating in a very polar solvent such as DMSO. The reaction of Tpm*Cu(I)-phthalimidate with iodobenzene afforded the expected C−N coupling product in 76% yield accounting for its role as an intermediate in this transformation.



INTRODUCTION

During the past few years we have witnessed a remarkable progress in synthetic applications of copper-assisted Ullmann and Goldberg condensations (Scheme 1).[1] The origin of the growing interest in this research area stems from the discovery by Buchwald and co-workers, at the end of the 1990s, that the use of certain chelating ligands produced an accelerating effect in these copper-mediated organic transformations.[2] Since then, different types of neutral bidentate chelators based on N,N-,[2c,d,3] O′O-[4], or mixed N,O[5]- donor atoms have been mainly employed, along with copper, allowing these processes to occur in a catalytic manner under mild conditions. Kinetic, experimental, and theoretical studies carried out on the mechanism of Cu(I)-catalyzed amidation of aryl iodides[6] (the Goldberg reaction) support the formation of a neutral, tricoordinated Cu^I(amidate) intermediate stabilized by a single molecule of the bidentate ligand. In this context, Hartwig et al. have recently isolated a closely related LCu^I(OPh) (L = chelating nitrogen-donor ligand) and demonstrated its kinetic and chemical competence in the Ullmann etherification of aryl halides.[7]

Scheme 1. Ullmann and Golberg Reactions



Very active catalytic systems based on the previous strategy (bidentate ligand) have been already described,[3−5] most of them upon in situ generation of the catalyst precursor. In contrast, examples describing the use of multidentate ancilliary ligands, other than bidentates, in the copper-assisted Ullmann and Goldberg condensations are yet scarce (Scheme 2). For example, Taillefer and co-workers have examined the effect of a range of polidentate oxyme type and pyridine-imine chelators in arylation of N-heterocycles[5d,e] and cyanation of aryl halides.[8a] These studies revealed that a combination of a tetradentate Schiff base with a suitable copper(I) source in situ generates a highly active catalyst for various type of cross-coupling processes.[5d,e,8] Recently, Zhou et al.[9] have prepared a tetra-coordinated Cu(II) complex bearing a tetradentatesulfonato-salen ligand and described its catalytic activity in different N-arylation reactions carried out in water. With regard to tripodal chelators, catalysts systems based on 1:1 mixtures of CuI and commercially available 1,1,1-tris(hydroxymethyl)ethane[10] or tris(2-aminoethyl)amine[11] tridentate ligands have proven to be efficient in carbon-heteroatom bond forming reactions. Of note, well-defined cationic trinuclear copper(I)

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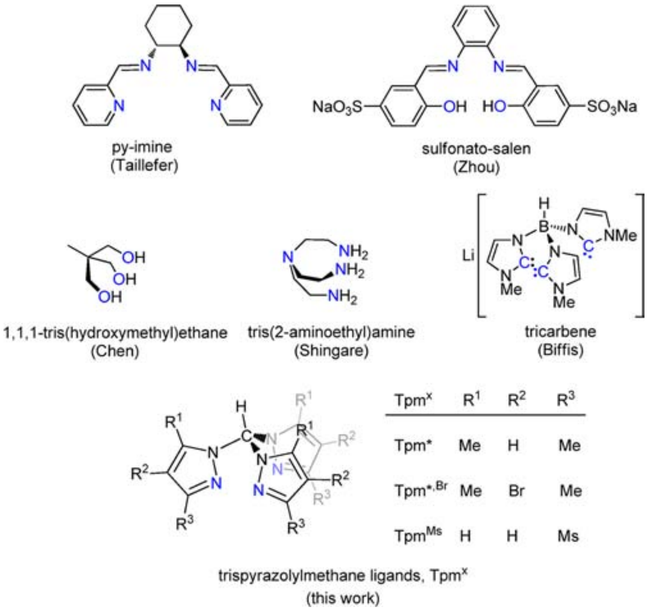
Scheme 2. Previously Employed Tri- and Tetradentate Ligands in Goldberg/Ullmann Reactions and Tpm^x Ligands Employed in This Work



Tpm^x	R^1	R^2	R^3
Tpm*	Me	H	Me
$\mathrm{Tpm}^{*,Br}$	Me	Br	Me
Tpm^{Ms}	H	H	Ms

complexes containing two anionic triscarbene ligands have been successfully tested as catalysts in arylation of N-, O-, and C-centered nucleophiles,[12] a rare example of the use of NHC-carbene ligands in copper-catalyzed cross-coupling reactions.

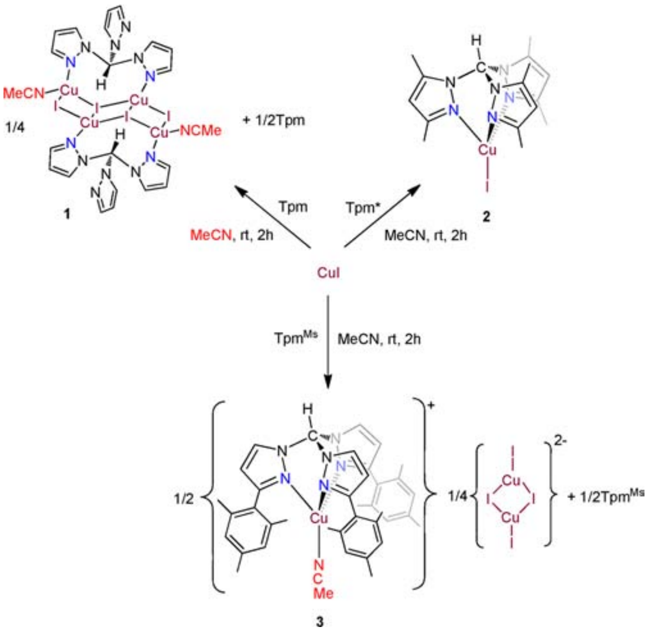
Noteworthy, the use of stable preformed copper(I) complexes as catalysts in copper-mediated C−C and C-heteroatom cross-coupling reactions is not a common practice,[3b,13] despite this methodology can overcome the drawbacks of the catalyst in situ generation strategy, such as the formation of metal species with different catalytic activities, the decrease of yield due to side reactions,[2e,14] or the contamination of products with the typically employed excess of ligand. In addition, such use of well-defined precatalysts could shed some light on the influence of the catalyst structure on the mechanism of the reaction.

We are interested in the preparation and characterization of stable copper(I) complexes that can serve as catalysts in cross-coupling processes, particularly those involving the formation of C-heteroatom bonds. In this context, we have recently reported the synthesis of two well-defined, isomeric, dinuclearCu(I) complexes $[Cu_2I_2L_2]$ (L = bis(azaindolyl)-methane) containing one molecule of the bidentate ligand per copper atom. Both complexes efficiently catalyzed the N-arylation of 2-pyrrolidinone and S-arylation of thiols with aryl iodides.[15] In that work, we briefly mentioned that the complex $[\mathrm{Tpm^*Cu(NCMe)}]BF_4$ induced, at a moderate extent, the N-arylation reaction of pyrrolidone. Given the tridentate mode of this ligand, we wondered if other related complexes bearing these Tpm^x ligands (Scheme 2) could catalyze these transformations effectively. Herein, we describe the preparation and full characterization as well as the catalytic activity in C-heteroatom bond-forming reactions of new Cu(I) derivatives bearing Tpm^x ligands. In order to compare this system with the well-established Cu^{I}(amidate) bearing bidentate ligands, we have prepared the complex Tpm*Cu(I)-phthalimidate, a potential intermediate in this transformation, for which NMR and chemical reactivity studies have also been carried out.

■ RESULTS AND DISCUSSION

Synthesis and Molecular Structures of Metal Complexes. The reaction of copper(I) iodide in acetonitrile with the Tpm^x ligands illustrated in Scheme 3 afforded several CuI-Tpm^x complexes with different Cu/ligand stoichiometry. Thus, when equimolar amounts of CuI and the parent ligand Tpm were reacted at room temperature, a rapid precipitation of the tetranuclear complex $[Tpm_2Cu_4I_4(NCMe)_2]$ (**1**) was observed. Despite the initial CuI/Tpm molar ratio of 1:1, we only isolated complex **1**. Subsequently, this compound was prepared in 87% yield by using a 2:1 stoichiometric mixture of CuI and Tpm, respectively. Conversely, the use of the dimethylpyrazolyl-containing Tpm* ligand yielded the expected mononuclear derivative [Tpm*CuI] (**2**) from a 1:1 initial ratio of reagents. The bulkier Tpm^{Ms} induced a somewhat distinct reactivity, since its addition to an acetonitrile solution containing one equiv of CuI resulted in the formation of $\{[\mathrm{Tpm}^{Ms}\mathrm{Cu(MeCN)}]^+\}_2\{[Cu_2I_4]^{2-}\}\cdot\mathrm{MeCN}$ (**3**), in which the empirical ratio of CuI to Tpm^{Ms} was 2:1. Not surprisingly, a high yield preparation of this complex (84%) was achieved from an initial CuI:Tpm^{Ms}, 2:1 ratio.

Scheme 3. Synthesis of Tpm^x-Copper(I) Complexes 1−3



All complexes were stable to air both in solution and in the solid state. Compounds **1** and **3** were only sparingly soluble in MeCN and DMSO, but complex **2** was well soluble in those solvents and also in $CHCl_3$. The coordination of Tpm^x ligands to the copper(I) center in the molecules of **1**−**3** was confirmed by a characteristic shift of resonances for the ligands to the downfield region in their ^{1}H NMR spectra recorded in DMSO-d_6 (see the Experimental Section). In addition, the IR spectra of **1** and **3** in Nujol mull showed weak stretching bands at 2133 and 2141 cm^{-1}, respectively, due to the presence of coordinated MeCN in these compounds. Nevertheless, spectroscopic and analytical data obtained for these copper derivatives were insufficient for unequivocally proposing a formulation for each of them. Therefore, the molecular structures of **1**−**3** were determined by X-ray diffraction studies carried out with single crystals of the complexes obtained from acetonitrile solutions.

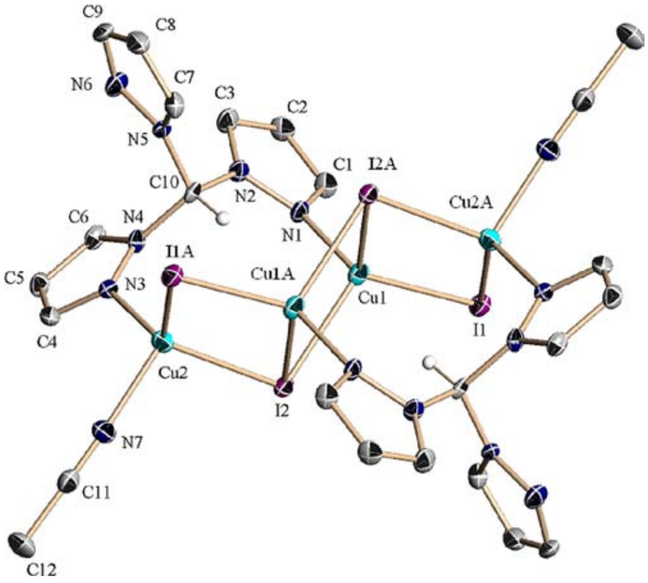


Figure 1. Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **1**: Cu(1)−N(1) = 2.037(4), Cu(1)−I(2) = 2.6469(7), Cu(1)−N(1) = 2.037(4), Cu(1)−I(2A) = 2.7040(7), Cu(2)−N(3) = 2.063(4), Cu(2)−N(7) = 1.996(4), Cu(2)−I(2) = 2.6694(7), Cu(2)−I(1A) = 2.5720(7), N(1)−Cu(1)−I(2A) = 104.76(11), N(1)−Cu(1)−I(2) = 112.00(11), I(1)−Cu(1)−I(2) = 114.67(2), I(1)−Cu(1)−I(2A) = 116.40(2), N(7)−Cu(2)−N(3) = 101.96(16), N(3)−Cu(2)−I(1A) = 117.37(10), N(7)−Cu(2)−I(2) = 103.61(12), I(1A)−Cu(2)−I(2) = 118.87(2).

The crystal structure of **1** (Figure 1) consists of two Tpm ligands, two acetonitrile molecules, and a step-Cu_4I_4 core which contains two types of I atoms (μ_2-I and μ_3-I) and two types of Cu(I) centers, both in tetrahedral environments. Cu(1) is bonded to three iodine atoms and to a nitrogen atom from one of the pyrazolyl rings of a Tpm ligand, whereas Cu(2) is coordinated by two iodine atoms and two nitrogen atoms, one from a pyrazolyl ring of the same Tpm moiety and one from the acetonitrile molecule: each Tpm ligand bridges between both types of Cu(I) centers in a kappa^{2}NN-coordination mode, the third pyrazolyl ring remaining uncoordinated. The bond angles around Cu(1) ranging from 104.76(11) to 116.40(2)° (see the caption of Figure 1) are normal for a tetrahedral coordination, although Cu(2) exists in a slightly more distorted tetrahedral arrangement with angles around Cu(2) being in the interval 101.96(16)−118.87(2)°. The Cu−N and Cu−I bond lengths are comparable with those of other tetrameric clusters.[16]

Single-crystal analyses of **2** revealed that it is a mononuclear complex (Figure 2). The Cu(I) ion is coordinated by the iodide anion and the three N atoms of the Tpm* ligand in a trigonally distorted tetrahedral geometry, with angles varying from 84.86(5) to 129.49(3). The Cu−N bond distances for the tridentate ligand (2.0863(13)−2.1416(13) Å) are similar to those previously described for other tris(pyrazolyl)methane copper derivatives,[17] with a shorter Cu−I distance (2.4667(2) Å) compared to tetrahedral L_3CuI complexes.[18]

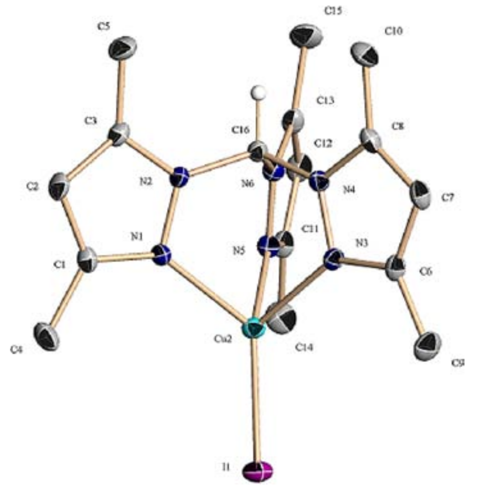


Figure 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **2**: Cu(2)−N(1) = 2.0994(5), Cu(2)−N(3) = 2.1416(13), Cu(2)−N(5) = 2.0863(13), Cu(2)−I(1) = 2.4667(2), N(5)−Cu(2)N(1) = 84.86(5), N(5)−Cu(2)−N(3) = 87.49(5), N(1)−Cu(2)−N(3) = 87.72(5), N(5)−Cu(2)−I(1) = 128.88(4), N(1)−Cu(2)−I(1) = 129.49(3), N(3)−Cu(2)−I(1) = 124.38(3).

The solid-state structure of **3** has shown its ionic nature. This compound contains two independent $[Tpm^{Ms}Cu(MeCN)]^+$cations and one $[Cu_2I_4]^{2-}$ as the counteranion, with the three Cu ions in the +1 oxidation state. The Cu(I) cation shows a distorted tetrahedron environment with a N4 donor set, one from the coordinated MeCN molecule and the other three N atoms from the tridentate ligand Tpm^{Ms} (Figure 3). In the $[Cu_2I_4]^{2-}$counteranion, both Cu(I) are symmetrically bridged by two I atoms and coordinated by a terminal iodide anion, leading to a trigonal planar geometry around each copper center. The structure of the cation has already been reported by our group as a PF_6^- salt,[17d] and the dianion $[Cu_2I_4]^{2-}$ has also been crystallographically characterized.[18b,19] Bond distances and angles are in good agreement with those already published.

NMR features of complexes **1**−**3** showed the equivalence of the three pyrazolyl rings of the Tpm^x ligands in their molecules. This observation is in agreement with the solid-state structures being maintained in solution for **2** and **3** but not for **1**. In the latter case, it is likely that the tetramer dissociates somehow in the presence of the solvent DMSO-d_6. As shown above, molecular structures of these three Tpm^xCu(I) complexes in the solid state are quite different. Despite the distinct electronic nature of the pyrazolyl substituents (i.e. H, Me, and Ms), we believe that it is the steric hindrance at the 3 position of the pyrazolyl rings that determines the structure adopted by complexes **1**−**3**. In this regard, both Tpm* and Tpm^{Ms} favor the formation of N_3-mononuclear complexes, but the larger size of the Ms group in the latter prevents the coordination of the iodine atom to the Cu(I) center, yielding the acetonitrile adduct.

N-Arylation and S-Arylation Reactions Catalyzed by 1−3. Although we were initially seeking for complexes with a 1:1 metal to ligand ratio for catalytic purposes, and only **2** met such a requirement, we decided to examine the catalytic properties of all these Tpm^xCu compounds in the aryl amidation reaction[2a,5e,10,13j,14b,20] of iodobenzene with 2-pyrrolidinone (Table 1). The experiments were performed with 5 mol % based on copper in the presence of K_3PO_4 as the base in dioxane at 110 °C for 24 h. Under these conditions

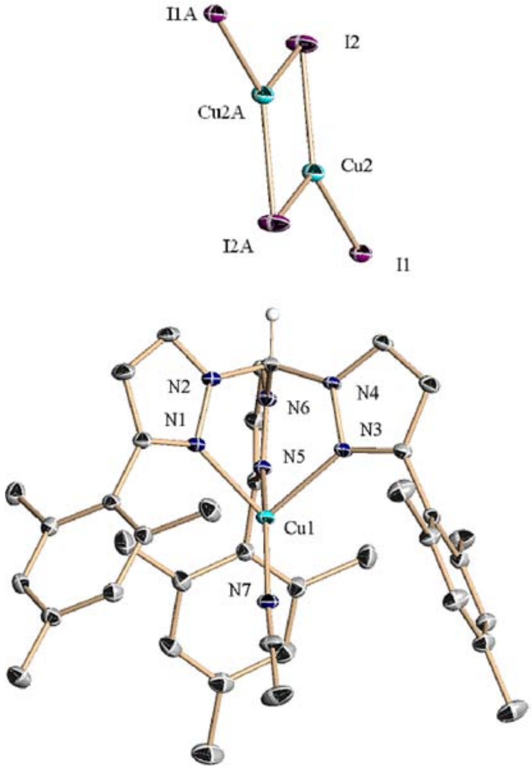
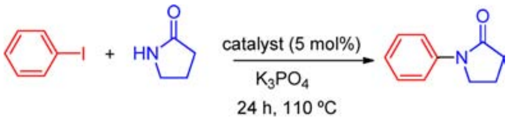


Figure 3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **3**: Cu(1)−N(5) = 2.034(2), Cu(1)−N(1) = 2.117(2), Cu(1)−N(3) = 2.1177(19), Cu(I)−N(7) = 1.874(2), Cu(2)−I(1) = 2.5011(4), Cu(2)−I(2) = 2.5666(4), Cu(2A)−I(2) = 2.5611(4), Cu(2)−I(2A) = 2.5611(4), Cu(2)−Cu(2A) = 2.6535(7), N(7)−Cu(1)−N(5) = 146.52(9), N(7)−Cu(1)−N(1) = 117.35(9), N(7)−Cu(1)−N(3) = 114.25(9), N(5)−Cu(1)−N(1) = 87.19(8), N(5)−Cu(1)−N(3) = 87.98(8), N(1)−Cu(1)−N(3) = 86.73(8), I(1)−Cu(2)−I(2A) = 116.568(14), I(1)−Cu(2)−I(2) = 125.754(15), I(2A)−Cu(2)−I(2) = 117.672(14), Cu(2A)−I(2)−Cu(2) = 62.328.

complexes **1**−**3** were active (Table 1, entries 1−3), although with variable efficiency. Taking into account the above-mentioned insolubility of complexes **1** and **3** in most organic solvents, we studied the effect of the solvent in this cross-coupling process. Thus, in toluene only **2** induced the reaction, affording the expected coupling product in 86% yield (entry 4). In more polar solvents such as MeCN and DMSO, the catalytic activity of **3** remained unchanged but that of **1** was increased as the result of the solubility enhancement of the latter in these polar solvents (entries 5−9). Next, we decided to compare the catalytic performance of well-defined precatalysts **1**−**3** with that of in situ prepared catalysts. For that purpose, the coupling reactions were performed in dioxane in the presence of 5 mol % of CuI and 5 mol % of the ligand. It was found that in the case of Tpm* and $\mathrm{Tpm^{Ms}}$ ligands similar yields of the coupling product were obtained under both protocols (entries 2, 3 vs 11, 12). On the contrary, the in situ made catalyst with the Tpm ligand resulted to be more effective than the preformed complex **1**, yielding the product in quantitative yield (entries 1 vs 10). Moreover, an experiment carried out using complex **1** and two additional equivalents of the ligand Tpm to match the overall 1:1 Cu:Tpm ratio, afforded the coupling product in 65% yield (entry 13), almost identical to that found when **1** was employed as the precatalyst (see entry 1). In a blank experiment performed under ligandless conditions,[21] it was found that the yield only reached 58% after 24 h. Thus, it seems that there is no effect of the use of well-defined or in situ generated catalyst precursors with the Tpm* or $\mathrm{Tpm^{Ms}}$ derivatives from the point of view of activity. But for the parent Tpm, the in situ strategy led to substantially higher yields. We believe that this is the result of a readily formation of a 1:1 TpmCu(I) adduct that would act as an effective catalyst precursor. Although the use of yields values to assess trends in catalytic activities must be considered with caution, we believe that the overall picture indicates that in all cases the species responsible for catalysis is the $\mathrm{Tpm^{x}Cu}$ core, showing that coordination of these ligands may exert a positive effect in catalysis.

Table 1. N-Arylation of 2-Pyrrolidinone Catalyzed by $\mathrm{Tpm^{x}Cu(I)}$ Complexes[a]



entry	precatalyst	solvent	yield (%)[b,c]
1	**1**	dioxane	63
2	**2**	dioxane	80
3	**3**	dioxane	80
4	**2**	toluene	86
5	**1**	MeCN	80
6	**2**	MeCN	80
7	**3**	MeCN	73
8	**1**	DMSO	93
9	**3**	DMSO	88
10	CuI + Tpm (1:1)	dioxane	95[d]
11	CuI + Tpm* (1:1)	dioxane	84[d]
12	CuI + $\mathrm{Tpm^{Ms}}$ (1:1)	dioxane	73[d]
13	**1** + Tpm (1:2)	dioxane	65
14	CuI	dioxane	58

[a] Reaction conditions: iodobenzene (1 mmol), 2-pyrrolidinone (1.2 mmol), K_3PO_4 (2 mmol), copper complex (5 mol % of copper, 0.0125 mmol for **1** and **3**, 0.05 mmol for **2** and CuI), solvent (1 mL). [b] Isolated yields (average of two runs). [c] Unreactive iodobenzene accounted for the overall mass balance. [d] The reaction was carried out in the presence of CuI (5 mol %) and $\mathrm{Tpm^{x}}$ (5 mol %) as the catalyst.

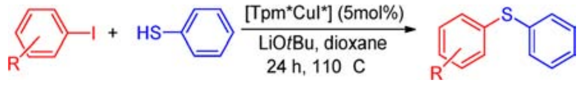
Next, we decided to study the scope of this Goldberg-type condensation using only precatalyst **2**, on the basis of its well-defined 1:1 Cu/ligand stoichiometry. The coupling reactions of pyrrolidinone with different aryl iodides were carried out using 5 mol % of **2** and K_3PO_4 as the base in dioxane at 110 °C (Scheme 4). Electron-deficient and electron-rich *para*-substituted aryl iodides were suitable for this reaction, providing N-arylated products in high yields. 2-Methoxy-1-iodobenzene afforded lower yield of the coupling product (62%), but the reaction yield could be significantly improved (up to 85%) by increasing the amount of catalyst employed (10 mol %). In addition, under the present reaction conditions the system was chemoselective toward iodides, providing a complete replacement of the iodo-group by the nucleophile in the presence of a bromo substituent on the aryl ring.

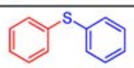
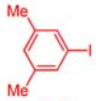
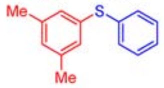
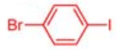
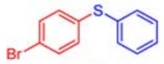
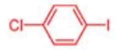
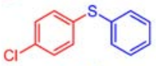
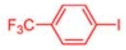
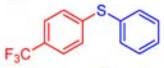
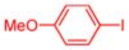
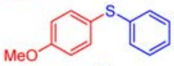
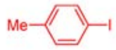
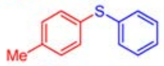
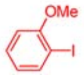
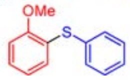
A comparison between the results illustrated in Scheme 4 and those reported by Chen et al.[10] using the in situ prepared CuI/1,1,1-tris(hydroxymethyl)ethane system revealed that our well-defined system behaves similarly. Thus, the coupling reaction of iodobenzene and pyrrolidinone in dioxane afforded

Scheme 4. Coupling of ArI with 2-Pyrrolidinone in the Presence of 2[a,b]

[a]Reaction conditions (as in Table 1): ArI (1 mmol), 2-pyrrolidinone (1.2 mmol), K_3PO_4 (2 mmol), precatalyst **2** (5 mol %), dioxane (1 mL), 110 °C, 24 h. [b]Isolated yields (average of two runs). [c]Reaction carried out with using 10 mol % of **2**.

Table 2. Coupling of ArI with Thiophenol in the Presence of 2[a]



Entry	ArI	Product	Yield[b] %
1			95
2			95
3			99
4			93
5			99
6			61 99^c
7			72
8			20 95^c

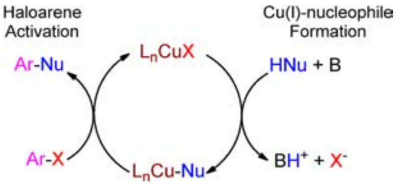
[a]Reaction conditions: ArI (1.2 mmol), thiophenol (1.0 mmol), LiO*t*Bu (2 mmol), precatalyst **2** (5 mol %), dioxane (1 mL), 110 °C, 24 h. [b]Isolated yields (average of two runs). [c]Reaction carried out with using 10 mol % of **2**.

80% yield of the coupling product, whereas the CuI/1,1,1-tris(hydroximethyl)ethane led to a 81% yield of the corresponding product under the same reaction conditions (K_3PO_4 as the base in dioxane at 110 °C for 24 h) but using 10 mol % catalyst loading. But, the Tpm*CuI precatalyst is considerably less active than Buchwald's catalytic system based on the use of CuI and excess of a diamine ligand.[2c] Under similar reaction conditions (temperature and time) the latter afforded quantitative yields of the amidation products by using 1 mol % of the copper source. However, our protocol avoids the removal of free ligand in the reaction workup and also prevents the formation of different CuL_n species that could affect the concentration of the active catalytic species in solution. In any case, our aim in this work is to demonstrate that tridentate Tpm^x ligands are beneficial to this reaction, in order to provide a new window for future catalyst development.

We have also extended this protocol to C−S bond-forming reactions[22] by examining the arylation of thiols with aryl iodides with complex **2** as the catalyst precursor. The coupling reactions were carried out under the optimal conditions found for the N-arylation reactions but with LiO*t*Bu (2 equiv) as the base. In order to minimize the formation of undesired phenyl disulfide (C_6H_5−S−S−C_6H_5) the experiments were done with a slight excess of the aryl iodide. The desired thioethers were prepared in good to excellent yields as shown in Table 2. We found that aryl iodides bearing electron-withdrawing groups at the *para* position were more prone to undergo this transformation (entries 3−5) than those bearing electron-donating substituents on that position (entries 6 and 7). In this regard, the coupling reaction of thiophenol and 4-methoxy-1-iodobenzene furnished quantitative yield of the S-arylated product in the presence of 10 mol % of precatalyst **2**. Like in the N-arylation of pyrrolidinone (see above), full selectivity toward iodo derivatives was highlighted on the coupling of 1-bromo or 1-chloro-4-iodobenzene with thiophenol affording the corresponding 4-bromo- or 4-chlorophenyl phenyl thioether as the only product (entries 3 and 4). In contrast to this result, the system developed by the group of Shingare[11a] based on the use of CuI and the ligand tris(2-aminoethyl)amine has been reported to be active in the coupling of thiols with both aryl iodides and aryl bromides. An increase in the catalyst loading was required with a sterically hindered substrate such as 2-iodoanisol (entry 8).

Synthesis of Cu(I)−Imidate Complex and Reactivity with Iodobenzene. In the past few years, different studies have been carried out with the aim to elucidate the mechanism of copper-catalyzed Goldberg and Ullmann-type reactions. However, up to date it is not possible to make a unique mechanistic proposal that satisfactorily explains the entire catalytic cycle. Experimental evidence[6a−c,7,23] and theoretical calculations[6d,24]support the formation of a ligated Cu(I)-nucleophile intermediate in the initial step of the reaction (Scheme 5). In this regard, complexes of the type LCu(I)-nucleophile (nucleophile = amidate,[6a−c] imidate,[6a−c] amido,[6a−c] phenoxide,[7] and pyrazolate[23d]) containing a bidentate o monodetate ligand have been prepared, characterized, and shown to react with aryl halides to form the corresponding coupling products. But how the activation of the aryl halide by the Cu(I)-nucleophile proceeds is still a matter of controversy. For example, experiments performed in the presence of a radical clock argued in favor of an oxidative addition pathway to form a Cu(III)-aryl(nucleophile) intermediate.[6,7,23a] Such species have not been yet detected nor isolated from the reaction mixture, although well-defined Cu(III)-aryl complexes have been reported recently to react with N-and O-base nucleophiles to afford C−N and C−O coupling products.[25] On the other hand, very recently Buchwald et al.[26] have examined the selectivity in Ullmann-type reactions by DFT calculations

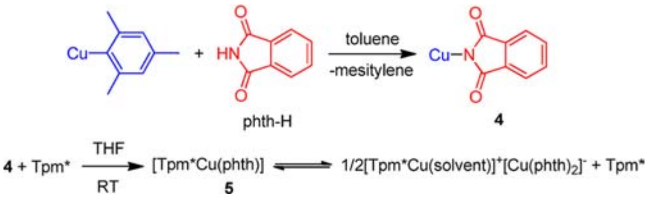
Scheme 5. Simplified Catalytic Cycle for Copper-Catalyzed Ullmann and Goldberg Reactions



coming to the conclusion that a Cu(I)/Cu(II) radical pathway is energetically favored over the formation of a Cu(III)-aryl intermediate.

Since examples of LCu(I) amidate and imidate compounds containing bidentate and monodentate ligands are known, we decided to prepare similar complexes with the tripod Tpm* ligand. The synthesis was carried out following a two-step procedure similar to that reported for the preparation of (1,2-diamine)Cu(I)-pyrrolidinonate.[6a] Initially, we attempted to synthesize the Tpm*Cu-pyrrolidonate, but it decomposed when trying to isolate it. Thus, we decided to prepare the phtalimidate derivative instead. First, Cu(I)-phthalimidate, **4**, was obtained from the reaction of mesitylcopper[27] and phthalimide as a pale yellow solid in 90% yield (Scheme 6).

Scheme 6. Synthesis of the Tpm*–Cu(I) Phthalimidate Complex



The room temperature ^{1}H NMR spectrum of **4** in C_6D_6 consists of two well-resolved doublet of doublets centered at 7.34 and 6.79 ppm, in contrast to the spectrum of the related Cu(I)-pyrrolidinonate for which the broadening of resonances are attributed to a rapid exchange between oligomeric species in solution.[6a] In addition, elemental analysis of **4** is in agreement with a 1:1 Cu/phthalimidate ratio. Then, the Tpm* ligand was added to a THF solution of **4**, a slightly cloudiness being observed within 15 min of reaction. Evaporation of solvent yielded compound **5** as a yellow solid of analytical purity that reflected a 1:1 ratio of the Tpm* ligand and the phthalimidate (phth) moiety. Any attempt to crystallize the complex led to decomposition preventing the elucidation of its molecular structure in the solid state. It has been described that in solution copper(I) amidate and imidate complexes ligated by bidentate chelators form ion pairs consisting on a L_2Cu^+cation and a CuX_2^- anion.[6b] To check such possible behavior for compound **5**, conductivity measurements were undertaken. Thus, the molar conductivity of a 1.0 mM solution of **5** in DMSO was 38.0 Ω^{-1} cm^2 mol^{-1}, a value higher than those measured for ferrocene (1.39 Ω^{-1} cm^2 mol^{-1}) or $[NBu_4][BPPh_4]$ (22.9 Ω^{-1} cm^2 mol^{-1}) as standards, and similar to that of the complex $[NBu_4][Cu(phth)_2]$[6b] (40.6 Ω^{-1} cm^2 mol^{-1}). We interpret these data as evidence that complex **5** predominantly forms ion pairs in polar solvents. Unfortunately, we could not gain any information about the molecular structure of **5** in a less polar solvent, such as THF due to its poor solubility in this medium.

NMR experiments were conducted to get a better knowledge about the identity of the species in solution. The ^{1}H NMR of **5** in DMSO-d_6 did not provide any useful information since resonances for both the anionic (phth) and the Tpm* ligands were very broad indicating that exchange processes were taking place. More informative was the room temperature ^{1}H NMR spectrum of **5** recorded in $CDCl_3$. Despite the broadness of the signals, two sets of resonance patterns for two different anionic phth ligands in ca. 1:1 ratio were clearly distinguished in the range of 7.4–8.0 ppm (Figure 4a). One group of these resonances could be assigned to the anionic species $[Cu(phth)_2]^-$ by the direct comparison with the ^{1}H NMR of the complex $[NBu_4][Cu(phth)_2]$ recorded in $CDCl_3$ (two multiplets centered at δ 7.63 and 7.49). Cooling the sample from 20 °C to −40 °C did not produce a significant change in the resonances of the phth ligands but led to the emergence in the spectrum of two patterns of signals for the methyl protons of the Tpm* ligand in a 2:1 ratio (Figure 4b). This observation together with the appearance of a new broad signal in the low field region of the spectrum (ca. 8.7 ppm) suggested the existence of Tpm* ligands in a different chemical environment. The pattern of Tpm* signals of greater intensity was very similar to that of the free ligand, whereas the minor Tpm* species seemed to be related by integration with the phth ligand that appeared at lower field. The insolubility of **5** in a more appropriate solvent to record lower temperature ^{1}H NMR spectra precluded collecting more information about the structure of all the species presented in solution. However, the data available so far allow proposing that $CDCl_3$ solutions of **5** consist of a mixture of a neutral form, Tpm*Cu(phth), and an ionic form. The latter contains $[Cu(phth)_2]^-$ as the anion, but the cationic part of the ion pair is not formed by the coordination of two molecules of the tripod Tpm* ligand to the metal atom, since Cu(I) does not favor an octahedral environment. Instead, we believe the cationic moiety contains only one molecule of the Tpm* ligand coordinated to the copper(I) center. The observation of the free Tpm* ligand in solution seems to support this proposal.

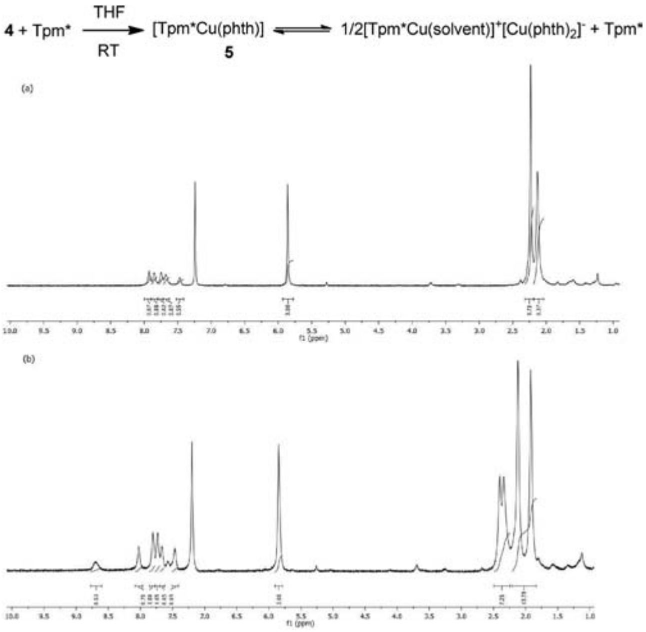
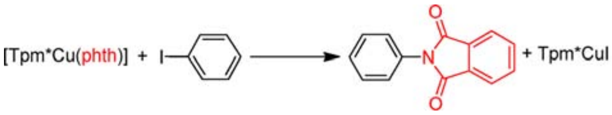


Figure 4. ^{1}H NMR spectra of a solution of **5** in $CDCl_3$ at (top) room temperature and (bottom) −40 °C.

Once the solution structure of complex **5** was established, we examined its reactivity toward iodobenzene. The reaction of a dioxane solution of **5** with 1 equiv of iodobenzene afforded the coupling product in 76% yield (isolated) after 24 h at 110 °C (eq 1). Interestingly, the coupling of phthalimide with iodobenzene catalyzed by 5 mol % of Tpm*CuI under the same conditions (temperature and reaction time) produced the coupling product with a very low yield. These contrasting



(1)

results can be explained if we assume that the stoichiometric reaction shown in eq 1 corresponds to a step beyond the rate determining step in the catalytic process, which complex **5** can be proposed as an intermediate in this transformation.

It is worth mentioning that the reaction shown in eq 1 slightly differs from the catalytic reaction. The Cu-amidate species, during catalysis, is formed upon the action of the base. In this stoichiometric reaction, the Cu-amidate species has already been formed, and therefore we have no base in the reaction mixture. This experiment resembles those by Hartwig and Buchwald,[6] with bidentate ligands. As mentioned above, we have tried to isolate the corresponding copper-pyrrolidonate compound but failed to characterize it due to its instability. However, upon generation and fast workup (as for the phth analog), reaction with iodobenzene was carried out, verifying the formation of the cross coupling product in a shorter reaction time than in the catalytic reaction. We believe that these experiments support the intermediacy of these amidate species in the catalytic cycle.

■ CONCLUSION

In summary, we have synthesized and fully characterized new Cu(I) complexes containing tripod ligands of type tris(pyrazolyl)methane, Tpm^x. The Cu/ligand stoichiometry encountered for these complexes markedly depends on the steric properties of the Tpm^x ligand. Only in the case of Tpm*, a neutral, tetrahedral compound Tpm*CuI, with a 1:1 metal to ligand ratio, was obtained. This well-defined complex was used as the precatalyst in the arylation of amides and aromatic thiols, allowing the efficient coupling of substrates under conditions similar to those described for CuI/tridentate ligand mixtures. Tpm*Cu-phthalimidate complex has also been prepared and been shown to be the active species in the arylation of amides with Tpm*CuI precatalyst. The design of special Tpm^x ligands that could provide stability to those copper-amidates is in progress in our laboratory.

■ EXPERIMENTAL SECTION

General Methods. All reactions and manipulations were carried out under an oxygen-free nitrogen atmosphere with standard Schlenk techniques. All substrates were purchased from Aldrich. Solvents were dried and degassed before use. Tris(pyrazolyl)methane ligands,[28] mesitylcopper,[27] and $[NBu_4][Cu(phth)_2]$[6b] (phth = phthalimidate) were prepared according to the literature procedures. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer. ^{1}H NMR shifts were measured relative to deuterated solvents peaks but are reported relative to tetramethylsilane. Elemental analyses were performed in Unidad de Análisis Elemental of the Universidad de Huelva.

Synthesis of $Tpm_2Cu_4I_4(NCMe)_2$ (1). To a stirred solution of CuI (0.190 g, 1 mmol) in acetonitrile (10 mL) was added a solution of the Tpm ligand (0.248 g, 1 mmol) in acetonitrile (5 mL). Precipitation of a white solid was immediately observed. The mixture was stirred for 2 h, and complex **1** was filtered, dried under vacuum, and obtained as a white solid (0.28 g, 87%).^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.36 (s, 2H), 8.14 (s, 6H), 7.80 (s, 6H), 6.51 (s, 6H), 2.08 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 142.9, 132.7, 118.9, 107.7, 78.7, 1.8. Anal. Calcd. for $C_{24}H_{26}N_{14}Cu_4I_4$: C, 22.26; H, 2.06; N, 15.41. Found: C, 22.65; H, 2.12; N, 15.32.

Synthesis of Tpm*CuI (2). Following the same procedure complex **2** was obtained as a white solid (0.49 g, 99%). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.64 (s, 1H), 5.85 (s, 3H), 2.39 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 150.5, 140.8, 107.1, 68.7, 14.2, 11.0. Anal. Calcd. for $C_{16}H_{22}N_6CuI$: C, 39.32; H, 4.54; N, 17.19. Found: C, 39.00; H, 4.54; N, 17.70

Synthesis of $Tpm^{Ms}{}_2Cu_4I_4(NCMe)_3$ (3). Following the same procedure, complex **3** was obtained as a white solid (0.42 g, 84%).^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.59 (s, 1H), 8.37 (s, 3H), 6.89 (s, 6H), 6.50 (s, 3H), 2.20 (s, 9H), 2.05 (s, 3H), 1.88 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d$_6$): δ 153.2, 138.6, 137.1, 134.1, 128.9, 128.4, 118.1, 108.0, 67.2, 21.1, 20.2, 1.6. Anal. Calcd. for $C_{84}H_{95}N_{17}Cu_4I_4$: C, 47.95; H, 4.54; N, 11.31. Found: C, 47.94; H, 4.55; N, 11.31.

Synthesis of Copper(I)-Phthalimidate (4). To a toluene solution (5 mL) of mesitylcopper (115 mg, 0.633 mmol) was added phthalimide (102 mg, 0.7 mmol). The colorless mixture was stirred for 30 min before volatiles were removed under vacuum. The residue was washed with THF (20 mL) and dried under vacuum to afford complex **4** (128 mg, 90%) as an air-sensitive pale yellow solid. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.62 7.34 (dd, J = 5.4, 3.1 Hz, 2H), 6.79 (dd, J = 5.5, 3.0 Hz, 2H). ^{13}C{^{1}H}NMR (100 MHz, DMSO-d$_6$): δ 179.8, 136.5, 132.8, 121.6. Anal. Calcd. for $C_8H_4CuNO_2\cdot 0.2THF$: C, 47.16; H, 2.50; N, 6.25. Found: C, 47.09; H, 2.89; N, 5.93.

Preparation of Tpm*Cu-(phthalimidate) (5). Inside a glovebox, a solution of copper(I)-phthalimidate (0.05 mmol) in THF (0.5 mL) was placed into a vial equipped with a magnetic stirbar. A THF solution of ligand (0.05 mmol) was then added. After 15 min, a fine precipitated was formed. The reaction mixture was stirred for 2 h at ambient temperature. The solvent was evaporated, and complex **5** was obtained as a bright yellow solid in quantitative yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.93 (s, 1H), 7.85 (s, 1H), 7.75 (s, 1H), 7.68 (s, 1H), 7.47 (s, 1H), 5.86 (s, 3H), 2.23 (s, 9H), 2.13 (s, 9H). ^{13}C{^{1}H}NMR (100 MHz, CDCl$_3$): δ 168.0, 134.7, 133.2, 131.3, 124.2, 121.2, 107.3, 67.2, 13.7, 11.4. Anal. Calcd. for $C_{24}H_{26}CuN_7O_2$: C, 56.75; H, 5.12; N, 19.31. Found: C, 56.64; H, 5.68; N, 18.61.

General Catalytic Procedure for the N-Arylation of Pyrrolidinone with Aryl Iodides. The catalyst (0.05 mmol) was dissolved in dioxane (1 mL) in an ampule. The aryl iodide (1.0 mmol), 2-pyrrolidinone (1.2 mmol), and the base, K_3PO_4 (2 mmol), were added under a nitrogen atmosphere. The reaction was stirred at 110 °C for 24 h in an oil bath. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (15 mL), and centrifuged for 5 min. The clean solution was evaporated to dryness, and the residue was purified by flash chromatography on silica gel.

General Catalytic Procedure for the S-Arylation of Thiols with Aryl Iodides. The catalyst (0.05 mmol) was dissolved in dioxane (1 mL) in an ampule. The aryl iodide (1.2 mmol), the thiol (1.0 mmol), and the base, LiO*t*Bu (2 mmol), were added under a nitrogen atmosphere. The reaction was stirred at 110 °C for 24 h in an oil bath. The reaction mixture was allowed to cool to room temperature and treated with ethyl acetate (15 mL) and water (5 mL). The organic and aqueous layers were then separated, and the organic layer was evaporated to dryness. The residue was purified by flash chromatography on silica gel.

X-ray Crystal Determinations. Data associated with the crystal structures of **1**−**3** are summarized in Tables S1, S7, and S13, respectively (see the Supporting Information). A single crystal of **1**, **2**, and **3** suitable for X-ray diffraction studies (obtained at −20 °C from acetonitrile solutions), coated with dry perfluoropolyether, was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173(2) K] to the goniometer head. Data collection[29] was carried out on a Bruker-Nonius X8 kappa APEX II CCD area-detector diffractometer using graphite-monochromatic radiation λ(Mo Kα) = 0.71073 Å, by means of ω and φ scans with narrow frames. Data reduction was performed using SAINT[29] and corrected for Lorentz polarization effects and absorption by a multiscan method applied by SADABS.[30] The structure was solved by direct methods (SIR-2002)[31] and refined against all F^2 data by full-matrix least-squares techniques with SHELXTL.[32] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, analytical and spectroscopic data. and crystallographic information files 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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