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COMMUNICATION

A Simple Access to Transition Metal Cyclopropenylidene Complexes

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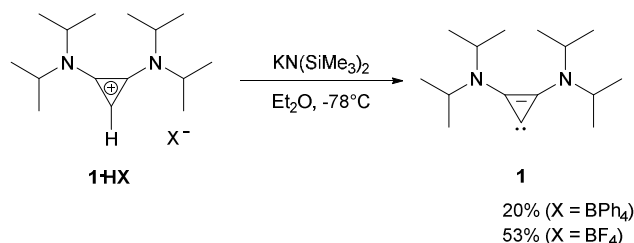
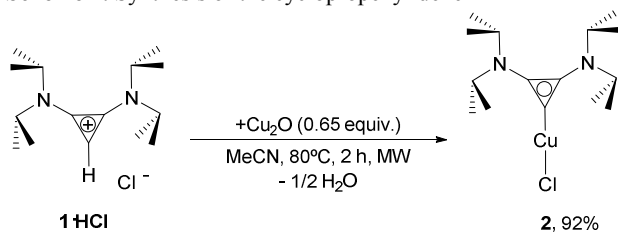
We report the first example of BAC-Cu complex (BAC = bis(diisopropylamino)cyclopropenylidene) and its use as a carbene-transfer reagent, allowing access to Au-, Pd-, Ir- and Rh-BAC compounds. Catalytic experiments show the high activity of the [CuCl(BAC)] complex in Click chemistry.

Cyclopropenylidenes, the simplest aromatic ring system displaying a carbene centre, are amongst the most discussed compounds within the carbocyclic carbene family.¹ Since the early 1970's,^{1a} various transition metal complexes bearing cyclopropenylidene ligands have been prepared. Their synthesis has been achieved *via* oxidative addition of dihalocyclopropenes,^{2d-f,3} by the reaction of cyclopropenium salts or lithium adducts,^{2d-f,4} or using deoxygenation, desulfurization and deselenization routes.^{2e,5} However these methodologies require harsh conditions that are not conducive to the generation of libraries of complexes.^{1a} The isolation of the cyclopropenylidene **1** in 2006⁶ (Scheme 1) allowed to broaden the number of complexes available,^{1a,7} but Group 11 remains to date scarcely studied, with no example of gold and copper compounds, and only one example of a silver derivative.⁸ As a consequence, the catalytic activity of cyclopropenylidene metal complexes has remained rather unexplored⁹ compared to that of the *N*-heterocyclic carbene (NHC) counterparts.¹⁰

As part of our ongoing efforts to develop straightforward synthetic accesses to NHC transition metal complexes, we have shown that Cu-NHC compounds could be obtained by simple reaction of the conjugate acid of NHCs with Cu₂O,¹¹ and subsequently used as NHC-transfer reagents.¹² Such a methodology provides a versatile synthetic access to a library of NHC complexes, without the formation of the highly reactive free carbene at any stage.¹³ Herein, we report that this synthetic strategy can also be applied to the cyclopropenylidene series, allowing access to Au, Pd, Ir and Rh complexes. In addition, we show that a BAC-Cu complex has a high catalytic activity in an important catalytic transformation namely the [3+2] cycloaddition of azides and alkynes.

The first step of the synthetic strategy consists of the formation of a BAC-Cu^I complex by reaction of the cyclopropenium chloride **1·HCl** with Cu₂O under microwave heating.¹⁴ Indeed such a reaction benefits from short reaction times, and in this manner the desired

complex [CuCl(BAC)] **2** was obtained in 92% yield after 2 hours at 80°C in acetonitrile (Scheme 2). It is worth mentioning that **2** is perfectly air and moisture stable, which allows for a convenient work-up procedure.

Scheme 1. Synthesis of the cyclopropenylidene **1**⁶Scheme 2. Synthesis of the Cu-BAC complex **2**

The ¹H NMR spectrum of **2** at room temperature contains three broad signals corresponding to the ¹Pr groups. Upon cooling the solution to 240 K, the signals significantly sharpen to the expected doublets and multiplet (assigned to CH₃ and CH, respectively). Such a dynamic behaviour has already been observed for the free carbene **1** and its corresponding salt **1·HBF₄**.^{6a} The free activation energy for site exchange of the ¹Pr groups was found to be 53 kJ/mol for the free carbene and 75 kJ/mol for the cyclopropenium salt. In the case of complex **2**, a ΔG[‡] of 63.5 kJ/mol was experimentally determined and is likely to be related to a similar dynamic process (see ESI for details). The structure of **2** was unambiguously confirmed by a single crystal X-ray diffraction study (Fig. 1).¹⁵ Complex **2** has a pseudo-linear geometry with a C11-Cu1-C1 angle of 175.6(2)°. The C1-Cu1 bond distance [1.880(6) Å] is strikingly shorter than previously reported C-Cu bond lengths for IPr^{16a} (IPr = (*N,N'*-bis-[2,6-diisopropylphenyl]imidazol-2-ylidene) [1.953(8) Å] and 1,2,3-

triazol-4-ylidene CuCl complexes [1.9577(16) Å].¹⁷ This is in agreement with the strong σ -donor ability of BAC.^{1b,18,19} Its steric hindrance was assessed by calculating its % V_{Bur}^{20} at 1.9 Å and found to be 31.6%. This value is slightly larger than that of ICy [30.5%, ICy = (*N,N'*-bis-[dicyclohexyl]imidazol-2-ylidene)] and significantly smaller than that of two common NHCs, IMes [38.0%, IMes = (*N,N'*-bis-[2,4,6-trimethylphenyl]imidazol-2-ylidene)] and IPr (49.6%).^{16,21,22}

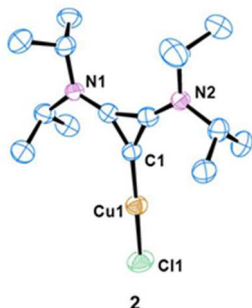
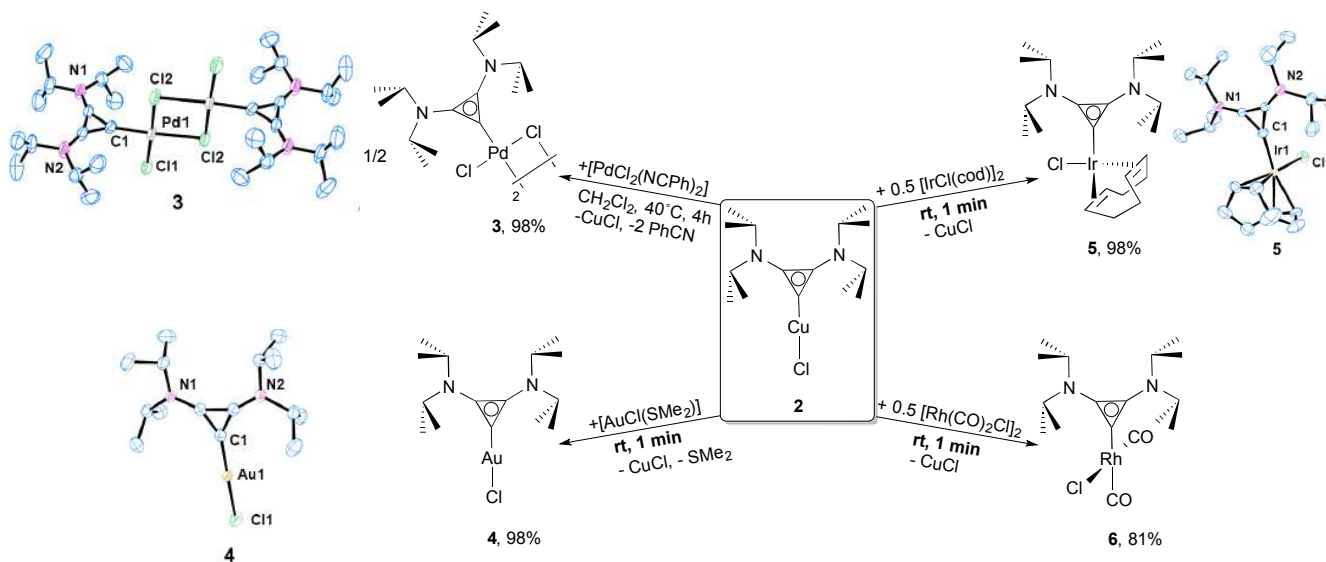


Figure 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu-C, 1.880(6); Cu-Cl, 2.107(2); C-Cu-Cl, 175.6(2).¹⁵

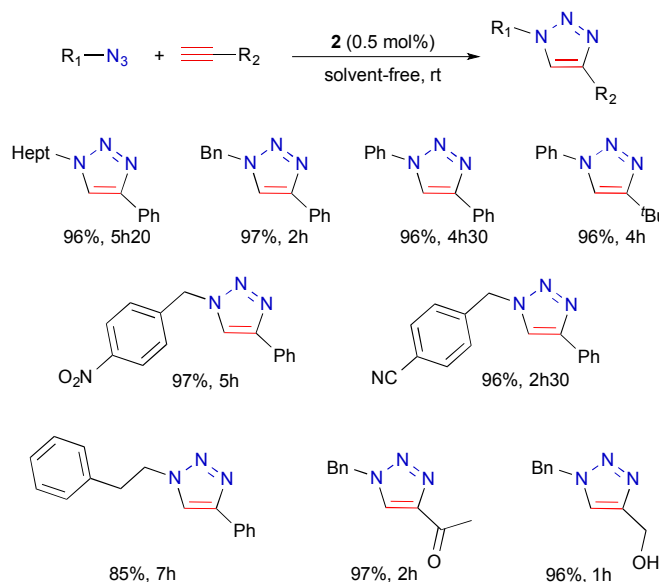
With complex **2** in hand, its ability to transfer the carbocyclic carbene was examined. Results are summarised in Scheme 3. Four metals (Rh, Ir, Pd, Au) belonging to Groups 9, 10 and 11 were selected to test the viability and versatility of the synthetic approach. In all cases, the transfer of the cyclopropenylidene occurs quantitatively and selectively. Spectacularly, for Au, Ir and Rh, the carbene transfer reaches completion within one minute at room temperature! In the case of palladium, while the transfer occurs quantitatively to form the targeted dimeric species, 4 hours and an operating temperature of 40°C are required to reach completion. This represents an outstandingly straightforward method compared

to previously reported procedures for palladium, that for example have made use of palladium black and the BAC·HCl salt (44% yield).^{1a,2d} The present methodology affords the desired complex with a 90% yield over the two synthetic steps. The NMR spectra of complexes **3-6** also show the presence of a dynamic phenomenon on the NMR timescale with ΔG^\ddagger for this process in the 50.0-64.2 kJ/mol range (see ESI for details). All complexes were obtained in micro-analytical purity and their structure was unambiguously confirmed by single crystal X-ray diffraction.¹⁵ The fact that [CuCl(BAC)] **2** and [AuCl(BAC)] **4** can be isolated in such a straightforward and pure manner is also a highlight of the approach. Indeed, all attempts to prepare **2** from the free BAC **1** failed. In the case of gold, similarly to the behaviour of the smallest CAAC carbenes,²³ BAC reacts with [AuCl(THT)] quantitatively affording the cationic [Au(BAC)₂]⁺ complex, regardless of the reagent stoichiometry used (see ESI for XRD data).

The key copper synthon **2** appeared a logical choice to initially evaluate the catalytic performance of transition metal BAC-containing complexes. We chose to test its catalytic activity in the [3+2] cycloaddition of azides and alkynes.²⁴ The reaction of heptyl azide with phenyl acetylene, under mild conditions (room temperature, solvent-free), using a low catalyst loading was investigated. Comparison with [CuCl(SIMes)] [SIMes = (*N,N'*-bis[2,4,6-(trimethyl)phenyl]imidazol-2-ylidene)], which represents the state-of-the-art²⁵ for such a reaction, showed that the cyclopropenylidene complex **2** has a higher catalytic activity than its NHC analogue. Relative kinetic profiling curves, under identical conditions, are presented in the ESI. Various substrates with a broad range of functionalities (-NO₂, -CN, -OH, -C=O) were tested. All desired compounds were obtained with an excellent isolated yield using 0.5 mol% of **2** under mild condition (solvent-free, 25°C) (Scheme 4).



Scheme 3. Transfer of cyclopropenylidene from copper to palladium, gold, iridium and rhodium. ORTEP representations of **3-5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): for **3**: Pd-C1, 1.926(4); Pd-Cl1, 2.2892(12); Pd-Cl2, 2.3311(12); Pd-Cl21, 2.4215(11); for **4**: Au-C1, 1.971(2); Au-Cl, 2.2843(7); C1-Au-Cl, 179.22(6); for **5**: Ir-C1, 2.011(2); Ir-Cl, 2.3596(7); C1-Ir-Cl, 91.75(6).¹⁵



Scheme 4. Scope of the [3+2] cycloaddition. Reaction conditions: **2** (0.5 mol%), azide (1.00 mmol), alkyne (1.10 mmol), 25°C, solvent-free.

Conclusions

In conclusion, the synthesis of the first cyclopropenylidene copper(I) complex and its use as an efficient carbene transfer reagent have been achieved. The approach results in the straightforward generation of Pd and Rh complexes, as well as the first isolation of Au and Ir complexes bearing a BAC ligand. Preliminary catalytic studies of the parent Cu-BAC complex are extremely promising and show that this ligand family may in certain instances surpass the NHC congeners. As one of the most important criteria for the development of catalysts is a versatile synthetic access to a library of complexes, we hope that the present work will encourage the study and development of highly active systems bearing cyclic carbenes other than the classical 5-membered heterocyclic standards.

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