

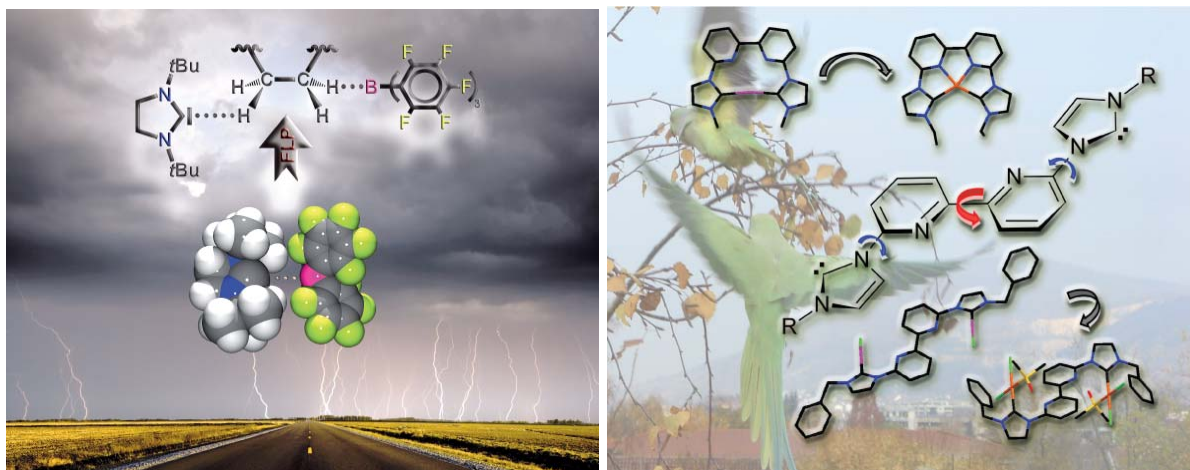
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N-Heterocyclic Carbenes

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Trinuclear copper(I) complexes with triscarbene ligands: catalysis of C–N and C–C coupling reactions†

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Novel synthetic routes for the preparation of trinuclear copper(I) complexes with triscarbene ligands are presented, which yield higher purity products than the one previously described. The first crystal structure of one of these complexes is reported and confirms the expected structure. The trinuclear complexes proved to be efficient catalysts of Ullmann-type reactions as well as of the Sonogashira reaction.

Introduction

Metal-catalyzed carbon–carbon and carbon–heteroatom coupling reactions have become one of the most important reaction classes in chemical synthesis.¹ Most of these reactions however need a noble metal catalyst, hence the cost may easily become a shortcoming of their technological application. Therefore, a flourishing area of research is the quest for catalysts made out of non-noble metals which exhibit comparable catalytic efficiency. In this connection, copper species are well-established promoters of C–N and C–O couplings (the so-called Ullmann, Goldberg and related reactions).² These applications were recently made much more technologically appealing by the discovery of novel catalysts and reaction protocols that allowed for high catalytic efficiency at comparatively mild temperatures.³ Moreover, copper species have also been occasionally proposed as an alternative to the more commonly employed Pd-based catalysts for technologically relevant C–C couplings, such as the Heck,⁴ Suzuki⁵ and Sonogashira⁶ reactions.

We have recently started a research program aimed at the synthesis, characterisation and catalytic application of copper(I) complexes with di- and tri-*N*-heterocyclic carbene (NHC) ligands.⁷ In particular, we have reported on the synthesis of complex **1** (Fig. 1) for which we have proposed a trinuclear structure in which every copper atom is coordinated to two imidazolin-2-ylidene rings, belonging to two different tricarbenic units.⁸

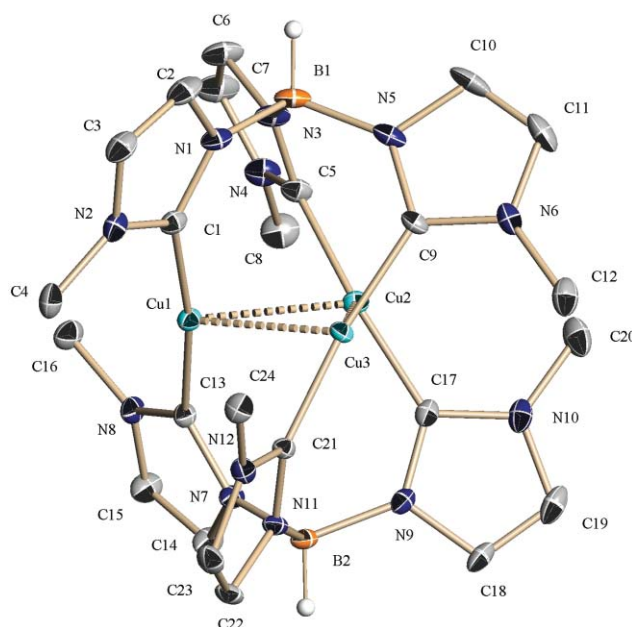


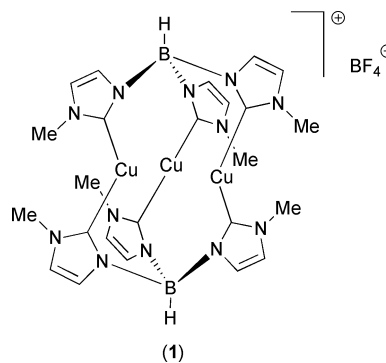
Fig. 1 ORTEP drawing (30% ellipsoids probability) of complex **1-PF₆**. Hydrogen atoms and PF₆[−] anion have been removed for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–Cu(2) 2.7049(10), Cu(2)–Cu(3) 2.6965(9), Cu(1)–Cu(3) 2.6169(9), Cu(1)–C(1) 1.915(5), Cu(1)–C(13) 1.912(5), Cu(2)–C(5) 1.901(6), Cu(2)–C(17) 1.905(5), Cu(3)–C(21) 1.908(5), Cu(3)–C(9) 1.908(5); C(1)–Cu(1)–C(13) 171.1(2), C(5)–Cu(2)–C(17) 168.0(3), C(21)–Cu(3)–C(9) 170.2(2).

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† Electronic supplementary information (ESI) available: Full listing of atomic coordinates, bond distances and angles, and CIF file for complex **1-PF₆**. CCDC reference number 726192 for complex **1-PF₆**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906730b



This complex exhibits an excellent catalytic activity in the Ullmann coupling between azoles or phenols and aryl halides; furthermore, its reactivity in these reactions is quite different from that of other copper-based catalytic systems, in that it exhibits an anomalous dependence on the nature of the substituents on the aryl halide.

In this contribution, we report alternative synthetic procedures for the preparation of trinuclear copper(I) complexes of this kind, the first crystal structure of one such complex which definitely confirms the expected structure, and further studies on the reactivity of these complexes in C–N, C–O and also C–C coupling reactions.

Results and discussion

Complex **1** was previously obtained upon deprotonation of the tris-imidazolium tetrafluoroborate salt precursor with *n*-BuLi and subsequent reaction with [CuBr(PPh₃)₃], following a procedure already employed by Fehlhammer *et al.* for the preparation of chelate triscarbene complexes of other transition metals.⁹ This procedure provides the product in good yield, but also in impure form, since the product invariably contains trace amounts of triphenylphosphine and, most notably, large amounts of inorganic salts that cannot be removed by recrystallisation.

Nevertheless, it has been possible to obtain a crystal structure of complex **1** bearing a PF₆[−] instead of a BF₄[−] counterion (complex **1-PF₆**). The complex was obtained through a modification of the same synthetic route, upon deprotonation of the trisimidazolium triflate precursor with *n*-BuLi and subsequent reaction with [Cu(NCMe)₄](PF₆). This synthetic procedure makes it easier to purify the complex from inorganic salts. Crystals suitable for an X-ray diffraction study were grown by slow diffusion of concentrated solutions of the complex in diethyl ether. Gratifyingly, the structure (Fig. 1 and Table 1) fully confirms the one previously proposed by some of us on the basis of spectroscopic and analytical methods.⁸ The asymmetric unit consists of two independent molecules of almost identical metrical parameters and only one of them will be discussed here.

Complex **1-PF₆** crystallizes in a *P* $\bar{1}$ space group with a *D*₃ symmetry. Each copper atom is bicoordinated with 1.91 Å (average) Cu–C_{carbene} bond distances, similar to other previously described NHC–Cu complexes.¹⁰ The C_{carbene}–Cu–C_{carbene} angles of 170° (average) are slightly deviating from linearity, in contrast with the results reported by Meyer on complex [Cu₃(TIME^{Me})₂](PF₆)₃ (TIME^{Me} = 1,1,1-tris[(3-methylimidazol-2-ylidene)-methyl]ethane) which shows C–Cu–C angles close to 178°. This deviation from linearity might be ascribed to the geometric constraints exerted by the less flexible tris(imidazolin-2-ylidene)borate ligand compared to the TIME^{Me} ligand. Furthermore, the C_{carbene}–Cu–C_{carbene} plane is not perpendicular to the plane of the three copper atoms, similarly to a recently reported structure of a polynuclear silver(I) complex with two hexacarbene ligands.¹¹ Consequently, the complex exhibits a twisted, chiral structure (Fig. 2). The imidazolin-ylidene rings in the complex are characterised by metrical parameters comparable to other reported Cu–NHC complexes showing N–C_{carbene} distances of 1.36 Å (average) and N–C_{carbene}–N angles of 105° (average). These bond distances and angles are usually different from those of the imidazolium precursors of the carbene ligands, but due to the lack

Table 1 Crystal data and structure refinement for complex **1-PF₆**

Empirical formula	C ₂₄ H ₃₂ B ₂ Cu ₃ F ₆ N ₁₂ P	
Formula weight	845.83	
Temperature/K	173(2)	
Wavelength/Å	0.71073	
Crystal system	Triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	<i>a</i> = 14.1659(6) Å	α = 86.910(1)°
	<i>b</i> = 15.2179(8) Å	β = 76.367(1)°
	<i>c</i> = 16.9149(9) Å	γ = 73.979(1)°
Volume/Å ³	3405.8(3)	
<i>Z</i>	4	
Density (calculated)/mg m ^{−3}	1.650	
Absorption coefficient/mm ^{−1}	1.973	
<i>F</i> (000)	1704	
Crystal size/mm ³	0.25 × 0.13 × 0.13	
Theta range for data collection	1.77 to 30.42°	
Index ranges	−20 ≤ <i>h</i> ≤ 14, −21 ≤ <i>k</i> ≤ 21, −24 ≤ <i>l</i> ≤ 24	
Reflections collected	55191	
Independent reflections	20099 [<i>R</i> (int) = 0.0306]	
Completeness to theta = 30.42°	98.4%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7735 and 0.7382	
Refinement method	Full-matrix-block least-squares on <i>F</i> ²	
Data/restraints/parameters	20099/0/865	
Goodness-of-fit on <i>F</i> ²	1.060	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> _i = 0.0462, <i>wR</i> ₂ = 0.1281	
<i>R</i> indices (all data)	<i>R</i> _i = 0.0623, <i>wR</i> ₂ = 0.1459	
Largest diff. peak and hole/e Å ^{−3}	1.447 and −0.956	

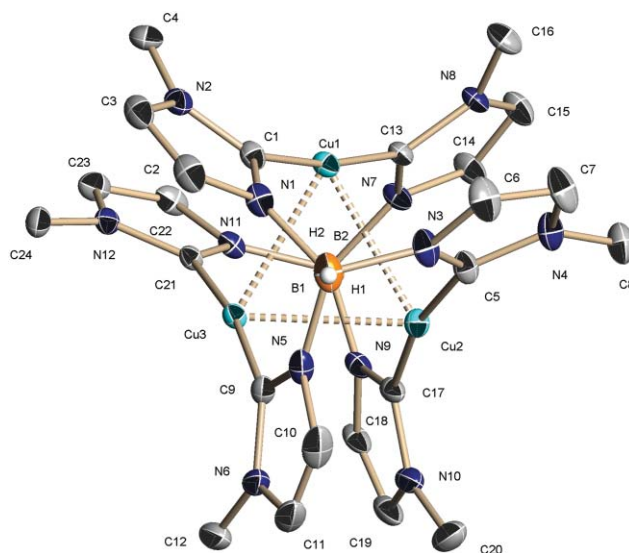


Fig. 2 Top view of complex [Cu₃{HB(MeIm)₂}]₂(PF₆).

of the X-ray structure of the precursor employed in this case no definite conclusions can be drawn.

The Cu–Cu separations of 2.71, 2.70 and 2.62 Å exceed the sum of atomic radii (2.56 Å). Some authors have suggested that bond

distances in the range 2.4–2.7 Å may indicate the existence of some weak d^{10} – d^{10} closed-shell metal–metal interactions,¹² although two of the distances fall beyond the upper limit commonly considered for such interactions (2.68 Å).

We have also developed an alternative synthetic pathway for copper(I) triscarbene complexes, based upon the synthesis of silver(I) triscarbene complexes as intermediates with subsequent transmetallation to copper(I) centers. The transmetallation from a silver(I) NHC complex, synthesized by treatment of the imidazolium salt with Ag_2O , is a useful coordination method in the preparation of chelating *N*-heterocyclic carbene complexes.¹³ In most cases this procedure can be carried out under aerobic conditions, and the process has been successfully applied to a variety of metal centers.¹⁴ Moreover, an efficient synthetic procedure for the preparation of the silver(I) triscarbene precursors has been very recently reported by our group.¹⁵

Using the intermediate silver triscarbene complex **2** and $\text{CuBr}(\text{SMe}_2)$ as the copper source, complex **3** could be prepared (Fig. 3), which was not accessible through the previously reported deprotonation route, presumably due to the acidity of the benzylic protons. The complex was obtained in lower yield compared to the original synthesis of **1** by the deprotonation route, but in higher purity.

The copper(I) complex **3** has been characterized by analytical and spectral data. The infrared spectrum carried out on the solid sample showed all the expected bands: weak absorptions in the range 3029–3115 cm^{-1} are due to the azolyl ring C–H stretchings, a medium absorption at 1554 cm^{-1} is related to ring “breathing” vibrations and a medium absorption at 2431 cm^{-1} is due to the B–H stretching. The ^1H -NMR spectra of the copper complex supports the proposed structure. The product appears spectroscopically pure, and exhibits signals slightly upfield compared to the parent tris-azolium salt as well as to the silver precursor **2**; as expected, the C_2 –H signal is absent. Correspondingly, the ^{13}C -NMR spectrum shows the characteristic coordinated C_2 signal at δ ca. 177 ppm, well downfield from the corresponding signal of the tris-azolium salt (δ ca. 140.52). Furthermore, there is only a single set of signals for the imidazolin-2-ylidene rings in both the ^1H and ^{13}C NMR spectra, which indicates a highly symmetric structure. It is interesting to remark that the benzylic protons in the complex give an AB system in the ^1H NMR spectrum, which is indicative of their diastereotopicity and consequently supports the hypothesis

that the complex is chiral, as in the case of the related complex **1**. The ESI-MS spectrum of **3** gives a unique ion at 1157 m/z ; this confirms that **3** does indeed possess an oligomeric structure, with two triscarbene ligands and three metal centers. No fragment ions were observed, showing that the copper(I) complex was stable under the conditions of the electrospray ionization and detection. However, despite the spectroscopic purity determined by NMR, the elemental analysis of complex **3** was lower than expected; the data however could be reasonably fitted by taking into account the presence of residual AgBr , which was experimentally confirmed by ICP-AAS analysis. Consequently, on the basis of these data and of their similarity to the spectral data of complex **1**, we also attributed to complex **3** a similar structure in which every copper atom is coordinated to two imidazolin-2-ylidene rings, belonging to two different triscarbene units, each one therefore coordinating in η^1 fashion (Fig. 3).

We have attempted to extend this synthetic procedure to the preparation of other copper(I) triscarbene complexes with bulkier wingtip substituents at the triscarbene ligand such as mesityl or *t*-butyl. Unfortunately, although we were able to detect formation of the desired complex in the reaction mixture by ESI-MS, we have been unable up to now to isolate the products in satisfactory yield and purity.

We have evaluated the catalytic efficiency of complex **3** in the Ullman coupling of aryl halides with azoles and phenols. The obtained data were compared with those obtained with the previously reported complex **1**. In parallel, we were also keen to perform a comparative evaluation of the catalytic activity of other copper–NHC complexes not possessing the trinuclear structure of **1** and **3**, in order to determine the effect of the trinuclear structure on the catalytic performance of the complex.¹⁶ Therefore, we have included in our studies an evaluation of the catalytic potential of the commercially available copper carbene complex **4** conventionally termed IPrCuCl .¹⁷ This complex is arguably the most efficient copper carbene complex catalyst known to date and it has proven useful for several reactions.¹⁸ To the best of our knowledge, though, no investigation on its catalytic efficiency in Ullmann-type couplings is available, although a related complex bearing a ligand with a saturated *N*-heterocyclic ring was recently reported to exhibit good catalytic activity for the amination of aryl and heteroaryl bromides with ammonia.¹⁹

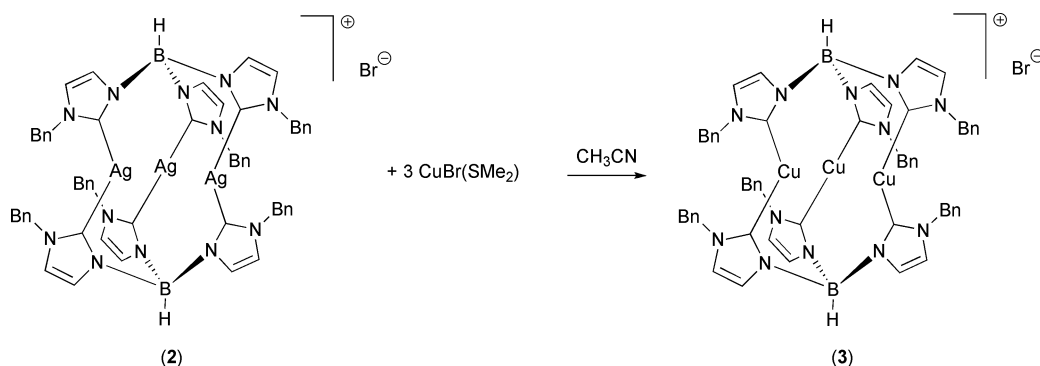
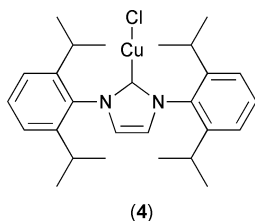


Fig. 3 Reaction scheme for the synthesis of complex **3**.



The tests were run under the optimised reaction conditions already employed with catalyst **1**, that is, using 3 mol% Cu in DMSO with Cs₂CO₃ as the base at 100 °C for 24 h.⁸ Only in the case of catalyst **4**, which turned out to be the least efficient catalyst in initial tests, the amount of catalyst was set to 10 mol% Cu in order to achieve conversions comparable with the trinuclear complexes. The results are reported in Table 2.

It can be appreciated that complexes **1** and **3** exhibit comparable catalytic activity, in that they are able to efficiently convert activated aryl iodides, bromides or even chlorides at a comparatively low temperature (100 °C). On the other hand, the observed yields were found to decrease smoothly on going from activated, electron-poor aryl halides to more electron-rich ones. The abnormally low reactivity of aryl halides bearing weakly electron-donating groups, previously recorded using complex **1**⁸ (see *e.g.* Table 2, entries 1–3 and 6–8), was not observed with complex **3**.

Complex **4** displayed a good catalytic activity, which was however significantly lower than that of the trinuclear complexes. In fact, 10 mol% catalyst (10 mol% Cu) was required to reach conversions attainable with just 1 mol% (3 mol% Cu) trinuclear complex. Therefore, the trinuclear structure of complexes **1** or **3** seems to make a positive contribution to the catalytic efficiency of such complexes in Ullmann-type reactions.

The catalytic activity of complexes **1**, **3** and **4** has also been studied in the Sonogashira coupling of aryl halides with terminal alkynes. The results are reported in Table 3.

Initially, we investigated the standard reaction between iodoacetophenone and phenylacetylene, and screened with the various catalysts for different solvents (DMSO, DMF) and bases (TBAA, Cs₂CO₃) in order to determine the best reaction conditions. The reaction time was set at a constant of 24 h and was not optimized further. Quite interestingly, the mononuclear complex **4** turned out to be completely inactive for the reaction under all the employed reaction conditions. On the other hand, complexes **1** and **3** turned out to be active. Cs₂CO₃ was found to be the best base in all cases. Concerning the solvent, DMSO provided slightly better results in terms of conversion (Table 3, entries 2 and 3), particularly with catalyst **3**. We soon realised however that DMSO also promoted an unwanted side reaction such as the homocoupling of the arene (Table 3, entry 3). An analogous but much more pronounced solvent effect was observed by us in the catalysis of the Sonogashira reaction by silver–polycarbene complexes.¹⁵ In that case, switching from DMF to DMSO as solvent led to a complete reversal of the reaction selectivity from the cross-coupling product to the alkyne homocoupling product.

We then investigated the scope of the synthetic procedure with respect to both the aryl halide and the alkyne. Interestingly, the reactivity of complex **3** with the more electron-rich aryl iodides dropped considerably in both DMF and DMSO (Table 3, entries 4–7), whereas the catalytic performance of complex **1** was still good, leading to a quantitative conversion in

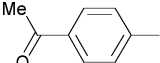
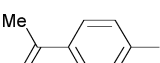
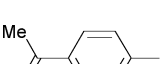
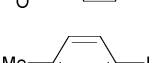
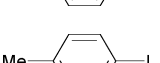
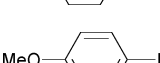
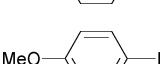

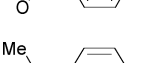
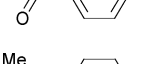
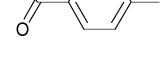
Table 2 Arylation of azoles and phenols with different copper(I) NHC complexes

Entry	ArX +	HN-azole	[Cu] 3–10 mol% Cs ₂ CO ₃ , DMSO	ArN-azole		
				Yield (%) ^a		
				1 ^{b,c}	3 ^c	4 ^d
1				93	nd	90
2				21	nd	54
3				50	nd	23
4				73	nd	60
5				44	nd	50
6				>99	85	86
7				20	93	nd
8				50	33	67
9				70	54	86
10				50	24	57
11				>99	>99	nd
12				>99	>99	85
13				15	nd	9
14				70	nd	86
15				50	nd	71

Reaction conditions: see Experimental section; ^a yields determined by ¹H NMR spectroscopy; ^b literature data, see ref. 6; ^c 3 mol% Cu; ^d 10 mol% Cu.

the case of 4-iodotoluene and to a 54% yield in the case of 4-iodoanisole.

Table 3 Sonogashira reactions with different copper(I) NHC complexes

$\text{ArX} + \text{H}-\text{C}\equiv\text{C}-\text{R}' \xrightarrow[\text{base, solvent}]{[\text{Cu}] 3 \text{ mol}\%} \text{Ar}-\text{C}\equiv\text{C}-\text{R}'$					
Entry	Aryl halide	Alkyne	Base Solvent	Yield (%) ^a	
				1	3
1		H—C≡C—Ph	TBAA DMF	95	nd
2		H—C≡C—Ph	Cs ₂ CO ₃ DMF	>99	42
3		H—C≡C—Ph	Cs ₂ CO ₃ DMSO	90 (5)	97 (1)
4		H—C≡C—Ph	Cs ₂ CO ₃ DMF	>99	9
5		H—C≡C—Ph	Cs ₂ CO ₃ DMSO	nd	0
6		H—C≡C—Ph	Cs ₂ CO ₃ DMF	54	8
7		H—C≡C—Ph	Cs ₂ CO ₃ DMSO	93	4
8		H—C≡C—Ph	Cs ₂ CO ₃ DMF	10	nd
9		H—C≡C—Ph	Cs ₂ CO ₃ DMF	0	nd
10		H—C≡C—C ₆ H ₁₃	Cs ₂ CO ₃ DMF	41	nd
11		H—C≡C—CO ₂ Et	Cs ₂ CO ₃ DMF	37	nd

Reaction conditions: see Experimental section; ^a Yields determined by ¹H NMR spectroscopy.

The reactivity of complex **1** towards aryl bromides and chlorides was low, but this appears at present to be a common feature of all copper-based catalytic systems for this reaction. Finally, a preliminary evaluation of the reactivity of complex **1** in the reaction with other alkynes was performed. Moderate yields were obtained upon reaction of 4-iodoacetophenone with both an electron-rich substrate such as 1-octyne and an electron-poor one such as ethyl propiolate. Given the lower reactivity of these alkynes in the Sonogashira reaction compared to phenylacetylene, these initial results represent a good starting point for further optimisation.

Conclusions

Trinuclear copper(I) complexes with triscarbene ligands are efficient catalysts of Ullmann-type reaction with activated aryl halide

reagents, as well as of the Sonogashira reaction with aryl iodides. Two novel routes for the preparation of these complexes have been described, which obtain the complexes in good yields and purity even in the presence of C–H acidic substituents on the ligand. Finally, the structure of one of these complexes has been elucidated and found to exhibit some peculiar features (*e.g.* chirality) with interesting implications for the development of a new generation of triscarbene complexes with tailored ligand structure and for novel applications.

Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of 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. Complexes [Cu(NCMe)₄](PF₆)²⁰ and [Ag₃{HB(BnIm)₃}₂](Br) **2**¹⁵ were prepared according to literature procedures. NMR spectra were recorded on a Bruker Avance 300 MHz (300.1 MHz for ¹H and 75.5 MHz for ¹³C); chemical shifts (δ) are reported in units of ppm relative to the residual solvent signals. ¹¹B NMR has been referenced to NaBH₄. IR spectra were run on a Perkin-Elmer FT-IR Spectrum 100. Electrospray mass spectra (ESI-MS) were obtained in positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer. The crystal structure was determined on a Bruker-AXSX8 kappa diffractometer.

Synthesis of hydrotris(3-methyl-imidazolium-1-yl)borate bis(triflate)

MeOTf (2.7 cm³, 23.7 mmol) was added at room temperature to a suspension of potassium hydrotris(imidazolyl)borate (2 g, 7.9 mmol) in 50 cm³ of CH₂Cl₂. The reaction mixture was stirred for 14 h. The solvent was then decanted and the white residue washed with THF (3 × 20 cm³) and diethyl ether (3 × 50 cm³) and dried under vacuum (76% yield). δ_B (100 MHz; CD₃CN; NaBH₄) 38.3 (d, *J*_{B-H} = 124 Hz); δ_H (300 MHz; CD₃CN; Me₄Si) 3.81 (s, 9H, CH₃), 7.22 and 7.38 (s, 3H each, =CH), 8.29 (s, 3H, NCH); δ_C (75 MHz; CD₃CN; Me₄Si) 36.3 (CH₃), 124.2, 125.5 (=CH), 140.0 (NCH). ESI-MS (positive ions, CH₃OH): *m/z* 129 ([M]²⁺).

Synthesis of complex [Cu₃{HB(MeIm)₃}₂](PF₆) **1**-PF₆

n-BuLi (1.6 M, 1 cm³, 1.62 mmol) was added to a cooled (−78 °C) suspension of the hydrotris(3-methyl-imidazolium-1-yl)borate bis(trifluoromethanesulfonate) (0.3 g, 0.54 mmol) in 4 cm³ of Et₂O. The mixture was allowed to warm to 0 °C and was further stirred at this temperature for 3 h and then for a further 3 h at room temperature. The solvent was removed under vacuum and the triscarbene formed was used without further purification (the ¹H-NMR spectrum in CD₃CN of the crude reaction mixture shows signals identical to those published by Fehlhammer,⁹ indicating quantitative formation of the triscarbene). 0.3 g (0.80 mmol) of [Cu(NCMe)₄](PF₆) were mixed with the freshly prepared triscarbene, cooled at −10 °C and 3 cm³ of MeCN were slowly added. The reaction mixture was warmed to room temperature and stirred for 3 h after which the solvent was removed under vacuum. The obtained off-white solid was washed with Et₂O

(2 × 20 cm³) and cold THF (2 × 3 cm³). Extraction with CH₂Cl₂ (3 × 20 cm³) yielded the complex [Cu₃{HB(MeIm)₃}₂](PF₆) in 41% yield. Crystals can be obtained by slow diffusion of diethyl ether in an acetonitrile solution of [Cu₃{HB(MeIm)₃}₂](PF₆). δ_B (100 MHz; CD₃CN; NaBH₄) 41.2 (d, J_{B-H} = 115 Hz); δ_H (300 MHz; CD₃CN; Me₄Si) 3.40 (s, 18H, CH₃), 7.04 and 7.13 (s, 6H each, =CH); δ_C (300 MHz; CD₃CN; Me₄Si) 38.3 (CH₃), 121.9 and 127.1 (=CH), 178.4 (NCH). Anal. calcd. for C₂₄H₃₂B₂Cu₃F₆N₁₂P: C, 34.1; H, 3.8; N, 19.9%. Found: C, 33.7; H, 3.6, N, 19.5%.

Synthesis of complex [Cu₃{HB(BnIm)₃}₂](Br) 3

A solution of CuBr(SMe₂) (0.145 g in 15 cm³ of anhydrous acetonitrile) was added to a solution of [Ag₃{HB(BnIm)₃}₂](Br) 2 (0.5 g in 15 cm³ of anhydrous acetonitrile). The reaction mixture was stirred at room temperature for 3 h, whereby a light-grey solid formed in suspension. The suspension was filtered and the filtrate was evaporated to dryness to yield a white solid, which was treated with methanol (2 cm³) and ether (5 cm³), filtered and dried. Yield 30%. δ_H (300 MHz; (CD₃)₂SO; Me₄Si) 7.41 (s, 1H, CH), 7.33 (s, 1H, CH), 7.12 (m, 1H, Ar), 6.98 (m, 2H, Ar), 6.85 (m, 2H, Ar), 5.30–5.70 (AB system, 2H, CH₂). δ_C (75 MHz; (CD₃)₂SO; Me₄Si) 176.7 (NCN), 137.6, 128.8, 127.6 and 127.0 (Ar), 128.0 and 120.9 (CH), 54.3 (CH₂). ν_{max}/cm⁻¹: 3029w, 3062w, 3115w (CH), 2431 m (BH), 1554 m (C=C + C=N). ESI-MS (positive ions, CH₃OH), m/z 1157 [Cu₃{HB(BnIm)₃}₂]⁺. Anal. calcd. for [Cu₃{HB(BnIm)₃}₂](Br)·0.5AgBr: C, 54.1; H, 4.2; N, 12.6; Cu, 14.3; Ag, 4.0%. Found C, 53.0; H, 3.6; N, 12.3; Cu, 14.0; Ag, 5.4%.

General procedure for C–N and C–O coupling reaction

The required amount of complex 3 (1 mol%, 3 mol% [Cu]) or 4 (10 mol%), the aryl halide (1.0 mmol), the base (2.0 mmol), the nitrogen- or oxygen-containing substrate (1.5 mmol), and 3 cm³ of solvent were placed in a Schlenk tube, previously evacuated and filled with argon. The resulting mixture was heated under stirring to 100 °C for 24 h and subsequently cooled to room temperature, diluted with dichloromethane (10 cm³) and filtered. The filtrate was washed with a 5% w/w aqueous KHCO₃ solution (2 × 10 cm³) and water (2 × 10 cm³), and finally dried over MgSO₄. The solvent was removed under vacuum to yield the crude product, which was analyzed by NMR to determine the yield. The products were identified by comparison with characterisation data found in the literature.²¹

General procedure for the Sonogashira reaction

An oven-dried Schlenk tube equipped with a magnetic stirring bar was charged with aryl halide (0.25 mmol), the base (0.3 mmol, 1.2 equiv.) and catalyst (3 mol% copper for complexes 1 and 3, 10% mol for complex 4). The tube was closed with a rubber septum, evacuated and filled with argon. The alkyne (0.3 mmol, 1.2 equiv.) and solvent (2 cm³) were subsequently injected, and the tube was placed in an oil bath preheated at 110 °C. The reaction mixture was stirred at 110 °C for 24 h, after which it was cooled to room temperature and diluted with 5 cm³ dichloromethane. The resulting suspension was filtered and the solvent was removed under vacuum to yield the crude product, which was analyzed by NMR to determine conversions and yields. The products were

identified by comparison with characterisation data found in the literature.^{6f}

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