Application of Indazolin-3-ylidenes in Catalysis: Steric-Tuning of Non-Classical Formally Normal *N*-Heterocyclic Carbenes with Dual Electronic Character for Catalysis

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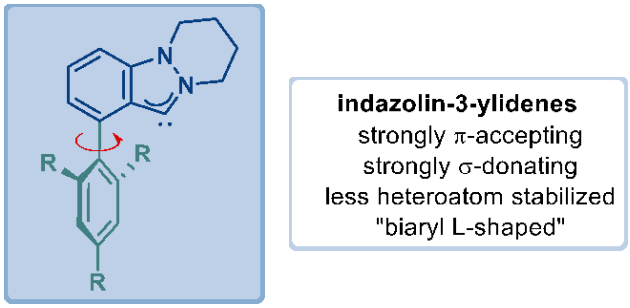
Supporting Information



ABSTRACT: N-Heterocyclic carbenes are pivotal ligands in chemistry and catalysis, providing essential tools for reactivity of metal centers. In particular, the development of non-classical less heteroatom-stabilized N-heterocyclic carbenes (NHCs) has attracted tremendous attention owing to higher ligand basicity. However, research on catalytic activity of non-classical NHCs has been challenging due to restrictions in modifying steric environment crucial for catalysis. Herein, we report a new class of indazolin-3-ylidene ligands derived from readily available indazole that feature steric differentiation around the metal center. Compared to classical imidazolin-2-ylidenes, these ligands feature strongly enhanced σ-donation resulting from repositioning of one of the nitrogen atoms. Simultaneously, the presence of the fused aromatic ring results in strongly enhanced π-accepting properties. The $\%V_{bur}$ is higher than the classic imidazolin-2-ylidene IMes ligand. We demonstrate that when used as ligands, the sterically-differentiated coordination environment of indazolin-3-ylidenes efficiently promote hydroamination reaction of alkynes to give valuable nitrogen-containing motifs, outcompeting the classical imidazolin-2-ylidenes. This protocol has also been applied to the challenging hydrohydrazination of alkynes and applied to the late-stage diversification. Comprehensive characterization, coordination chemistry as well as the evaluation of steric, σ-donating and π-accepting properties is demonstrated. Computational studies to gain insight into the reaction mechanism are reported. We anticipate that sterically-differentiated non-classical indazolin-3-ylidenes will accelerate the development of well-defined less heteroatom-stabilized N-heterocyclic carbene ligands in transition-metal-catalysis.

Introduction

Since the breakthrough studies by Arduengo in 1991,[1] the field of N-heterocyclic carbenes has experienced a tremendous growth, resulting in now widespread application of N-heterocyclic carbenes in various fields of science, ranging from organometallic chemistry and catalysis to medicine and materials science.[2,3] The pivotal utility of NHCs as ligands to transition-metals results from strong σ-donation of carbene centers outperforming phosphine ligands.[4] After the pioneering studies by Bertrand on CAACs (cyclic (alkyl)(amino)carbenes)[5] as a flagship example of NHCs with decreased heteroatom stabilization, special attention has been given to non-classical less heteroatom-stabilized N-heterocyclic carbenes (Figure 1A). These mesoionic and related NHCs (**B–F**) feature higher basicity of the ligand, resulting in enhanced donor properties, while the availability of heterocycles beyond imidazolin-2-ylidenes **A** enables to vary the electronic properties across a broad range unattainable with imidazolin-2-ylidenes through wingtip or backbone modifications.[6] To date, several ligand systems have been developed, such as the aforementioned CAACs **B**,[5] 1,2,3-triazolylidenes **C**,[7] and mesoionic imidazol-4-ylidenes **D**.[8] However, research on catalytic activity of non-classical NHCs has been challenging due to restrictions in modifying

steric environment crucial for catalysis.[9, 10] The presence of two nitrogen atoms in imidazolin-2-ylidenes provides adaptable handles for steric differentiation around the metal center, which is not easily

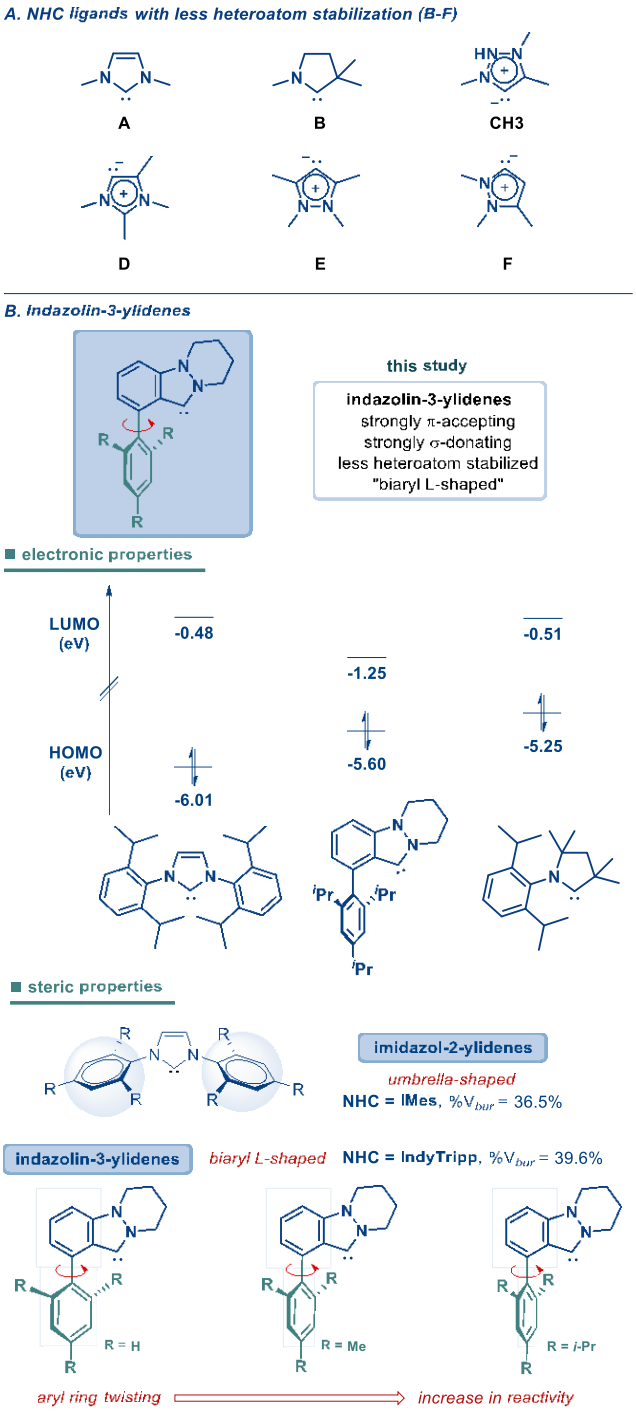


Figure 1. (A) Structures of classical (**A**) and less heteroatom stabilized NHCs (**B–F**). (B) Indazolin-3-ylidenes. Energies calculated at B3LYP 6-311++g(d,p) level, R = Dipp. R'R'' = IndyTripp.

accessible in other classes of less heteroatom stabilized N-heterocyclic carbenes. The steric tuning of NHC ligands is now recognized as a crucial component necessary for catalysis with extensive studies devoted to pinpoint the effect of catalytic pockets on the reactivity.[11]

Herein, we report a new class of indazolin-3-ylidene ligands derived from readily available indazole that feature steric differentiation around the metal center (Figure 1B). Compared to classical imidazolin-2-ylidenes, these ligands feature strongly enhanced σ-donation resulting from the repositioning of one of the nitrogen atoms. Simultaneously, the presence of the fused aromatic ring results in strongly enhanced π-accepting properties. The $\%V_{bur}$ is higher than the classic imidazolin-2-ylidene IMes ligand. We demonstrate that when used as ligands, the sterically-differentiated coordination environment of indazolin-3-ylidenes efficiently promote hydroamination reaction of alkynes to give valuable nitrogen-containing motifs, outcompeting the classical imidazolin-2-ylidenes. This protocol has also been applied to the challenging hydrohydrazination of alkynes and applied to the late-stage diversification. Comprehensive characterization, coordination chemistry as well as the evaluation of steric, σ-donating and π-accepting properties is demonstrated. Computational studies to gain insight into the reaction mechanism are reported. We anticipate that the sterically-defined coordination environment non-classical indazolin-3-ylidenes will accelerate the development of well-defined less heteroatom-stabilized N-heterocyclic carbene ligands in transition-metal-catalysis.

Results and Discussion

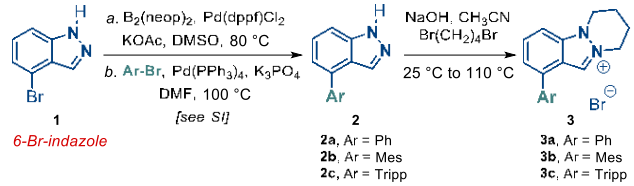
Non-classical formally normal N-heterocyclic carbenes that feature a directly linked nitrogen atom to the carbene center are expected to have a tremendous impact on homogenous catalysis.[9a,9c] For our study, we selected indazolin-3-ylidenes owing to the facile availability from indazole and the unique electronic characteristics incorporating the reshuffling of one of the nitrogen atoms (cf. imidazolin-2-ylidenes) and the presence of the fused aromatic ring as the key drivers of electronic properties. We hypothesized that the unique L-shaped biaryl steric arrangement could be achieved by the cross-coupling of readily available 6-bromo-indazole with sterically-demanding di-ortho-substituted arenes (Scheme 1). For the study, we selected structural analogues of classic IMes and IPr imidazolin-2-ylidenes (Ar = Mes, **2b**; Ar = Tripp, **2c**) as well as unsubstituted aryl analogue (Ar = Ph, **2a**). Notably, after optimization, the cross-coupling can be accomplished from the unprotected, commercially-available 6-bromoindazole by a sequence of Suzuki–Miyaura borylation and Suzuki–Miyaura cross-coupling on 2.6-3.0 g scale in 40-74% yields. The conversion to the indazolium precursors was accomplished by a double N-alkylation with 1,4-dibromobutane in 69-77% yields (see SI).

With access to sterically-differentiated indazolium precursors, we next comprehensively evaluated steric and electronic properties of these novel NHC ligands. Most importantly, the gold complexes [Au(**NHC**)Cl] (**4a–c**) were

prepared by a transmetallation route of [Ag(**NHC**)Br] with AuCl·SC_4H_8 (Scheme 2). The complexes **4a–4c** ([Au(**IndyPh**)Cl] (**4a**), [Au(**IndyMes**)Cl] (**4b**) and [Au(**IndyTripp**)Cl] (**4c**) (Indy = indazolinylidene)) were found to be stable to air and moisture and could be fully characterized by X-ray crystallography (Figure 2).

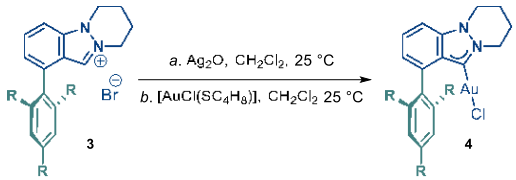
In this regard, studies by Cavallo and co-workers demonstrated that the % buried volume (%V_{bur}) and steric maps of [Au(NHC)Cl] complexes represent the best model for quantifying the steric impact of NHC ligands.[12] In the case of sterically-differentiated indazolin-3-ylidenes, [Au(**NHC**)Cl] are linear (C–Au–Cl, 179.6°; C–Au, 1.985 Å, **4a**; 178.9°; C–Au, 1.991 Å, **4b**; 176.3°; C–Au, 1.974 Å, **4c**), making it a good model for

Scheme 1. Synthesis of Indazolin-3-ylidene Precursors[a]



[a]See SI.

Scheme 2. Synthesis of Au(I) Complexes[a]



[a]Conditions: Ag_2O (1.2 equiv), 25 °C, CH_2Cl_2, 6 h, then [AuCl(SC_4H_8)] (1.0 equiv), 25 °C, CH_2Cl_2, 6 h, **4a**: 96%; **4b**: 86%; **4c**: 82%.

evaluating %V_{bur}. The (%V_{bur}) of 35.0%, 36.8%, 39.6% for complexes **4a–4c** increases in the series with the higher demand of the sterically-substituted ortho-biaryl ring. *Importantly, the steric demand of both **IndyMes** and **IndyTripp** ligands of 36.8% and 39.6% are higher than that of the classic imidazolin-2-ylidene IMes ligand (%V_{bur}) of 36.5% vs. IPr (%V_{bur}) of 45.6%.* There is a difference in quadrant distribution with unsymmetrical quadrants for indazolin-3-ylidenes (**4b**: 45.8%, 47.3%, 26.6%, 27.6%; **4c**: 54.3%, 51.4%, 24.6%, 28.2%), which can be compared with the symmetrical quadrant distribution for the classic imidazolin-2-ylidene IMes (**IMes**: 36.3%, 36.7%, 36.3%, 36.7%) and IPr (**IPr**: 49.4%, 42.3%, 50.3%, 40.6%). A graphical representation of steric maps in **4a–4c** in comparison with **IMes** in linear [Au(**NHC**)Cl] complexes is shown in Figure 3.

There are several other interesting structural features of indazolin-3-ylidenes that indicate increased steric impact in the series **4a–4c**. (1) First, the dihedral angle between the C6-Ar and the indazole ring increases from 61.0° in ortho-unsubstituted **4a** to 88.5° and 82.4° in ortho-substituted **4b** and **4c**. This indicates fixed and near fully perpendicular arrangement of the biaryl rings in sterically-tuned **4b–4c**. (2) Second, the distance between the new biaryl ring and metal, C^{ipso}(Ar)–Au, decreases in the series **4a–4c** (**4a**: 3.462 Å; **4b**: 3.429 Å; **4c**: 3.399 Å), indicating enhanced proximity of the di-ortho-substituted biaryl ring to the metal center. (3) Third, the distance between the metal and the center of the new biaryl ring for perpendicular **4b–4c** is 3.682 Å and 3.848 Å, respectively, indicating opening of the catalytic pocket for **4c**. Overall, to our knowledge, sterically-differentiated complexes **4b–4c** represent the most sterically-demanding non-classical less heteroatom stabilized N-heterocyclic carbenes in indazolidene and related ligands.[9c,13]

We next comprehensively evaluated electronic properties of these indazolin-3-ylidene ligands (Scheme 3). As shown, Rh(I) complexes, [Rh(**IndyPh**)$(CO)_2$Cl] (**5a**), [Rh(**IndyMes**)$(CO)_2$Cl] (**5b**) and [Rh(**IndyTripp**)$(CO)_2$Cl] (**5c**) were prepared by a mild two-step procedure via

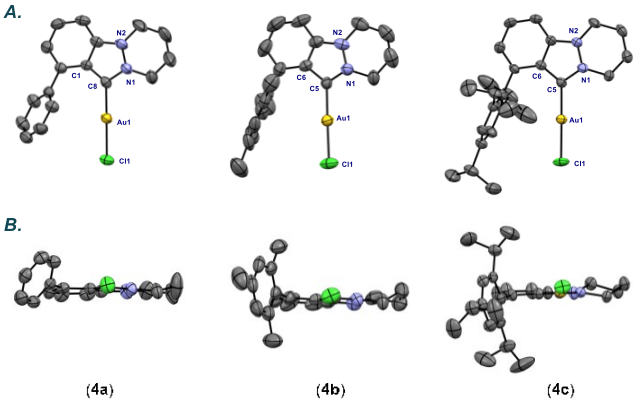


Figure 2. X-ray crystal structure of Au(I) complexes **4a-4c**. Two views: front (top); side (bottom). Hydrogen atoms and counterion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: **4a**: Au–C8, 1.985(4); Au-Cl, 2.294(1); N1–C8, 1.347(5); C8–C1, 1.418(5); N1–N2, 1.376(5); C1-C8-N1, 105.1(3); C8–Au–Cl, 179.6(1). **4b**: Au–C5, 1.991(5); Au-Cl, 2.289(1); N1–C5, 1.313(8); C6–C5, 1.437(8); N1–N2, 1.391(6); C6-C5-N1, 105.8(4); C5–Au–Cl, 178.9(2). **4c**: Au–C5, 1.974(7); Au-Cl, 2.306(2); N1–C5, 1.357(9); C6–C5, 1.420(1); N1–N2, 1.398(8); C6-C5-N1, 105.0(6); C5–Au–Cl, 176.3(2). **4a**: CCDC 2129509; **4b**: CCDC 2129510; **4c**: CCDC 2129511. Note gradual increase of C–Ar twist in **4a-4c**.

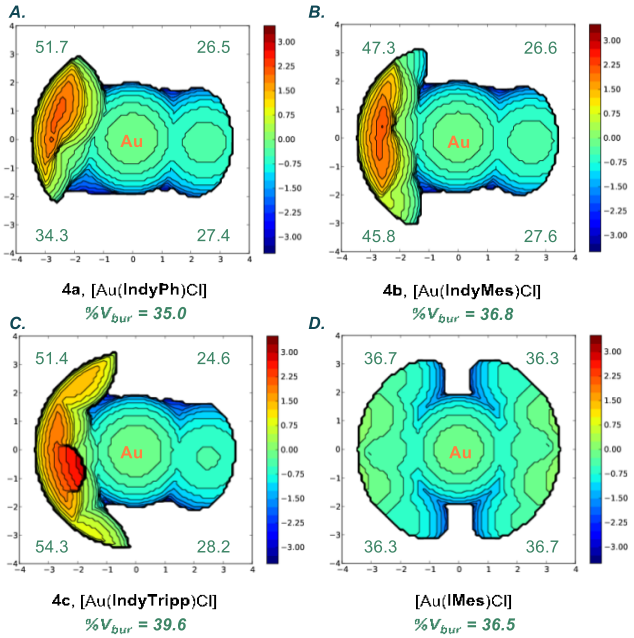
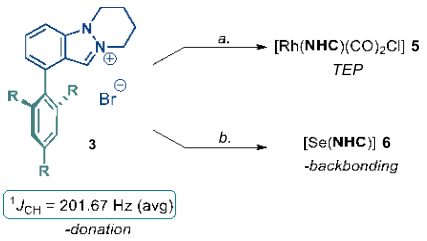


Figure 3. Topographical steric maps of Au(I) complexes **4a–4c** and [Au(**IMes**)Cl] showing % V_{bur} per quadrant.

[Rh(**NHC**)(cod)Cl] and the reaction with carbon monoxide after deprotonation with KO*t*Bu. Selenium adducts [Se(**IndyPh**)] (**6a**), [Se(**IndyMes**)] (**6b**) and [Se(**IndyTripp**)] (**6c**) were prepared by adding the free carbene generated in situ with KO*t*Bu to excess of selenium.

The Tolman electronic parameter (TEP) of **5a–5c** is 2041.4 cm^{-1}, 2038.2 cm^{-1}, 2043.4 cm^{-1}, respectively, with the CO stretching frequencies of ν_{sym} = 2064 cm^{-1} and ν_{asym} = 1989 cm^{-1} ; ν_{sym} = 2062 cm^{-1} and ν_{asym} = 1983 cm^{-1} ; ν_{sym} = 2066 cm^{-1} and ν_{asym} = 1992 cm^{-1} (CH_2Cl_2, 0.20 M). This allows to evaluate a

Scheme 3. Synthesis of Indazolin-3-ylidene Complexes[a]



[a]Conditions: (a) $[Rh(cod)Cl]_2$ (1.0 equiv), KO*t*-Bu (2.0 equiv), THF, 25 °C, 8 h, then CO, CH_2Cl_2, 0 °C, 1 h, **5a**: 79%; **5b**: 70%; **5c**: 54%. (b) Se (1.5 equiv), KO*t*-Bu (1.2 equiv), THF, 25 °C, 12 h, **6a**: 88%, **6b**: 88%, **6c**: 82%.

combined measure of the electronic properties of the sterically-differentiated indazolin-3-ylidene ligands, which can be compared with the classic imidazolin-2-ylidene IPr ligand (TEP of 2051.5 cm^{-1}) and model cyclic (alkyl)amino)carbenes $CAAC^{Cy}$ (TEP of 2048.6 cm^{-1}).[5a] *The values indicate strongly enhanced σ-donation of indazolin-3-ylidene as compared with imidazolin-2-ylidenes.*

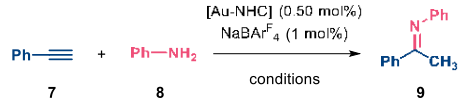
The δ_{Se} values of selenourea adducts **6a–6c** from the ^{77}Se NMR spectra are 230.3 ppm, 203.7 ppm and 245.7 ppm ($CDCl_3$), respectively, which can be compared with the classic imidazolin-2-ylidene IPr (δ_{Se} = 90 ppm).[14] This allows to evaluate π-backbonding, indicating that *indazolin-3-ylidenes feature significantly enhanced π-accepting properties compared with imidazolin-2-ylidenes (vide infra, Figure 5).*

Furthermore, one-bond CH J coupling constants from ^{13}C satellites of the ^1H NMR spectrum of salts **3a–3c** are 202.14 Hz, 201.68 Hz and 201.18 Hz, which can be compared with the classic imidazolin-2-ylidene IPr ($^1J_{CH}$ = 223.70 Hz).[15] This provides good indication of σ-donating properties of an NHC ligand and is consistent with *indazolin-3-ylidenes as strongly σ-donating NHC ligands.*

Overall, the structural and electronic characterization points at sterically-differentiated indazolin-3-ylidenes as ambiphilic NHCs superseding classical imidazolin-2-ylidenes in both donor and electrophilic properties with a significant steric demand superseding model IMes ligand.

With structural and electronic characterization of indazolin-3-ylidenes, we next proceeded to evaluate their activity in catalysis (Table 1, Schemes 4-6). At the outset we were interested in Au-promoted hydroamination of alkynes because of the fundamental role of this process in the synthesis of nitrogen-containing motifs. Our motivation in selecting this reaction stems from the fact that Au-catalyzed hydroamination is one of the most important methods to introduce nitrogen into organic molecules utilizing feedstock chemicals.[16,17] Thus, identification of new active ligand systems that promote hydroamination is of broad synthetic interest, The reaction between phenylacetylene and aniline was selected as a model system. We were delighted to find that the complex [Au(**IndyTripp**)Cl] (**4c**) promoted the reaction in excellent 94% yield at 0.50 mol% catalyst loading in the presence of 1.0 mol% of $NaBAr^F_4$ as activator at 80 °C (Table 1, entry 3). The use of less sterically-demanding [Au(**IndyMes**)Cl] (**4b**) and especially ([Au(**IndyPh**)Cl] (**4a**) resulted in less efficient reactions, 92% and 40% yield, respectively (Table 1, entries 1-2).

Table 1. Optimization of Au–NHC-Catalyzed Hydroamination of Alkynes[a]



entry	catalyst	[Au–NHC] (mol%)	additive	yield (%)
1	[Au(**IndyPh**)Cl]	0.50	$NaBAr^F_4$	40
2	[Au(**IndyMes**)Cl]	0.50	$NaBAr^F_4$	92
3	[Au(**IndyTripp**)Cl]	0.50	$NaBAr^F_4$	94
4	[Au(**IMes**)Cl]	0.50	$NaBAr^F_4$	81
5	[Au(**IPr**)Cl]	0.50	$NaBAr^F_4$	82

[a]Conditions: **7** (1.0 equiv), **8** (1.1 equiv), Au–NHC (0.5 mol%), $NaBAr^F_4$ (1 mol%), neat, 80 °C, 12 h. See SI for details.

Under these conditions, both [Au(**IndyTripp**)Cl] (**4c**) and [Au(**IndyMes**)Cl] (**4b**) outperformed the classic imidazolin-2-ylidenes [Au(**IMes**)Cl] (81% yield) and [Au(**IPr**)Cl] (82% yield) (Table 1, entries 4-5). The more sterically-demanding indazolin-3-ylidene complex [Au(**IndyTripp**)Cl] (**4c**) is

more reactive than less sterically-demanding [Au(**IndyMes**)Cl] (**4b**) (**4c**: 73%, RT; **4b**: 47%, RT) (not shown) and was selected for the scope studies. Thus, the reactivity trend of **Indy** ligands is in order of their sterically-differentiated environment (**IndyTripp** > **IndyMes** > **IndyPh**).

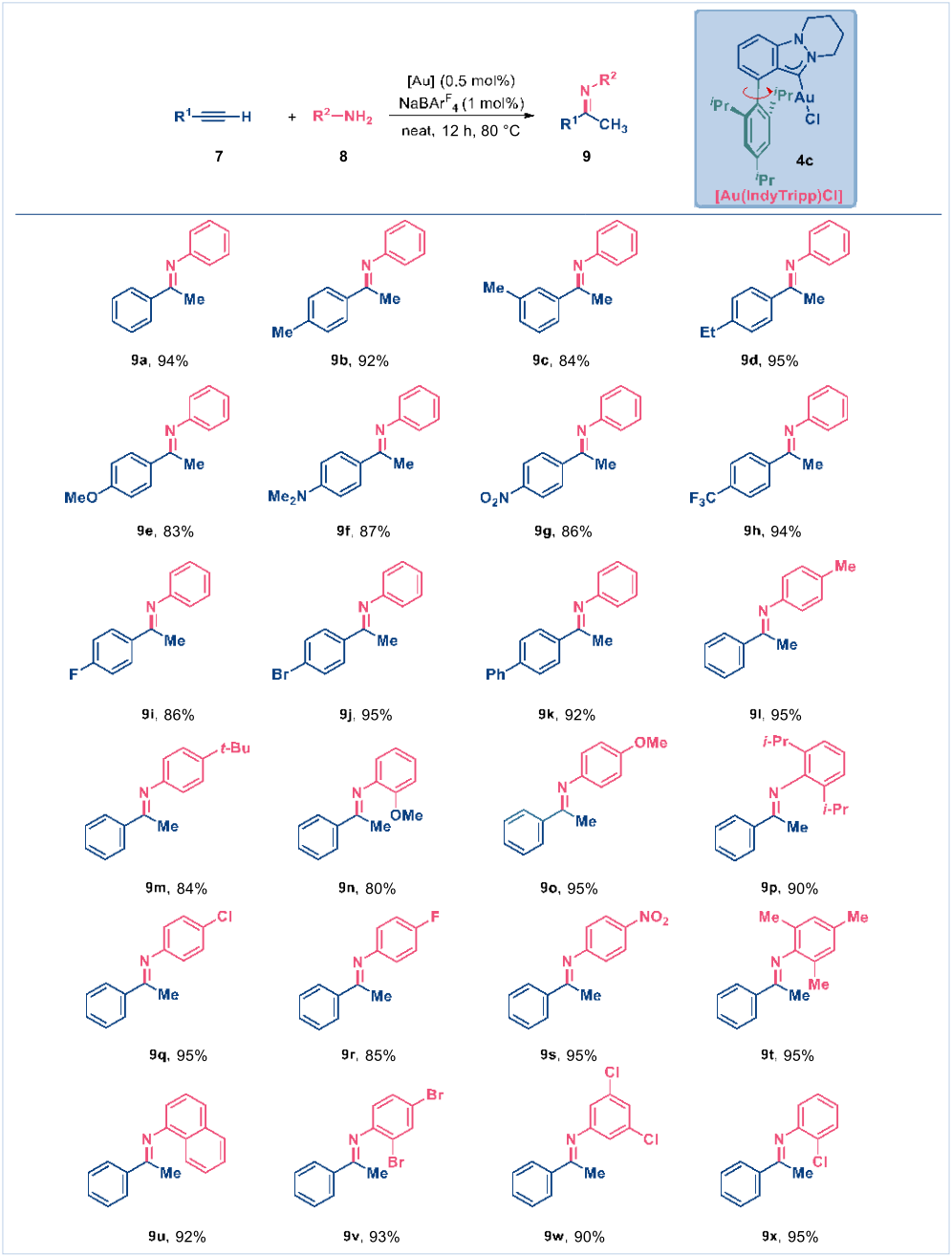
As shown in Scheme 4, the scope of the hydroamination of alkynes catalyzed by [Au(**IndyTripp**)Cl] is broad and encompasses a palette of electronically- and sterically-differentiated alkynes and anilines. As such, arylacetylenes with neutral (**9a–9d**), electron-donating (**9e–9f**) and electron-withdrawing (**9g–9j**) substituents are well tolerated. Importantly, sensitive functional groups, such as amino (**9f**), nitro (**9g**) and bromo (**9j**) are compatible, providing handles for further functionalization. Alkynes containing biologically-relevant substituents, such as trifluoromethyl (**9h**) and fluoro (**9i**) are applicable. Biaryl alkynes are also amenable to the hydroamination conditions (**9k**), providing extended conjugated systems. Various anilines were found to be well tolerated under the reaction conditions. As such, anilines substituted with alkyl groups (**9l–9m**), electron-donating groups (**9n–9o**), electron-withdrawing groups (**9q–9s**) as well as sterically hindered anilines (**9p**, **9t**) provided the hydroamination products in high yields. 1-Napthylaniline that represents a privileged motif in medicinal chemistry is also tolerated (**9u**).

This protocol was extended to halogenated anilines, including challenging ortho-substitution (**9v-9x**). At present stage, alkyl substrates are not compatible with the reaction.

Importantly, this hydroamination reaction could be extended to the challenging hydrohydrazination of alkynes (Scheme 5). Pleasingly, hydrohydrazination of electronically-differentiated arylacetylenes, including electron-neutral (**11a–11c**), electron-rich (**11d**) and electron-deficient (**11e–11h**) substituted arenes, proceeded in high yields. The N–N cleavage often complicating the process was not observed, showing the potential applicability of the [Au(**IndyTripp**)Cl] catalyst in organic synthesis.

This protocol could be applied to the direct late-stage derivatization of complex molecules (Scheme 6). Hydroamination of

Scheme 4. Scope of Au–NHC-Catalyzed Hydroamination of Alkynes[a]

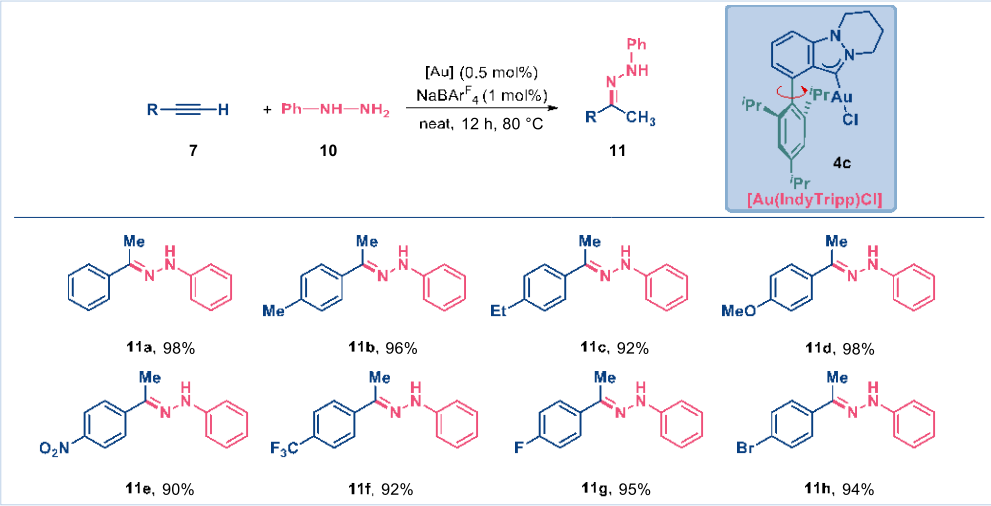


[a]Conditions: alkyne (1.0 equiv), amine (1.1 equiv), **4c** (0.5 mol%), NaBAr$^F_4$ (1 mol%), neat, 80 °C, 12 h. See SI for details.

propargylic ester of Clodinafop (Clodinafop-propargyl), a registered herbicide for spring wheat, performed well in the presence of several sensitive functional groups and coordinating pyridine ring, further demonstrating the generality of the catalyst and revealing potential for chemical research. Note that the product was isolated after hydrolysis due to imine instability (see SI).

To gain insight into the hydroamination mechanism catalyzed by indazolin-3-ylidenes, the transition states were studied by DFT computations (Figure 4). Based on the previous work by Bertrand and co-workers,[16c] the coordination of Au–NHC with aniline or phenylhydrazine would give intermediate **A-1** or **B-1**, respectively. Next, the ligand exchange between alkyne and aniline or phenylhydrazine would generate intermediate **A-2** or **B-2**, respectively. The free energy of activation for this step is 18.2 and 16.5 kcal/mol for **A-TS1** and **B-TS1**. After formation of **A-2** or **B-2**, the nucleophilic attack of aniline or

Scheme 5. Scope of Au–NHC-Catalyzed Hydrohydrazination of Alkynes[a]



[a]Conditions: alkyne (1.0 equiv), hydrazine (1.1 equiv), **4c** (0.5 mol%), NaBAr$^F_4$ (1 mol%), neat, 80 °C, 12 h. See SI for details.

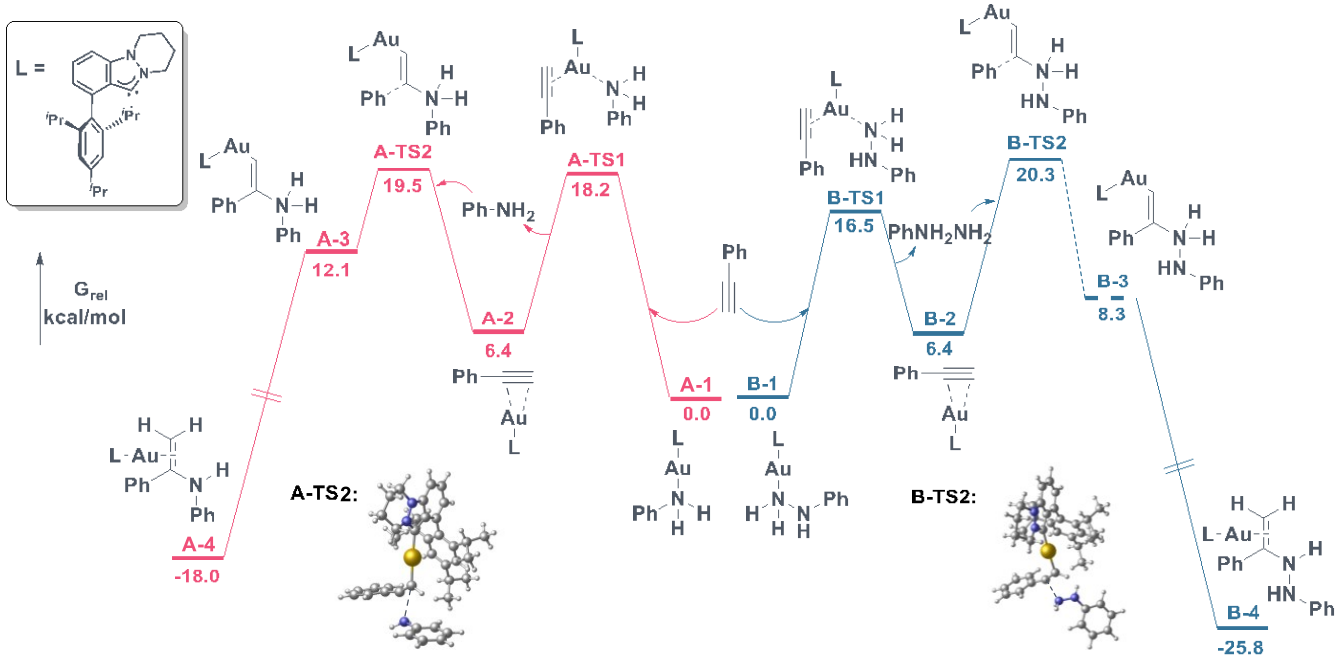


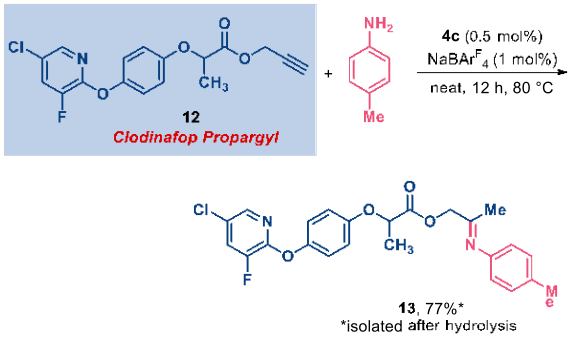
Figure 4. DFT-computed free energy profile of Au–NHC catalyzed hydroamination and hydrohydrazination. See SI for computational details.

phenylhydrazine would give intermediate **A-3** or **B-3** with the free energies of activation of 19.5 and 20.3 kcal/mol, respectively. Finally, proton migration gives product complexes **A-4** and **B-4**, which is exergonic by -30.1 and -34.1 kcal/mol, respectively.

The barriers for proton migration (from **A-3** to **A-4** and from **B-3** to **B-4**) have not been calculated because these steps are consistent with the computational data by Ujaque[18] and the energy is very low. These calculation results are consistent with the computational data of Ujaque and co-workers,[18] and highlight the potential of indazolin-3-ylidenes in electrophilic catalysis.

To further determine the electronic effect of nitrogen repositioning in indazolin-3-ylidenes, HOMO and LUMO energy levels of carbenes **IndyPh**, **IndyMes** and **IndyTripp** were determined at the B3LYP 6-311++g(d,p) level (Figure 5 and SI). The donor ability of carbenes is closely associated with the HOMO orbital (higher HOMO, more σ-donating), while the electron acceptance is associated with the LUMO orbital (lower

Scheme 6. Late-Stage Functionalization[a]



[a]Standard conditions. See SI.

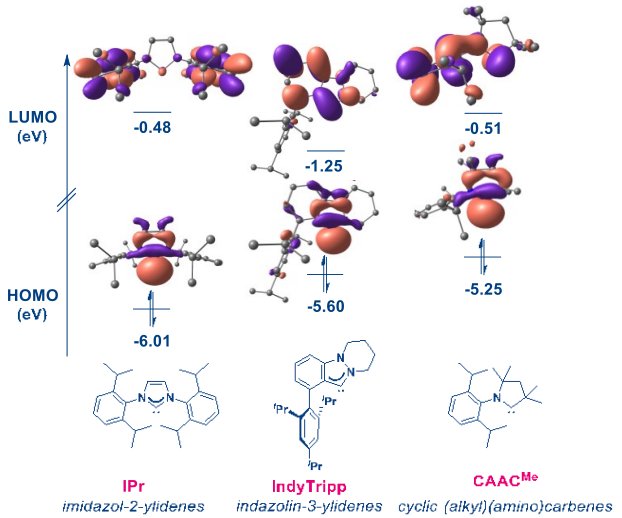


Figure 5. HOMO and LUMO energy levels (eV) calculated at B3LYP 6-311++g(d,p). See SI for details.

LUMO, more π-accepting). In some cases, π-donor orbital should also be considered. It is now accepted that computation of frontier orbitals is the most accurate evaluation of nucleophilicity and electrophilicity of NHC ligands, while the comparison must be made at the same level of theory.

The HOMO of the most reactive **IndyTripp** (-5.60 eV, σ-bonding orbital) is much higher than **IPr** (-6.01 eV), which is a reference for σ-donating imidazolin-2-ylidenes. The HOMO of **IndyMes** and **IndyPh** are -5.56 eV and –5.59 eV, respectively. These values can be further compared with **CAAC^{Me}** (-5.33 eV), which is a model for cyclic (alkyl)(amino)carbenes. Moreover, the LUMO of **IndyTripp** (-1.25 eV, π-accepting orbital) is significantly lower than for the model imidazolin-2-ylidene **IPr** (-0.48 eV) of the corresponding π-accepting orbital. The LUMO of **IndyMes** and **IndyPh** are -1.21 eV and -1.39 eV, respectively. These values can be compared with **CAAC^{Me}** (-0.51 eV). Furthermore, π-donating orbital of -6.22 eV, -6.17 eV, -6.61 eV in **IndyTripp**, **IndyMes** and **IndyPh** can be compared with the π-donating orbital for the reference imidazolin-2-ylidene **IPr** (-6.55 eV).

Overall, this indicates that sterically-differentiated indazolin-3-ylidenes (1) are significantly stronger donors than classical imidazolin-2-ylidenes with donor properties between imidazolin-2-ylidenes and cyclic (alkyl)amino)carbenes; and (2) feature significantly enhanced electrophilicity than classical imidazolin-2-ylidenes, also superseding cyclic (alkyl)(amino)carbenes. Thus, in combination with a significant steric demand superseding IMes, electronic properties of sterically-differentiated indazolin-3-ylidenes make them well-poised to make an impact on the development of new pursuits in organometallic catalysis.

Conclusions

In conclusion, the development of non-classical less heteroatom-stabilized N-heterocyclic carbenes has attracted tremendous attention owing to higher ligand basicity. In this study, we reported a new class of indazolin-3-ylidene ligands derived from readily available indazole that feature steric differentiation around the metal center. These non-classical indazolin-3-ylidenes feature strongly enhanced σ-donation, while, simultaneously, the presence of the fused aromatic ring results in strongly enhanced π-accepting properties. The $\%V_{bur}$ is comparable to the classic imidazolin-2-ylidene IMes ligand. The sterically-differentiated indazolin-3-ylidenes promote hydroamination reaction of alkynes to give valuable nitrogen-containing motifs, outcompeting the classical imidazolin-2-ylidenes. We further presented comprehensive characterization, coordination chemistry, the evaluation of steric, σ-donating, π-accepting properties. DFT studies provided insight into the mechanism. Application to the late-stage derivatization of complex molecules and challenging hydrohydrazination has been described. Overall, the results presented strongly suggest that sterically-differentiated non-classical indazolin-3-ylidenes featuring nitrogen re-shuffling might provide attractive ligands for transition-metal-catalysis and accelerate the development of broadly applicable well-defined non-classical NHC ligands.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, computational details, .cif files of **4a-4c**, coordinates and energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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