N-Heterocyclic Carbenes

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Cyclic (Amino)(aryl)carbenes (CAArCs) as Strong σ-Donating and π-Accepting Ligands for Transition Metals

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: *Cyclic (amino)(aryl)carbenes (CAArCs) result from the replacement of the alkyl substituent of cyclic (alkyl)-(amino) carbenes (CAACs) by an aryl group. This structural modification leads to enhanced electrophilicity of the carbene center with retention of the high nucleophilicity of CAACs, and therefore CAArCs feature a small singlet–triplet gap. The isoindolium precursors are readily prepared in good yields, and deprotonation at low temperature, in the presence of [RhCl(cod)]$_2$ and [(Me$_2$S)AuCl] lead to air-stable rhodium and gold CAArC-supported complexes, respectively. The rhodium complexes promote the [3+2] cycloaddition of diphenylcyclopropenone with ethyl phenylpropiolate, and induce the addition of 2-vinylpyridine to alkenes by CH activation. The gold complexes allow for the catalytic three-component preparation of 1,2-dihydroquinolines from aniline and phenyl acetylene. These preliminary results illustrate the potential of CAArC ligands in transition-metal catalysis.*

The introduction of N-heterocyclic carbenes (NHCs) as ligands for transition metals has generated many breakthroughs in catalysis.[1–3] This is mostly the result of their strong σ-donor properties, which are due to the lower electronegativity of carbon compared to Group 15 and 16 elements. Several types of carbenes have been prepared,[4] but a wider diversity is still needed to match their phosphorus-based counterparts. It has been shown that cyclic (alkyl)-(amino)carbenes (CAACs) **B**[5,6] are both stronger σ-donors and π-acceptors than classical imidazolin-2-ylidene **A**[7] (Figure 1). Consequently, they feature a smaller singlet–triplet gap, and their complexes are more thermally robust, as a result of stronger metal–carbon bonds.[8] In addition, the peculiar electronic properties of CAACs **B** allow for the stabilization of transition-metal centers and main-group elements in different oxidation states,[9] including paramagnetic species,[10] and for the activation of small molecules and enthalpically strong bonds.[11]

Herein we report that the replacement of the alkyl substituent of CAACs by an aryl group[12] results in enhanced electrophilicity of the carbene center, with retention of the high nucleophilicity of CAACs. Thus, cyclic (amino)-(aryl)carbenes (CAArCs) **E** (Figure 1) feature an even smaller singlet–triplet gap than CAACs. To illustrate the utility of this novel type of singlet carbene, we show that air stable [(CAArC)RhCl(COD)] and [(CAArC)AuCl] complexes are efficient catalysts for several chemical processes.

The enhanced σ-donor and π-acceptor properties of CAACs **B** compared to classical NHCs **A** is due to replacement of one of the σ-withdrawing and π-electron donating amino substituent by a σ-donating alkyl group. Note that other strategies have been developed to lower the energy of the LUMO, as exemplified by the anti-Bredt NHCs **C**[13] and diamidocarbenes **D** (Figure 1).[14] Carbenes **C** are very comparable to CAACs, whereas in the case of **D**, the increased electrophilicity is accompanied by a significant decrease of the energy of the HOMO, and thus **D** are weak σ-donating ligands. We hypothesized that the simple replacement of the alkyl group of CAACs **B** by an aryl group will further enhance the electrophilicity of the carbene center, without disrupting the energy of the HOMO, which is ruled by the σ-effects. To test our hypothesis, we first carried out a computational study using density functional theory (DFT; B3LYP/TZVP). The results show that CAArC **E** displays a remarkably low-energy LUMO compared to that observed for CAAC **B** and concomitantly, it features a high energy HOMO as observed for CAACs. As a result, CAArCs have the smallest singlet–triplet gap of the series (41.5 kcal mol^{-1}) (Figure 1).

Encouraged by these results, we attempted the synthesis of CAArCs (Scheme 1). Starting from readily available primary amines **1** and 2-bromobenzaldehydes **2**, imines **3** are accessible in almost quantitative yields. Then, lithiation with *n*-butyl lithium, addition of benzophenone, followed by treatment with trifluoromethanesulfonic anhydride, afford the desired isoindolium salts **4** in a one-pot procedure. A wide range of CAArC precursors **4a**–**4i** were prepared in moderate to good yields by variation of the nitrogen substituent and aryl scaffold, including chiral isoindolium salt **4f** from an enantiomerically pure amine. Note that the synthesis can be conducted on a multiple-gram scale (**4a**), and the salts can be isolated by filtration without further purification.

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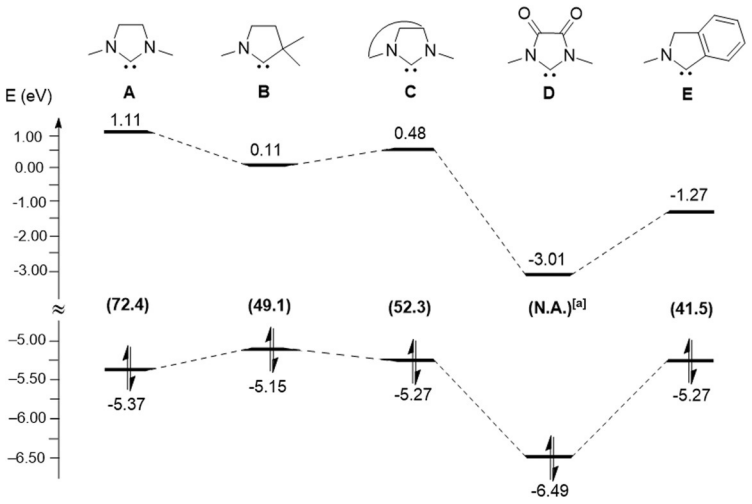
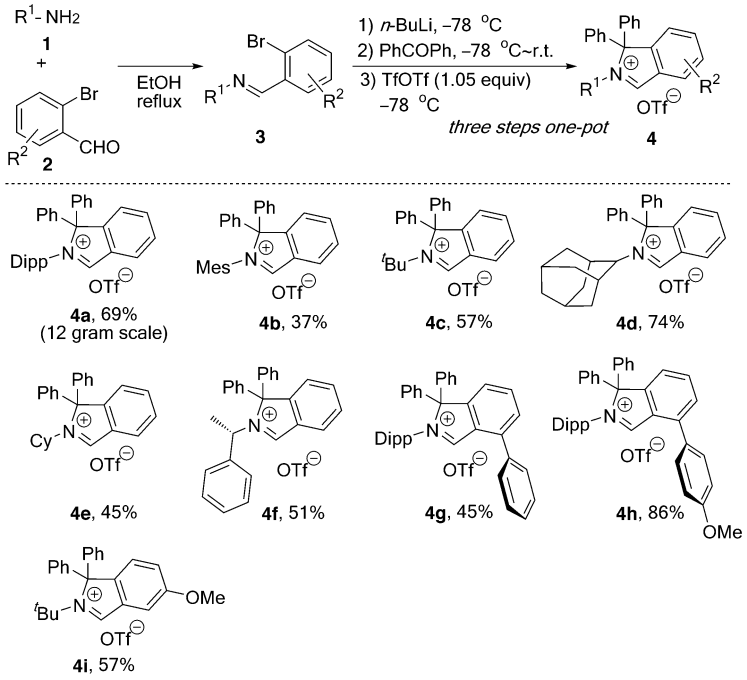


Figure 1. Energy (eV) of the HOMO and LUMO of carbenes **A**–**E**, and singlet–triple gap in parentheses (kcal mol^{-1}) of carbenes **A**–**C** and **E** calculated at the B3LYP/TZVP level of theory. [a] The triplet state of **D** is a biradical involving the carbonyl groups, and thus the singlet–triplet gap cannot be compared with those of the other carbenes.



Scheme 1. Synthesis of a variety of substituted isoindolium salts **4**.

With the isoindolium salts in hand, we attempted to prepare the free CAArCs by low-temperature deprotonation using different bases such as MN(SiMe$_3$)$_2$ (M = K, Na, Li), KO*t*Bu, and NaH, but in all cases a complex mixture was obtained. However, addition of S_8 at −78 °C to a THF solution of **4a** and LiN(SiMe$_3$)$_2$ led to the corresponding thioamide **5** in 62% yield, suggesting that the free CAArC **Ea** is formed but has only a short lifetime even at low temperature (Figure 2a).

The optimized structure of **Ea** (Figure 2b) shows a planar isoindoline-type core. The N-C$_{carbene}$-C$_{aryl}$ angle (105.0 °C) and the C$_{carbene}$–C$_{aryl}$ bond length (1.473 Å) are smaller and shorter, respectively, than those of CAACs (106.5 °C and 1.516 Å).[6a] The HOMO is a lone-pair of electrons that is mainly localized on the carbene center (Figure 2c). The LUMO is a π-type orbital that is distributed predominantly on the isoindolium motif, confirming that the aryl substituent serves as a π-acceptor, increasing the electrophilicity of the carbene center (Figure 2d).

Importantly, despite the instability of free CAArCs, treatment of isoindolium salts **4a–e** and **4i** with LiN(SiMe$_3$)$_2$ at −78 °C, in the presence of [RhCl(cod)]$_2$, leads to air-stable [(CAArC)RhCl(cod)] complexes **6a–e** and **6i**, which were isolated in moderate to good yields (43–82%; Scheme 2).[16] The structure of **6a** was ascertained by a single-crystal X-ray diffraction study (Figure 3). The ^{13}C NMR signal for the carbene carbon of complexes **6** appeared as a doublet around δ = 250 ppm ($^1J_{CRh} \approx 45$ Hz), which is significantly downfield and upfield shifted compared to those observed for rhodium complexes of NHCs (δ ≈ 190 ppm)[17] and CAACs (δ ≈ 278 ppm), respectively.[18] Bubbling carbon monoxide through dichloromethane solutions of **6a**,**b**,**d**,**e** gave the *cis*-chlorodicarbonylrhodium complexes **7a**,**b**,**d**,**e** in almost quantitative yield (Scheme 2). The average IR stretching frequencies for the carbonyl ligands (2032–2036 cm^{-1}) indicate that the overall donor properties of CAArCs are superior to those of NHCs (2039–2041 cm^{-1}), and similar to those of CAACs (2036 cm^{-1}).[19] Interestingly, the ^{77}Se NMR chemical shift of derivatives **8c** and **8d** (δ ^{77}Se: 601 and 616 ppm, respectively), prepared following the same procedure as for the sulfur adduct **5** but employing selenium, indicate that CAArCs are even more π-accepting than the bis(diisopropylamino)carbene (δ ^{77}Se: 593 ppm)[7c,d] and therefore than CAACs and of course NHCs[7a] (Scheme 3).

CAArC supported gold complexes can also be prepared by treatment of isoindolium salts with LiN(SiMe$_3$)$_2$ at −78 °C in the presence of [(Me$_2$S)AuCl]. [(CAArC)AuCl] complexes **9a–9d** were isolated in 37–88% yields (Scheme 4). The signals for the carbene carbon are upfield shifted by 20 ppm compared to those of [(CAAC)AuCl], but again greatly downfield shifted compared to those of NHCs. A single-crystal X-ray diffraction study of **9d** shows that gold is in a nearly linear environment (C$_{carbene}$-Au-Cl angle 177.5°) with a C$_{carbene}$–Au bond length of 1.998(38) Å (Figure 3, right).

As a proof of principle, we briefly tested the influence of the CAArC ligands on the catalytic activity of rhodium and gold centers. By using 2 mol% of rhodium complex **6a**, the [3+2] cycloaddition of diphenylcyclopropenone and ethyl phenylpropiolate proceeded at 110 °C, giving the cyclopenta-

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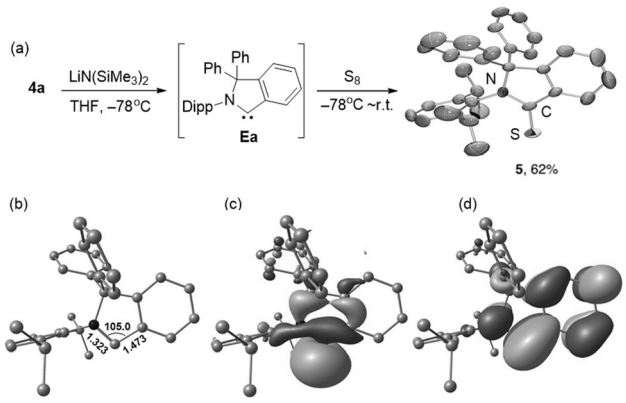
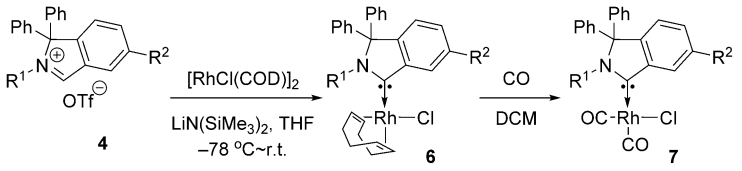


Figure 2. a) Trapping reaction with elemental sulfur and solid-state structure of **5** with thermal ellipsoids set at 30% probability (all hydrogen atoms are omitted for clarity).[15] b) Optimized structure of carbene **Ea** at the B3LYP/Def2SVP level of theory. c) HOMO of carbene **Ea** (isovalue = 0.03). d) LUMO of carbene **Ea** (isovalue = 0.03).



6a: R^1 = Dipp, R^2 = H: 69%
6b: R^1 = Mes, R^2 = H: 70%
6c: R^1 = *t*-Bu, R^2 = H: 82%
6d: R^1 = Ad, R^2 = H: 71%
6e: R^1 = Cy, R^2 = H: 48%
6i: R^1 = *t*-Bu, R^2 = OMe: 43%

Scheme 2. Synthesis of CAArC-ligated rhodium complexes **6** and **7**.

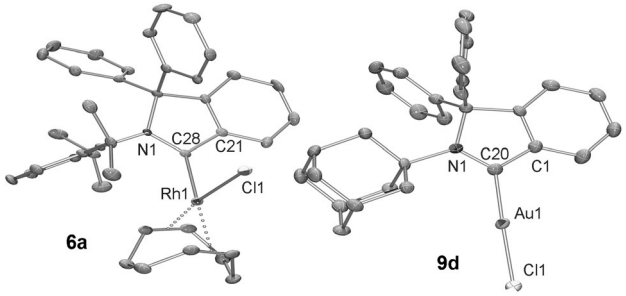
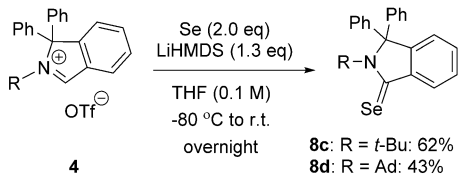
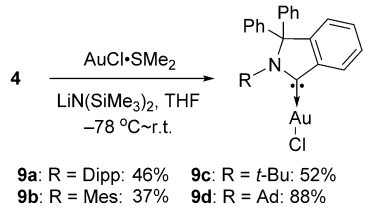


Figure 3. X-ray structures of complexes **6a** and **9d** with thermal ellipsoids set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **6a**, N1-C28 1.334(42), C28-C21 1.473(32), C28-Rh1 2.008(31), Rh1-Cl1 2.397(1); N1-C28-C21 105.5(2), N1-C28-Rh1 129.6(2), C21-C28-Rh1 124.1(2); **9d**, N1-C20 1.324(45), C20-C1 1.455(51), C20-Au1 1.998(38), Au1-Cl1 2.290(10); N1-C20-C1 108.8(3), N1-C20-Au1 129.8(3), C1-C20-Au1 121.3(3), C20-Au1-Cl1 177.5(11).



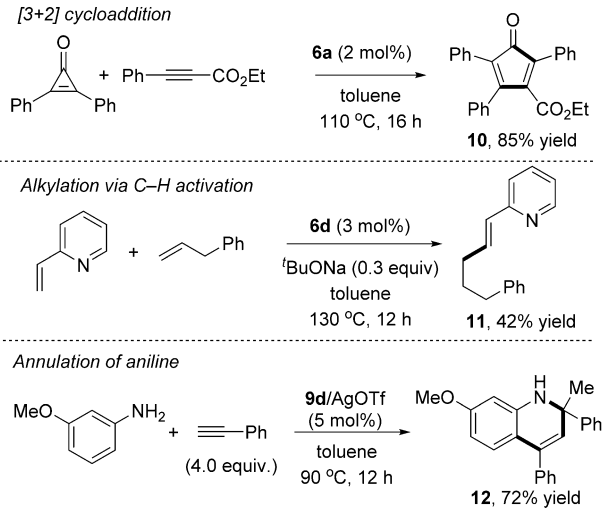
Scheme 3. Synthesis of CAArC-ligated seleno-amides.



Scheme 4. Synthesis of CAArC-supported gold complexes.

2,4-dienone derivative **10** in 85% yield after 16 h (Scheme 5).[20] Note that this result compares favorably with those obtained with NHC-Rh complexes (74% yield after 18 h at 110 °C).[20b] Recently, C–H activation reactions have emerged as one of the most powerful tools in the preparation of synthetically useful molecules.[21] To our delight, the *N*-adamantyl-substituted [(CAArC)RhCl(cod)] (**6d**) activates the terminal vinyl-CH bond of 2-vinylpyridine, which allows for the addition to an alkene as shown by the formation of **11**.[22] Lastly, the CAArC-ligated gold complex **9d** allows for the catalytic three-component preparation of 1,2-dihydroquinoline **12** from aniline and phenyl acetylene.[23]

In summary, isoindolium salts, which can be decorated at will on the nitrogen and on the aryl scaffold, are readily available in large quantities. They are precursors of five-membered carbenes that we name CAArCs. These species feature both strong σ-donating and π-accepting properties, and consequently a small singlet–triplet gap. Despite their instability, they can be used as ligands for transition metals, and our preliminary studies indicate that their peculiar electronic properties give rise to catalytically active metal complexes.



Scheme 5. The application of CAArC-ligated rhodium and gold complexes as active catalysts for the promotion of [3+2] cycloaddition, C–H bond activation, and three-component preparation of 1,2-dihydroquinoline.

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Experimental Section

General procedure for the preparation of **4**: *n*BuLi (5.25 mmol, 1.05 equiv) was added dropwise at −78 °C to an ether solution (14 mL) of mines **3** (5 mmol), and the resulting mixture was stirred at the same temperature for 1 h. Subsequently, a solution of diphenyl ketone (5.25 mmol, 1.05 equiv) in ether (3 mL) was added and the mixture warmed to room temperature and stirred for another 30 min. Then trifluoromethanesulfonic anhydride (5.25 mmol, 1.05 equiv) was added dropwise at −78 °C. The reaction mixture was stirred at room temperature for 1 h. After filtration, the solid was washed with Et_2O (10 × 3 mL), and extracted with CH_2Cl_2 (30 mL). The organic solvent was removed by evaporation to give the corresponding isoindolium salts **4** as white or pale yellow solids.

5: THF (2 mL) was added at −78 °C to a dry Schlenk flask containing **4a** (0.2 mmol, 116 mg), $LiN(SiMe_3)_2$ (0.2 mmol, 37 mg), and S_8 (0.2 mmol, 6.4 mg). The reaction mixture was warmed to room temperature and stirred overnight. The volatiles were removed under reduced pressure and thioamide **5** was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50:1) (57 mg, 62 %).

General procedure for the synthesis of CAArC-Rh complexes **6**: THF (4 mL) was added at −78 °C to a dry Schlenk flask containing isoindolium triflate **4** (0.42 mmol, 1.05 equiv), $LiN(SiMe_3)_2$ (0.44 mmol, 1.1 equiv, 73 mg), and $[Rh(COD)Cl]_2$ (0.2 mmol, 98.6 mg). After stirring at room temperature for 6 h, the volatiles were removed under vacuum, and CAArC-Rh complexes **6** obtained after purification by column chromatography (petroleum ether/ethyl acetate) as orange powders.

General procedure for the synthesis of CAArC-Rh complexes **7**: Carbon monoxide was bubbled (60 min) at room temperature into a solution of rhodium complex **6** (50 mg) in dichloromethane (5 mL). The color of the solution changed from red to yellow. After removing the volatiles under vacuum, Rh-CO complexes **7** were obtained as yellow powders in almost quantitative yields.

General procedure for the synthesis of CAArC-Au complexes **9**: THF (2 mL) was added at −78 °C to a dry Schlenk flask containing isoindolium triflate **4** (0.21 mmol, 1.05 equiv), $LiN(SiMe_3)_2$ (0.22 mmol, 1.1 equiv, 37 mg), and $[AuCl(SMe_2)]$ (0.2 mmol, 58.6 mg). The mixture was warmed to room temperature and stirred for 6 h. After removing the volatiles under vacuum, CAArC-Au complexes **9** were obtained after purification by column chromatography (petroleum ether/ethyl acetate) as white or gray powders. Single crystals of **9d** were obtained from a THF/hexane solution at room temperature.

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