

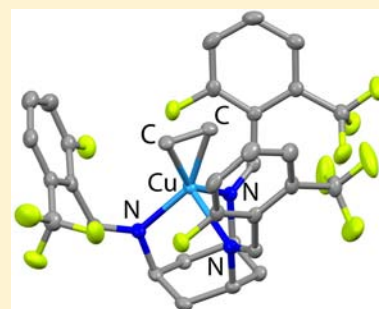
# New Cu(I)-Ethylene Complexes Based on Tridentate Imine Ligands: Synthesis and Structure

Parisa Ebrahimpour, Mairi F. Haddow, and Duncan F. Wass\*

School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

## Supporting Information

**ABSTRACT:** A new bulky facially coordinating  $N_3$ -donor tach-based ligand (tach: *cis,cis*-1,3,5-triaminocyclohexane) [**1**: *cis,cis*-1,3,5-tris(2-fluoro-6-(trifluoromethyl)benzylideneamino)cyclohexane] has been obtained from the condensation of tach with 3 equiv of the appropriate benzaldehyde. Reaction of **1** with  $[Cu(NCMe)_4][PF_6]$  gave the complex  $[(1)Cu(NCMe)] [PF_6]$ . Displacement of the acetonitrile ligand is possible with CO and  $C_2H_4$  (3–5 bar). Cu(I)-ethylene complexes of ligands **1** and **2** [**2**: *cis,cis*-1,3,5-(mesitylideneamino)cyclohexane] were prepared successfully by treatment of the ligands with CuBr and  $AgSbF_6$  in the presence of ethylene. These complexes display reversible complexation of the ethylene molecule under mild changes to pressure, suggesting possible application in olefin separation and extraction.



## INTRODUCTION

Ligands based on a *cis,cis*-1,3,5-tris(arylamino)cyclohexane framework have attracted attention as they provide a face-capping  $N_3$ -coordination environment around a metal center which is a versatile mimic for metalloenzyme active sites.<sup>2,3</sup> More generally, these ligands form a protected cavity around the metal center which has been exploited in biomimetic and catalysis research.<sup>4</sup> Our interest in such ligands stems from the potential of their group 11 complexes to separate simple substrates (such as CO and ethylene) from the mixture of waste gases that are common in petrochemical plants and refining, by weakly binding to such molecules.<sup>5,6</sup>

We have previously communicated the synthesis and preliminary study of one derivative of these ligands, namely, *cis,cis*-1,3,5-tris(mesitylideneamino)cyclohexane, its copper(I) complex and substrate binding selectivity of this complex,<sup>7,1</sup> together with a broader study of novel nonfluorinated and fluorinated  $N_3$ -donor ligands, their Cu(I) complexes and the propensity of such complexes to bind CO.

The ability of Cu(I) to coordinate ethylene has important ramifications in biochemistry (e.g., in fruit ripening),<sup>8</sup> in synthetic methodology (e.g., copper-catalyzed aziridination),<sup>8f,9</sup> and in industrial applications (e.g., epoxidation, paraffin separation).<sup>10</sup> As model intermediates for these processes, and in general as novel coordination compounds, a number of Cu(I)-ethylene complexes have been isolated and in many cases structurally characterized. Supporting ligands are almost exclusively based on nitrogen donors, with bidentate imines including  $\alpha$ -diimines or  $\beta$ -diketimines, and particularly tridentate pyrazolylborate derivatives pre-eminent.<sup>11,8d,e</sup> Stability is a function of the supporting ligands used and in some cases sensitivity toward heat, light, and ethylene-loss is reported. To date, and perhaps surprisingly given the success of other tridentate N-donor ligands, efforts to isolate olefin

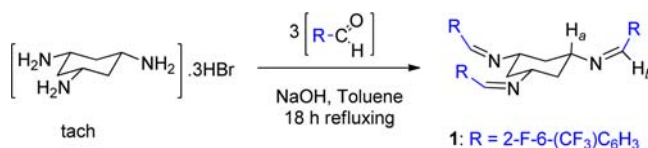
complexes supported by *cis,cis*-1,3,5-tris(arylamino)cyclohexane ligands have proved unsuccessful.

In this paper, we report the synthesis of copper complexes supported by a new fluorinated face-capping  $N_3$  donor ligand, and copper ethylene complexes supported by a range of related ligands. The reversible nature of olefin binding augers well for application in olefin separation.

## RESULTS AND DISCUSSION

**Synthesis and Structural Study of *cis,cis*-1,3,5-Tris(2-fluoro-6-(trifluoromethyl)benzylideneamino)cyclohexane (1).** *cis,cis*-1,3,5-Tris(2-fluoro-6-(trifluoromethyl)benzylideneamino)cyclohexane (**1**) was prepared using the same method as used to obtain previous *cis,cis*-1,3,5-tris(arylamino)cyclohexane ligands.<sup>7,1</sup> Treatment of *cis,cis*-1,3,5-triaminocyclohexane (tach) with 3 equiv of 2-fluoro-6-(trifluoromethyl)benzaldehyde in toluene and removal of water by azeotropic distillation over an 18 h period gives **1** in 86% yield (Scheme 1). The  $^1H$  NMR spectrum of the ligand exhibited a characteristic quartet at 8.64 ppm and a broad triplet of triplets around 3.72 ppm, corresponding to the imine protons ( $=N-CH-$ ,  $H_b$  in Scheme 1) and cyclohexane protons ( $=N-C_{tach}H-$ ,  $H_a$  in Scheme 1) respectively. Ligand **1** is stable under ambient conditions.

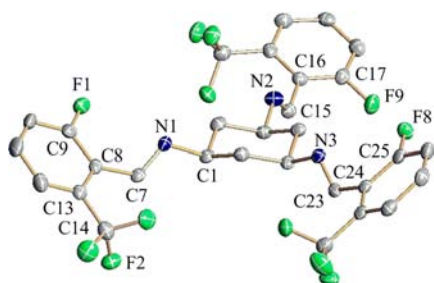
### Scheme 1. Synthesis of tach-Based Ligand 1



Received: October 24, 2012

Published: March 15, 2013

Crystals of **1** suitable for X-ray structure determination were obtained by slow evaporation of a  $\text{CH}_2\text{Cl}_2$  solution of the complex. Crystals of **1** form in the space group  $P2_1/c$ . The molecular structure shows that the three fluorinated benzyl imino arms inherit the *cis,cis*-stereochemistry, the cyclohexane backbone is in the chair conformation, and each imine moiety adopts the sterically favorable position (see Figure 1 and Table 1 for selected bond lengths and angles).



**Figure 1.** Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms have been omitted for clarity.

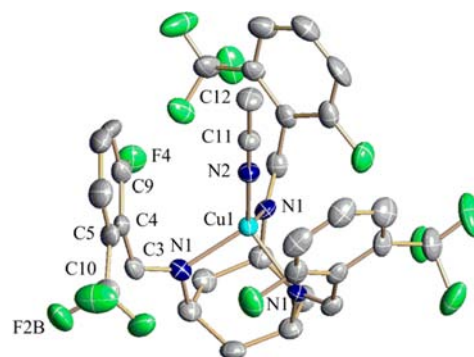
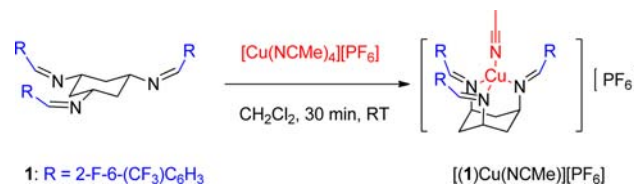
To compare this new ligand with the derivatives we have previously reported, its complexation chemistry with copper was explored. Reaction of **1** with  $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$  in  $\text{CH}_2\text{Cl}_2$  gives  $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$  in 85% yield as an intense yellow solid (Scheme 2).

Crystals of  $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$  were grown by slow diffusion of *n*-hexane into a saturated  $\text{CH}_2\text{Cl}_2$  solution of  $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$  at room temperature. Crystals of  $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$  form in a  $P2_13$  space group (see Figure 2 and Table 1 for selected bond lengths and angles). The fluorinated phenyl rings are arranged facially around the copper center, producing a cavity in which one molecule of acetonitrile is accommodated. A slight shortening of the  $\text{C}_{\text{NCMe}}-\text{N}_{\text{NCMe}}$  bond length (1.137 Å) in comparison with free acetonitrile (1.155 Å) is observed as expected upon coordination to a metal center. The Cu(I) center adopts a pseudotetrahedral geometry with  $\text{N}_{\text{tach}}-\text{Cu}-\text{N}_{\text{tach}}$  bond angles of  $94.10^\circ$ , and  $\text{N}_{\text{NCMe}}-\text{Cu}-\text{N}_{\text{tach}}$  bond angles of  $122.31^\circ$ .

Bubbling CO through the intensely yellow  $\text{CH}_2\text{Cl}_2$  solution of  $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$  resulted in decolorization and spectroscopic data consistent with CO coordination (Scheme 3).

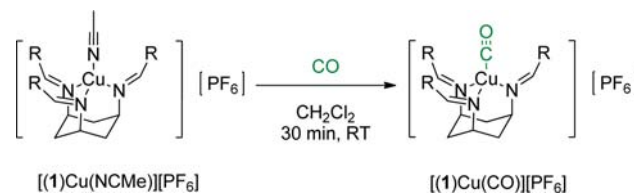
The IR spectrum of  $[(\mathbf{1})\text{Cu}(\text{CO})][\text{PF}_6]$  exhibited  $\nu(\text{CO})$  at  $2091\text{ cm}^{-1}$  indicative of only a moderate degree of  $\pi$ -back-bonding. As previously reported, copper can cause fast relaxation of proximal nuclei, and it was not possible to

### Scheme 2. Synthesis of $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$



**Figure 2.** Molecular structure of  $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$ . Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and  $[\text{PF}_6]^-$  counterion have been omitted for clarity.

### Scheme 3. Reaction of $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$ with Carbon Monoxide



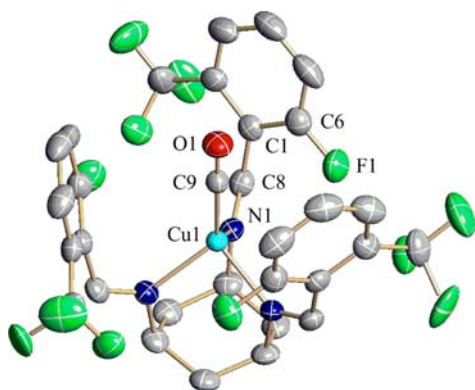
observe the  $^{13}\text{C}\{^1\text{H}\}$  NMR resonance for the coordinated carbon monoxide ligand in this case.<sup>1,7</sup>

Crystals of  $[(\mathbf{1})\text{Cu}(\text{CO})][\text{PF}_6]$  suitable for X-ray structure determination were grown by slow diffusion of *n*-hexane into a  $\text{CH}_2\text{Cl}_2$  solution of the complex. Crystals of  $[(\mathbf{1})\text{Cu}(\text{CO})][\text{PF}_6]$  form in the space group  $P2_13$  (see Figure 3 and Table 1 for selected bond lengths and angles). The fluorine atoms on the  $-\text{CF}_3$  group and  $[\text{PF}_6]^-$  counterion in the molecular structure of  $[(\mathbf{1})\text{Cu}(\text{CO})][\text{PF}_6]$  were disordered, requiring the use of some restraints to ensure a smooth refinement. The copper carbonyl complex adopts a *pseudo*-tetrahedral geometry very similar to the related Cu-NCMe complex.

**Synthesis of Cu(I)- $\text{C}_2\text{H}_4$  Complexes of *cis,cis*-1,3,5-Tri(arylideneamino)cyclohexanes:  $[(\mathbf{1})\text{Cu}(\text{C}_2\text{H}_4)][\text{X}]$ , ( $\text{X} = \text{PF}_6$  or  $\text{SbF}_6$ ) and  $[(\mathbf{2})\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ .** In a preliminary

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for **1**,  $[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$ , and  $[(\mathbf{1})\text{Cu}(\text{CO})][\text{PF}_6]$

<b>1</b>		$[(\mathbf{1})\text{Cu}(\text{NCMe})][\text{PF}_6]$	$[(\mathbf{1})\text{Cu}(\text{CO})][\text{PF}_6]$
N1–C7	1.269(3)	Cu1–N2	1.897(6)
N2–C15	1.256(3)	N2–C11	1.137(9)
N3–C24	1.265(3)	Cu1–N1	2.050(3)
N1–C7–C8–C9	45.5(4)	N1–C3	1.257(5)
N2–C15–C16–C17	118.6(3)	N2–C11–C12	180.0
N3–C23–C24–C25	–46.4(4)	N1–Cu1–N2	122.1(1)
		N1–Cu1–N1	94.32(13)
		C3–C4–C9–F4	2.2(6)
		C9–O1	1.134(6)
		Cu1–C9	1.810(4)
		N1–C8	1.271(3)
		Cu1–C9–O1	180.0
		N1–Cu1–C9	123.25(6)
		N1–C8–C1–C6	65.3(4)



**Figure 3.** Molecular structure of  $[(1)\text{Cu}(\text{CO})][\text{PF}_6]$ . Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and  $[\text{PF}_6]^-$  counterion have been omitted for clarity.

experiment, bubbling ethylene through a  $\text{CH}_2\text{Cl}_2$  solution of  $[(1)\text{Cu}(\text{NCMe})][\text{PF}_6]$  did not result in the desired substitution at the copper center. This result is in line with our previous unsuccessful attempts to isolate such species with a range of tach ligand derivatives.<sup>17</sup> However, upon subjecting the solution of  $[(1)\text{Cu}(\text{NCMe})][\text{PF}_6]$  to a slightly higher pressure of ethylene (3–5 bar), a signal corresponding to coordinated ethylene was observed by  $^1\text{H}$  NMR spectroscopy. Compound  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{PF}_6]$  was only stable under a pressure of ethylene (3–5 bar), suggesting a rapid displacement of ethylene from the Cu(I) center by recoordination of the liberated acetonitrile ligand (see Scheme 4). An ethylene saturated  $\text{CD}_2\text{Cl}_2$  solution of  $[(1)\text{Cu}(\text{NCMe})][\text{PF}_6]$  exhibited  $^1\text{H}$  NMR signals for both free and coordinated ethylene (and acetonitrile), suggesting a mixture of olefin and nitrile complexes.

To avoid this exchange between ethylene and the acetonitrile liberated from  $[(1)\text{Cu}(\text{NCMe})][\text{PF}_6]$ , a route to a Lewis base-free Cu(I)-tach precursor was sought. This was achieved by the one pot reaction of ligand **1** with  $\text{CuBr}$  and  $\text{AgSbF}_6$  under a pressure of ethylene (5–10 bar). Following passage through a short plug of Celite, a colorless solution of  $[(1)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  was concentrated while under a stream of ethylene to prevent further loss of the potentially labile olefin ligand (see Scheme 5). Compound  $[(1)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  was characterized by  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{19}\text{F}$  NMR spectroscopy, Elemental Analysis and electrospray ionization (ESI) mass spectrometry (and also structurally characterized *vide infra*).

The  $^1\text{H}$  NMR spectrum of  $[(1)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  in ethylene-saturated  $\text{CD}_2\text{Cl}_2$  displayed a resonance at 3.12 ppm corresponding to the ethylene coordinated to the copper center. The  $^{13}\text{C}\{^1\text{H}\}$  NMR resonance for the coordinated ethylene was observed at 85.3 ppm, an upfield shift of 38 ppm relative to free ethylene (123.5 ppm).<sup>1,1f a-c,e</sup> It is noteworthy

that, because of the highly labile nature of the copper-olefin bonding interaction,  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts cannot always be reported.<sup>11b,d,f,12</sup>

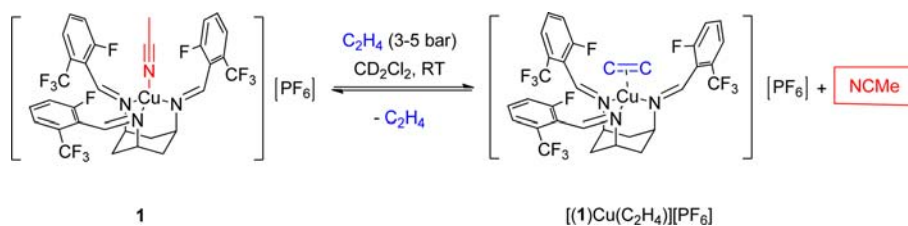
Following the successful synthesis and characterization of an ethylene-Cu(I) complex with this fluorinated tach-based ligand, a nonfluorinated tach-based ligand **2** (previously reported)<sup>7</sup> was subjected to the same protocol. Upon coordination of ethylene to the copper center in  $[(2)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$ , the  $^1\text{H}$  NMR signal corresponding to ethylene moved upfield from 5.27 ppm to 3.09 ppm. The  $^1\text{H}$  NMR upfield shift of the coordinated ethylene proton has been attributed to increased shielding caused by copper-to-ethylene  $\pi$ -back-donation.<sup>11b,c,13</sup> However, Walton et al. and Pérez et al. suggested that such an upfield shift may also be caused by an anisotropic effect generated by the  $\pi$ -system of the aromatic rings.<sup>14</sup> Certainly, the coordinated ethylene is sandwiched between three aromatic rings, such that the effects of the aromatic ring currents on the chemical shifts of the ethylene protons cannot be discounted. Similar shifts were reported by Vitagliano et al. for Cu(I)-ethylene complexes with a chiral diamine ligand.<sup>14d,15</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[(2)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  displayed a peak at 85.8 ppm which was assigned to the carbon atoms of coordinated ethylene (free ethylene: 123.5 ppm).<sup>11a-c,12a,14a</sup>

Compounds  $[(1)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  are stable if kept under an atmosphere of ethylene, both in solution and in the solid state. In weakly or noncoordinating solvents (e.g.,  $\text{CH}_2\text{Cl}_2$ ), these complexes are observed to lose ethylene under a stream of dinitrogen or under reduced pressure, illustrating reversible complexation of ethylene.

The selective coordination of ethylene over higher olefins was examined to test the applicability of complexes  $[\text{Cu}(1)\text{-(C}_2\text{H}_4)]\text{[SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  as mass-separation agents. Reactions between the labile copper-ethylene complexes and 2-butene (1:1 *cis* and *trans*), 1-pentene, 1-hexene, 1-octene, and norbornene were monitored by  $^1\text{H}$  NMR spectroscopy. However, no signals due to replacement of coordinated ethylene were observed, the signals for  $[\text{Cu}(1)(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  or  $[(2)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  remaining unchanged. Using the same protocol for the synthesis of the ethylene complexes with these other olefins also resulted in no reaction, as did attempted substitution reactions from the acetonitrile complexes. We speculated that the cavity imposed by the tridentate ligand is too small to accommodate these larger olefins.

Colorless crystals of  $[(1)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  suitable for X-ray analysis were obtained from concentrated  $\text{CH}_2\text{Cl}_2$  solutions of these compounds under 1 bar of ethylene at  $-18^\circ\text{C}$ . Crystals of  $[(1)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)]\text{[SbF}_6]$  belong to the triclinic space group  $P\bar{1}$  (see Figure 4 and Table 2 for selected bond lengths and angles).

#### Scheme 4. Reaction of Compound $[(1)\text{Cu}(\text{C}_2\text{H}_4)]\text{[PF}_6]$ with $\text{C}_2\text{H}_4$ (3–5 bar)



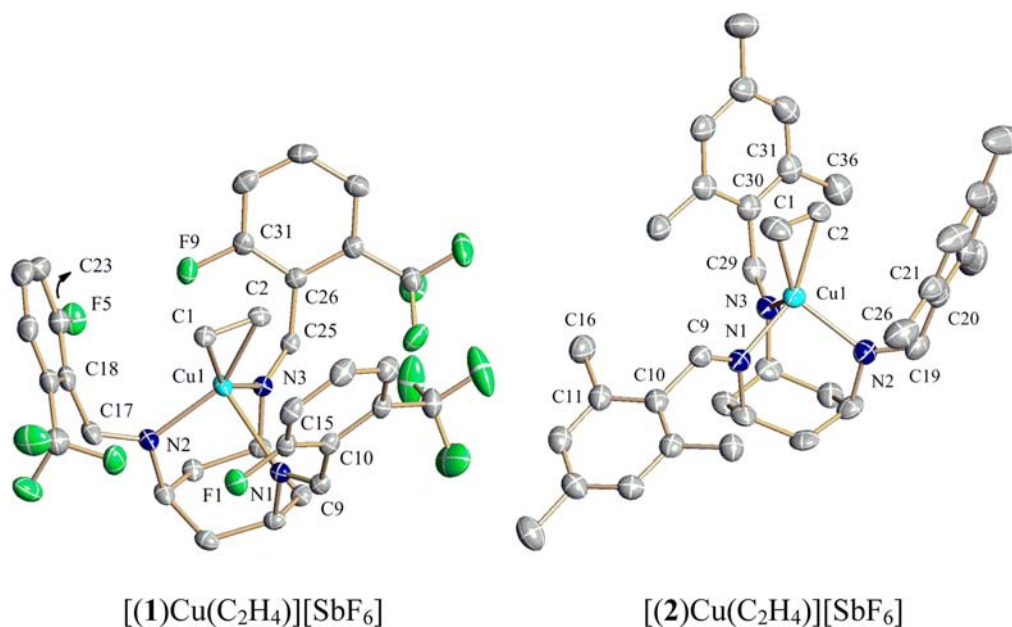
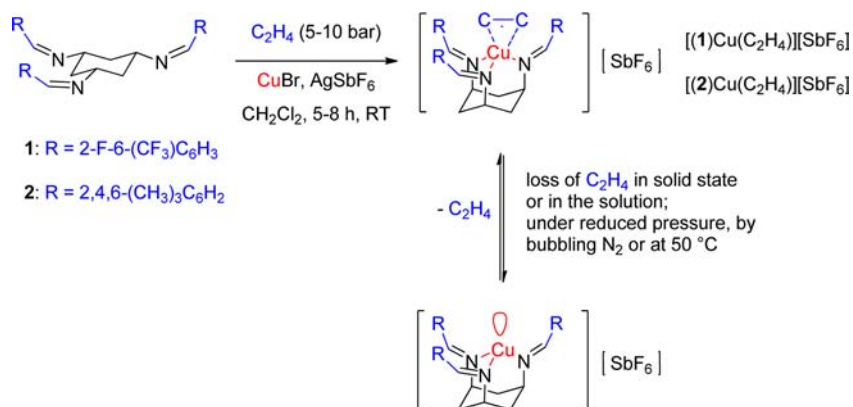
Scheme 5. Synthesis of  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ 

Figure 4. Molecular structures of  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ . Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and the  $[\text{SbF}_6]$  counterions have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$

$[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$		$[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$	
C1–C2	1.352(3)	C1–C2	1.347(6)
N1–C9	1.267(3)	N1–C9	1.282(5)
Cu1–N1	2.3085(19)	N2–C19	1.268(5)
Cu1–N2	2.036(2)	N3–C29	1.273(5)
Cu1–N3	2.0611(18)	Cu1–N1	2.030(3)
N1–Cu1–N2	91.09(7)	Cu1–N2	2.083(3)
N1–Cu1–N3	89.01(7)	Cu1–N3	2.128(3)
N2–Cu1–N3	95.85(8)	N1–Cu1–N2	94.47(12)
C9–C10–C15–F1	–1.5(3)	N1–Cu1–N3	91.46(12)
C17–C18–C23–F5	1.6(3)	N2–Cu1–N3	92.30(12)
C25–C26–C31–F9	1.1(3)	C9–C10–C11–C16	–0.7(6)
		C19–C20–C21–C26	–1.7(6)
		C29–C30–C31–C36	0.3(6)

In both  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  one molecule of ethylene is coordinated to Cu(I) in the typical  $\eta^2$ -fashion.<sup>11b–e,12a</sup> The ethylene protons were located on the difference map and were refined isotropically. The C–C distance of coordinated ethylene is 1.325(3) Å and 1.347(6) Å

in  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ , respectively, which does not differ significantly from the corresponding distance in free ethylene [1.3369(16) Å],<sup>11b,f,16</sup> consistent with the weak nature of the Cu–C<sub>2</sub>H<sub>4</sub> interaction. This observation supports the hypothesis that the upfield chemical

shifts observed in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are largely due to anisotropic ring effects originating from the aromatic arms rather than back-donation from the metal center.

The X-ray structure of  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  reveals a sterically constrained pocket around the fourth coordination site of the Cu(I) center, in which the arms adopt the expected *trans* imine geometry. By contrast, the structure of  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  shows two imine arms with the expected *trans* geometry, and the third imine arm with a *cis* geometry.

To investigate the origins of the geometry differences in structures  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ , the complexes were modeled computationally. Crystal structure geometries were used to generate input files, modifying substituents as required to access a range of different conformers for the *trans,trans,trans*- and *trans,trans,cis*- geometric isomers of the  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  respectively (see Table 3 and Figure 5).

**Table 3. Comparison of Relative Energies of the *trans,trans,cis*- and *trans,trans,trans*-Geometry of Complexes  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ <sup>a</sup>**

	relative energy (/kcalmol <sup>-1</sup> ) of isolated molecules		
	DFT	DFT-D	
<i>trans,trans,cis</i> - $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ : 2A	0.00	2.21	from crystal structure
<i>trans,trans,trans</i> - $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ : 2B	0.22	0.00	
<i>trans,trans,trans</i> - $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ : 1A	1.01	0.00	from crystal structure
<i>trans,trans,cis</i> - $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ : 1B	0.35	0.95	
<i>trans,trans,cis</i> - $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ : 1C	0.00	1.64	
<i>trans,trans,cis</i> - $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ : 1D	0.27	1.44	

<sup>a</sup>Because of the asymmetry of the aryl substituents in complex  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ , there are three possible conformations, for *trans,trans,cis*- geometry, the energies of which are listed in the table.

Geometry optimizations were carried out on isolated molecules using Jaguar<sup>18</sup> and the standard B3LYP density functional<sup>19</sup> with a 6-31G\* basis set on all atoms apart from copper, where the LACV3P basis set was implemented. Since the main aim was to compare the different possible conformers, frequency calculations were not performed. It was deemed unlikely that these large complexes of low symmetry would optimize to a saddle point. Dispersion corrections were calculated in ORCA<sup>20</sup> for the B3LYP-D<sup>21</sup> approach and added to the Jaguar energies; geometries were not reoptimized in this case.

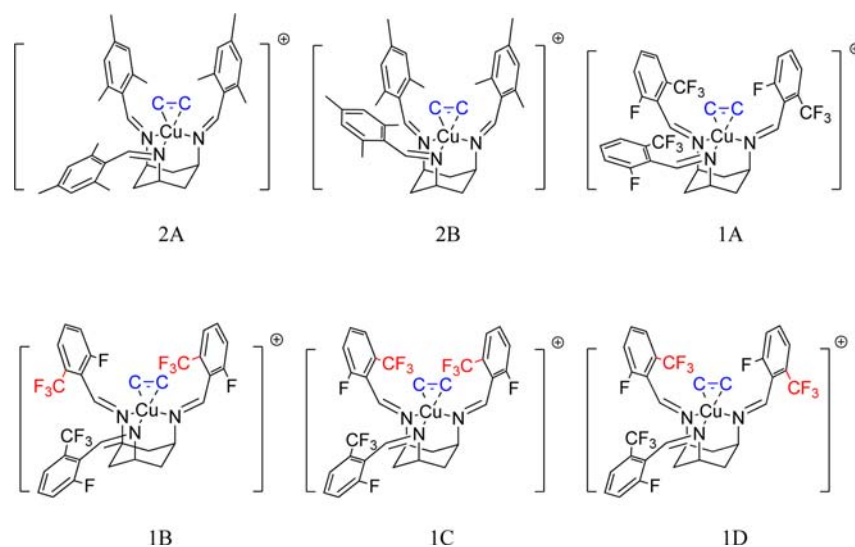
The calculated energy differences are within computational error, and it may be concluded that all conformers are likely to be accessible in solution, the different structures observed crystallographically due not to significant energy differences between conformers but to more subtle effects such as crystal packing.

## CONCLUSION

A new bulky facially coordinating  $\text{N}_3$ -donor tach-based ligand *cis,cis*-1,3,5-tris(2-fluoro-6-(trifluoromethyl)benzylideneamino)cyclohexane **1** has been obtained. Reaction of **1** with  $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$  gave the complex  $[(1)\text{Cu}(\text{NCMe})][\text{PF}_6]$  in which displacement of the acetonitrile ligand is possible with CO and  $\text{C}_2\text{H}_4$  (3–5 bar). Cu(I)-ethylene complexes of ligands **1** and *cis,cis*-1,3,5-(mesitylideneamino)cyclohexane **2** were prepared by treatment of the ligands with CuBr and AgSbF<sub>6</sub> in the presence of ethylene, the absence of other potentially coordinating ligands such as acetonitrile being essential for clean reactions. These complexes display reversible complexation of the ethylene molecule under mild changes to pressure, suggesting possible application in olefin separation and extraction.

## EXPERIMENTAL DETAILS

**General Considerations.** All operations were carried out under an inert atmosphere of Ar or  $\text{N}_2$  using standard Schlenk line techniques or an MBraun glovebox MB-BL-01. Dry  $\text{N}_2$ -saturated solvents were purified using an anhydrous engineering Grubbs-type solvent system. A Parr Instrument Company Autoclave (0.3L) was used for reactions



**Figure 5.** Imine geometric isomers of  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$  and  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ . Input files for 2A (*trans,trans,cis*-) and 1A (*trans,trans,trans*-) were generated directly from crystallographic data; 2B (*trans,trans,trans*-) was modeled by modification of crystallographic data for  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ . Because of the asymmetry of the aryl substituents in  $[(1)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ , three conformers of the (*trans,trans,cis*-) geometry were considered (1B, 1C, and 1D), modeled from crystallographic data for  $[(2)\text{Cu}(\text{C}_2\text{H}_4)][\text{SbF}_6]$ .

under high pressure (5–10 bar). NMR spectra of complexes under a pressure of ethylene were recorded in a 5 mm Heavy Wall (Pressure/Vacuum) Value NMR Sample tube (7" L) 522-PV-7 (Wilmad). Chemicals were obtained from Sigma-Aldrich and used without further purification unless otherwise stated. Ethylene (99.92%) was obtained from BOC UK.

All the X-ray diffraction experiments were carried out at 100 K on a Bruker Apex II Kappa CCD diffractometer using Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Intensities were integrated from several series of exposures measuring  $0.5^{\circ}$  in  $\omega$  or  $\varphi$  using the Apex II or proteum programs. Absorption corrections were based on equivalent reflections using SADABS, and structures were refined against all  $F_o^2$  data with hydrogen atoms (on carbon atoms) riding in positions calculated using SHELXL.<sup>22</sup>

Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemistry at the University of Bristol. Mass spectra were recorded on a VG Analytical Quattro spectroscope (ESI) by the Mass Spectrometry Service at the University of Bristol.  $^{19}\text{F}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^1\text{H}$  NMR spectra were recorded at  $25^{\circ}\text{C}$  in deuterated solvents to provide the field/frequency lock.  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra were referenced to residual NMR solvent peaks; chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane standard.  $^{19}\text{F}$  NMR spectra are reported in ppm relative to  $\text{BF}_3 \cdot \text{OEt}_2$  standard.

**Synthesis of *cis,cis*-1,3,5-Tris(2-fluoro-6-(trifluoromethyl)benzylideneamino)cyclohexane 1.** *cis,cis*-1,3,5-Triaminocyclohexane-3HBr (0.5 g, 1.3 mmol) was dissolved in a solution of 3 equiv of sodium hydroxide (0.16 g, 3.9 mmol) in water (10 mL), followed by addition of toluene (30 mL) and 3 equiv of 2-fluoro-6-(trifluoromethyl)benzaldehyde (0.41 mL, 3.9 mmol). The reaction was heated to  $150^{\circ}\text{C}$  in an oil bath for 18 h, during which time water was removed via azeotropic distillation with a Dean–Stark trap. The solution was allowed to cool, passed through a short Celite plug, and concentrated under reduced pressure to leave a pale yellow solid. The crude material was recrystallized from a minimum volume of hot diethyl ether and dried in vacuo. **1** (0.73 g, 86% yield) was obtained as a white microcrystalline solid.  $^1\text{H}$  NMR (399.77 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.64 (q, 3H,  $^4J_{\text{HF}}$  2.69,  $\text{HC}=\text{N}$ ), 7.49 (m, 6H,  $H_{\text{meta-Ar}}$ ), 7.33 (m br, 3H,  $H_{\text{para-Ar}}$ ), 3.72 (t, 3H,  $^3J_{\text{HH}}$  11.39 Hz,  $^3J_{\text{HH}}$  3.91 Hz,  $-\text{CH-N}=\text{}$ ), 2.16 (q, 3H,  $^2J_{\text{HH}}$  11.97 Hz, *trans*-CHH-), and 2.02 (m, 3H,  $^2J_{\text{HH}}$  11.97,  $^3J_{\text{HH}}$  3.67 Hz, *cis*-CHH-).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.63 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  160.9 (d,  $^1J_{\text{CF}}$  253.29 Hz, Ar-C<sub>2</sub>), 152.2 (s, C=N), 130.7 (d,  $^2J_{\text{CF}}$  9.23 Hz, Ar-C<sub>3</sub>), 130.3 (q,  $^2J_{\text{CF}}$  32.85 Hz, Ar-C<sub>6</sub>), 123.9 (d,  $^4J_{\text{CF}}$  13.80 Hz, Ar-C<sub>5</sub>), 123.5 (q,  $^1J_{\text{CF}}$  274.00 Hz, Ar-CF<sub>3</sub>), 121.9 (s br, Ar-C<sub>1</sub>), 120.2 (d,  $^3J_{\text{CF}}$  22.50 Hz, Ar-C<sub>4</sub>), 67.4 (s, Cy-CH), and 39.9 (s, Cy-CH<sub>2</sub>).  $^{19}\text{F}$  NMR (282.78 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -57.75 (s, 9F, Ar-CF<sub>3</sub>) and -112.81 (s, 3F, Ar-F). ESI mass spectrometry: calculated exact mass for  $\text{C}_{30}\text{H}_{21}\text{F}_{12}\text{N}_3$ : 651.15. Found:  $m/z$  674.14  $[\text{M}+\text{Na}]^+$ , 652.16  $[\text{M}+\text{H}]^+$ . ESI HR mass spectrum:  $m/z$  674.1436  $[\text{M}+\text{Na}]^+$  (calcd 674.1449), 652.1635  $[\text{M}+\text{H}]^+$  (calcd 652.1616). Elemental analysis: calcd (%) For  $\text{C}_{30}\text{H}_{21}\text{F}_{12}\text{N}_3$ : C, 55.31. H, 3.25. N, 6.45. Found: C, 55.38. H, 3.59. N, 6.14.

**Synthesis of [(1)Cu(NCCH<sub>3</sub>)]PF<sub>6</sub>.** **1** (0.10 g, 0.15 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL), and an equivalent amount of  $[\text{Cu}(\text{NCMe})_4][\text{PF}_6]$  (0.06g, 0.15 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added dropwise. An instantaneous color change from pale to intense yellow was observed. The reaction was stirred for 30 min under an inert atmosphere at room temperature. The product was precipitated by addition of *n*-hexane, collected by filtration, and dried in vacuo to obtain [(1)Cu(NCCH<sub>3</sub>)]PF<sub>6</sub> (0.13 g, 97%) as a bright yellow powder.  $^1\text{H}$  NMR (399.77 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.47 (s, 3H,  $\text{HC}=\text{N}$ ), 7.57 (m br, 3H,  $H_4$ -Ar), 7.50 (m, 3H,  $H_4$ -Ar), 7.24 (m, 3H,  $H_5$ -Ar), 4.24 (s br, 3H,  $-\text{CH-N}=\text{}$ ), 2.47 (dt, 3H,  $^2J_{\text{HH}}$  15.15 Hz,  $^3J_{\text{HH}}$  4.00 Hz, *trans*-CHH-), 2.12 (d br, 3H,  $^2J_{\text{HH}}$  14.66 Hz, *cis*-CHH-), and 1.24 (s, 3H, -NCCH<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.63 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  159.9 (d,  $^1J_{\text{CF}}$  253.29 Hz, Ar-C<sub>2</sub>), 155.5 (s, C=N), 131.9 (d,  $^2J_{\text{CF}}$  9.23 Hz, Ar-C<sub>3</sub>), 130.1 (q,  $^2J_{\text{CF}}$  32.85 Hz, Ar-C<sub>6</sub>), 124.5 (d,  $^4J_{\text{CF}}$  13.80 Hz, Ar-C<sub>5</sub>), 123.5 (q,  $^1J_{\text{CF}}$  274.00 Hz, Ar-CF<sub>3</sub>), 121.6 (s br, Ar-C<sub>1</sub>), 119.8 (d,  $^2J_{\text{CF}}$  22.50 Hz, Ar-C<sub>4</sub>), 67.4 (s, Cy-CH), 39.9 (s, Cy-CH<sub>2</sub>) and 1.1 (s, -NCCH<sub>3</sub>).  $^{19}\text{F}$  NMR (282.78 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -58.83 (s, 9F, Ar-

CF<sub>3</sub>), -73.19 (d, 6F,  $^1J_{\text{PF}}$  708.76 Hz, PF<sub>6</sub>), and -110.54 (s, 3F, Ar-F). ESI mass spectrometry: calculated exact mass for  $\text{C}_{32}\text{H}_{24}\text{CuF}_{12}\text{N}_3\text{PF}_6$ : 900.07. Found:  $m/z$  714.09  $[\text{M}(-\text{NCCH}_3, \text{PF}_6)]^+$ . ESI HR mass spectrum:  $m/z$  714.0834  $[\text{M}(-\text{NCCH}_3, \text{PF}_6)]^+$  (calcd 714.0838). Elemental analysis: calcd (%) for  $\text{C}_{32}\text{H}_{24}\text{CuF}_{12}\text{N}_4\text{PF}_6$ : C, 42.65. H, 2.68. N, 6.22. Found: C, 41.42. H, 2.83. N, 6.40.

**Synthesis of [(1)Cu(CO)]PF<sub>6</sub>.** Carbon monoxide was bubbled through a  $\text{CH}_2\text{Cl}_2$  solution (5 mL) of [(1)Cu(NCCH<sub>3</sub>)]PF<sub>6</sub> (0.05 g, 0.06 mmol) for 30 min to give a light yellow solution. The product was precipitated by addition of *n*-hexane (10 mL), collected and dried under stream of carbon monoxide to afford [(1)Cu(CO)]PF<sub>6</sub> (0.047 g, 95%) as a pale yellow solid.  $^1\text{H}$  NMR (399.77 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.67 (s, 3H,  $\text{HC}=\text{N}$ ), 7.61 (t, 3H,  $^3J_{\text{HH}}$  7.91 Hz,  $H_4$ -Ar), 7.59 (m, 3H,  $H_3$ -Ar), 7.26 (m, 3H,  $H_5$ -Ar), 4.39 (s, 3H,  $-\text{CH-N}=\text{}$ ), 2.58 (dt, 3H,  $^2J_{\text{HH}}$  15.15 Hz,  $^3J_{\text{HH}}$  3.79 Hz, *trans*-CHH-), and 2.16 (d, 3H,  $^2J_{\text{HH}}$  14.90 Hz, *cis*-CHH-).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.63 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  159.4 (d,  $^1J_{\text{CF}}$  252.90 Hz, Ar-C<sub>2</sub>), 159.3 (s, C=N), 133.0 (d,  $^2J_{\text{CF}}$  9.23 Hz, Ar-C<sub>3</sub>), 130.0 (q,  $^2J_{\text{CF}}$  32.29 Hz, Ar-C<sub>6</sub>), 127.2 (d,  $^4J_{\text{CF}}$  9.23 Hz, Ar-C<sub>5</sub>), 123.5 (q,  $^1J_{\text{CF}}$  274.00 Hz, Ar-CF<sub>3</sub>), 122.4 (s br, Ar-C<sub>1</sub>), 120.2 (d,  $^3J_{\text{CF}}$  22.50 Hz, Ar-C<sub>4</sub>), 66.2 (s, Cy-CH), and 36.2 (s, Cy-CH<sub>2</sub>).  $^{19}\text{F}$  NMR (282.78 MHz,  $\text{CD}_2\text{Cl}_2$ ): -58.69 (s, 9F, Ar-CF<sub>3</sub>), -73.26 (d, 6F,  $^1J_{\text{PF}}$  708.76 Hz, PF<sub>6</sub>) and -110.81 (s, 3F, Ar-F). IR/cm<sup>-1</sup> ( $\text{CD}_2\text{Cl}_2$ ):  $\nu$  coordinated (CO) 2094 s,  $\nu$  free (CO) 2143 m. ESI mass spectrometry: calcd exact mass for  $\text{C}_{31}\text{H}_{21}\text{CuF}_{12}\text{N}_3\text{O-PF}_6$ : 887.04. Found:  $m/z$  714.09  $[\text{M}(-\text{CO}, \text{PF}_6)]^+$ , 742.08  $[\text{M}(-\text{PF}_6)]^+$ . ESI HR mass spectrum:  $m/z$  714.0834  $[\text{M}(-\text{CO}, \text{PF}_6)]^+$  (calcd 714.0836), 742.0783  $[\text{M}(-\text{CO}, \text{PF}_6)]^+$  (calcd 742.0762).

**Synthesis of [(1)Cu(C<sub>2</sub>H<sub>4</sub>)]PF<sub>6</sub>.** A high pressure NMR tube, charged with  $\text{CD}_2\text{Cl}_2$  (0.3 mL) and [(1)Cu(NCCH<sub>3</sub>)]PF<sub>6</sub> (0.05 g, 0.06 mmol), was pressurized with ethylene (3–5 bar).  $^1\text{H}$  NMR (299.90 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.43 (s, 3H,  $\text{HC}=\text{N}$ ), 7.53 (t br, 3H,  $^3J_{\text{HH}}$  7.57 Hz,  $H_4$ -Ar), 7.44 (d br, 3H,  $^3J_{\text{HH}}$  7.40 Hz,  $H_5$ -Ar), 7.20 (m br, 3H,  $H_3$ -Ar), 5.27 (s, free C<sub>2</sub>H<sub>4</sub>), 4.20 (s, 3H,  $-\text{CH-N}=\text{}$ ), 3.11 (s br, coordinated C<sub>2</sub>H<sub>4</sub>), 2.44 (dt, 3H,  $^2J_{\text{HH}}$  14.27 Hz,  $^3J_{\text{HH}}$  3.70 Hz, *trans*-CHH-), 2.07 (d br, 3H,  $^2J_{\text{HH}}$  14.27 Hz, *cis*-CHH-), and 1.19 (s, -NCCH<sub>3</sub>).

**Synthesis of [(1)Cu(C<sub>2</sub>H<sub>4</sub>)]SbF<sub>6</sub>.** Dry, degassed  $\text{CH}_2\text{Cl}_2$  (10 mL) was added to CuBr (0.15 g, 1.0 mmol), AgSbF<sub>6</sub> (0.37 g, 1.0 mmol), and **1** (0.65 g, 1.0 mmol) in an autoclave. The mixture was stirred under positive pressure of ethylene (5–10 bar) for 8 h. The mixture was passed through a plug of Celite. The resulting colorless solution was reduced to 3 mL under a stream ethylene and layered with *n*-hexane to give colorless crystals of [(1)Cu(C<sub>2</sub>H<sub>4</sub>)]SbF<sub>6</sub> (0.85 g, 80%) after 20 h at  $-18^{\circ}\text{C}$ .  $^1\text{H}$  NMR (399.77 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.66 (s, 3H,  $\text{HC}=\text{N}$ ), 7.58 (t br, 3H,  $^3J_{\text{HH}}$  8.36 Hz,  $H_4$ -Ar), 7.51 (d br, 3H,  $^3J_{\text{HH}}$  8.36 Hz,  $H_5$ -Ar), 7.35 (m br, 3H,  $H_3$ -Ar), 5.33 (s, free C<sub>2</sub>H<sub>4</sub>), 4.30 (s br, 3H,  $-\text{CH-N}=\text{}$ ), 3.12 (s, coordinated C<sub>2</sub>H<sub>4</sub>), 2.55 (dt, 3H,  $^2J_{\text{HH}}$  15.37 Hz,  $^3J_{\text{HH}}$  4.15 Hz, *trans*-CHH-), and 2.18 (d br, 3H,  $^2J_{\text{HH}}$  15.40 Hz, *cis*-CHH-).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.71 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  160.2 (d,  $^1J_{\text{CF}}$  252.93 Hz, Ar-C<sub>2</sub>), 157.8 (s, C=N), 132.0 (d,  $^2J_{\text{CF}}$  9.24 Hz, Ar-C<sub>3</sub>), 129.9 (q,  $^2J_{\text{CF}}$  32.19 Hz, Ar-C<sub>6</sub>), 127.0 (d,  $^4J_{\text{CF}}$  9.23 Hz, Ar-C<sub>5</sub>), 123.5 (q,  $^1J_{\text{CF}}$  272.80 Hz, Ar-CF<sub>3</sub>), 122.3 (s, Ar-C<sub>1</sub>), 120.2 (d,  $^3J_{\text{CF}}$  22.26 Hz, Ar-C<sub>4</sub>), 85.3 (s, coordinated C<sub>2</sub>H<sub>4</sub>), 66.4 (s, Cy-CH), and 35.5 (s, Cy-CH<sub>2</sub>).  $^{19}\text{F}$  NMR (282.78 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -59.19 (s, 9F, -CF<sub>3</sub>) and -112.19 (s, 3F, CF). ESI mass spectrometry: calcd exact mass for  $\text{C}_{32}\text{H}_{25}\text{CuF}_{12}\text{N}_3\text{SbF}_6$ : 977.00. Found:  $m/z$  742.10  $[\text{M}(\text{SbF}_6)]^+$ , 714.09  $[\text{M}(-\text{C}_2\text{H}_4, \text{SbF}_6)]^+$ . ESI HR mass spectrum:  $m/z$  742.1147  $[\text{M}(\text{SbF}_6)]^+$  (calcd 742.1147). Elemental analysis: calcd (%) for  $\text{C}_{32}\text{H}_{25}\text{CuF}_{12}\text{N}_3\text{SbF}_6$ : C, 39.27. H, 2.57. N, 4.29. Found: C, 39.08. H, 2.43. N, 4.25.

**Synthesis of [(2)Cu(C<sub>2</sub>H<sub>4</sub>)]SbF<sub>6</sub>.** Dry, degassed  $\text{CH}_2\text{Cl}_2$  (10 mL) was added to CuBr (0.15 g, 1.0 mmol), AgSbF<sub>6</sub> (0.38 g, 1.0 mmol), and **2** (0.52 g, 1.0 mmol) in an autoclave. The mixture was stirred under positive pressure of ethylene (5–10 bar) for 10 h. The mixture was passed through a plug of Celite. The resulting colorless solution was reduced to 3 mL under a stream of ethylene and layered with *n*-hexane to give colorless crystals of [(2)Cu(C<sub>2</sub>H<sub>4</sub>)]SbF<sub>6</sub> (0.70 g, 83%) after 20 h at  $-18^{\circ}\text{C}$ .  $^1\text{H}$  NMR (399.77 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.53 (s, 3H,  $\text{HC}=\text{N}$ ), 6.73 (s, 6H,  $H_{\text{meta-Ar}}$ ), 5.28 (s, free C<sub>2</sub>H<sub>4</sub>), 4.13 (s br, 3H,  $-\text{CH-N}=\text{}$ ), 3.09 (s, 3H, coordinated C<sub>2</sub>H<sub>4</sub>), 2.50 (dt, 3H,  $^2J_{\text{HH}}$

15.19 Hz,  $^3J_{\text{HH}}$  4.47 Hz, *trans*-CHH-), 2.13 (s, 9H, *para*-ArCH<sub>3</sub>), 2.01 (s, 18H, *ortho*-ArCH<sub>3</sub>), and 1.95 (d, 3H,  $^2J_{\text{HH}}$  14.85 Hz, *cis*-CHH).  $^{13}\text{C}\{\text{H}\}$  NMR (100.63 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  166.1 (s, C=N), 139.5 (s, Ar-C<sub>para</sub>), 135.1 (s, Ar-C<sub>ortho</sub>), 132.3 (s, Ar-C<sub>ipso</sub>), 128.5 (s, Ar-C<sub>meta</sub>), 85.8 (s, coordinated C<sub>2</sub>H<sub>4</sub>), 65.7 (s, Cy-CH), 32.8 (s, Cy-CHH), 20.7 (s, *ortho*-ArCH<sub>3</sub>), and 19.4 (s, *para*-ArCH<sub>3</sub>). ESI mass spectrometry: calcd exact mass for C<sub>38</sub>H<sub>49</sub>CuN<sub>3</sub>SbF<sub>6</sub>: 845.22. Found: *m/z* 582.29 [M-(C<sub>2</sub>H<sub>4</sub>, SbF<sub>6</sub>)]<sup>+</sup>. ESI HR mass spectrum: *m/z* 582.2904 [M-(C<sub>2</sub>H<sub>4</sub>, SbF<sub>6</sub>)]<sup>+</sup> (calcd 582.2909).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Crystallographic details and cif files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [Duncan.Wass@bristol.ac.uk](mailto:Duncan.Wass@bristol.ac.uk).

### Notes

The authors declare no competing financial interest.

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