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**PAPER**

# Copper(II) complexes incorporating poly/perfluorinated alkoxyaluminate-type weakly coordinating anions: Syntheses, characterization and catalytic application in stereoselective olefin aziridination†

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The synthesis and characterization of a series of cationic copper(II) complexes of the type $[Cu(NCR)_6][Al(OC(CF_3)_2R')_4]_2$ ($R = CH_3$, Ph; $R' = CF_3$, Ph, $PhCH_3$), incorporating poly/perfluoronated alkoxyaluminates as weakly coordinating anions (WCAs) is presented. Aziridination of various olefins, such as the unreactive olefins *e.g.* ethylhex-2-enoate and 1-decene, with *N*-tosyliminophenyliodinane catalyzed by $[Cu(NCR)_6][Al(OC(CF_3)_2R')_4]_2$ affords very good yields (up to 96%) and high TOFs (up to 5000 $h^{-1}$) under mild conditions. Using disubstituted olefins as substrates, high stereoselectivities are obtained at room temperature. The to date highest *cis* : *trans* ratio (98 : 2) of the obtained aziridines is achieved for *cis*-stilbene in good yield (85%) as well as promising TOF (> 2000 $h^{-1}$). The investigation of the solvent effect on yield and selectivity reveals that for certain oleophilic substrates (1-decene), less polar solvents, such as dichloromethane are a better choice than acetonitrile, which is commonly considered as the best solvent for olefin aziridination. Accordingly, a mechanism involving a paramagnetic copper nitrene intermediate with both concerted and stepwise pathways is proposed.

## Introduction

The development of weakly coordinating anions (WCAs)[1] has drawn increasing attention since 2001,[2] when Krossing reported a facile synthesis of silver polyfluoroalkoxyaluminates $AgAl(OR)_4$, ($R = CH(CF_3)_2$, $C(CH_3)(CF_3)_2$, $C(CF_3)_3$). The robustness, non-oxidizing and weak coordinating ability of the perfluoroalkoxyaluminate $[Al(OC(CF_3)_3)_4]^-$ make it a very good candidate for stabilizing extremely sensitive and electrophilic cations, such as $Ag(P_4)^+$ [3] and related Ag salts,[4] $P_5X_2^+$,[5] $CI_3^+$,[6] $[Bi_4OF_2Cl_6]^{2+}$ [7] and $[Zn_2]^{2+}$.[8] Meanwhile, as is the case with perfluoroborates and carboranes, per/polyfluoroalkoxyaluminates are of great interest for catalysis, *e.g.* C–C bond formation,[1k] enantioselective hydrogenation,[9] asymmetric cycloisomerization,[10] olefin polymerization[11] and ethylene oligomerization.[12] In all cases, complexes incorporating $[Al(OC(CF_3)_3)_4]^-$ show at least the same or superior catalytic activities than other types of WCAs.

Our group has been investigating the role of WCAs as counteranions of catalytically active cationic metal complexes since 2003.[13] We recently disclosed a straightforward and cost efficient synthetic procedure for acetonitrile ligated silver perfluoroalkoxyaluminate $[Ag(NCCH_3)_4][Al(OC(CF_3)_3)_4]$,[14] which avoids using ultrasound and expensive/toxic AgF. Using $[Ag(NCCH_3)_4][Al(OC(CF_3)_3)_4]$ as metathesis reagent, we communicated the synthesis and characterization of $[Cu(NCCH_3)_4][Al(OC(CF_3)_3)_4]$ and $[Cu(NCCH_3)_6][Al(OC(CF_3)_3)_4]_2$, as well as their catalytic application for olefin aziridination.[15] Aziridination of various olefins with *N*-tosyliminophenyliodinane (PhINTs) catalyzed by $[Cu(NCCH_3)_6][Al(OC(CF_3)_3)_4]_2$ affords good to excellent yields (up to 96%) and high turnover frequencies (> 5000 $h^{-1}$) with low catalyst loadings (0.1–1 mol%) under mild conditions. These promising results demonstrate that the perfluoroalkoxyaluminate $[Al(OC(CF_3)_3)_4]^-$ has significant advantages over other anions in copper-catalyzed olefin aziridination. Thus, we now extend our research to analogous polyfluoroalkoxyaluminates, such as $[Al(OC(CF_3)_2Ph)_4]^-$ and $[Al(OC(CF_3)_2PhCH_3)_4]^-$, which are expected to provide better solubility to the complexes in commonly used non-polar organic solvents.

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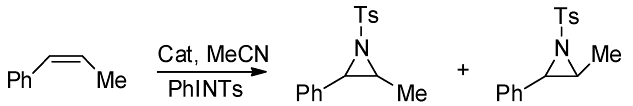
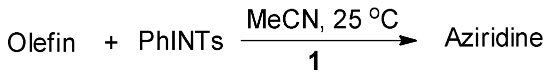
**Table 1** Anion effect on yield and regioselectivity for olefin aziridination[20b]



| Catalyst | Yield (%) | *cis* : *trans* |
|---|---|---|
| $Cu(ClO_4)_2$ | 76 | 95 : 5 |
| $Cu(acac)_2$ | 64 | 26 : 74 |
| $CuBr_2$ | 40 | 30 : 70 |

**Table 2** Anion effect on yield for the aziridination of cyclooctene and cyclopentene[17b]



| Olefin | Anion | Yield (%) |
|---|---|---|
| Cyclooctene | $BAr^F{}_4{}^-$ | 80 |
|  | $BAr^F{}_4{}^-$ | 98 |
| Cyclopentene | $Cl^-$ | 14 |
|  | $OTf^-$ | 25 |
|  | $BAr^F{}_4{}^-$ | 65 |

L = tripyridine ligand [2.1.1]-(2,6)-pyridinophane

To date, literature reports on the catalytic olefin aziridination are mainly focused on the effects of cations,[16] ligands,[17] substrates[18] and nitrene sources.[18b,19] Only a few mentioned the anion effect.[17b,20] Nevertheless, it is commonly accepted that catalysts incorporating WCAs are superior to those with normal anions. The earlier work of Evans[20b,21] showed that simple copper salts with classic WCAs such as $ClO_4^-$, $OTf^-$ and $BF_4^-$, are superior to those with halides or $acac^-$ as counteranions, affording much higher yields and better stereoselectivities (Table 1).

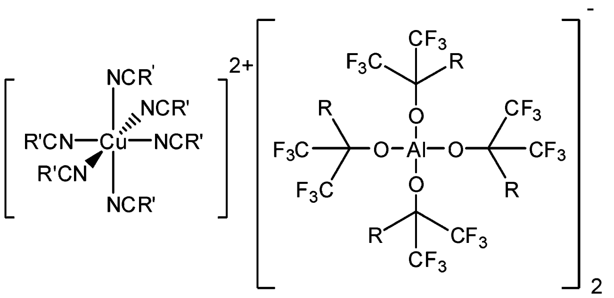
Caulton *et al.* [17b] demonstrated that high catalyst activity could be achieved in dichloromethane when the halide ligands were removed by $NaB(C_6F_5)_4$. The same group also reported that the use of the fluorinated $[B(C_6F_5)_4]^-$ afforded higher catalytic activity and better thermal stability compared to the non-fluorinated congener $[B(C_6H_5)_4]^-$. Furthermore, Vedernikov showed that the catalytic activity of Cu(II) complexes increased significantly (Table 2) when, for instance, $OTf^-$ was replaced by the bulky, fluorinated $BPh^F{}_4{}^-$($BAr^F{}_4 = [B(C_6F_5)_4]^-$ or $[B(C_6H_3(m\text{-}CF_3)_2)_4]^-$). In a previous communication,[15] we have shown that $[Cu(NCCH_3)_6][Al(OC(CF_3)_3)_4]_2$ affords a higher yield than $[Cu(NCCH_3)_6][BAr^F{}_4]_2$.

The work presented here is our continuing investigation of the anion effect on the copper-catalyzed olefin aziridination. We now report on the synthesis and characterization of copper(II) complexes with the general formula $[Cu(NCR')_6][Al(OC(CF_3)_2R)_4]_2$ ($R' = CH_3$, Ph; $R = CF_3$, Ph, $PhCH_3$), as well as their catalytic application in olefin aziridination.

## Results and Discussion

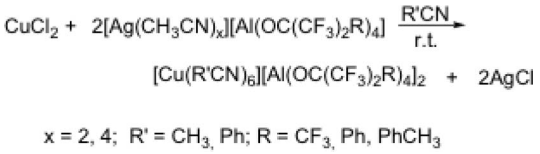
### Synthesis and characterization

Reaction of anhydrous copper(II) chloride with the silver salts of various WCAs in acetonitrile or benzonitrile readily affords copper complexes **1–6** (Fig. 1, Scheme 1). A slight excess of silver salt allows the complete chloride elimination.[22] However, this method can only be applied to compound **1**, due to the fact that **1** is the only complex soluble in polar solvents such as acetonitrile and the unreacted silver salt can be readily removed by product extraction with dichloromethane.



**1**: $R = CF_3$, $R' = CH_3$; **2**: $R = CF_3$, $R' = Ph$; **3**: $R = Ph$, $R' = CH_3$;
**4**: $R = Ph$, $R' = Ph$; **5**: $R = PhCH_3$, $R' = CH_3$; **6**: $R = PhCH_3$, $R' = Ph$

**Fig. 1** Copper(II) complexes of the general formula $[Cu(NCR')_6][Al(OC(CF_3)_2R)_4]_2$.



**Scheme 1** Synthesis of copper(II) complexes **1–6**.

Complex **1** can be further purified by slow diffusion of an acetonitrile solution of **1** into dichloromethane at −35 °C. For the synthesis of **2–6**, a slight excess of copper(II) chloride is added. The unreacted salt can be easily removed by re-dissolving the products in dichloromethane. Further recrystallization of **2–6** with dichloromethane and pentane–hexane only resulted in green oily compounds.

### Solid-state structures

Blue crystals of **1** suitable for X-ray diffraction can be obtained by slow diffusion of toluene into a concentrated acetonitrile solution of **1** at −35 °C. The X-ray crystal structure of **1** (Fig. 2) proves the octahedral symmetry of the Cu(II) cation and the non-coordinating nature of the anion. However, due to severe unresolvable disorder problems in the anionic part, a detailed discussion of the molecular structure of complex **1** is not possible. The same problem was also reported previously for acetonitrile ligated lanthanide complexes by Helm *et al.*[22] Nevertheless, it is very clear that the anion $[Al(OC(CF_3)_3)_4]^-$ has no interactions with the copper(II) cation in solid state, proving the non-coordinating character of $[Al(OC(CF_3)_3)_4]^-$.

### FT-IR spectroscopic studies

Complexes **1–6** were characterized by FT-IR using Nujol oil as matrix. It was observed that when using KBr, the color of the pellets often changed from green–blue to brown shortly after

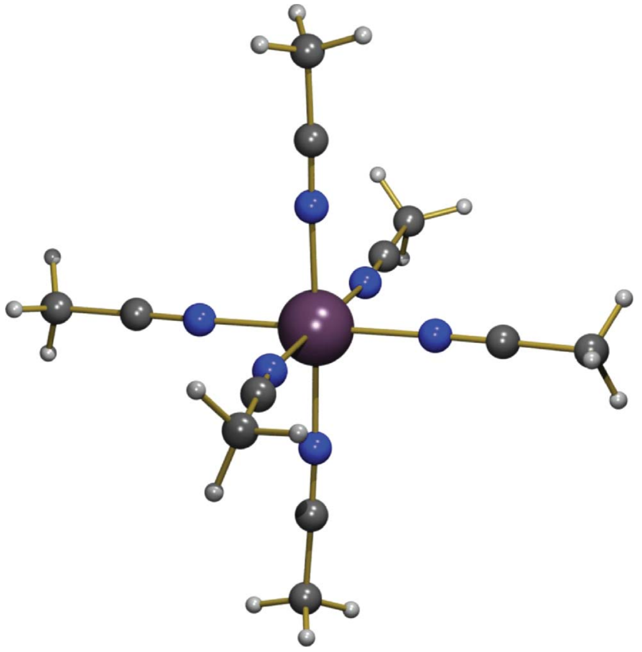


**Fig. 2** Ball-and-stick style plot of the cationic part of complex **1** in the solid state.[23]

the measurement. This is probably a consequence of complex decomposition by forming M–Br bonds.

The IR spectra of acetonitrile coordinated complexes **1**, **3**, **5** exhibit two sharp $\nu$(CN) absorptions with medium intensity at 2332, 2304 (**1**), 2332, 2301 (**3**) and 2331, 2302 cm$^{-1}$ (**5**), respectively (Fig. 3, upper half), which can be assigned to the fundamental $\nu_2$(CN) stretching mode and a combination mode of ($\nu_3 + \nu_4$),[24] respectively. On the other hand, only one broad $\nu$(CN) absorption is observed for the benzonitrile congeners **2**, **4**, **6** at 2280, 2274 and 2275 cm$^{-1}$, respectively (Fig. 3, lower half). The higher energies of all $\nu$(CN) absorptions compared to those of free acetonitrile (2254 and 2293 cm$^{-1}$) and benzonitrile (2256 cm$^{-1}$) are caused by σ-donation of electron density from the free electron pair of nitrogen to the metal center.[24b,25] It is noteworthy that the $\nu$(CN) absorptions are almost identical for acetonitrile coordinated complexes **1**, **3**, **5**, as well as for the benzonitrile congeners **2**, **4**, **6**. This observation indicates that changing counteranions from $[Al(OC(CF_3)_3)_4]^-$ to $[Al(OC(CF_3)_2PhCH_3)_4]^-$ has little influence on the coordination environment of the copper(II) cation. Based on the IR data and the solid-state structure of **1** (Fig. 2), it can be argued that the anions in complexes **2–6** are also truly non-coordinating in solid state.

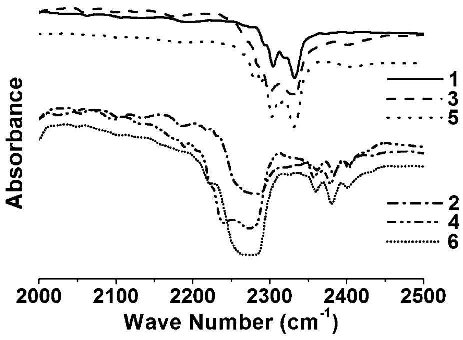


**Fig. 3** IR spectra of the copper(II) complexes **1–6** of the range 2000–2500 cm$^{-1}$.

### EPR spectroscopic studies

The EPR spectra of the copper(II) complexes **1–6** (Fig. 4) are typical for copper(II) systems (3d$^9$, $S = 1/2$) in the distorted octahedral coordination (tetragonal elongation) due to the Jahn–Teller effect. The copper(II) compounds can be described by an axially symmetric spin Hamiltonian in accordance with the symmetry of the molecule (see the crystal structure). The $^{63,65}$Cu hyperfine splitting (quartet of lines) is resolved only for the parallel part of the EPR spectra of frozen solutions due to the interaction of the unpaired electron with the nuclear spins of $^{63}$Cu and $^{65}$Cu ($I = 3/2$, natural abundance ≈69 and 31% respectively, isotopic splitting not resolved). The clear relationship $g_{II} > g_\perp > 2.0$ indicates a $d_{(x^2-y^2)}$ ground state for the unpaired electron.[26] The small deviations of $g$ values (see Table 3) and hyperfine coupling constants $A_{II}$ ($^{63,65}$Cu) are probably due to different nitrile ligands of the complexes,[13h] different frozen solutions as well as packing effects in solid state.

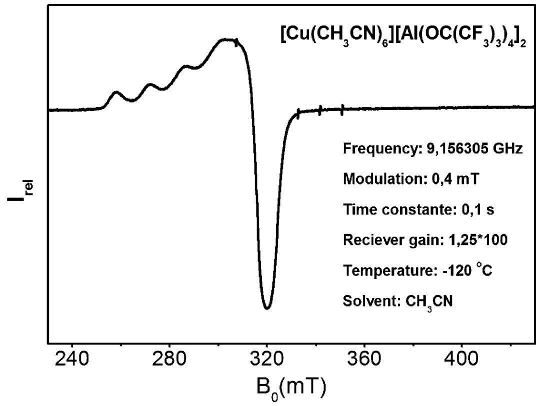


**Fig. 4** EPR spectrum of a frozen solution of complex **1**.

### Catalytic olefin aziridination with complexes 1–6

Acetonitrile coordinated complexes **1**, **3**, **5** were examined for their catalytic activities for olefin aziridination, using styrene as model substrate. It was found that complexes **3** and **5** are as active as **1** under standard conditions (Table 4, entry 1, 3, 5), affording very good yields (> 90%) in less than 5 min. However, the yields of aziridine decreased significantly to *ca.* 65% when only 0.1 mol% catalysts were applied (Table 4, entry 4, 6). The significantly lower activity of the two complexes probably results from complex decomposition, indicated by the color change of the

**Table 3** EPR parameters of the copper(II) complexes **1–6**

| Complex | $g_{II}$ | $g_\perp$ | $A_{II}$ (mT) |
|---|---|---|---|
| **1**[a] | 2.353 | 2.098 | 14.72 |
| **2**[a] | 2.355 | 2.091 | 13.72 |
| **3**[a] | 2.346 | 2.095 | 14.72 |
| **4**[b] | 2.317 | 2.078 | 15.48 |
| **5**[a] | 2.328 | 2.081 | 14.65 |
| **6**[b] | 2.323 | 2.078 | 15.07 |

[a] frozen acetonitrile solution; [b] frozen benzonitrile solution.

**Table 4** Aziridination of styrene with complexes **1–6**[a]

| Entry | Cat. | Load. (mol%) | Time (min) | Yield[b] |
|---|---|---|---|---|
| 1[c] | **1** | 0.5 | 3 | 91 |
| 2[c] | **1** | 0.1 | 360 | 90 |
| 3 | **3** | 0.5 | 3 | 93 |
| 4 | **3** | 0.1 | 360 | 65 |
| 5 | **5** | 0.5 | 3 | 90 |
| 6 | **5** | 0.1 | 360 | 67 |
| 7 | **6** | 0.5 | 3 | 89 |
| 8 | **6** | 0.1 | 360 | 68 |
| 9[d] | **6** | 0.5 | 120 | 75 |

[a] All reactions were performed in 2 mL dry acetonitrile with 1 equiv. of PhINTs and 5 equiv. of olefin at 25 °C. [b] Isolated yield. [c] Data from Ref. 15. [d] dichloromethane as solvent.

reaction solution from yellow–green to orange. Previous studies also showed that the anion $[Al(OC(CF_3)_2PhCH_3)_4]^-$ is less robust, decomposing in the presence of zinc(II) cation and small amounts of water.[27]

It is reasonable to assume that under the standard conditions, benzonitrile complexes would behave as do their acetonitrile congeners, due to the presence of a large excess of acetonitrile. Indeed, the assumption is supported by the catalytic results obtained from complexes **5** and **6** (Table 4, entries 5, 7 and entries 6, 8). Yet, when dichloromethane is used as solvent (Table 4, entry 9), the reaction time and the yield are much lower. Hence, the catalytic activity of complexes **2** and **4** were not tested.

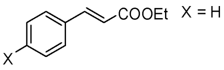
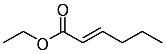
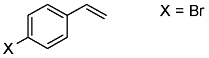
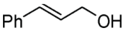
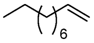
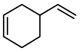
## Olefin aziridination catalyzed by complex 1

Following the preliminary investigation,[15] the scope of olefin substrates was further extended. Various olefins were tested for catalytic aziridination using the most active and robust complex **1** as catalyst. As shown in Table 5, all substrates except cinnamyl alcohol (entry 7) were successfully aziridinated with very good isolated yields.

Electron deficient cinnamate ester and its *p*-substituted derivatives afford high yields of aziridines (entries 1–3) within very short reaction times. The influence of the *p*-substitutes at the aromatic ring is clearly reflected by the necessary reaction times: the moderately electron-donating methoxy group (entry 3) is much more favored than the electron-withdrawing bromide (entry 2). The same effect is also observed for *p*-substituted styrenes (entry 5, 6).

A noteworthy example is ethylhex-2-enoate (entry 4), which was first reported as substrate for olefin aziridination. The very low reactivity of ethylhex-2-enoate is caused by the strong electron withdrawing character of the ester and the inert aliphatic chain. Nevertheless, a satisfactory yield (70%) of aziridine **2d** could be obtained within a relatively short reaction time (1.5 h). Not unexpectedly, the system was not compatible with allyl alcohols (entry 7). The only isolated product, $TsNH_2$, suggests decomposition of PhINTs in the presence of hydroxyl functionality, which has been assumed to act as proton source, accounting for undesired hydrolysis of PhINTs.[20b] A small amount of $TsNH_2$ was also detected in other cases, especially when the reaction time was prolonged due to less active substrates (entry 2, 4). This is in accordance with our previous results[15] as well as the findings of Evans *et al.*,[21] who demonstrated that the decomposition of PhINTs to $TsNH_2$ is increasingly pronounced with long reaction times. Despite the insolubility in acetonitrile, the aziridination of highly oleophilic 1-decene (entry 8) still affords a relatively high yield (73%) within 10 min. The non-conjugated diene 4-vinylcyclohex-1-ene (entry 9) was also tested. Only the ring double bond yields the aziridine, whereas the C═C vinyl group does not exhibit any reactivity. This is in good accordance with our earlier work,[15] where 80% yield had been obtained within 20 min for cyclohexene, *versus* 25% within 8 h for vinylcyclohexane, showing that the C═C bound of the vinyl substituent is not prone to aziridination.

**Table 5** Aziridination of various olefins catalyzed by **1**[a]

| Entry | Olefin | Time | Prod. | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  | 15 min | **2a** | 90 |
| 2 | x = Br | 1.5 h | **2b** | 84 |
| 3 | x = OMe | 5 min | **2c** | 92 |
| 4 |  | 1.5 h | **2d** | 70 |
| 5 |  | 5 min | **2e** | 90 |
| 6 | x = OMe | 1 min | **2f** | 93 |
| 7[c] |  | 10 min | | N. A. |
| 8 |  | 10 min | **2g** | 73 |
| 9 |  | 1 min | **2h** | 84 |

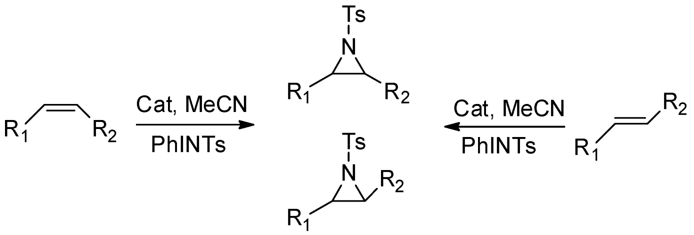
[a] All reactions were performed in 2 mL dry acetonitrile with 3 mol% catalyst, 1 equiv. of PhINTs and 5 equiv. of olefin at 25 °C unless otherwise noted. [b] Isolated yield. [c] $TsNH_2$ was formed quantitatively.

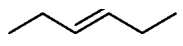
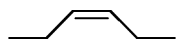
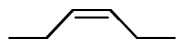
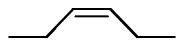
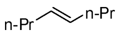
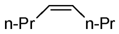
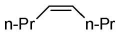
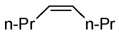
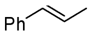
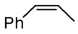
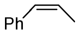
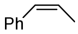
## Stereoselectivity

Evans' copper system[20b] involving classic WCAs, such as $ClO_4^-$ and $OTf^-$, was found to be very efficient in the stereoselective aziridination of 1,2-disubstituted olefins. The investigation of the influence of per/polyfluoroalkoxyaluminates on the stereoselectivity in olefin aziridination is of great interest (Table 6). As expected, all *trans* olefins lead to the desired *trans* disubstituted aziridines in high yields (entries 1, 5, 9, 13) in the presence of **1**. The aziridination of*cis*-disubstituted aliphatic olefins also exhibits excellent stereoselectivities (entry 2, 6, 10), affording almost exclusively *cis* aziridines.

In comparison, up to 10 mol% catalyst loading and sometimes low temperatures (– 20 °C) are required to achieve moderate yields and relatively high stereoselectivities when the classic WCAs are applied.[20b] When *cis*-β-methylstyrene is used as substrate, the stereoselectivity is only slightly lower (entry 10). In the cases of **3** (entry 3, 7, 11) and **5** (entry 4, 8, 12), similar yields and indistinguishable stereoselectivities are obtained, only with slightly longer reaction times. From Evans' results and those presented in this work, it is very clear that counteranions have significant influence on the stereoselectivity of olefin aziridination, with the trend from high to low: $[Al(OC(CF_3)_2R)_4]^-$> $ClO_4^-$, OTf> $Br^-$, $acac^-$. From this observation, it can be deduced that classic

**Table 6** Aziridination of *cis* and *trans* disubstituted olefins catalyzed by **1**, **3**, **5**[a]



| Entry | Olefin | Cat. | Time (min) | Prod. | Yield (%)[b] | *cis* : *trans* ratio[c] |
|---|---|---|---|---|---|---|
| 1 |  | **1** | 12 | **3a** | 83 | < 1 : 99 |
| 2 |  | **1** | 12 | **3b** | 85 | > 99 : 1 |
| 3 |  | **3** | 15 | **3b** | 87 | > 99 : 1 |
| 4 |  | **5** | 13 | **3b** | 85 | 99 : 1 |
| 5 |  n-Pr, n-Pr | **1** | 15 | **3c** | 80 | 2 : 98[e] |
| 6 |  n-Pr, n-Pr | **1** | 20 | **3d** | 81 | 97 : 3[e] |
| 7 |  n-Pr, n-Pr | **3** | 25 | **3d** | 78 | 98 : 2[e] |
| 8 |  n-Pr, n-Pr | **5** | 22 | **3d** | 80 | 98 : 2[e] |
| 9[d] |  Ph | **1** | 5 | **3e** | 90 | < 1 : 99 |
| 10[d] |  Ph | **1** | 3 | **3f** | 95 | 3 : 97 |
| 11[d] |  Ph | **3** | 5 | **3f** | 93 | 3 : 97 |
| 12[d] |  Ph | **5** | 5 | **3f** | 92 | 4 : 96 |

[a] All reactions were performed in 2 mL dry acetonitrile with 1–3 mol% catalyst, 1 equiv. of PhINTs and 5 equiv. of olefin at 25 °C unless otherwise noted. [b] Isolated yield. [c] The ratio of *cis* and *trans* isomers was detected by 400 MHz $^1$H NMR. [d] 1 mol% catalyst loading. [e] The lower stereoselectivity was due to small amount of *cis*/*trans* impurities in the *trans*/*cis* 1,2-disubstituted olefins.

WCAs have a stronger interaction ability than WCA of the type $[Al(OC(CF_3)_2R)_4]^-$. Indeed, in certain cases, the classical WCAs actually coordinate to the metal center, even in coordinating solvents such as acetonitrile.[24a]

## Aziridination of *cis*-stilbene

To further investigate the influence of counteranions on the stereoselectivity of olefin aziridination, *cis*-stilbene was aziridinated under various conditions (Table 7). Only very moderate stereoselectivity (*cis*/*trans* = 63 : 37) can be achieved in the presence of **1** (entry 1) under standard conditions. Yet at 0 °C, *cis*-2,3-diphenylaziridine is obtained almost exclusively (*cis*/*trans* = 98 : 2) with prolonged reaction time (4 h) and in similar high yield (93%) (entry 2). This is consistent with Evans' report,[20b] in which the *cis*/*trans* ratio of the aziridines was increased from 83 : 17 to 90 : 10 when the temperature was decreased from 0 °C to –20 °C. Moreover, examination of the reaction with higher catalyst loading (3 mol%) at room temperature gives similar results with respect to yield (85%), reaction time (1 min) and stereoselectivity (97 : 3) (entry 3). With complex **3** as catalyst, slightly lower yield (86%) and stereoselectivity (*cis*/*trans* = 60 : 40) is obtained (entry 4).

**Table 7** Aziridination of *cis*-stilbene under various reaction conditions[a]

| Entry | Cat. | Time (min) | Temp. (°C) | Yield[b] | *cis* : *trans* ratio[c] |
|---|---|---|---|---|---|
| 1 | **1** | 5 | 25 | 92% | 63 : 37 |
| 2 | **1** | 240 | 0 | 93% | 98 : 2 |
| 3[d] | **1** | 1 | 25 | 85% | 97 : 3 |
| 4 | **3** | 25 | 25 | 86% | 60 : 40 |
| 5[e] | **3** | 180 | 25 | 81% | 55 : 45 |
| 6[e] | **2** | 30 | 25 | 91% | 53 : 47 |
| 7[e] | **4** | 300 | 25 | 55% | 48 : 52 |
| 8[d,e] | **4** | 5 | 25 | 70% | 53 : 47 |

[a] All reactions were performed in 2 ml dry acetonitrile with 1 mol% catalyst, 1 equiv. of PhINTs and 5 equiv. of olefin at 25 °C unless otherwise noted. [b] isolated yield. [c] The ratio of *cis* and *trans* isomers was detected by $^1$H NMR measurement and was the average value of three parallel reactions. [d] with 3 mol% loading. [e] dichloromethane as solvent.

Comparable results could be obtained using dichloromethane as solvent, only when applying significantly prolonged reaction times (entry 5). The replacement of acetonitrile ligands by benzonitrile leads to lower yields and worse stereoselectivities (entry 5, 7),

**Table 8** Aziridination of 1-decene under various conditions[a]

| Entry | Cat. | Solvent | Time | Yield[b] |
|---|---|---|---|---|
| 1 | **1** | MeCN | 10 min | 73% |
| 2 | **3** | MeCN | 8 min | 75% |
| 3 | **3** | DCM | 2 min | 76% |
| 4 | **4** | DCM | 2 min | 80% |

[a] All reactions were performed in 2 mL dry acetonitrile with 1 mol% catalyst **3**, 1 equiv. of PhINTs and 5 equiv. of olefin at 25 °C unless otherwise noted. [b] Isolated yield

which can be attributed to the lesser thermal stability of benzonitrile coordinated complexes.[13h] The result can be significantly improved with higher loading of **4** (entry 8), yet still far away from the best records. Again, the complex with $[Al(OC(CF_3)_3)_4]^-$ as counteranion (**2**) shows a higher catalytic activity than the one incorporating $[Al(OC(CF_3)_2Ph)_4]^-$ (**4**) (entry 6, 7).

### Solvent effects

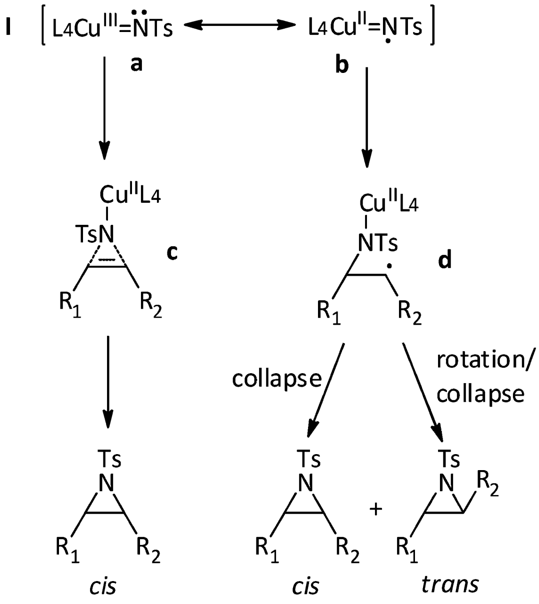
It is well established that for olefin aziridination reactions polar solvents afford better results than non-polar solvents, mainly because the nitrene source PhINTs dissociates much faster in polar solvents such as acetonitrile or nitromethane. However, this is not always the case. From Table 8 it is apparent that dichloromethane provides better results than acetonitrile for the aziridination of 1-decene (entry 2, 3).

Additionally, in contrast to the results obtained for *cis*-stilbene, complex **3** shows a higher catalytic activity than **1** (entry 1, 2). The benzonitrile coordinated complex **4** is superior to its acetonitrile congener **3** (entry 3, 4). These observations can be attributed to the very high lipophilic 1-decene having higher affinity to the catalysts of lower polarity, *e.g.* **3** and **4**.

### Mechanistic considerations

The reaction mechanism of metal-catalyzed olefin aziridination reactions has been subject of extensive debate. Previous investigations by Mansuy,[28] Evans,[20b] Jacobsen[29] and Che[16a] indicate that the mechanism is system dependent both respect to the metals, the ligands and on the nature of the counteranions. As for copper systems, two mechanisms have been suggested. While Evans assumed a non-radical concerted mechanism with copper(II) as the catalytically active oxidation state in nitrene transfer;[20b] Jacobsen argued for a discrete Cu(III)-nitrene as reactive intermediate.[29b,30] Herein, a mechanism, which involves both concerted and stepwise pathways is proposed (Scheme 2).

Pérez *et al.*[31] suggested a paramagnetic copper nitrene **I** as intermediate in copper-catalyzed olefin aziridination. The assumption was supported by Norrby's theoretical investigation,[30] which assigned the resonance species **a** and **b** to singlet and triplet states, respectively. Results from Table 6 suggest that the aziridination of 1,2-disubstituted aliphatic olefins and *cis*-β-methylstyrene proceeds *via* a concerted mechanism[20b] *via* transition state **c**. Yet, the results obtained with *cis*-stilbene indicate that the stepwise[32] pathway would be favored, if radical **d** is stable enough. It is apparent that a hypothetic radical **d** originating from *cis*-stilbene has lower energy than that of *cis*-β-methylstyrene; therefore more *trans* product was obtained for *cis*-stilbene under the same conditions.



**Scheme 2** Proposed mechanism for copper-catalyzed olefin aziridination.

The influence of the counteranions on stereoselectivity can be explained by the assumption that the coordination/interaction of an anion to the copper center would influence the equilibrium of the two nitrene forms in favor of triplet **b** (Scheme 2). Accordingly, the stepwise pathway would be preferred. Compared to normal anions and classical WCAs, WCAs of the type $[Al(OC(CF_3)_2R)_4]^-$ ($R = CF_3$, Ph, $PhCH_3$) are less likely to have interactions with the cation $[Cu(NCR')_6]^{2+}$ and the nitrene $[(NCR')_4Cu{=}NTs]^+$ ($R' = CH_3$, Ph). Therefore, rendering the catalysts higher stereoselectivity. Table 5 and 6 also show that the stereoselectivity is only slightly lower when $[Al(OC(CF_3)_3)_4]^-$ is replaced by $[Al(OC(CF_3)_2Ph)_4]^-$ or $[Al(OC(CF_3)_2PhCH_3)_4]^-$, demonstrating that the latter two are almost as weakly coordinating as the former. On the other hand, Norrby's theoretical calculations[30] showed that the smaller the copper-nitrene is, the lower energy of the singlet **a** will be compared to the triplet **b**, and *vice versa*. This straightforwardly explains why acetonitrile ligated copper complexes lead to a better stereoselectivity than their benzonitrile congeners (Table 7, entry 5, 7) and other larger copper systems.[20b,33]

## Conclusion

Copper(II) complexes **1–6** of the general formula $[Cu(NCR')_6][Al(OC(CF_3)_2R)_4]_2$ ($R' = CH_3$, Ph; $R = CF_3$, Ph, $PhCH_3$) are very efficient catalysts for olefin aziridination with PhINTs as nitrene source. Highly inert substrates such as ethylhex-2-enoate and 1-decene can be successfully aziridinated under mild conditions. Contrary to previous reports, aziridination of *cis*-stilbene is also stereoselective under certain conditions, providing *cis* : *trans* ratio of the resulting aziridines up to 98 : 2. The very weak coordinating ability of WCAs $[Al(OC(CF_3)_2R)_4]^-$ ($R = CF_3$, Ph, $PhCH_3$) is considered to be responsible for the superior results obtained with respect to reactivity and stereoselectivity. Interestingly, for highly lipophilic olefins, such as 1-decene, dichloromethane provides better results than the commonly used acetonitrile. Further work to extend the substrate scope and mechanistic studies are currently under way in our laboratories.

## Experimental Section

All preparations and manipulations were carried out under argon atmosphere using standard Schlenk techniques. All solvents used were dried by standard procedures. $^{1}$H, $^{13}$C and $^{19}$F NMR measurements were performed on a JEOL 400 MHz spectrometer. $^{27}$Al NMR measurements were performed on a Bruker AVANCE-DPX-400 MHz spectrometer. IR spectra were recorded on a Perkin Elmer FT-IR spectrometer using Nujol. EPR spectra were recorded with a JEOL JES-RE2X at X-band frequency ($v \approx 9.05$ GHz, microwave power 2 mW, modulation frequency 100 kHz). Elemental analyses were carried out at the Mikroanalytisches Labor of TU München. Metal analyses were determined with a Vario EL/1100 metal analyzer.

### General procedure for the synthesis of K[Al(OC(CF$_3$)$_2$Ph)$_4$] and K[Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$]

The synthesis and characterization of K[Al(OC(CF$_3$)$_3$)$_4$] were carried out according to the literature.[14]

Purified LiAlH$_4$[2] (1.4 equiv.) was suspended in toluene (30 mL) and HOC(CF$_3$)$_2$R (R = Ph, PhCH$_3$) (4.0 equiv.) was added at room temperature. The mixture was refluxed for 3 h, whereupon a yellow–orange solution formed. The volatiles were removed *in vacuo*, affording a yellow–orange oily solid, which was re-dissolved in diethyl ether (20 mL) and treated with saturated aqueous KCl solution (20 mL). The mixture was then stirred vigorously for 3 h at room temperature. After separating the aqueous layer and precipitation, the organic phase was washed by saturated aqueous KCl solution (10 mL × 3), dried by MgSO$_4$, filtered and brought to dryness *in vacuo* to afford the crude product as a white to pale yellow solid, which was re-dissolved in dry DCM (5 mL) and layered with *n*-pentane (15 mL) at 0 °C. The desired product was obtained as white to pale yellow crystals. Yield: 50–75%.

**K[Al(OC(CF$_3$)$_2$Ph)$_4$].** LiAlH$_4$ (0.158 g, 4.2 mmol), HOC(CF$_3$)$_2$Ph (2.0 mL, 11.9 mmol); Yield: 70%. Elemental Anal. Calc.(%) for $C_{36}H_{20}AlF_{24}KO_4$ (1038.58): C, 41.63; H, 1.94; F, 43.90; K 3.76;Found: C, 42.30; H, 2.28; F, 44.30; K, 4.00. $^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 7.70 (d, $J$ = 7.6, 2H), 7.28 (t, $J$ = 7.4, 1H), 7.15 (t, $J$ = 7.8, 2H); $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): −74.50.

**K[Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$].** LiAlH$_4$ (0.129 g, 3.4 mmol), HOC(CF$_3$)$_2$PhCH$_3$ (2.0 mL, 9.7 mmol); Yield: 55%. Elemental Anal. Calc.(%) for $C_{40}H_{28}AlF_{24}KO_4$ (1094.69): C, 43.89; H, 2.58; F, 41.65; K, 3.57; Found: C, 44.20; H, 2.89; F, 41.20; K, 3.32. $^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 7.56 (d, $J$ = 8.3, 2H), 6.95 (d, $J$ = 8.4, 2H), 2.25 (d, $J$ = 5.8, 3H); $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): −74.52.

### General procedure for the synthesis of [Ag(NCCH$_3$)$_4$]-[Al(OC(CF$_3$)$_3$)$_4$], [Ag(NCCH$_3$)$_2$] [Al(OC(CF$_3$)$_2$Ph)$_4$] and [Ag(NCCH$_3$)$_2$][Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$]

An acetonitrile (10 mL) solution of AgNO$_3$ (1.0 equiv.) was added to an acetonitrile (10 mL) solution of K[Al(OC(CF$_3$)$_2$R)$_4$] (1.0 equiv.) (R = CF$_3$, Ph, PhCH$_3$) in a pre-dried Schlenk in darkness. The reaction mixture was stirred for 15 min. Thereafter, 20 mL of diethyl ether was added. The mixture was stirred for another 15 min and the volatiles were removed *in vacuo*, affording the product as a white solid, which was re-dissolved in dry DCM (10 mL). Filtration and removal of the volatiles in darkness afforded the product as a white powder. Yield: 85–93%.

**[Ag(NCCH$_3$)$_4$][Al(OC(CF$_3$)$_3$)$_4$].** AgNO$_3$ (0.408 g, 2.4 mmol), K[Al(OC(CF$_3$)$_3$)$_4$] (2.415 g, 2.4 mmol); Yield: 2.78 g (93%). Elemental Anal. Calc. (%) for $C_{24}H_{12}AgAlF_{36}N_4O_4$ (1239.17): C, 23.26; H, 0.98; N, 4.52; F, 55.19; Found: C, 23.48; H, 0.93; N, 4.47; F, 55.36;$^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 2.01 (CH$_3$, s, 12H); $^{13}$C NMR(101 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 126.43, 123.51, 120.60, 119.68, 117.70, 79.97, 2.25; $^{27}$Al NMR (104.3 MHz, CD$_2$Cl$_2$, 25 °C,$\delta$ (ppm)): 29.33 (s); $^{19}$F NMR (376.5 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): −79.91 (s).

**[Ag(NCCH$_3$)$_2$][Al(OC(CF$_3$)$_2$Ph)$_4$].** AgNO$_3$ (0.238 g, 1.4 mmol), K[Al(OC(CF$_3$)$_2$Ph)$_4$] (1.45 g, 1.4 mmol); Yield: 1.50 g (90%). Elemental Anal. Calc. (%) for $C_{40}H_{26}AgAlF_{24}N_2O_4$ (1189.46): C, 40.39; H, 2.20; N, 2.36;F, 38.33; Found: C 39.60, H 2.03, N 2.32; F, 37.98;$^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 7.85 (d, $J$ = 7.6, 8H), 7.27 (t, $J$ = 7.2, 4H), 7.19 (t, $J$ = 7.5, 8H), 2.00 (s, 6H); $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 136.03, 128.18, 128.04, 127.92, 126.80, 125.28, 122.38, 119.48, 118.88, 79.86, 1.18;$^{27}$Al NMR (104.3 MHz,CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 30.18 (s); $^{19}$F NMR (376.5 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): −74.63 (s).

**[Ag(NCCH$_3$)$_2$][Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$].** AgNO$_3$ (0.238 g, 1.4 mmol), K[Al(OC(CF$_3$)2PhCH$_3$)$_4$] (1.519 g, 1.4 mmol); Yield: 1.48 g (85%). Elemental Anal. Calc. (%) for $C_{44}H_{34}AgAlF_{24}N_2O_4$ (1245.56): C, 42.43; H, 2.75; N, 2.25;F, 36.61; Found: C, 42.39, H, 3.02, N, 2.24; F, 36.14;$^{1}$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 7.70 (d, $J$ = 8.1, 8H), 6.99 (d, $J$ = 8.2, 8H), 2.23 (s, 12H), 1.95 (s, 6H);$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 139.73, 133.49, 128.77, 128.32, 127.81, 125.88, 122.98, 120.09, 119.35, 80.41, 21.30, 2.15;$^{27}$Al NMR (104.3 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): 30.27 (s); $^{19}$F NMR (376.5 MHz, CD$_2$Cl$_2$, 25 °C, $\delta$ (ppm)): −74.62 (s).

### General procedure for the synthesis of [Cu(NCCH$_3$)$_6$]-[Al(OC(CF$_3$)$_3$)$_4$]$_2$(1), [Cu(NCCH$_3$)$_6$][Al(OC(CF$_3$)$_2$Ph)$_4$]$_2$ (3) and [Cu(NCCH$_3$)$_6$][Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$]$_2$ (5)

CuCl$_2$ (0.95–1.1 equiv.) was added to an acetonitrile solution (10 mL) of [Ag(CH$_3$CN)$_x$][Al(OC(CF$_3$)$_2$R)$_4$] (2.0 equiv.) ($x$ = 2, 4; R = CF$_3$, Ph, PhCH$_3$). The resulting mixture was stirred for 3 h under exclusion of light. After filtration, the volatiles were removed *in vacuo*, affording the product as a green–blue solid. For **1**, the crude product was re-dissolved in 1.5 mL dry acetonitrile, filtered and layered by 10 mL dichloromethane to afford purified product; for **3** and **5**, the crude product was re-dissolved in 10 mL dichloromethane, filtered and the volatiles were removed *in vacuo* to afford purified products.

**[Cu(NCCH$_3$)$_6$][Al(OC(CF$_3$)$_3$)$_4$] (1).** CuCl$_2$ (0.0128 g, 0.1 mmol), [Ag(CH$_3$CN)$_4$][Al(OC(CF$_3$)$_3$)$_4$] (0.248 g, 0.2 mmol); Yield: 0.18 g (80%); Elemental Anal. Calc. (%) for $C_{44}H_{18}Al_2CuF_{72}N_6O_8$ (2244.04): C, 23.55; H, 0.81; N, 3.75;

F, 60.96; Found: C 23.42, H 0.72, N 3.81; F, 61.10; Selected IR (Nujol, cm$^{-1}$): $\nu$(CN), 2332, 2304, 1036, 972;

**[Cu(NCCH$_3$)$_6$][Al(OC(CF$_3$)$_2$Ph)$_4$]$_2$ (3).** CuCl$_2$ (0.0148 g, 0.11 mmol), [Ag(NCCH$_3$)$_2$] [Al(OC(CF$_3$)$_2$Ph)$_4$] (0.238 g, 0.2 mmol); Yield: 0.21 g (89%); Elemental Anal. Calc. (%) for $C_{84}H_{58}Al_2CuF_{48}N_6O_8$ (2308.83): C, 43.70; H, 2.53; F, 39.50; N, 3.64; Found: C, 43.98; H, 2.64; N, 3.06; F, 38.80; Selected IR (Nujol, cm$^{-1}$): $\nu$(CN), 2332, 2301, 1082, 1036, 967;

**[Cu(NCCH$_3$)$_6$][Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$]$_2$ (5).** CuCl$_2$ (0.0148 g, 0.11 mmol), [Ag(NCCH$_3$)$_2$][Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$] (0.249 g, 0.2 mmol); Yield: 0.20 g (85%) Elemental Anal. Calc. (%) for $C_{92}H_{74}Al_2CuF_{48}N_6O_8$ (2421.04): C, 45.64; H, 3.08; N, 3.47; F, 37.67; Found: C, 44.74; H, 3.08; N, 3.10; F, 36.90; Selected IR (Nujol, cm$^{-1}$): $\nu$(CN), 2331, 2302, 1036, 1023, 966;

### General procedure for the synthesis of [Cu(NCC$_6$H$_5$)$_6$]-[Al(OC(CF$_3$)$_3$)$_4$]$_2$ (2), [Cu(NCC$_6$H$_5$)$_6$][Al(OC(CF$_3$)$_2$Ph)$_4$]$_2$ (4) and [Cu(NCC$_6$H$_5$)$_6$][Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$]$_2$ (6)

CuCl$_2$ (1.1 equiv.) was added to a dry benzonitrile solution (4 mL) of [Ag(CH$_3$CN)$_x$][Al(OC(CF$_3$)$_2$R)$_4$] (2.0 equiv.) ($x = 2, 4$; R = CF$_3$, Ph, PhCH$_3$). The resulting mixture was stirred for 4 h in darkness. After filtration, the volatiles were removed *in vacuo* to afford the product as a green solid, which was re-dissolved in 10 mL dry DCM, filtered and the volatiles were removed *in vacuo* to afford purified product.

**[Cu(NCC$_6$H$_5$)$_6$][Al(OC(CF$_3$)$_3$)$_4$]$_2$ (2).** CuCl$_2$ (0.0148 g, 0.11 mmol), [Ag(CH$_3$CN)$_4$][Al(OC(CF$_3$)$_3$)$_4$] (0.248 g, 0.2 mmol); Yield: 0.22 g (85%); Elemental Anal. Calc. (%) for $C_{74}H_{30}Al_2CuF_{72}N_6O_8$ (2616.46): C, 33.97; H, 1.16; N, 3.21; F, 52.28; Found: C, 34.97; H, 0.92; N, 3.51; F, 52.50; Selected IR (Nujol, cm$^{-1}$): $\nu$(CN), 2280, 1067, 1027, 974;

**[Cu(NCC$_6$H$_5$)$_6$][Al(OC(CF$_3$)$_2$Ph)$_4$]$_2$ (4).** CuCl$_2$ (0.0148 g, 0.11 mmol), [Ag(NCCH$_3$)$_2$] [Al(OC(CF$_3$)$_2$Ph)$_4$] (0.238 g, 0.2 mmol); Yield: 0.22 g (83%); Elemental Anal. Calc. (%)for $C_{114}H_{70}Al_2CuF_{48}N_6O_8$ (2681.24): C, 51.07; H, 2.63; N, 3.13; F, 34.01; Found: C, 49.48; H, 2.33; N, 3.05; F, 33.00; Selected IR (Nujol, cm$^{-1}$): $\nu$(CN), 2274, 1036, 1024, 965;

**[Cu(NCC$_6$H$_5$)$_6$][Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$]$_2$ (6).** CuCl$_2$ (0.0148 g, 0.11 mmol), [Ag(NCCH$_3$)$_2$][Al(OC(CF$_3$)$_2$PhCH$_3$)$_4$] (0.249 g, 0.2 mmol); Yield: 0.24 g (86%) Elemental Anal. Calc. (%) for $C_{122}H_{86}Al_2CuF_{48}N_6O_8$ (2793.46): C, 52.45; H, 3.10; N, 3.01; F, 32.64; Found: C, 51.70; H, 2.99; N, 2.92; F, 32.70; Selected IR (Nujol, cm$^{-1}$): $\nu$(CN), 2275, 1040, 1024, 964;

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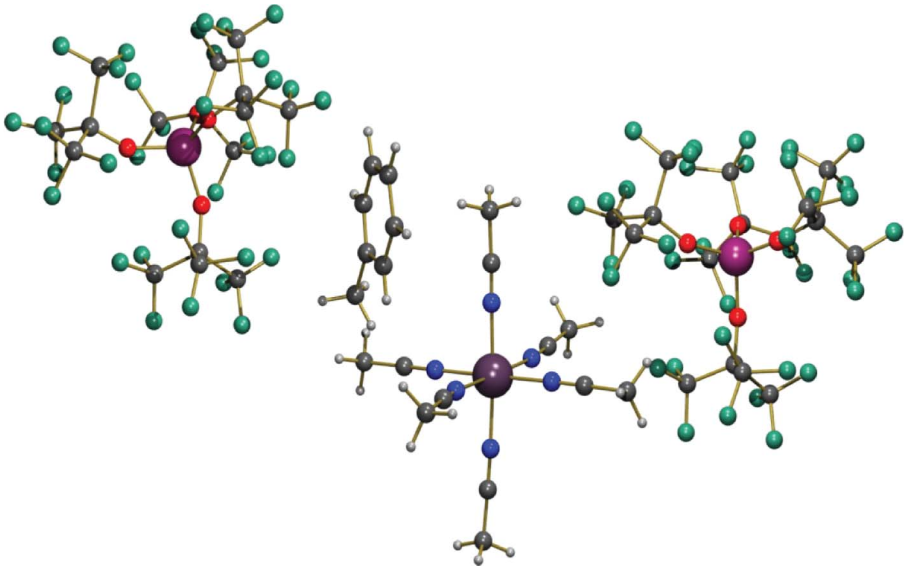

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