

Indazolin-3-ylidenes (Indy*): Easily Accessible, Sterically-Hindered Indazole-Derived *N*-Heterocyclic Carbenes and Application in Gold Catalysis

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Sterically-hindered *N*-heterocyclic carbenes (NHCs) with functionalized *N*-wingtips are a pivotal class of ligands in organic synthesis. Herein, we report the first class of sterically-hindered *N*-heterocyclic carbenes based on the indazole framework. These ligands combine strong σ -donation of the carbene center characteristic to the carbene placement at the C3-indazole position with the sterically-hindered and flexible *N*-substitution with the versatile 2,6-bis(diphenylmethyl)aryl moiety that extends beyond the metal centre for the first time in non-classical *N*-heterocyclic carbenes. The ligands are readily accessible by the rare Cadogan indazole synthesis of sterically-hindered *N*-aryl-1-(2-nitrophenyl)methanimines. Steric and electronic characterization as well as catalytic studies in the synthesis of oxazolines are described. Considering the unique properties of indazole-derived carbenes, we anticipate that this class of compounds will find broad application in organic synthesis and catalysis.

Introduction

In the past two decades, *N*-heterocyclic carbenes (NHCs) have evolved into an essential class of ligands in modern organic synthesis (Figure 1A).¹ In particular, *N*-heterocyclic carbenes have been exploited as ancillary ligands in transition-metal complexes, where they impart remarkable stability as well as beneficial steric and electronic properties on the metal center owing to the umbrella-type steric arrangement of *N*-aromatic wingtips and strong σ -donation superseding phosphines.² The development of new, sterically-hindered NHC ligands has been a dominant direction in ligand development, allowing for fine-tuning the reactivity and selectivity of organic processes at the metal center in a variety of transformations and catalytic pathways.³

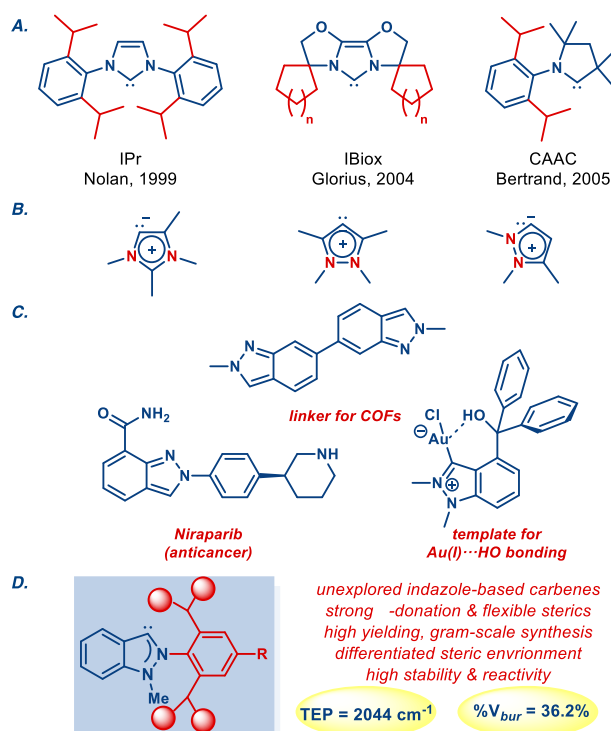


Figure 1. (A) Sterically-demanding *N*-heterocyclic carbenes. (B) Abnormal and less heteroatom stabilized carbenes. (C) Prevalence of indazoles in chemistry. (D) This study: Sterically-hindered indazolin-3-ylidenes.

Although imidazol-2-ylidenes are by far the most common class of *N*-heterocyclic carbenes currently used in organic synthesis,⁴ the past decade has witnessed the development of less heteroatom stabilized *N*-heterocyclic carbenes, where the carbene site is not stabilized by two nitrogen atoms (Figure 1B).⁵ These non-classical carbenes are significantly stronger σ -donors than imidazol-2-ylidenes due to higher basicity, while the deployment of different heterocyclic scaffolds offers novel opportunities for steric tuning for applications in the field of organic synthesis not available in the classical imidazole scaffolds.⁶ In this context, indazole-derived carbenes have garnered particular attention owing to their distinct structural

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and electronic characteristics merged with facile access to the indazole ring.⁷⁻¹⁰

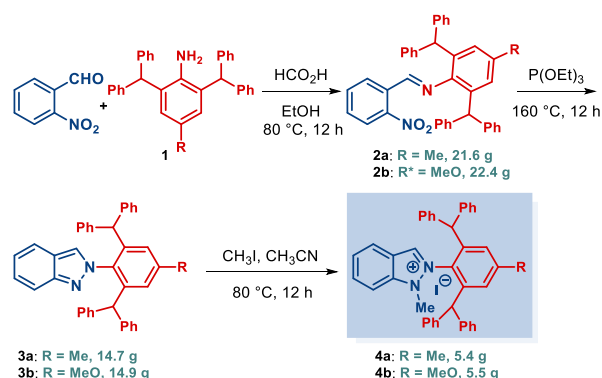
In 2009, the Huynh group reported a seminal study on the synthesis of indazolin-3-ylidenes and demonstrated their strong σ -donor character significantly superior to the classical NHC ligands (TEP = 2041 cm⁻¹ vs. 2051 cm⁻¹).⁷ In organic synthesis, the indazole ring system is one of the most common *N*-heterocycles in pharmaceutical, agrochemical and advanced materials research with recent examples including the synthesis of uniquely linked covalent organic frameworks, anticancer drugs and organic electroluminescence devices (Figure 1C).^{8, 9} Attractive methods for the synthesis of indazoles by C–H activation and refined classical methods have been developed.¹⁰

Our interest in *N*-heterocyclic carbenes and heterocycles¹¹ led us to question whether sterically-hindered indazolin-3-ylidenes with the versatile *N*-2,6-bis(diphenylmethyl)aryl moiety might be possible. The vast majority of the known indazolin-3-ylidenes feature *N*-alkyl substitution,¹² which, taking lessons from the imidazol-2-ylidene chemistry, imposes an important limitation in exploring the catalytic activity of this class of *N*-heterocyclic carbenes. We were cognizant of the recent spectacular advances in using IPr*-type imidazol-2-ylidenes and related ligands, where the flexible steric substitution of the 2,6-bis(diphenylmethyl)aryl wingtips dynamically accommodates to the catalytic pocket in close proximity to the metal center and extends beyond the metal coordination sphere.¹³ Note that the 2,6-bis(diphenylmethyl) substituent is referred to as IPr* in the imidazol-2-ylidene framework. Herein, we report the first class of *N*-sterically-hindered *N*-heterocyclic carbenes based on the indazole framework with the flexible *N*-substitution that extends beyond the metal centre from the versatile *N*-wingtip for the first time in non-classical *N*-heterocyclic carbenes (Figure 1D). These ligands combine strong σ -donation of the carbene center with sterically-hindered and modular sterics. Considering the unique electronic properties of indazole-derived carbenes, their ease of synthesis by the modular Cadogan cyclization, and the versatility of *N*-substitution, we anticipate that this class of compounds will find broad application in organic synthesis and catalysis.

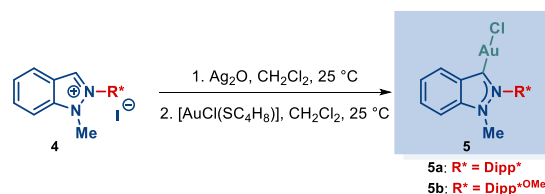
Results and Discussion

Our study commenced with developing a robust synthetic route to the proposed class of ligands (Scheme 1). Facile, scalable and readily accessible ligand synthesis is arguably the most crucial requirement for the use in catalysis and metal stabilization. The ligands targeted in this study included the parent Indy*, featuring 2,6-bis(diphenylmethyl)-4-tolyl moiety, and the more electron-donating Indy*MeO, featuring 2,6-bis(diphenylmethyl)-4-anisyl group. The developed synthetic sequence involves formic acid-promoted condensation of the readily available 2,6-dibenzhydryl-4-methylaniline or 2,6-dibenzhydryl-4-methoxyaniline with 2-nitrobenzaldehyde (**2a**: 21.6 g, 94% yield; **2b**: 22.4 g, 95% yield). The key Cadogan cyclization was smoothly performed using triethyl phosphite at 160 °C (**3a**: 14.7 g, 91% yield; **3b**: 14.9 g, 89% yield). Finally, *N*-

alkylation with MeI readily afforded the desired indazolium salts (**4a**: 5.4 g, 80% yield; **4b**: 5.5 g, 79% yield).



Scheme 1. Cadogan Cyclization for the Synthesis of Sterically-Hindered Indazolium Salts^a. ^aConditions: (a) *o*-nitrobenzaldehyde (1.0 equiv), **1** (1.2 equiv), EtOH, 80 °C, 12 h. **2a**: 94%; **2b**: 95%. (b) **2** (1.0 equiv), P(OEt)₃ (5 equiv), 160 °C, 12 h. **3a**: 91%; **3b**: 89%. (c) **3** (1.0 equiv), MeI (5 equiv), CH₃CN, 80 °C, 12 h. **4a**: 80%; **4b**: 79%. See SI for details.



Scheme 2. Synthesis of Au(I) Complexes^a. ^aConditions: Ag₂O (1.0 equiv), 25 °C, CH₂Cl₂, 6 h, then [AuCl(SC₄H₉)] (1.0 equiv), 25 °C, CH₂Cl₂, 6 h, **5a**: 87%; **5b**: 88%. Dipp* = 2,6-(Ph₂CH)₂-4-Me-C₆H₃; Dipp*MeO = 2,6-(Ph₂CH)₂-4-MeO-C₆H₃.

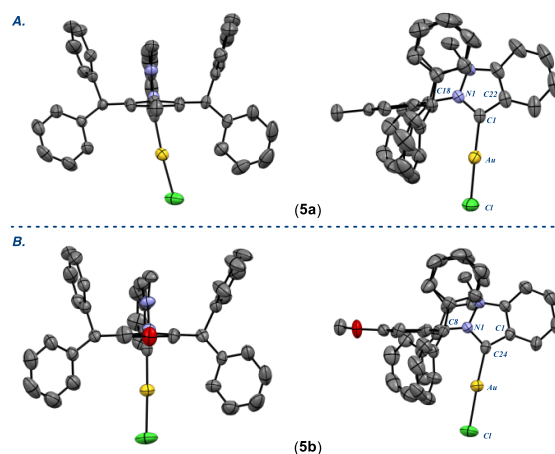


Figure 2. X-ray crystal structure of Au(I) complexes **5a–5b**. Two views: front (left); side (right). Hydrogen atoms have been omitted for clarity. See SI for selected bond lengths [Å] and angles [°]. **5a**: CCDC 2158126; **5b**: CCDC 2158125.

The route involves a rare Cadogan indazole synthesis of sterically-hindered *N*-aryl-1-(2-nitrophenyl)methanimines.¹⁴ The developed route is highly modular and smoothly affords gram scale quantities of ligand precursors from simple and readily available starting materials.

Having developed a scalable access to indazolium salts, next we performed comprehensive steric and electronic characterization of these new ligands (Scheme 2 and Figure 2). First, in order to quantify the steric impact, Au(I)–NHC

complexes, [Au(Indy*)Cl] (**5a**) and [Au(Indy*MeO)Cl] (**5b**) were prepared by transmetalation from Ag(I)–NHC complexes using

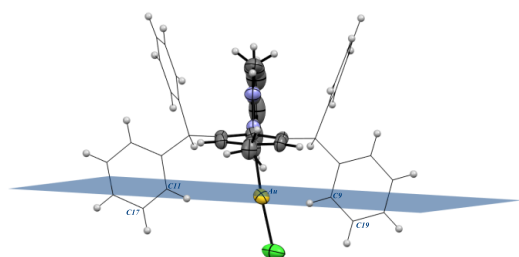


Figure 3. Graphical representation of C11–Au–C9 plane in **5a**. Note that the *N*-aryl wingtip extends beyond the metal coordination sphere.

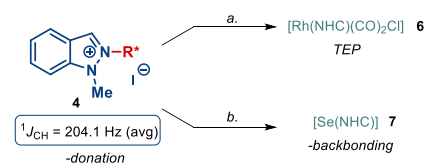
Au(SC₄H₈)Cl at 25 °C (**5a**: 87% yield; **5b**: 88% yield) (Scheme 2). The complexes were found to be stable to air and moisture. The identity of complexes **5a–5b** was confirmed by elemental analysis. To further exclude the possibility of halogen scrambling, ion chromatography studies have been conducted. The chromatographic data revealed a distinct peak corresponding to the chloride anion, while no discernible peak for the iodide anion was detected (see SI). Complexes **5a** and **5b** were fully characterized by x-ray crystallography (Figures 2–3). Complex **5b** crystallized as two molecules in the unit cell.

The %buried volume (%V_{bur}) and steric maps method developed by Nolan, Cavallo et al. was used to determine the steric impact (see SI).^{3a, 15} Both [Au(Indy*)Cl] complexes are linear (**5a**: C–Au–Cl, 175.4°; C–Au, 1.981 Å; **5b**: mol1, C–Au–Cl, 177.0°; C–Au, 1.983 Å; mol2, C–Au–Cl, 173.6°; C–Au, 1.970 Å). The (%V_{bur}) of [Au(IPr*)–Indy]Cl is 34.8%, while the (%V_{bur}) of [Au(Indy*MeO)Cl] is 36.2% (mol1) and 34.4% (mol2). These values can be compared with the seminal *N,N*-diethyl-indazol-3-ylidene reported by the Huynh group ([Au(NHC)Cl], C–Au–Cl, 178.8°; C–Au, 1.977 Å; %V_{bur} of 26.3)^{7b} and standard imidazol-2-ylidene, IMes ([Au(NHC)Cl], C–Au–Cl, 180.0°; C–Au, 1.999 Å; %V_{bur} of 36.5%).^{3a}

Next, to evaluate electronic properties, Rh(I) complexes, [Rh(Indy*)(CO)₂Cl] (**6a**) and [Rh(Indy*MeO)(CO)₂Cl] (**6b**) were prepared after generating the free carbene in situ by deprotonation with a slight excess of KOt-Bu and the reaction with [Rh(cod)Cl]₂ followed by bubbling with CO (**6a**: 89% yield; **6b**: 88% yield) (Scheme 3). The CO stretching frequencies of [Rh(Indy*)(CO)₂Cl] are $\nu_{\text{sym}} = 2070 \text{ cm}^{-1}$ and $\nu_{\text{asym}} = 1990 \text{ cm}^{-1}$ (CH₂Cl₂, 0.20 M), and of [Rh(Indy*MeO)(CO)₂Cl] are $\nu_{\text{sym}} = 2070 \text{ cm}^{-1}$ and $\nu_{\text{asym}} = 1989 \text{ cm}^{-1}$ (CH₂Cl₂, 0.20 M), which corresponds to a TEP of 2044.2 cm⁻¹ and 2043.8 cm⁻¹. These values can be compared with the standard imidazol-2-ylidene, IMes (TEP of 2051 cm⁻¹)^{2f} or strongly donating cyclic (alkyl)(amino)carbenes, CAAC^{cy} (TEP of 2049 cm⁻¹),^{1c} indicating a very significant donor effect of the indazol-3-ylidene framework.

Selenourea adducts, [Se(Indy*)] (**7a**) and [Se(Indy*MeO)] (**7b**) were prepared by deprotonation with KOt-Bu in the presence of selenium (**7a**: 85% yield; **7b**: 86% yield) (Scheme 3). The δ_{Se} value of 153.40 ppm for [Se(Indy*)] (CDCl₃) and 152.88 ppm for [Se(Indy*MeO)] (CDCl₃) indicates higher π -accepting properties than the standard imidazol-2-ylidene,

IMes ($\delta_{\text{Se}} = 27 \text{ ppm}$),¹⁶ as expected from indazole benzannulation. Moreover, one-bond CH *J* coupling constants



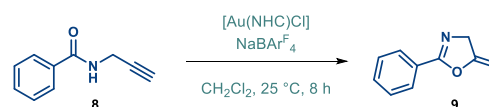
Scheme 3. Synthesis of Rh(I) and Se Complexes^a. ^aConditions: (a) [Rh(cod)Cl]₂ (1.0 equiv), KOt-Bu (2.0 equiv), THF, 25 °C, 8 h, then CO, CH₂Cl₂, 0 °C, 1 h, **6a**: 89%; **6b**: 88%; (b) Se (1.5 equiv), KOt-Bu (1.2 equiv), THF, 25 °C, 12 h, **7a**: 85%, **7b**: 86%.

from ¹³C satellites of the ¹H NMR spectra are 204.1 Hz and 204.2 Hz for Indy*·HI (CDCl₃) and Indy*MeO·HI (CDCl₃), respectively. These values are consistent with the Indy* ligands as significantly more σ -donating than imidazole-2-ylidenes IMes·HCl (225.2 Hz, CDCl₃).¹⁷

We next evaluated the catalytic activity of Indy*–Au complexes. Cycloisomerization of *N*-propargylamides to oxazolines was selected as a model reaction due to the importance of oxazoline products in medicinal chemistry and the capacity of NHC–Au(I) catalysis platform to promote electrophilic cyclization reactions in a general fashion.

The screening of the reaction conditions using Au–NHC at 1 mol% loading was performed in the presence of 1 mol% of NaBARF₄ at room temperature (Table 1). As shown, this study revealed that both [Au(Indy*)Cl] (**5a**) (95% yield) and [Au(Indy*MeO)Cl] (**5b**) (97% yield) significantly outperform standard imidazol-2-ylidene complexes, [Au(IMes)Cl] (52% yield) and [Au(IPr)Cl] (76% yield). Literature survey revealed few examples of silver-free cycloisomerization of *N*-propargylamines promoted by Au(I)–NHC complexes.¹⁸

Table 1. Au–NHC-Catalyzed Amide Cycloisomerization^a



entry	catalyst	[Au–NHC] (mol%)	additive	yield (%)
1	[Au(Indy*)Cl]	1.0	NaBARF ₄	95
2	[Au(Indy*MeO)Cl]	1.0	NaBARF ₄	97
3	[Au(IMes)Cl]	1.0	NaBARF ₄	52
4	[Au(IPr)Cl]	1.0	NaBARF ₄	76

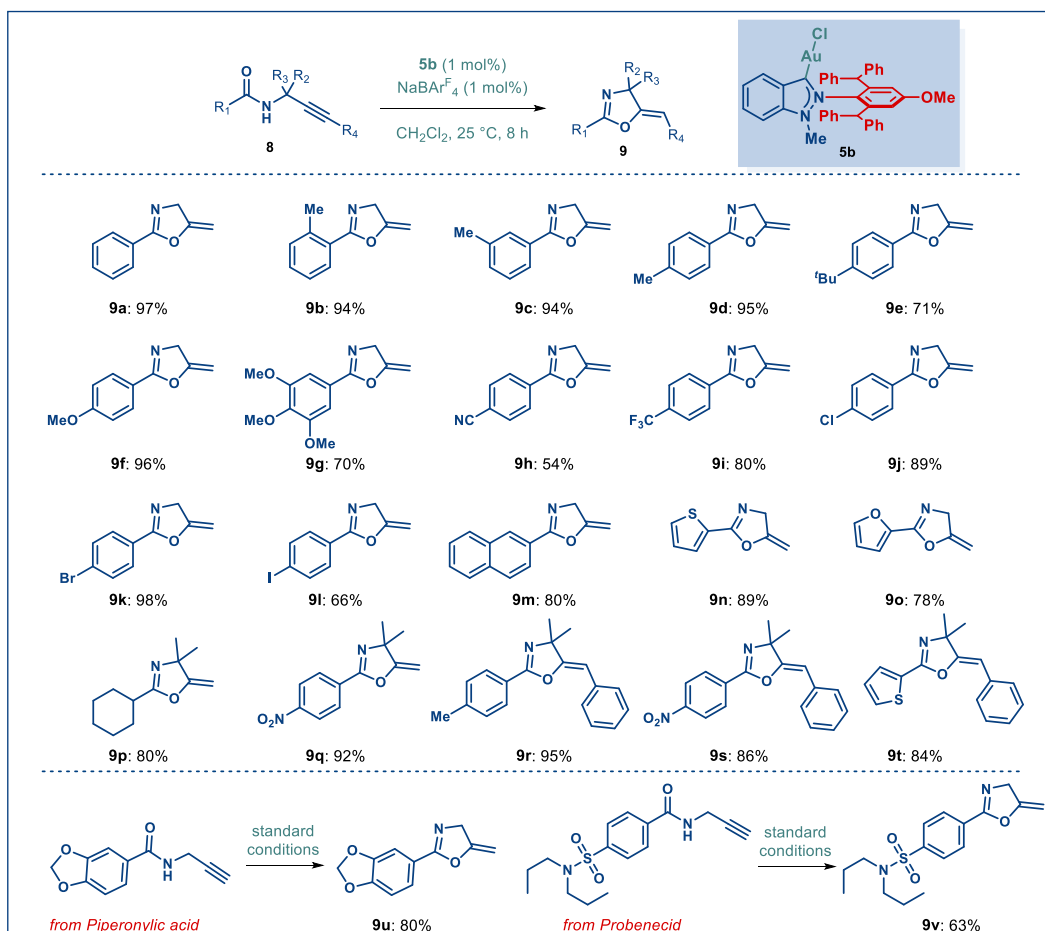
^aConditions: **8** (1.0 equiv), Au–NHC (1.0 mol%), NaBARF₄ (1.0 mol%), CH₂Cl₂, 25 °C, 8 h.

Evaluation of the substrate scope (Table 2) demonstrated broad generality of this cycloisomerization reaction with high efficiency for various aryl (**9a–9m**), heteroaryl (**9n–9o**), alkyl (**9p**) and substituted propargylic (**9q–9t**) substrates. It is notable that the reaction shows high functional group tolerance towards halides, such as Cl, Br, I (**9j–9l**) and electrophilic functions such as cyano (**9h**) and nitro (**9q**). The potential utility in medicinal chemistry has been demonstrated by the direct late-stage functionalization of *Piperonylic Acid* and *Probenecid* amides (**9u–9v**).

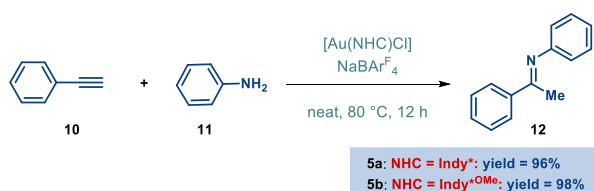
Encouraged by the high activity of Indy* complexes, we have also evaluated their performance in hydroamination of alkynes (Scheme 4). Pleasingly, both catalysts showed

excellent reactivity in the model hydroamination (96–98% yield), which outperformed related but not *N*-sterically-

Table 2. Scope of Au–NHC-Catalyzed Amide Cycloisomerization^a



^aConditions: propargylic amides (1.0 equiv), **5b** (1 mol%), NaBARF₄ (1 mol%), CH₂Cl₂ (0.5 M), 25 °C, 8 h. See SI for details.



Scheme 4. Au–NHC-Catalyzed Alkyne Hydroamination^a. ^aConditions: phenylacetylene (1.0 equiv), aniline (1.1 equiv), Au–NHC (0.5 mol%), NaBARF₄ (1.0 mol%), neat, 80 °C, 12 h.

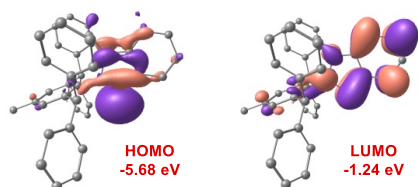


Figure 4. HOMO (σ-donating orbital) and LUMO (π-accepting orbital) of Indy*. B3LYP 6-311++g(d,p) level. See SI for details.

mechanism of hydroamination of terminal alkynes, it is now established that the rate-determining step is the nucleophilic

attack of the amine to the coordinated alkyne. However, strong donor ligands have been shown to be highly active in Au-catalyzed hydroaminations, which has been ascribed to the protodemetalation as the rate limiting step.¹⁹

To further evaluate the effect of IPr*-type substitution on the indazol-3-ylidene ligands, HOMO and LUMO energy levels of Indy* and Indy*MeO were determined at the B3LYP 6-311++g(d,p) level (Figure 4 and SI). The HOMO of Indy* (-5.68 eV) and Indy*MeO (-5.64 eV) indicate significantly stronger σ-donation than IPr (-6.01 eV), which is a standard electronic model for σ-donating NHCs. These values can be further compared with the standard SiPr (HOMO of -5.85 eV; LUMO of -0.42 eV) and MeCAAC (CAAC = cyclic (amino)(alkyl)carbene) (HOMO of -5.33 eV; LUMO of -0.51 eV).²⁰ Thus, Indy* ligands combine the steric properties of 2,6-bis(diphenylmethyl)aryl N-wingtip substitution with σ-donating and π-electronic character of non-classical *N*-heterocyclic carbenes.

Conclusions

In conclusion, we have reported the first class of sterically-hindered *N*-heterocyclic carbenes based on the indazole framework. The unique features of this class of ligands are (1) strong σ-donation of the carbene center imparted by the

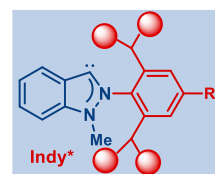
carbene placement at the C3 position of the versatile indazole ring, and (2) sterically-hindered, flexible *N*-substitution with the 2,6-bis(diphenylmethyl)aryl moiety that extends beyond the metal centre for the first time in non-classical *N*-heterocyclic carbenes. Considering the unique properties of indazole-derived carbenes, we anticipate that this class of ligands will find broad application in organic synthesis and catalysis.

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ABSTRACT



novel indazole-based carbenes
amide cycloisomerization
strong π -donation & flexible sterics
gram-scale Cadogan synthesis
differentiated steric environment
high stability & reactivity

TEP = 2044 cm⁻¹

%V_{bur} = 36.2%

