# Polynuclear Copper(I) Complexes with Chelating Bis- and Tris-N-Heterocyclic Carbene Ligands: Catalytic Activity in Nitrene and Carbene Transfer Reactions

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dinuclear complexes.

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Di- and trinuclear complexes of copper(I) bearing bis- or tris-N-heterocyclic carbene ligands have been prepared and evaluated as catalysts in nitrene transfer reactions from PhI=NTs to unsaturated and saturated substrates (olefin aziridination and C–H bond amidation) and carbene transfer re-

## Introduction

Research into copper(I) complexes with N-heterocyclic carbenes (NHC)<sup>[1]</sup> as ligands has attracted considerable attention in recent years. In particular, copper(I) complexes containing an NHC ligand have been reported as catalysts for a number of synthetically useful reactions such as selective reductions, cyclopropanations, aziridinations, 1,3-dipolar cycloadditions, and hydrosilylations.<sup>[2]</sup> Encouraged by these results, further research efforts focused on the synthesis and characterisation of this type of complex has led to the development of a wide variety of synthetic strategies and complex structures.<sup>[3,4]</sup> Thus, copper(I) complexes containing polycarbene ligands, that is, multidentate ligands with two or more NHC units, have been widely studied,<sup>[4,5]</sup> affording mono- or polynuclear complexes by virtue of the different chelating<sup>[6,7]</sup> or bridging<sup>[8-14]</sup> modes that such ligands can adopt when interacting with a metal centre. Despite the wide variety of (NHC)Cu<sup>I</sup> complexes available, the majority of catalytic studies have been carried out with mononuclear compounds, in particular, with complex [IPrCuCl] [Scheme 1, left; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], first described by Buchwald and co-workers<sup>[15]</sup> and further extensively studied by Diez-Gonzalez and Nolan.<sup>[2b,2c]</sup>

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actions from diazo compounds to olefins. The complexes ex-

hibited moderate-to-high catalytic activity in both processes.

The tosylamidation of C-H bonds, previously unreported

with a NHC-containing copper catalyst, was promoted by the

Scheme 1. Mono- and trinuclear NHC-copper(I) complexes.

We have described the first example of a catalytic system based on the trinuclear tricarbene-copper(I) complexes 1 and 2 (Scheme 1, right) for C-N and C-C coupling reactions.<sup>[10]</sup> Encouraged by these results, we have now extended our investigation on the catalytic efficiency of such compounds to nitrene and carbene transfer reactions. Copper complexes have been reported to catalyse these transformations in which a carbene group from a diazo compound (Scheme 2) or a nitrene group from an iodine hypervalent compound can be transferred to unsaturated or saturated acceptors.<sup>[16c,16e]</sup> The former route leads to the formation of cyclopropanes or aziridines, whereas the second leads to the functionalisation of C-H bonds. Of the catalysts employed in these transformations, mononuclear copper(I)-NHC complexes<sup>[16,17]</sup> have successfully been used in carbene transfer as well as in olefin aziridination reactions. However, the use of the NHCCu core to promote the functionalisation of C-H bonds by nitrene insertion is, to the best of our knowledge, hitherto unknown. Thus, we have prepared a series of dinuclear copper complexes bearing bidentate NHC ligands (Scheme 3) and tested them, along with the complexes 1 and 2 with a tris-carbene ligand (Scheme 1), in the above transformations; the first example of C-H amidation induced by a NHCCu-based catalyst was observed.

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Scheme 2. Carbene and nitrene transfer reactions catalysed with copper complexes.



Scheme 3. Dinuclear copper(I) complexes employed in this work.

#### **Results and Discussion**

#### Synthesis of Bis-carbene-Silver and -Copper Complexes

We have previously described the syntheses of the trinuclear tris-carbene–copper(I) complexes 1 and 2 (Scheme 1).<sup>[10]</sup> We were also interested in preparing related dinuclear bis-carbene–copper(I) complexes such as **3b** (Scheme 3), the preparation of which has just recently been reported.<sup>[12,13]</sup> Following the same methodology, we have synthesised the complexes **4b–6b** (Scheme 3).

The reactions of the bis-imidazolium precursors **3–6** with  $Ag_2O^{[18]}$  and subsequent anion exchange afforded the corresponding dinuclear bis-carbene–silver complexes **3a–6a**. Although complexes **3a**<sup>[12,13]</sup> and **4a**<sup>[19]</sup> have previously been reported in the literature (**4a** with a different counter-ion), the related complexes **5a** and **6a** are hitherto unreported. Note, the use of a bis-imidazolium salt similar to **5** but with chloride counter-ions has been reported to afford a silver complex with a different dinuclear structure, with only one bridging dicarbene ligand and one chloride coordinated to each silver atom.<sup>[20]</sup>

Complexes **3a–6a** were employed as starting materials in the transmetallation reaction in which the NHC ligands were transferred from silver to copper to yield the complexes **3b–6b**. Their spectroscopic data compare well with those of the previously reported, structurally characterised complex **3b**<sup>[12,13]</sup> and also suggest for the novel complexes a dinuclear structure with two bridging dicarbene ligands. Support for the dinuclear structures is also provided by ESI-MS analyses in which only signals attributable to dinuclear bis-carbene complexes are visible (see the Exptl. Sect.). Interestingly, a signal related to a dioxygen adduct of the dinuclear complex is sometimes detected in the ESI-MS spectrum and in the case of complex **5b** it is the major signal. We are currently investigating the preparative synthesis of such adducts and their detailed characterisation.

Compounds 3b-6b are somewhat unstable in solution and, in some cases, attempts to obtain pure analytical samples failed. Complex 3b, which has a methylene bridge between the two carbene ligands and methyl groups on the N atoms, is the most stable complex. It seems that elongation of the bridge between the carbene units or an increase in the steric bulk of the N substituents, that is, the cases of 4-6, negatively affected the stability of the complexes, which invariably showed decomposition in their <sup>1</sup>H NMR spectra after 1-2 d in solution. In contrast, the complexes were stable in the solid state without special precautions, although upon prolonged storage in air they invariably showed a light-blueish tinge, which indicates slow oxidation of the metal by atmospheric oxygen. In this context, the instability of copper(I)-NHC complexes towards air oxidation has very recently been reported.<sup>[13,21]</sup>

#### **Catalytic Activity: Nitrene Transfer Reactions**

We first screened the potential of these copper complexes in nitrene transfer reactions. As a test reaction, we focused on the aziridination of styrene and employed 3b as the catalyst precursor and N-tosylimino(phenyl)iodinane (PhI=NTs) as the nitrene source. The results are shown in Table 1. The reaction was found to proceed at room temperature with only 1 mol-% catalyst, although the yield greatly depended on the excess of olefin employed (Table 1, entries 1-5). Addition of molecular sieves to the reaction mixture did not significantly alter the results (Table 1, entries 4 and 6). The in situ generation of PhI=NTs by mixing PhI(OAc)<sub>2</sub> and TsNH<sub>2</sub> gave a poor yield of the product. The use of acetonitrile as solvent led to a decrease in the aziridination yield at room temperature, which significantly increased at 50 °C (Table 1, entry 10); furthermore, in this solvent, in situ generated PhI=NTs gave higher yields than in dichloromethane (Table 2, entry 11).

The use of alternative nitrene sources gave mixed results. Anhydrous chloramine T was unsuitable as a reagent in dichloromethane, whereas moderate yields of aziridine were achieved in acetonitrile. The presence of water was found to be highly detrimental in this case; the reaction yield improved upon the addition of molecular sieves and decreased drastically when using commercial chloramine T trihydrate (Table 1, entries 12–17). In contrast, very high yields were obtained with the system PhI=O + H<sub>2</sub>NTs at 50 °C in acetonitrile (Table 1, entry 18).

Following these preliminary investigations, complexes 1, 2 and 3b–6b were tested in the styrene aziridination reaction under the optimised conditions. Table 2 shows the results, allowing the catalytic capabilities of the series of catalysts in this reaction to be assessed. Although all the complexes

Table 1. Styrene aziridination catalysed by complex 3b.[a]



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Entry	Nitrene source	Т [°С]	Styrene/ nitrene	Solvent	Yield <sup>[b]</sup> [%]
1	PhI=NTs	25	5:1	CH <sub>2</sub> Cl <sub>2</sub>	14
2	PhI=NTs	25	10:1	$CH_2Cl_2$	25
3	PhI=NTs	25	20:1	$CH_2Cl_2$	44
4	PhI=NTs	25	30:1	$CH_2Cl_2$	76
5	PhI=NTs	25	50:1	$CH_2Cl_2$	80
6	PhI=NTs	25	30:1	$CH_2Cl_2$	78 <sup>[c]</sup>
7	$PhI(OAc)_2 + H_2NTs$	25	30:1	$CH_2Cl_2$	14
8	PhI=NTs	25	30:1	CH <sub>3</sub> CN	26
9	$PhI(OAc)_2 + H_2NTs$	25	30:1	CH <sub>3</sub> CN	25
10	PhI=NTs	50	30:1	CH <sub>3</sub> CN	82
11	$PhI(OAc)_2 + H_2NTs$	50	30:1	CH <sub>3</sub> CN	91
12	chloramine T	25	30:1	$CH_2Cl_2$	4
13	chloramine T	25	30:1	$CH_2Cl_2$	6 <sup>[c]</sup>
14	chloramine T	25	30:1	CH <sub>3</sub> CN	26
15	chloramine T	25	30:1	CH <sub>3</sub> CN	37 <sup>[c]</sup>
16	chloramine T commercial (•3H <sub>2</sub> O)	25	30:1	CH <sub>3</sub> CN	8
17	chloramine T	50	30:1	CH <sub>3</sub> CN	43
18	$PhI=O + H_2NTs$	50	30:1	CH <sub>3</sub> CN	95 <sup>[c]</sup>

[a] Reaction conditions: 0.263 mmol nitrene source, 4 mL solvent, 2 mol-% [Cu], 17 h. [b] Yields were determined by NMR spectroscopy. [c] With addition of 100 mg of molecular sieves (4 Å).

Table 2. Aziridination of styrene with PhI=NTs catalysed by polynuclear copper(I)–NHC complexes.<sup>[a]</sup>

Entry	Catalyst	Yield [%] <sup>[b]</sup>
1	1	34
2	2	64
3	3b	82
4	<b>4</b> b	67
5	5b	41
6	6b	35

[a] Reaction conditions: 0.263 mmol PhI=NTs, 30 equiv. styrene, 4 mL acetonitrile, 2 mol-% [Cu], 50 °C, 17 h. [b] Yields were determined by NMR spectroscopy.

catalysed the aziridination reaction, significant differences in catalytic activity were found. In the case of the triscarbene derivatives, complex 1 is less active than the related 2. With the bis-carbene series, the activity follows the trend 3b > 4b > 5b > 6b. In fact, this trend correlates to a certain extent with the stability of the complexes in solution mentioned above.

To compare the catalytic efficiency of complex 3b with that of the standard complex [IPrCuCl], we determined the conversion curves for the aziridination of styrene for both catalysts with in situ formed PhI=NTs (Figure 1). It is apparent that the initial activity is very similar for the two catalysts, but [IPrCuCl] is deactivated faster and the reaction stops after about 5 h and 60% yield whereas 3b retains its activity for a longer period of time allowing a much higher yield to be obtained. Thus, the catalytic efficiency of 3b compares favourably not only with the other polynuclear

copper catalysts in our series (Table 2), but also with [IPrCuCl], and the reason appears to be the higher stability of **3b** under the reaction conditions.



Figure 1. Conversion curves for the aziridination of styrene with in situ formed PhI=NTs catalysed by **3b** ( $\Box$ ) and [IPrCuCl] ( $\diamond$ ). Reaction conditions: 0.263 mmol PhI(OAc)<sub>2</sub> + H<sub>2</sub>NTs, 30 equiv. styrene, 4 mL acetonitrile, 2 mol-% [Cu], 50 °C.

To complete the aziridination screening, a series of olefins bearing aromatic and aliphatic substituents as well as electron-withdrawing and -donating groups were employed as substrates using 3b as catalyst. The results are reported in Table 3. p-Substituted styrenes showed moderate aziridination yields (Table 3, entries 1-7), which were quite unaffected by the nature of the group located at the para position, but they were affected by the use of in situ generated PhI=NTs (Table 3, entries 3 and 4). Geminal-disubstituted olefins also gave moderate yields, provided the substituents were not too bulky (entries 8 and 9). On the other hand, vicinal-disubstituted olefins and cyclic olefins gave rather low aziridination yields (entries 10-12). Interestingly, when cis-propenylbenzene was used as the substrate, most of the aziridination product was found to be in the trans configuration (entry 11). This inversion of stereochemistry can be interpreted to be a result of the existence of a radical pathway for the aziridination reaction.<sup>[22]</sup>

Having demonstrated the catalytic capabilities of these compounds, and particularly that of complex **3b**, to catalyse the nitrene transfer reactions, we decided to investigate its potential in the functionalisation of the C–H bond given that, as mentioned before, there are no examples of the use of a NHCCu-based catalyst for this reaction. The selection of the model substrate was somewhat limited by the poor solubility of **3b** in non-polar solvents. Because of this we first targeted 1,4-dioxane as a suitable substrate. Thus, the reaction of several nitrene sources in 1,4-dioxane as solvent in the presence of catalytic amounts of **3b** led to the product derived from the formal insertion of an NTs group into the  $\alpha$ -C–H bond of the cyclic ether (Scheme 4 and Table 4).

Although negligible reactivity was observed at 50 °C, moderate yields of the insertion product were obtained upon raising the reaction temperature to 70 °C (Table 4, entries 1–4). Under these conditions, anhydrous chloramine T was found to be a significantly better nitrene source than

Table 3. Aziridination of olefins with PhI=NTs catalysed by complex 3b.<sup>[a]</sup>

Entry	Nitrene source	Olefin	Yield <sup>[b]</sup> [%]
1	PhI=NTs	styrene	82
2	$PhI(OAc)_2 + H_2NTs$	styrene	91
3	PhI=NTs	4-chlorostyrene	39
4	$PhI(OAc)_2 + H_2NTs$	4-chlorostyrene	78
5	PhI=NTs	4-fluorostyrene	36
6	PhI=NTs	4-methylstyrene	45
7	PhI=NTs	4-methoxystyrene	38
8	PhI=NTs	α-methylstyrene	36
9	PhI=NTs	1,1-diphenylethylene	15
10	PhI=NTs	cis-propenylbenzene	7(11 <sup>[c]</sup> )
11	PhI=NTs	trans-propenylbenzene	28
12	PhI=NTs	cis-cyclooctene	11

[a] Reaction conditions: 0.263 mmol nitrene source, 30 equiv. olefin, 4 mL acetonitrile, 2 mol-% [Cu], 50 °C, 17 h. [b] Yields were determined by NMR spectroscopy. [c] Yield of the *trans*-aziridine product.



Scheme 4. C–H bond functionalisation by nitrene insertion catalysed by **3b**.

Table 4. C–H bond functionalisation of 1,4-dioxane catalysed by complex  $3b.^{\rm [a]}$ 

Entry	Substrate	Nitrene source	<i>T</i> [°C]	Yield <sup>[b]</sup> [%]
1	1,4-dioxane	PhI=NTs	50	0
2	1,4-dioxane	$PhI(OAc)_2 + H_2NTs$	50	0
3	1,4-dioxane	$PhI(OAc)_2 + H_2NTs$	70	20
4	1,4-dioxane	$PhI(OAc)_2 + H_2NTs$	70	38 <sup>[c]</sup>
5	1,4-dioxane	chloramine T	70	51 <sup>[c]</sup>
6	tetrahydrofuran	chloramine T	70	48 <sup>[c]</sup>
7	1,4-dioxane [d]	chloramine T	70	32 <sup>[c]</sup>

[a] Reaction conditions: 0.263 mmol nitrene source, 4 mL substrate, 20 mol-% [Cu], 17 h. [b] Yields were determined by NMR spectroscopy. [c] With addition of 100 mg of 4 Å molecular sieves. [d] The reaction was performed with 1 mmol 1,4-dioxane and 1.3 mmol chloramine T in 6 mL acetonitrile.

PhI=NTs (Table 4, entries 5 and 7); the reaction could be performed in acetonitrile as solvent with nearly stoichiometric amounts of reagents. Under similar reaction conditions, tetrahydrofuran was also functionalised in moderate yields (Table 4, entry 6).

#### Catalytic Activity: Carbene Transfer Reactions

We also tested the polynuclear copper complexes in carbene transfer reactions using ethyl diazoacetate (EDA) as the carbene source. An interesting feature of the mononuclear [IPrCuCl] complex is that it suppresses the diazo coupling reaction that leads to the formation of diethyl maleate and fumarate, an unwanted side-reaction in carbene transfer processes.<sup>[16a]</sup> Catalysis only takes place if the chloride ligand on the complex is displaced by a non-coordinating anion or a donor ligand. We investigated the same reaction with complexes 1 and 3b under comparable reaction conditions (1-4 mol-% catalyst, dichloromethane, room temperature) and found that, in contrast to [IPrCuCl], the decomposition reaction was catalysed by both complexes. The reaction was faster with 3b, reaching completion with 1 mol-% catalyst after only 2 h and yielding a 60:40 fumarate/ maleate ratio, whereas in the case of 1 the reaction was slower, reaching a conversion of 90% with a 77:23 fumarate/maleate ratio after 24 h with 4 mol-% catalyst. Apparently, the inherent cationic nature and consequent electrophilicity of our polynuclear complexes is high enough to trigger EDA decomposition in spite of the presence of two strongly coordinated ligands such as the two NHC moieties in the coordination sphere of the copper(I) centres.

The olefin cyclopropanation reaction also proved to be effective with these di- and trinuclear copper(I) complexes. Ethyl diazoacetate and methyl phenyldiazoacetate (PhDA) were employed along with an excess of the olefin acceptor (10 equiv. with respect to the diazo compound) and 1 mol-% of the copper catalyst. The results are reported in Table 5. The reaction of EDA with the trinuclear catalyst 1 was very slow, yielding a negligible amount of the cyclopropane even after 24 h. The catalytic performances of the dinuclear catalysts 3b, 4b and 6b were somewhat better, but the yields of cyclopropane were still only moderate after 24 h. The diastereoselectivity of the reaction with EDA was also moderate (ca. 70:30), whereas the use of the phenyl-containing diazo compound induced a much higher diastereoselectivity, although the yields remained only moderate (entries 5-7).[23]

Table 5. Cyclopropanation of styrene catalysed by polynuclear copper(I)–NHC  $complexes^{[a]}$ 



Entry	Catalyst	Diazo compound	Yield <sup>[b]</sup> [%]	$dr^{[c]}$
1	1	EDA	3	38:62
2	3b	EDA	45	73:27
3	<b>4b</b>	EDA	21	71:29
4	6b	EDA	41	71:29
5	3b	PhDA	25	>95:5
6	<b>4b</b>	PhDA	33	>95:5
7	6b	PhDA	45	>95:5

[a] Reaction conditions: see the Exp. Sect. [b] Yields were determined by NMR spectroscopy. [c] Diastereomeric ratio (E/Z).

## Conclusions

We have found that polynuclear poly-NHC copper complexes catalyse the transfer of carbene (from diazo com-



pounds) or nitrene (from iodine hypervalent compounds) fragments to unsaturated and saturated substrates in moderate-to-high yields. In particular, this system has provided the first example of the tosylamidation of C–H bonds with a catalyst containing the NHCCu core, which was known to induce other transformations (olefin cyclopropanation, aziridination and C–H bond functionalisation by carbene insertion).

## **Experimental Section**

**General Methods:** All manipulations were carried out by using standard Schlenk techniques under dry argon or dinitrogen. The reagents were purchased by Aldrich or Merck as high-purity products and generally used as received. All solvents were dried by standard procedures and distilled under dinitrogen immediately prior to use. *N*-Tosylimino(phenyl)iodinane (PhI=NTs),<sup>[24]</sup> complexes 1,<sup>[10a]</sup> 2,<sup>[10b]</sup> 3a<sup>[25]</sup> and 3b<sup>[12]</sup> and ligand precursors 4,<sup>[19]</sup> 5<sup>[26]</sup> and 6<sup>[27]</sup> were prepared according to literature procedures. NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer (300.1 MHz for <sup>1</sup>H and 75.5 MHz for <sup>13</sup>C). Chemical shifts ( $\delta$ ) are reported in units of ppm relative to the residual solvent signals.

General Procedure for the Synthesis of the Silver Complexes 4a–6a: The bis-imidazolium ligand precursor (1 mmol) and Ag<sub>2</sub>O (2.5 mmol) were placed in a 100 mL two-necked round-bottomed flask equipped with a magnetic stirring bar under an inert atmosphere under light exclusion. Deionised water (50 mL) was subsequently added and the reaction mixture was maintained at room temperature whilst stirring for 24 h. Subsequently, the reaction mixture was filtered through Celite under an inert atmosphere and the filtrate was treated with NH<sub>4</sub>PF<sub>6</sub> (2.1 mmol). The resulting white precipitate was filtered off under an inert atmosphere and dried under reduced pressure under light exclusion.

**Complex 4a:** Yield 49%. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.56 (s, 4 H, CH), 7.34 (s, 4 H, CH), 4.67 (s, 8 H, CH<sub>2</sub>), 3.76 (s, 12 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta$  = 124.0 (CH), 123.0 (CH), 52.3 (CH<sub>2</sub>), 39.4 (CH<sub>3</sub>) ppm, carbene carbon not detected. C<sub>20</sub>H<sub>28</sub>Ag<sub>2</sub>F<sub>12</sub>N<sub>8</sub>P<sub>2</sub> (886.15): calcd. C 27.09, H 3.19, N 12.65; found C 26.46, H 3.37, N 12.25.

**Complex 5a:** Yield 45%. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.68 (s, 4 H, CH), 7.57 (s, 4 H, CH), 4.07 (m, 8 H, CH<sub>2</sub>), 3.49 (s, 12 H, CH<sub>3</sub>), 2.50 (m, 4 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta$  = 124.8 (CH), 121.9 (CH), 48.4 (CH<sub>2</sub>), 38.7 (CH<sub>3</sub>), 30.6 (CH<sub>2</sub>) ppm, carbene carbon not detected. C<sub>22</sub>H<sub>32</sub>Ag<sub>2</sub>F<sub>12</sub>N<sub>8</sub>P<sub>2</sub> (914.21): calcd. C 28.89, H 3.53, N 12.26; found C 28.67, H 3.67, N 11.95.

**Complex 6a:** Yield 41%. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.84 (s, 4 H, CH), 7.72 (s, 4 H, CH), 6.89 and 6.37 (AB system, 4 H, CH<sub>2</sub>), 4.25 (m, 4 H, CH), 0.90–2.10 (m, 40 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]-DMSO):  $\delta$  = 123.3 (CH), 121.9 (CH), 65.2 (CH<sub>2</sub>), 62.2 (CH), 35.1 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 25.9 (CH<sub>2</sub>) ppm, carbene carbon not detected. C<sub>38</sub>H<sub>56</sub>Ag<sub>2</sub>F<sub>12</sub>N<sub>8</sub>P<sub>2</sub> + 3H<sub>2</sub>O (1184.16): calcd. C 38.51, H 5.28, N 9.46; found C 38.59, H 4.78, N 9.55.

**General Procedure for the Synthesis of the Copper(I) Complexes 4b–6b:** The dinuclear dicarbene silver complex was placed in a 50 mL two-necked round-bottomed flask equipped with a magnetic stirring bar under an inert atmosphere. Acetonitrile (3–5 mL) was subsequently added followed by CuI (2 equiv. with respect to the introduced silver complex). The reaction mixture was maintained at room temperature whilst stirring for 30 min. Subsequently, the reaction mixture was filtered through Celite under an inert atmosphere.

sphere and the filtrate was concentrated to about 1-2 mL under reduced pressure and finally treated with diethyl ether (ca. 20 mL). The resulting white precipitate was filtered off under an inert atmosphere, washed diethyl ether ( $2 \times 5 \text{ mL}$ ) and dried under reduced pressure.

**Complex 4b:** Yield 52%. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.33 (s, 4 H, CH), 7.28 (s, 4 H, CH), 4.66 (s, 8 H, CH<sub>2</sub>), 3.73 (s, 12 H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 176.7 (NCN), 123.2 (CH), 122.4 (CH), 51.2 (CH<sub>2</sub>), 39.2 (CH<sub>3</sub>) ppm. MS (ESI, CH<sub>3</sub>CN): *m/z* (%) = 253.22 (74) [Cu<sub>2</sub>L<sub>2</sub>]<sup>2+</sup>, 269.19 (100) [Cu<sub>2</sub>L<sub>2</sub>·O<sub>2</sub>]<sup>2+</sup>; the simulated isotopic pattern of the ions matches the experimental pattern.

**Complex 5b:** Yield 48%. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.67 (s, 4 H, CH), 7.55 (s, 4 H, CH), 4.12 (m, 8 H, CH<sub>2</sub>), 3.37 (s, 12 H, CH<sub>3</sub>), 2.50 (m, 4 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 177.2 (NCN), 125.7 (CH), 122.5 (CH), 47.5 (CH<sub>2</sub>), 39.0 (CH<sub>3</sub>), 31.3 (CH<sub>2</sub>) ppm. MS (ESI, CH<sub>3</sub>CN): *m*/*z* = 283.21 (100) [Cu<sub>2</sub>L<sub>2</sub>·O<sub>2</sub>]<sup>2+</sup>; the simulated isotopic pattern of the ion matches the experimental pattern. C<sub>22</sub>H<sub>32</sub>Cu<sub>2</sub>F<sub>12</sub>N<sub>8</sub>P<sub>2</sub> (825.56): calcd. C 31.99, H 3.91, N 13.57; found C 32.04, H 4.06, N 13.34.

**Complex 6b:** Yield 45%. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 7.75$  (s, 4 H, CH), 7.66 (s, 4 H, CH), 6.56 (br. s, 4 H, CH<sub>2</sub>), 4.26 (m, 4 H, CH), 1.00–2.00 (m, 40 H, CH<sub>2</sub>) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 176.7$  (NCN), 123.7 (CH), 121.3 (CH), 62.2 (CH<sub>2</sub>), 64.2 (CH), 25–41 (CH and CH<sub>2</sub>) ppm. MS (ESI, CH<sub>3</sub>CN): m/z (%) = 375.43 (100) [Cu<sub>2</sub>L<sub>2</sub>]<sup>2+</sup>, 749.33 (56) [Cu<sub>2</sub>L<sub>2</sub>]<sup>+</sup>, 769.34 (56) [Cu<sub>2</sub>L<sub>2</sub>·HF]<sup>+</sup>, 895.16 (57) [Cu<sub>2</sub>L<sub>2</sub>PF<sub>6</sub>]<sup>+</sup>; the simulated isotopic pattern of the ions matches the experimental pattern.

**Decomposition of Ethyl Diazoacetate:** The copper(I) complex (10  $\mu$ mol) was placed in a 50 mL three-necked round-bottomed flask under an inert atmosphere. Dichloromethane (20 mL for complex 1, 5 mL for complex 3b) was subsequently added and the mixture was stirred until dissolution of the catalyst was complete. Ethyl diazoacetate (EDA, 0.25 mmol for complex 1, 1 mmol for complex 3b) was then added and the mixture was stirred at room temperature for 24 h. Aliquots (0.2 mL) of the reaction mixture were removed after 2, 5 and 24 h, evaporated to dryness and analysed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> using 4-bis(trimethylsilyl)benzene as internal standard.

General Procedure for the Cyclopropanation Reactions: The copper(I) complex (10  $\mu$ mol) was placed in a 50 mL three-necked round-bottomed flask under an inert atmosphere. Styrene (1.25 mmol for complex 1, 10 mmol for the others) and dichloromethane (20 mL for complex 1, 5 mL for the others) were subsequently added and the mixture was stirred until dissolution of the catalyst was complete. The diazo compound was then added (0.25 mmol in one portion for complex 1, 1 mmol in 1 mL dichloromethane over 1 h with a syringe pump for the others) and the mixture was stirred at room temperature for 24 h. After this time the reaction mixture was evaporated to dryness and analysed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> using 4-bis(trimethylsilyl)benzene as internal standard. The products were identified by comparison of the <sup>1</sup>H NMR spectra with literature data.<sup>[28]</sup>

General Procedure for the Aziridination Reactions: The nitrene source (0.263 mmol), the copper(I) complex (2.63 µmol for the dinuclear complexes and 1.75 µmol for the trinuclear complexes, 2 mol-% [Cu]), the olefin, if solid (5–50 equiv. with respect to the nitrene source), and, if appropriate, 4 Å molecular sieves (100 mg) were placed in a 50 mL two-necked round-bottomed flask under an inert atmosphere. The flask was thermostatted at the desired temperature (25 or 50 °C) and solvent (4 mL) and olefin, if liquid (5–50 equiv. with respect to the nitrene source), were then added.

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The mixture was maintained at the desired temperature whilst stirring for 17 h. After this time, the reaction mixture was evaporated to dryness and analysed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> using 4-bis(trimethylsilyl)benzene as internal standard. The products were identified by comparison of the <sup>1</sup>H NMR spectra with literature data.<sup>[22a,29]</sup>

General Procedure for the Nitrene Insertion Reactions: The nitrene source (0.263 mmol) and the copper(I) complex **3b** (13.1 µmol, 10 mol-% [Cu]) were placed in a 50 mL two-necked round-bot-tomed flask under an inert atmosphere. The flask was thermostatted at the desired temperature (50 or 70 °C) and nitrene acceptor (4 mL) was then added. If appropriate, molecular sieves (4 Å, 100 mg) were added at this stage. The mixture was maintained at the desired temperature whilst stirring for 17 h. After this time the reaction mixture was evaporated to dryness and analysed by <sup>1</sup>H NMR spectroscopy in CDCl<sub>3</sub> using 4-bis(trimethylsilyl)benzene as internal standard. The products were identified by comparison of the <sup>1</sup>H NMR spectra with literature data.<sup>[30]</sup>

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- For general references on NHC ligands, see: a) S. Diez-Gonzalez (Ed.), N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools, RSC Catalysis Series, RSC, Cambridge, 2010; b) C. S. J. Cazin (Ed.), N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis, in: Catalysis by Metal Complexes, vol. 32, Springer, Heidelberg, Germany, 2010; c) F. E. Hahn, M. C. Jahnke, Angew. Chem. 2008, 120, 3166; Angew. Chem. Int. Ed. 2008, 47, 3122; d) F. Glorius (Ed.), N-Heterocyclic Carbenes in Transition Metal Catalysis, in: Topics in Organometallic Chemistry, vol. 21, Springer, Heidelberg, Germany, 2007; e) S. P. Nolan (Ed.), N-Heterocyclic Carbenes in Synthesis, Wiley-VCH, Weinheim, Germany, 2006.
- [2] a) S. Diez-Gonzalez, N. Marion, S. P. Nolan, *Chem. Rev.* 2009, 109, 3612–3676; b) S. Diez-Gonzalez, S. P. Nolan, *Aldrichim. Acta* 2008, 41, 43–51; c) S. Diez-Gonzalez, S. P. Nolan, *Synlett* 2007, 2158–2167.
- [3] a) A. J. Arduengo, H. V. R. Dias, J. Calabrese, F. Davidson, Organometallics 1993, 12, 3405–3409; b) H. G. Raubenheimer, S. Cronje, P. H. van Rooyen, P. J. Olivier, J. G. Toerien, Angew. Chem. 1994, 106, 687; Angew. Chem. Int. Ed. Engl. 1994, 33, 672–673; c) H. G. Raubenheimer, S. Cronje, P. J. Olivier, J. Chem. Soc., Dalton Trans. 1995, 313–316.
- [4] J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* 2009, 109, 3561–3598.
- [5] a) J. A. Mata, M. Poyatos, E. Peris, *Coord. Chem. Rev.* 2007, 251, 841–859; b) A. T. Normand, K. J. Cavell, *Eur. J. Inorg. Chem.* 2008, 2781–2800; c) M. Poyatos, J. A. Mata, E. Peris, *Chem. Rev.* 2009, 109, 3677–3707.
- [6] X. J. Wan, F. B. Xu, Q. S. Li, H. B. Song, Z. Z. Zhang, *Inorg. Chem. Commun.* 2005, 8, 1053–1055.
- [7] R. McKie, J. A. Murphy, S. R. Park, M. D. Spicer, S. Zhou, Angew. Chem. 2007, 119, 6645–6648; Angew. Chem. Int. Ed. 2007, 46, 6525–6528.
- [8] P. L. Arnold, A. C. Scarisbrick, A. J. Blake, C. Wilson, *Chem. Commun.* 2001, 2340–2341.
- [9] a) X. Hu, K. Meyer, J. Organomet. Chem. 2005, 690, 5474– 5484; b) X. Hu, Y. Tang, P. Gandzel, K. Meyer, Organometallics 2003, 22, 612–614; c) X. Hu, I. Castro-Rodriguez, K.

Meyer, Organometallics **2003**, *22*, 3016–3018; d) X. Hu, I. Castro-Rodriguez, K. Meyer, J. Am. Chem. Soc. **2003**, *125*, 12237– 12245.

- [10] a) C. Tubaro, A. Biffis, E. Scattolin, M. Basato, *Tetrahedron* 2008, 64, 4187–4195; b) C. Tubaro, A. Biffis, E. Scattolin, M. Basato, G. Papini, C. Santini, E. Alvarez, S. Conejero, *Dalton Trans.* 2009, 7223–7229.
- [11] I. V. Shishkov, F. Rominger, P. Hofmann, *Dalton Trans.* 2009, 1428–1435.
- [12] K. Matsumoto, N. Matsumoto, A. Ishii, T. Tsukuda, M. Hasegawa, T. Tsubomura, *Dalton Trans.* 2009, 6795–6801.
- [13] S. Sabiah, C.-S. Lee, W.-S. Hwang, I. J. B. Lin, Organometallics 2010, 29, 290–293.
- [14] C. Ellul, G. Reed, M. F. Mahon, S. I. Pascu, M. K. Whittlesey, Organometallics 2010, 29, 4097–4104.
- [15] a) V. Jurkauskas, J. P. Sadighi, S. L. Buchwald, Org. Lett. 2003, 5, 2417–2420.
- [16] a) M. R. Fructos, T. R. Belderrain, M. C. Nicasio, S. P. Nolan, H. Kaur, M. M. Díaz-Requejo, P. J. Pérez, J. Am. Chem. Soc. 2004, 126, 10846–10847; b) R. E. Gawley, S. Narayan, Chem. Commun. 2005, 5109–5111; c) M. M. Díaz-Requejo, P. J. Pérez, J. Organomet. Chem. 2005, 690, 5441–5450; d) M. R. Fructos, P. de Fremont, S. P. Nolan, M. M. Díaz-Requejo, P. J. Pérez, Organometallics 2006, 25, 2237–2241; e) M. M. Díaz-Requejo, P. J. Pérez, Chem. Rev. 2008, 108, 3379–3394.
- [17] a) B. M. Trost, G. Dong, J. Am. Chem. Soc. 2006, 128, 6054–6055; b) R. Liu, S. R. Herron, S. A. Fleming, J. Org. Chem. 2007, 72, 5587–5591; c) Q. Xu, D. H. Appella, Org. Lett. 2008, 10, 1497–1500; d) B. M. Trost, G. Dong, Chem. Eur. J. 2009, 15, 6910–6919; e) S. Simonovic, A. C. Whitwood, W. Clegg, R. W. Harrington, M. B. Hursthouse, L. Male, R. E. Douthwaite, Eur. J. Inorg. Chem. 2009, 1786–1795.
- [18] I. J. B. Lin, C. S. Vasam, Coord. Chem. Rev. 2007, 251, 642– 670.
- [19] X.-Q. Xiao, G.-X. Jin, Dalton Trans. 2009, 9298-9303.
- [20] S. Ahrens, A. Zeller, M. Taige, T. Strassner, *Organometallics* 2006, 25, 5409–5415.
- [21] I. I. F. Boogaerts, G. C. Fortman, M. R. L. Furst, C. S. J. Cazin, S. P. Nolan, Angew. Chem. Int. Ed. 2010, 49, 8674–8677.
- [22] a) D. A. Evans, M. M. Faul, M. T. Bilodeau, J. Am. Chem. Soc. 1994, 116, 2742–2753; b) W. Zhang, N. H. Lee, E. N. Jacobsen, J. Am. Chem. Soc. 1994, 116, 425–426; c) S.-M. Au, J.-S. Huang, W.-Y. Yu, W.-H. Fung, C.-M. Che, J. Am. Chem. Soc. 1999, 121, 9120–9132; d) M. M. Díaz-Requejo, P. J. Pérez, M. Brookhart, J. L. Templeton, Organometallics 1997, 16, 4399–4402.
- [23] H. M. L. Davies, E. G. Antoulinakis, Org. React. 2004, 57, 1-326.
- [24] Y. Yamada, T. Yamamoto, M. Okawara, *Chem. Lett.* 1975, 361–362.
- [25] C. A. Quezada, J. C. Garrison, M. J. Panzner, C. A. Tessier, W. J. Young, *Organometallics* **2004**, *23*, 4846–4848.
- [26] F. M. Nachtigall, Y. E. Corilo, C. C. Cassol, G. Ebeling, N. H. Morgon, J. Dupont, M. N. Eberlin, *Angew. Chem.* 2008, 120, 157–160; *Angew. Chem. Int. Ed.* 2008, 47, 151–154.
- [27] K. Okuyama, J. Sugiyama, R. Nagahata, M. Asai, M. Ueda, K. Takeuchi, J. Mol. Catal. A 2003, 203, 21–27.
- [28] a) J. S. Yadav, B. V. S. Reddy, P. Narayana Reddy, Adv. Synth. Catal. 2004, 346, 53–56; b) J. P. Deleux, G. Leroy, J. Weiler, Tetrahedron 1973, 29, 1135–1144.
- [29] a) Y. Cui, C. He, J. Am. Chem. Soc. 2003, 125, 16202–16203;
  b) G. Y. Gao, J. D. Harden, X. P. Zhang, Org. Lett. 2005, 7, 3191–3193.
- [30] a) L. He, J. Yu, J. Zhang, X.-Q. Yu, Org. Lett. 2007, 9, 2277– 2280; b) A. K. Chakrabarti, A. Kondaskar, S. Rudrawar, Tetrahedron 2004, 60, 9085–9091.

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