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Indol-2-ylidene (IdY): Ambiphilic N-heterocyclic Carbene Derived from Indole

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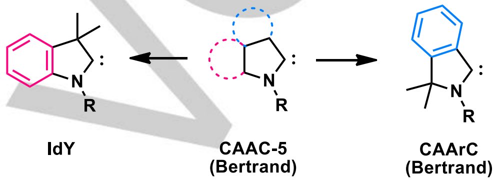
Abstract: The synthesis of ambiphilic N-heterocyclic carbene ligand, indol-2-ylidene (IdY, **A**), is described. A series of indolenium precursors (**2a**-**f**) were prepared on a gram scale in good yields. Trapping experiments with elemental selenium, $[RhCl(cod)]_2$ and CuCl provided the expected carbene adducts. Further computational and spectroscopic studies supported the ambiphilicity of IdY, which lies between cyclic (alkyl)(amino)carbenes (CAAC-5) and cyclic (amino)(aryl)carbene (CAArC). The copper complexes (**6**) show high percent buried volume (%V_{bur} = 58.1) and allow for carboboration of terminal alkynes within 30 minutes in a demonstration of synthetic utility with good yields and high regioselectivity.



- **Ambiphilic N-heterocyclic carbene**
- **Facile preparation & Gram scale synthesis**
- **Catalytic activity - Fast & High regioselective carboboration**

Figure 1. Strategies for increasing ambiphilicity of CAACs

Introduction

N-heterocyclic carbenes (NHCs) have been widely used in transition metal catalysis,[1] nanoparticle stabilization,[2] organocatalysis,[3] and main group chemistry[4] for three decades. One of the representative NHC scaffolds is imidazol-2-ylidene derived from imidazole - an abundant motif in natural products[5] and drug molecules.[6] Derivatization of the imidazole scaffold has been studied extensively and the synthetic studies[7] paved the way to development of new types of NHCs such as asymmetric NHCs[8], unsymmetric NHCs[9] and hemilabile NHCs.[10]

Cyclic (alkyl)(amino)carbenes (CAACs) are also receiving remarkable attention because of their ambiphilic properties.[11] The formal replacement of one nitrogen atom (π-electron donating, σ-withdrawing) by an alkyl group (σ-donating) makes these carbenes more electrophilic while retaining the nucleophilic character. In addition, the small HOMO-LUMO energy gap facilitates the smaller singlet-triplet (S/T) gap and it is an important factor in the context of reactivity of NHCs towards inert small molecules such as carbon monoxide.[12] Thanks to the ambiphilicity, CAAC ligands have been applied in diverse fields such as light emitting materials as CAAC-Cu complexes[13] and novel transition metal catalysis.[14] Furthermore, isolated CAACs were used for stabilization of paramagnetic species[4b, 15] and activation of small molecules or enthalpically strong bonds.[16]

Following the pioneering work on CAACs, other classes of ambiphilic NHCs have been developed. Ambiphilicity could be increased by structural modification strategies, such as replacement of the amino group by an amido group[17a, b, f, j, k] or an aryl group [17e, h, j, k]. Tuning the ring properties also increased the ambiphilicity [17c, d, g, i]. These ambiphilic NHCs exhibit unique reactivity such as exchange reactions at main group elements[17g] and (2+1) cycloaddition with dimethyl maleate or fumarate.[17k] In the same vein, the indole scaffold is a promising candidate for ambiphilic NHCs due to its cyclic (alkyl)(amino) fragment and the presence of an aryl group (**Figure 1**), in close resemblance to known ambiphilic NHCs.[17e, h, j, k] Moreover, because the indole motif is one of the most common N-heterocycles found in drug molecules and natural products[18] numerous synthetic methods[19] for the indole moiety have been reported to date. In this context, it is surprising that indole based NHCs had not yet been studied well. In order to fill this research gap we decided to explore the potential of indole derived NHCs and designed 'Indol-2-ylidene (IdY)'. Very recently, the Hahn group reported new N-alkylated, anionic and protic CAAC ligands based on the indole skeleton.[17l] Their indole-based CAAC ligands were successfully demonstrated as a new entity of auxiliary ligands in palladium and platinum complexes, which was prepared by oxidative addition method.

In the present study, we demonstrated (i) more diverse yet facile synthesis of indole-based CAAC ligands (IdY), (ii) fundamental studies of electronic properties of IdY with various tools, and (iii) the first transition metal catalysis of the ligand system. To enlighten the ambiphilicity and practical usage of IdY, various IdY precursors and their selenium, rhodium, and copper complexes were prepared. Thus, we successfully characterized the strong electrophilicity and tunable electronic structure of IdY by ^{77}Se

NMR and computational studies. In addition, the strong nucleophilicity of IdY was also successfully demonstrated by FT-IR analysis of IdY–Rh(CO)$_2$ complex. Most importantly, the catalytic carboboration of terminal alkynes by IdY–Cu complexes was described as the first catalysis of indole-based CAAC ligand.

Results and Discussion

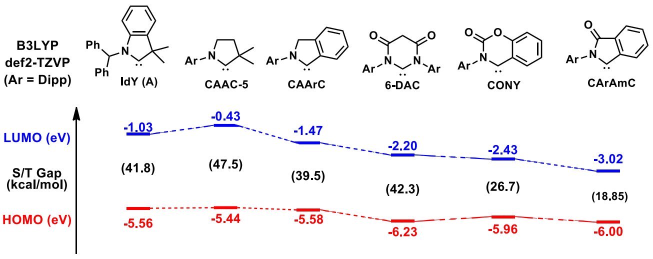
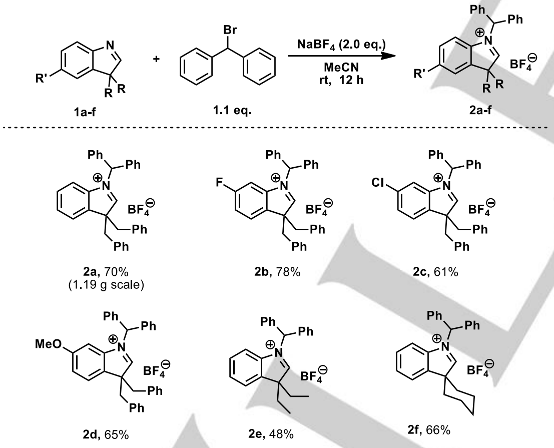


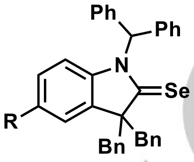
Figure 2. HOMO-LUMO Energy Level (eV) and Singlet-Triplet Transition Energy (kcal/mol) of NHCs Calculated at the B3LYP/def2-TZVP Level of Theory.

We started by performing a computational study to access electronic properties of IdY (**A**) and compare it with other hitherto reported ambiphilic NHCs (**Figure 2**). Hence, the HOMO energy level of **A** (-5.56 eV) is similar to the HOMO energy level of CAAC-5 (-5.44 eV), while the LUMO energy level of **A** (-1.03 eV) is intermediate between CAAC-5 (-0.43 eV) and cyclic (amino)(aryl)carbene (CAArC, -1.47 eV). Furthermore, the S/T gap of **A** (41.8 kcal/mol) is comparable to the one in CAArC (39.5 kcal/mol). The computational results therefore predicted the ambiphilic nature of **A**.



Scheme 1. Synthesis of substituted indolenium precursor (**2**). 'Bn' - benzyl

After confirming the ambiphilicity of **A** by computational studies, we proceeded to the synthesis of the indolenium salts (**2**), expected to provide **A** (**Scheme 1**) after deprotonation. The desired indolenium precursors (**2a**-**f**) were obtained in a simple two step reaction on a multigram scale in good yields. In the first step, the quaternary indolenine derivatives (**1**) were prepared following Fischer indole synthesis[19b] and Yang's indolenine synthesis[19c] (See SI). For the subsequent alkylation step, the sterically bulky benzhydryl group was chosen, since attempts to introduce the tBu group and aryl group commonly used for NHC into **1** are not accessible. Introduction of a bulky substituent on the nitrogen atom was supposed to improve the stability of **A** due to the steric protection of the carbene center.[20] Indeed, in the single crystal structure of **2f** the benzhydryl group is effectively shielding the C2 position (**Figure S1**). Since the aromatic ring substituent R can be varied easily, the LUMO energy levels of **A** can be tuned in a rational fashion (See SI).



3

Entry	R	^{77}Se NMR (ppm)
3a	H	542
3b	F	550
3c	Cl	570 [a]
3d	OMe	508

Figure 3. Carbene-selenium Adducts (**3**) and their ^{77}Se Chemical Shifts (solvent: (CD$_3$)$_2$CO). 'Bn' - benzyl group. [a]: in CDCl$_3$

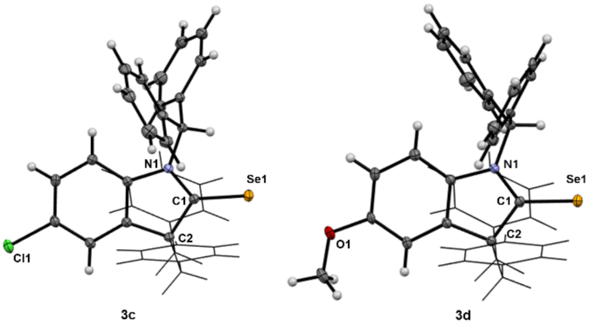


Figure 4. X-ray crystallographic analysis of compound **3c** and **3d**. Selected experimental bond lengths [Å] and angles [°]. **3c**: C1–N1 1.354(1), C1–C2 1.527(2), C1-Se1 1.801(1), N1–C1–C2 108.38(9); **3d**: C1–N1 1.344(5), C1–C2 1.530(5), C1–Se1 1.811(3), N1–C1–C2 108.3(3)

With the indolenium precursors (**2**) in hand, we attempted to generate the free **A** by deprotonation at -78 ˚C using various non-nucleophilic bases such as MN(SiMe$_3$)$_2$ (M=K, Na, Li), MOtBu (M=K, Na), LDA and NaH. Unfortunately, a complicated mixture of products was obtained in each case, in similarity to CAArCs. Being unable to obtain the free **A**, we performed trapping experiments with elemental selenium and were pleased to isolate the corresponding IdY-selenium adducts (**3** in **Figure 3**). The structures of **3c** and **3d** were clearly confirmed by a single crystal X-ray diffraction analysis (**Figure 4**). In the solid state structures, non-classical hydrogen bonding (NCHB) between C(sp^3)H and selenium was observed (See SI).[21]

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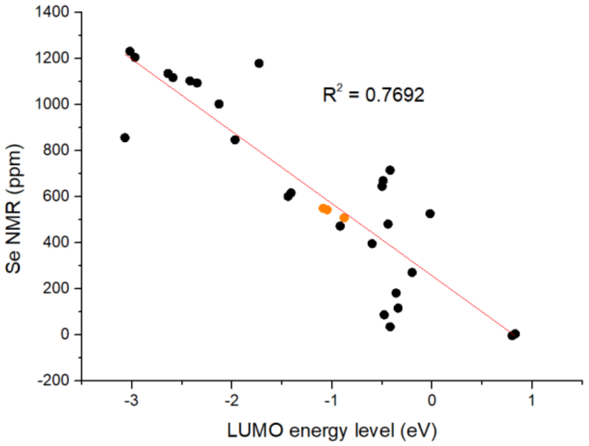
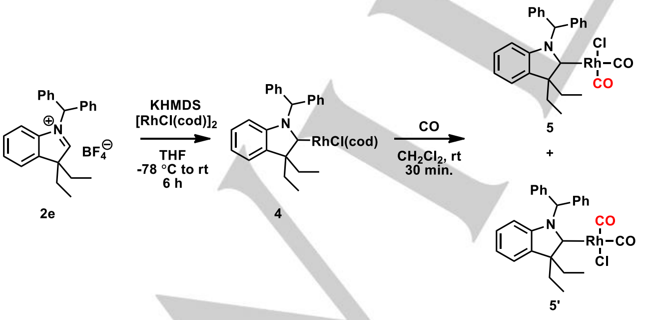


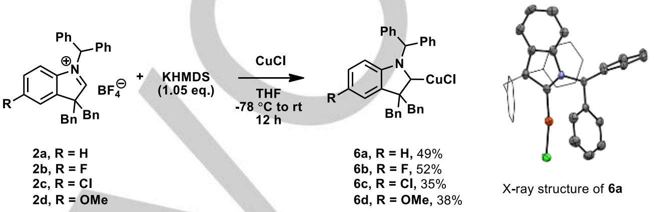
Figure 5. ^{77}Se NMR shifts (ppm, in d_6-acetone) of carbene-selenium adducts (data for **3** are in orange, all typical carbene-selenium adducts excluding **3** are in black) vs LUMO of the free NHCs (calculated at B3LYP/def2-TZVP)

To test the π-accepting properties of **A**, we measured the ^{77}Se NMR shifts of **3a**-**d** and compared them with values obtained for other NHCs as suggested by Ganter.[22] **3a** exhibits an intermediate ^{77}Se NMR shift (542 ppm) between CAAC-5 (481 ppm) and CAArC (601 ppm), as expected from the trend in LUMO energie levels (**Figure 2**). Indeed, plotting the LUMO energy level versus ^{77}Se NMR shifts of 29 analogues[17h, 22-23] (**Figure 5**, See SI) provides an approximate linear relation (R^2 = 0.7692). To explore further, we considered two conformers, **3a** and **3a'** (See SI), differing in the orientation of the benzhydryl group with respect to the selenium atom. ^{77}Se NMR shifts of 498 (**3a**) and 584 (**3a'**) ppm were predicted (BP86/def2-TZVP) and their average value (541 ppm) is in a good agreement with the experimental data (542 ppm). Since **3a'** is energetically accessible (+3.48 kcal/mol) in the solution phase, we suggest that **3a** and **3a'** exist in equilibrium in solution and the observed ^{77}Se NMR shift is a result of their rapid exchange. Moreover, the inductive effect of the R substituent on the aryl backbone was reflected by the ^{77}Se NMR shifts, with the most electron deficient **3c** having the highest (570 ppm) and electron rich **3d** the lowest (508 ppm) chemical shift (**Figure 3**).



Scheme 2. Synthesis of Rhodium Complexes of IdY (**4**, **5** and **5'**).

In addition to selenium trapping experiments, we demonstrated the presence of IdY free carbene by formation of IdY–metal complexes. In contrast to platinum and palladium complexes *via* oxidative addition of IdY precursor,[17l] IdY–Rh complex (**4**) could be synthesized by metalation of the *in-situ* generated free carbene (**Scheme 2**). This complex features a highly deshielded carbene–metal ^{13}C NMR peak (**4**: 276 ppm (J_{Rh-C} = 47.4 Hz) in $CDCl_3$), in close resemblance to the previously reported CAAC-5–metal complexes (CAAC-5–RhCl(cod): 278 ppm (J_{Rh-C} = 45.0 Hz) in $CDCl_3$). The carbonylation of **4** generated two inseparable rotamers (**5**, **5´**) which exhibited three different IR absorption signals at 1972, 1995 and 2074 cm^{-1} (ATR, **Figure S6**). DFT calculations allowed to assign these signals to the CO *cis* to IdY (red, **Scheme 2**) and *trans* to IdY (black, **Scheme 2**, see SI). The average values of the experimental data are 2023 cm^{-1} and 2035 cm^{-1}, indicating that **A** is a strong electron-donating ligand, comparable to CAAC-6 (ν^{av}_{CO} = 2029 cm^{-1}) and BICAAC (ν^{av}_{CO} = 2032 cm^{-1}).



Scheme 3. Synthesis of Copper complexes of IdY (**6**) and X-ray structure of **6a**. 'Bn' - benzyl group

Apart from the rhodium complexes, a series of IdY–CuCl complexes **6** was synthesized successfully (**Scheme 3**). Similar to **4** and **5**, these copper complexes showed highly deshielded carbene-metal peaks (**6a**: 246 ppm) in ^{13}C-NMR spectra, comparable to CAAC-5–CuCl (250 ppm)[24]. The complex **6a** could also be characterized by X-ray crystallographic analysis (see SI). In the solid state structure, the benzhydryl group effectively shields the copper center.

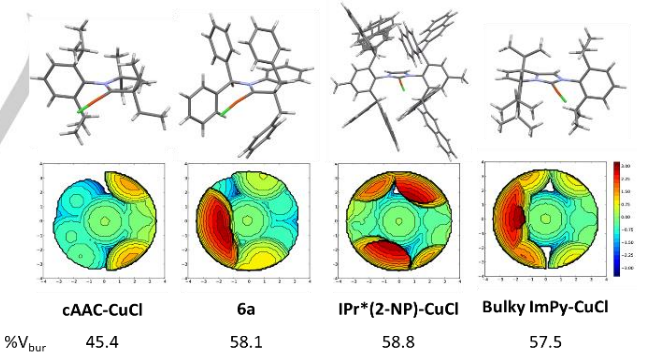
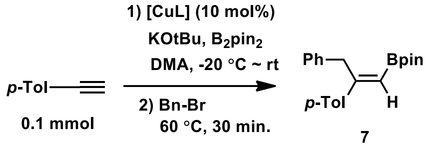


Figure 6. Structure of the CAAC-5–CuCl,[24b] **6a**, IPr*(2-NP)–CuCl[24a] and bulky ImPy–CuCl,[24c] and their steric maps calculated via SambVca 2.0[25] with a sphere radius of 3.5 Å; a distance from sphere 0.0 Å; Mesh step 0.10 Å; bondi radii scaled by 1.17; H atom omitted.

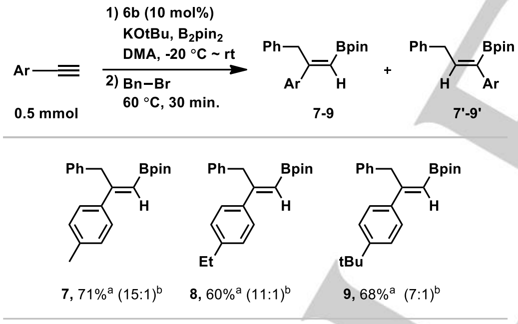
The observation of the crowded environment around the Cu center in **6a** in the solid state prompted us to further explore the steric properties of **6a** by percent buried volume calculation (%V_{bur}) based on solid state structure. Hence, we compared the %V_{bur} of **6a** and previously reported CAAC-5–CuCl (**Figure 6**). Due to the benzhydryl group, **6a** shows a more crowded environment (%V_{bur} = 58.1) around the Cu center than the CAAC-5–CuCl (%V_{bur} = 45.4). In fact, the %V_{bur} value of **6a** is similar to the one obtained for NHCs with the largest steric hindrance reported so far (%V_{bur} = 57.5 [Bulky ImPy–CuCl]) and 58.8 [IPr*(2-NP) –CuCl]).



[CuL]	Yields	[CuL]	Yields
6a	33 %	6d	49 %
6b	63 %	L = IPr	39 %
6c	37 %	L = CAAC-5	23 %

Scheme 4. Catalyst performance in benzylboration of *p*-tolyl acetylene. Yields were determined by NMR analysis with internal standard (CH_2Br_2).

Having confirmed the ambiphilic nature and considerable steric bulkiness of IdY, we seeked to demonstrate the utility of IdY-metal complexes in organic synthesis. Following the previous work in the field, NHC complexes of large buried volume[26] and strong π-accepting NHC ligands[27] find application in regioselective carboboration of alkynes. Inspired by these works, we investigated the benzylboration of *p*-tolyl acetylene in presence of **6** as a catalyst. Interestingly, in case of **6a** the reaction was terminated after only 30 minutes with the appropriate yields of 35%. Further optimization (**Scheme 4**) indicated a superior performance of **6b** compared to the other IdY–CuCl and representative NHC–CuCl complexes (IPr–CuCl and CAAC-5–CuCl). After this simple optimization, we chose **6b** as the optimal catalyst and expanded the substrate scope of the alkyne (**7**-**9**, **Scheme 5**). In case of each substrate, synthetically useful yields and high regioselectivity were observed.



Scheme 5. Substrate scope of benzylboration using **6b** as a catalyst. Yields: isolated yields. 'Bn' - benzyl group. a) combined yields, b) ratio of **7**-**9** and **7'**-**9'**

Conclusion

In summary, we developed a convenient and scalable synthesis of indolenium precursors (**2**) for a highly ambiphilic carbene, indol-2-ylidene (IdY, **A**). The ambiphilicity and tunability of **A** was demonstrated by computational studies and indirectly by spectroscopic characterization of the corresponding selenium adducts and transition metal complexes. The IdY–CuCl complexes (**6**) showed good catalytic activity, which is the first transition metal catalysis of the indole-based CAAC ligands, in a carboboration reaction. Further development of the IdY framework for free carbene isolation are currently underway in our laboratory and will be reported in due course.

Experimental Section

Full experimental details and characterization data for all compounds and details of the DFT calculations are included in the Supporting Information.

Acknowledgements

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Conflict of interest

The authors declare the following competing financial interest: A patent application has been led through POSTECH on methods and reagents presented in this manuscript.

Keywords: N-heterocyclic carbenes • ambiphilic carbenes • ligand design • indole • copper catalysis

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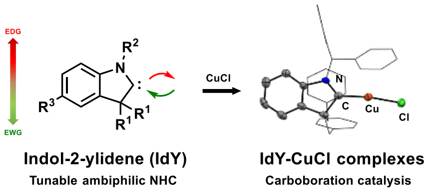
Entry for the Table of Contents



Ambiphilic N-heterocyclic carbene, indol-2-ylidene(**IdY**), is reported. The ambiphilicity is characterized by **IdY**-supported materials. The non-classical hydrogen bonding(NCHB) of **IdY**–Se complex is characterized by X-ray and computational studies. Furthermore, the carboboration of terminal alkynes using **IdY**–Cu complexes can be performed within 30 minutes with good yields and high regioselectivity.