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IPr*^{Thia} – Wingtip-Flexible, Sterically-Hindered, Modular, N,C/S,C-Chelating Thiazole-Donor N-Heterocyclic Carbene Ligands

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PAPER

IPr*Thia – Wingtip-Flexible, Sterically-Hindered, Modular, N,C/S,C-Chelating Thiazole-Donor N-Heterocyclic Carbene Ligands

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N-Heterocyclic carbenes (NHCs) represent a pivotal class of ligands in coordination chemistry owing to their unique electronic and electronic properties. In particular, hemilabile N-heterocyclic carbenes have garnered significant attention over the past decade due to their capacity to transiently coordinate to metals and open coordination sites. However, hemilabile NHC ligands have been predominantly limited to N, O and P donors, while NHC ligands bearing versatile S-donors have been severely underdeveloped. Herein, we report wingtip-flexible, sterically-hindered NHC ligands that feature N,C/S,C-chelating thiazole donors in combination with the powerful IPr* (IPr* = (2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) scaffold. These ligands are prepared by a highly modular S_NAr arylation of thiazole derivatives. Full structural and electronic characterization is reported. The ligands feature high barrier to rotation around the N–thiazole axis (10 kcal/mol). The ligands are evaluated for their steric, electron-donating and π-accepting properties as well as coordination chemistry to Ag(I), Pd(II), Rh(I) and Se. Preliminary catalytic studies in Ag, Pd and Rh-catalysis are presented. The efficiency of the approach is highlighted by preparing a library of unsymmetrical imidazolium precursors. The mono-IPr* wingtip provides a highly-hindered yet sterically-flexible environment adjusting to metal centers, while the N-thiazolyl wingtip displays a fluxional behavior that interchanges from the hard/soft N,C to soft/soft S,C coordination. Considering the importance of hemilabile N-heterocyclic carbene ligands in metal stabilization in inorganic and organometallic chemistry, we expect that this class of ligands will be of broad interest.

Introduction

Hemilabile ligands play a central role in coordination chemistry.[1] In particular, in the past decade, tremendous progress has been made in using chelating N-heterocyclic carbene ligands, where the unique steric and electronic properties of the carbenic center in combination with a chelating heteroatom, such as O, N, P, provide access to stabilizing metal centers and opening coordination sites at the metal (Figure 1A).[2,3] However, despite a very significant progress in using O, N and P donors, NHC ligands bearing versatile S-donors are less developed.[4] Furthermore, despite the extensive research efforts to introduce sterically-hindered N-heterocyclic carbene ligands, which are now among the most frequently utilized NHCs in various areas of science ranging from inorganic chemistry through transition-metal-catalysis to surface chemistry and biological applications, as elegantly demonstrated by the groups of Nolan,[5] Glorius,[6] Bertrand,[7] Marko[8] and others[9] (Figure 1B), the introduction of hemilability on sterically-hindered NHC frameworks in a modular and practical manner has been a challenge.

In view of diverse applications of hemilabile NHC ligands and our own interest in ligand development,[10] we considered a new class of NHC ligands featuring N-thiazole wingtip in imidazol-2-ylidene architecture. The exocyclic N-thiazolyl wingtip is related to but structurally-distinct from thiazol-2-ylidenes, where the S-substituent is a part of the N-heterocyclic motif. We were particularly attracted to thiazoles because these heterocycles are among the most common S-heterocycles in organic synthesis and many methods for their generation are available.[11] Furthermore, thiazoles are considered privileged scaffolds in medicinal chemistry,[12] which might spur biomedical applications of imidazole–thiazole NHC ligand hybrids. A plethora of medicinal applications of NHC–metal complexes are worth noting.[13] Most importantly, following the Pearson's hard-soft acid-base principle, these ligands should exhibit unique chelation behavior spanning C,N and C,S orthogonal donor sites, and there are only few examples of such ligands reported.[14] Although at the outset of our study no examples of synthetically-useful N-Aryl-N-thiazolyl NHC ligands have been reported,[15] we hypothesized that the powerful S_NAr heteroarylation chemistry can be deployed to access the desired scaffolds in a highly practical and generic fashion.[15g] As the second key design element, we were cognizant of the recent advances made using bulky, wingtip-flexible NHCs, such as IPr*, where the inherent spatial properties of the ortho-benzhydryl substitution of the NHC wingtip enable precise control of the NHC geometry, protecting the metal centers, while simultaneously retaining strong σ-donation inherent to the imidazol-2-ylidene scaffold.[3c,3d, 4a,16]

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Electronic Supplementary Information (ESI) available: Experimental details and computational data. See DOI: 10.1039/x0xx00000x

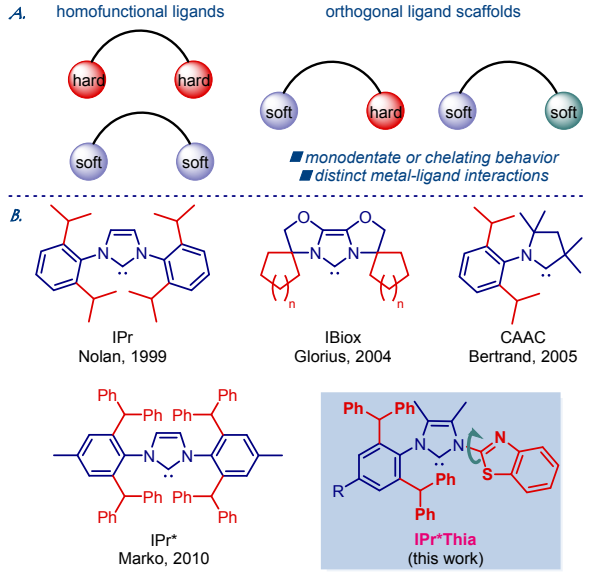
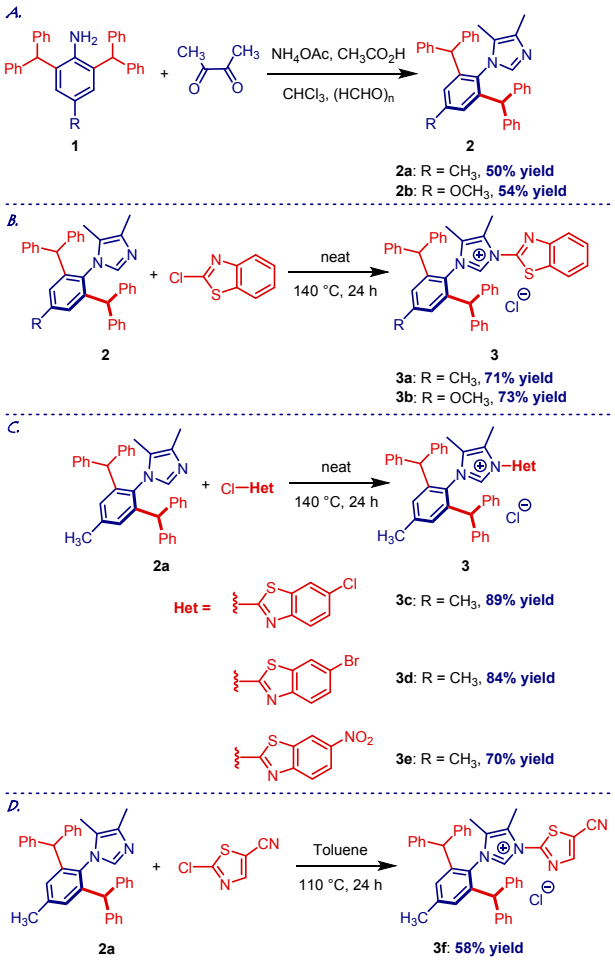


Fig. 1. (A) Graphical representation of homofunctional and orthogonal ligands. (B) State-of-the-art of sterically-demanding N-heterocyclic carbenes in inorganic and organometallic chemistry.

Results and Discussion

Our study commenced with the synthesis of imidazolium precursors featuring N-thiazolyl wingtips (Scheme 1). Two anilines, **1a–1b**, bearing 4-alkyl and 4-methoxy substitution were selected as model compounds, justified by the fact that IPr* and IPr*^{MeO}, the parent imidazol-2-ylidenes, are the most commonly used sterically-hindered, wingtip-flexible NHC derivatives in organometallic and inorganic arena (Scheme 1A).[3c,3d] 4,5-Dimethyl-substitution on the imidazole ring has been selected due to higher stability of imidazolium salts and the corresponding NHC–metal complexes. Initial assays were conducted using 2-chlorobenzimidazole as an S_NAr electrophile (Scheme 1B). After optimization, we determined that the desired condensation took place under neat conditions by heating a mixture of N-Ar-imidazole with 2-chlorobenzothiazole at 140 °C for 20 h.[17] This procedure allowed for isolation of N-thiazolyl imidazolium precursors **3a–3b** in 71-73% yields after simple recrystallization (**3a**, mp = 250-252 °C; **3b**, mp = 258-260 °C). In consideration of the biomedical importance of thiazolyl scaffolds, we next decided to evaluate the generality of this protocol (Scheme 1C). In the event, commercially-available 2-chlorobenzothiazoles bearing sensitive functional handles such as chloro (**3c**), bromo (**3d**) and nitro (**3e**) underwent the S_NAr coupling in good to excellent yields (70-89%). Furthermore, the procedure is not limited to benzothiazoles, and simple thiazoles can also participate in the coupling as illustrated by 2-chloro-5-cyanothiazole (**3f**) (Scheme 1D). In this case a more dilute conditions in toluene at 110 °C had to be used to prevent product decomposition. It is worth noting that in all cases, the products could be purified by recrystallization from the reaction mixtures, thus streamlining the synthesis. Furthermore, the functional group tolerance to Cl, Br, NO_2 and CN substitution provides ample handles for product manipulation by standard electrophilic or cross-coupling chemistry. Finally, it is worth noting that 2-chlorothiazoles are among the most common thiazole precursors available, which bodes well for the generation of analogues by this approach.

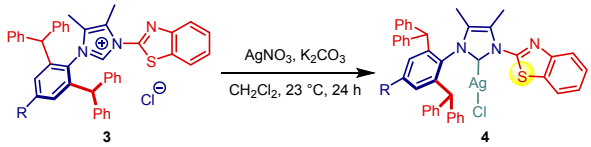
Scheme 1 Synthesis of Imidazolium Precursors



With the access to imidazolium salts, we next evaluated coordination chemistry of these novel ligands (Schemes 2–5). First, we were focused on determining the steric impact of these wingtip-flexible, hemilabile, thiazole-donor carbenes. For this purpose, we synthesized linear Ag(I)–NHC complexes using representative imidazoliums **3a–3b**. Thus, [Ag(IPr*^{Thia})Cl] (**4a**) and [Ag(IPr*^{MeOThia})Cl] (**4b**) were synthesized in 73-76% yields by the procedure reported by Gimeno and co-workers using $AgNO_3/K_2CO_3$ in CH_2Cl_2 at room temperature (Scheme 2).[18] The complexes were found to be stable to air and moisture.

Complexes **4a–4b** were characterized by x-ray crystallographic analysis (Figure 2). Complexes **4a–4b** were found to be monomeric. The complexes are characterized by linear coordination around silver ([Ag(IPr*^{Thia})Cl], C–Ag–Cl, 172.23 (14)°, C–Ag, 2.092 (5) Å, Ag–Cl, 2.3202 (16) Å; [Ag(IPr*^{MeThia})Cl], C–Ag–Cl, 175.8 (2)°; C–Ag, 2.088 (7) Å; Ag–Cl, 2.314 (2) Å). Interestingly, both complexes **4a–4b** feature syn-coplanar conformation of the thiazolyl ring with the sulfur atom oriented towards the metal in both [Ag(IPr*^{Thia})Cl] (**4a**) and [Ag(IPr*^{MeOThia})Cl] (**4b**) (**4a**: [Ag(IPr*^{Thia})Cl], S–Ag, 3.120 Å; **4b**: [Ag(IPr*^{MeOThia})Cl], S–Ag, 3.231 Å), indicating weak stabilization of the metal center by sulfur. The dihedral angle in [Ag(IPr*^{Thia})Cl] (**4a**) of $C_{(carbene)}$–N–C–S is 24.8 (6)°, while the angle between the planes of the imidazolyl and thiazolyl ring is 22.5°. The dihedral angle in [Ag(IPr*^{MeOThia})Cl] (**4b**) of $C_{(carbene)}$–N–C–N is 43.5 (9)°, while the angle between the planes of the imidazolyl and thiazolyl ring is 41.2°, indicating a slight tilt of the thiazolyl ring with respect to the imidazolyl ring.

Scheme 2 Synthesis of Ag(I)–NHC Complexes **4a–4b**



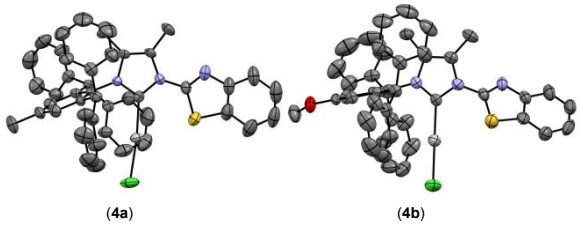


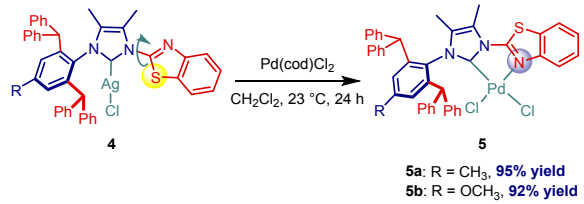
Fig. 2. X-ray crystal structures of complexes **4a–4b**. CCDC 2354247, **4a**; CCDC 2354248, **4b**. See SI for selected bond lengths and angles.

The geometry of complexes **4a–4b** was further analyzed by the buried volume method pioneered by Nolan and Cavallo (Chart 1A–1B).[19] The analysis revealed an exceptionally high % buried volume (%V_{bur}) of the [Ag(IPr*^{Thia})Cl] (**4a**) complex of 54.7% with quadrant distribution of SW, 67.2%; NW, 58.0%; NE, 33.0%; SE, 60.7%. This high buried volume is a result of a steric interaction of the ortho-benzylidene wingtip with the catalytic pocket of the complex. This value is significantly higher than that of the model imidazol-2-ylidene, IPr, [Ag(IPr)Cl], (%V_{bur}) = 43.8% with quadrant distribution of SW, 38.1%; NW, 51.1%; NE, 52.4%; SE, 33.7%, and matches the sterically-demanding and symmetrical IPr*, [Ag(IPr*)Cl], (%V_{bur}) = 53.5% with quadrant distribution of SW, 41.0%; NW, 52.6%; NE, 52.2%; SE, 68.3%. The % buried volume (%V_{bur}) of [Ag(IPr*^{MeOThia})Cl] (**4b**) complex is 46.6% with quadrant distribution of SW, 66.9%; NW, 46.2%; NE, 43.9%; SE, 29.6%.

As a next step of our investigation, we prepared chelating Pd(II)–NHC complexes, [Pd(IPr*^{Thia})Cl_2] (**5a**) and [Pd(IPr*^{MeOThia})Cl_2] (**5b**) to force the N,C coordination of these hemilabile N-thiazolyl-imidazol-2-ylidene ligands (Scheme 3). Thus, [Pd(IPr*^{Thia})Cl_2] (**5a**) and [Pd(IPr*^{MeOThia})Cl_2] (**5b**) were synthesized by transmetallation of Ag(I)–NHC complexes **4a–4b** with [Pd(cod)Cl_2] at room temperature.[20] Pd(II)–NHC complexes **5a–5b** were crystalline, and their structures were determined by x-ray crystallography (Figure 3).

As expected, the complexes are characterized by a square planar geometry around palladium with N–C coordination, while the imidazolyl and thiazolyl rings are coplanar ([Pd(IPr*^{Thia})Cl_2] (**5a**), $C_{(carbene)}$–N–C–N, 0.2 (7)°; [Pd(IPr*^{MeOThia})Cl_2] (**5b**), $C_{(carbene)}$–N–C–N, 7.1 (3)°. The C–Pd/N–Pd bond lengths are [Pd(IPr*^{Thia})Cl_2] (**5a**), $C_{(carbene)}$–Pd, 1.985 (5) Å; $N_{(thiazolyl)}$–Pd, 2.091 (4) Å; [Pd(IPr*^{MeOThia})Cl_2] (**5b**), $C_{(carbene)}$–Pd, 1.966 (2) Å; $N_{(thiazolyl)}$–Pd, 2.091 (2) Å, and the complexes are characterized by a strong trans influence of the NHC ligand, [Pd(IPr*^{Thia})Cl_2] (**5a**), $C_{(carbene)}$Pd–Cl, 2.3563 (12) Å; $N_{(thiazolyl)}$Pd–Cl, 2.2752 (14) Å; [Pd(IPr*^{MeOThia})Cl_2] (**5b**), $C_{(carbene)}$Pd–Cl, 2.3508 ’(6) Å; $N_{(thiazolyl)}$Pd–Cl, 2.2642 (6) Å. The geometry of complexes **5a–5b** was further analyzed by the buried volume method (Chart 1C–1D). Thus, the [Pd(IPr*^{Thia})Cl_2] (**5a**) complex is characterized by (%V_{bur}) of 40.7% with quadrant distribution of SW, 30.3%; NW, 34.4%; NE, 51.1%; SE, 46.8%, and the [Pd(IPr*^{MeOThia})Cl_2] (**5b**) complex features (%V_{bur}) of 40.8% with quadrant distribution of SW, 32.1%; NW, 34.5%; NE, 50.9%; SE, 45.9%. Thus, the change of coordination from linear Ag(I)–NHC to square planar Pd(II)–NHC enforces a full rotation around the $N_{(imidazolyl)}$–$C_{(thiazolyl)}$ axis, indicating flexibility of the thiazolyl ring in this class of ligands.

Scheme 3 Synthesis of Pd(II)–NHC Complexes **5a–5b**



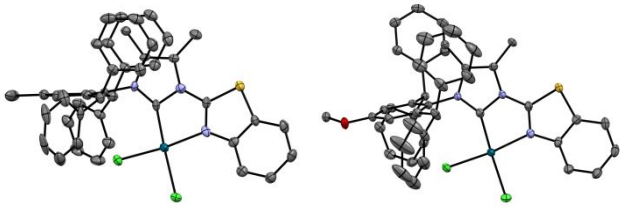


Fig. 3. X-ray crystal structures of complexes **5a–5b**. CCDC 2354249, **5a**; CCDC 2354250, **5b**. See SI for selected bond lengths and angles.

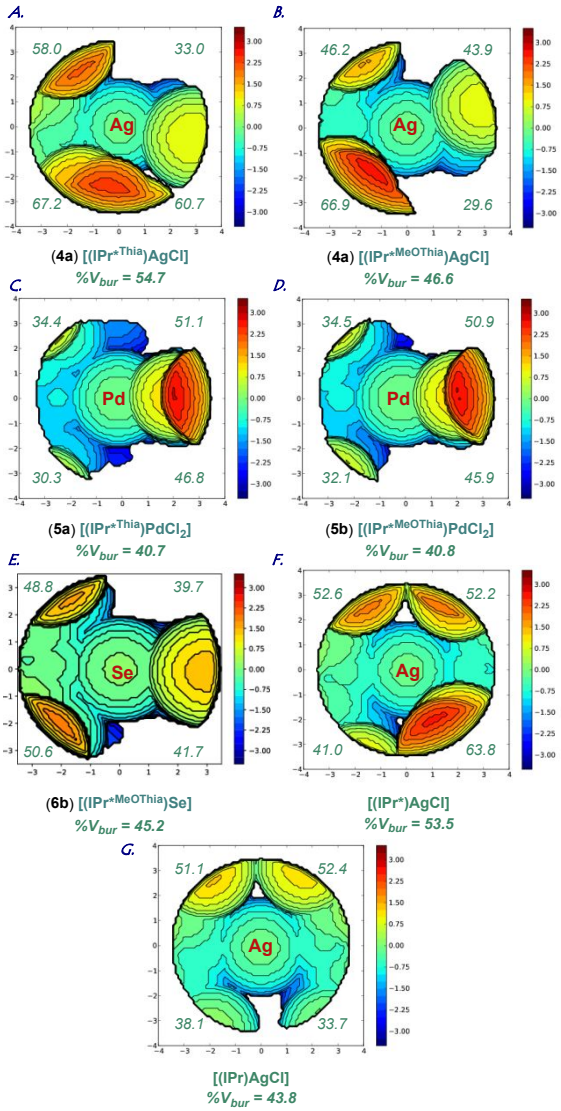


Chart 1. Topographical steric maps of (A) [(IPr*^{Thia})AgCl] (**4a**), (B) [(IPr*^{MeOThia})AgCl] (**4b**), (C) [(IPr*^{Thia})$PdCl_2$] (**5a**), (D) [(IPr*^{MeOThia})$PdCl_2$] (**5b**), (E) [(IPr*^{MeOThia})Se] (**6b**) showing %V_{bur} per quadrant. (F) [(IPr*)AgCl] and (G) [(IPr)AgCl] are shown for comparison.

Scheme 4 Synthesis of Se–NHC Complex **6b**

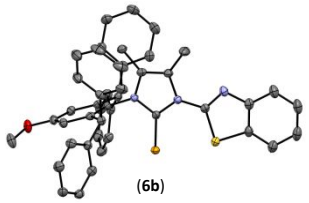
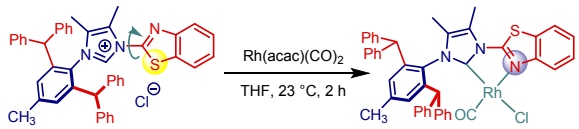


Fig. 4. X-ray crystal structure of complex **6b**. CCDC 2372438. See SI for selected bond lengths and angles.

Scheme 5 Synthesis of [RhCl(NHC)(CO)] Complex **7a**



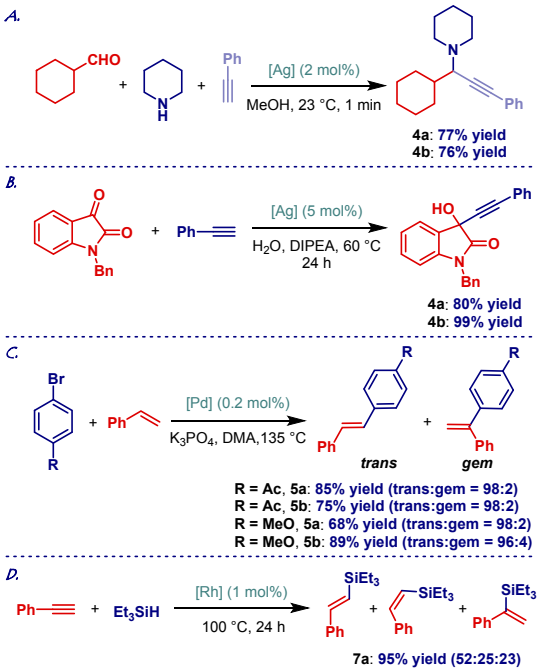
To gain insight into the electronic properties of these N-thiazolyl NHC ligands, we synthesized a representative selenourea adducts **6a–6b**, [Se(IPr*^{Thia})] and [Se(IPr*^{MeOThia})] (Scheme 4), and a representative Rh(I)–NHC complex **7a**, [Rh(IPr*^{Thia})(CO)Cl] (Scheme 5). The seleourea adduct **6b** was crystalline and, the structure was characterized by x-ray crystallography (Figure 4). Despite extensive efforts, we were unable to obtain x-ray quality crystals of the Rh(I)–NHC complex **7a**.

Complex **6b** crystallized as a single molecule in the unit cell. The C–Se bond length in [Se(IPr*^{MeOThia})] (**6b**) is 1.820. The complex is characterized by a syn-coplanar conformation of the thiazolyl and imidazolyl rings with the sulfur atom towards selenium, $C_{(carbene)}$–N–C–S, 6.5°; Se–S, 3.076 Å. Analysis of the selenourea adduct [Se(IPr*^{MeOThia})] (**6b**) by the buried volume method revealed the (%V_{bur}) of 45.2% with quadrant distribution of SW, 50.6%; NW, 48.8%; NE, 39.7%; SE, 41.7% (Chart 1E), further confirming rotational flexibility of the N-thiazolyl wingtip.

From the electronic characterization standpoint, the synthesis of selenoaurea adducts permits to gauge π-backbonding properties of NHC ligands. Thus, the [Se(IPr*^{Thia})] (**6a**) complex is characterized by the δ Se value of 151.94 ppm ($CDCl_3$), which can be compared with IPr (δ Se = 90 ppm) and IPr* (δ Se = 106 ppm). Thus, the thiazolyl ring substitution results in an enhancement of π-acceptance of these ligands. In contrast, the Rh(I)–NHC complex, [Rh(IPr*^{Thia})(CO)Cl] (**7a**), is characterized by the CO stretching of 1995 cm^{-1}. This value can be compared with related N,C chelating Rh(I)–NHC complexes, and indicates an enhancement of π-backbonding of the ligand.

Next, we briefly investigated the catalytic activity of these sterically-hindered hemilabile thiazolyl-donor NHC ligands in Ag(I), Pd(0) and Rh(I) catalysis (Scheme 6). As shown, [Ag(IPr*^{Thia})Cl] (**4a**) and [Ag(IPr*^{MeOThia})Cl] (**4b**) showed promising activity in Ag(I)-catalyzed A3-coupling and alkynylation of isatins, while [Pd(IPr*^{Thia})Cl_2] (**5a**), [Pd(IPr*^{MeOThia})Cl_2] (**5b**) and [Rh(IPr*^{Thia})(CO)Cl] (**7a**) performed well in Heck coupling and alkyne hydrosilylation. The results indicate generality in C–N, C–C and C–Si bond formation. The catalytic activity of the obtained complexes is comparable to their symmetrical analogues in this type of reactions.[21]

Scheme 6 Catalytic Activity of [IPr*^{Thia}–M] Complexes



To gain further insight into the electronic properties of the IPr*^{Thia} ligands, we determined HOMO and LUMO energy levels at the B3LYP 6-311++g(d,p) level (Figure 5 and SI). It is now established that calculated HOMO and LUMO energy levels provide the most accurate determination of nucleophilicity (more σ-donating, higher HOMO) and electrophilicity (more π-accepting, lower LUMO) of N-heterocyclic carbene ligands. The σ-donor orbital of IPr*^{Thia} (HOMO-1 due to required symmetry, -6.41 eV) is in the same range as IPr* (-6.12 eV), and can be compared with the classical IPr (-6.01 ev). The π-accepting orbital (LUMO+6 due to required symmetry) of IPr*^{Thua} (-0.52 eV) can be compared with IPr* (-0.90 eV) and IPr (-0.48 eV). The π-donor orbital of IPr*^{Thia} (HOMO, -6.08 eV) can be compared with the corresponding π-donor orbitals of IPr* (-6.28 eV) and IPr (-6.55 eV). The LUMO orbital of IPr*^{Thia} (-1.30 eV) is located on the benzothiazole ring. Thus, these results indicate that IPr*^{Thia} ligands can be electronically characterized as strongly σ-nucleophilic, yet sterically rotationally-flexible at both imidazol-2-ylidene wingtips.

Next, we also performed rotational studies to gain information about the rotatable character of the thiazolyl wingtip (Figure 6). We obtained a detailed rotational profile of the parent carbene IPr*^{Thia} by a systematic rotation around the $C_{(Me)}$–N–$C_{(thia)}$–S dihedral angle. The rotation was performed in both directions. The rotational profile of IPr*^{Thia} identified the energy minimum at ca. 180° $C_{(Me)}$–N–$C_{(thia)}$–S angle in a syn eclipsing $C_{(carbene)}$–N–$C_{(thia)}$–S conformation (ca. 0.0°) (0 kcal/mol). The energy maximum is located at ca. 0° $C_{(Me)}$–N–$C_{(thia)}$–S dihedral angle (9.9 kcal/mol) in a syn eclipsing $C_{(carbene)}$–N–$C_{(thia)}$–N conformation (ca. 0.0°). Thus, the rotational profile of IPr*^{Thia} provides further insight into the fluxional character of the N-thiazolyl wingtip. The overall barrier to rotation (ca. 10 kcal/mol) is much higher than in the related N-oxazolyl ligands (ca. 3.5 kcal/mol), a result of much larger radius of oxygen to sulfur substitution, indicating access to more sterically defined catalytic pockets in IPr*^{Thia} ligands in combination with soft sulfur stabilization.

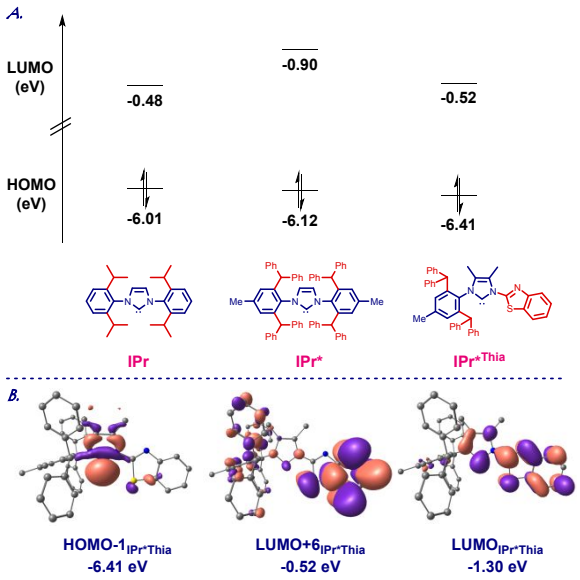


Fig. 5. (A) HOMO and LUMO energy levels (eV). (B) HOMO-1, LUMO+6 and LUMO (eV) of IPr*^{Thia} calculated at B3LYP 6-311++g(d,p). See SI.

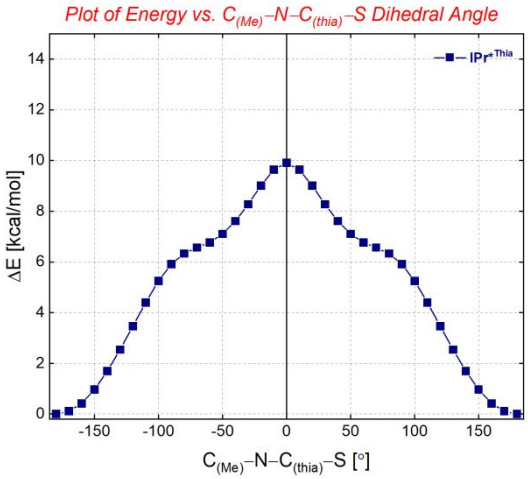


Fig. 6. Rotational profile of IPr*^{Thia} (ΔE, kcal/mol, vs. C(Me)–N–C(thia)–S [°]).

Conclusions

In summary, hemilabile S-donor N-heterocyclic carbenes have been underutilized as ancillary ligands in metal stabilization. We have reported a new class of hemilabile sterically-hindered NHC ligands that combine the characteristics of N,C/S,C-chelating thiazole donors in combination with the broadly popular IPr*-sterically-demanding and wingtip-flexible scaffold. These ligands are characterized by a modular synthetic access by a practical, chromatography-free arylation with readily available thiazole derivatives. The ligands have been evaluated in their coordination chemistry to Ag(I), Pd(II), Rh(I) and Se. Full structural and electronic characterization has been reported, with one of the Ag(I)–NHC derivatives characterized by one of the highest (%V_{bur}) of unsymmetrical imidazol-2-ylidene derivatives reported to date (54.7%). The study established a N,C/S,C fluxional behaviour of the N-thiazolyl wingtip, adjusting to metal centres. Considering the importance of metal stabilization by orthogonal soft and hard donor functions in combination with the carbenic centers, we expect that this class of ligands will be of broad interest in inorganic and organometallic synthesis.

Experimental

General methods. All experiments involving metal complexes were performed using standard Schlenk techniques under nitrogen or argon unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Compounds **1a**,[22] **1b**,[23] and **2a**[24] have been previously reported in the literature. Spectroscopic properties matched literature data. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker spectrometers at 400 (^{1}H NMR) and 100 MHz (^{13}C NMR). Infrared spectra were recorded on a Nicolet Nexus 2002 FTIR spectrometer. High-resolution mass spectra (HRMS) and elemental analyses were measured on a 7T Bruker Daltonics FT-MS and Vario EL II (CHNS) instrument respectively.

General Procedure for the Synthesis of Anilines. Anilines were synthesized according to literature procedures.[22, 23]

2,6-Dibenzhydryl-4-methylaniline (1a).[22] The product was obtained in 52% yield (24.00 g, 54.60 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.2 Hz, 8H), 7.20 (d, *J* = 7.2 Hz, 4H), 7.09 (d, *J* = 7.0 Hz, 8H), 6.38 (s, 2H), 5.44 (s, 2H), 3.27 (s, 2H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.90, 139.78, 129.68, 129.36, 129.18, 128.62, 126.73, 52.50, 21.16.

4-Methoxy-2,6-bis(diphenylmethyl)aniline (1b).[23] The product was obtained in 93% yield (44.00 g, 96.57 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.3 Hz, 8H), 7.19 (t, *J* = 7.2 Hz, 4H), 7.09 (d, *J* = 7.3 Hz, 8H), 6.20 (s, 2H), 5.47 (s, 2H), 3.40 (s, 3H), 3.12 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.92, 142.61, 136.03, 130.92, 129.63, 128.67, 126.84, 114.48, 55.23, 52.60.

General Procedure for the Synthesis of 1-Arylimidazoles. *N*-Aryl imidazoles were synthesized according to a modified literature procedure.[24] To a aniline derivative (12 mmol) in dry $CHCl_3$ (20 mL), diacetyl (10 mmol), acetic acid (50 mmol), NH_4OAc (12 mmol), paraformaldehyde (10 mmol), and H_2O (0.5 mL) were added and the mixture was refluxed for 48 h. After removal of the solvent, the dark residue was dissolved in Et_2O and basified to pH 14 in an ice bath with aqueous 40% KOH solution. The resulting mixture was extracted with Et_2O, and the combined organic layers were washed with H_2O and dried over Na_2SO_4. Concentration and purification through silica gel column chromatography gave the desired product.

1-(2,6-Dibenzhydryl-4-methylphenyl)-4,5-dimethyl-1*H*-imidazole (2a).[24] The product was obtained in 50% yield (2.00 g, 3.85 mmol) as a pale brown solid. Purification by flash chromatography (hexane/AcOEt = 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 12H), 6.97 – 6.93 (m, 4H), 6.91 – 6.88 (m, 4H), 6.86 (s, 2H), 6.61 (s, 1H), 4.99 (s, 2H), 2.26 (s, 3H), 2.15 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.92, 142.86, 142.48, 138.90, 135.67, 133.92, 132.37, 129.66, 129.62, 129.26, 128.53, 128.37, 126.65, 123.46, 51.51, 21.93, 13.07, 7.91.

1-(2,6-Dibenzhydryl-4-methoxyphenyl)-4,5-dimethyl-1*H*-imidazole (2b).[10a] The product was obtained in 54% yield (2.17g, 4.06 mmol) as a pale yellow solid. Purification by flash chromatography (hexane/AcOEt = 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 12H), 6.98 – 6.95 (m, 4H), 6.92 – 6.89 (m, 4H), 6.58 (d, *J* = 1.2 Hz, 3H), 5.00 (s, 2H), 3.61 (s, 3H), 2.15 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.39, 144.62, 142.64, 142.22, 135.95, 133.86, 129.58,

129.19, 128.57, 128.41, 127.84, 126.76, 123.56, 114.44, 55.38, 51.76, 13.10, 7.88.

General Procedure for the Synthesis of Imidazolium Salts. Imidazolium salts were synthesized according to a modified literature procedure.[17,26] 1-Arylimidazole (2a or 2b) and the thiazole derivatives were stirred in a closed pressure tube for 20 h at 140 °C. The reaction mixture was then allowed to cool to room temperature and washed with diethyl ether until the supernatant was colorless. The products (**3a**, **3b**, **3c**, **3d**) were then dried in vacuo to give the desired imidazolium salt.

1-(Benzo[*d*]thiazol-2-yl)-3-(2,6-dibenzhydryl-4-methylphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium Chloride (3a). *New compound.* The product was obtained in 71% yield (0.35 g, 0.51 mmol) as beige powder of mp 250 - 252 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.27 - 7.23 (m, 14H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.99 (d, *J* = 6.7 Hz, 4H), 6.76 (s, 2H), 5.36 (s, 2H), 2.50 (s, 3H, CH_3), 2.21 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.13, 149.66, 142.04, 141.53, 140.96, 140.74, 139.40, 134.32, 130.59, 129.64, 129.39, 129.25, 128.97, 128.77, 128.40, 127.33, 127.21, 127.06, 123.77, 122.34, 52.21, 21.97, 10.95, 7.95. HRMS (ESI/Q-TOF)_m/z (%) $[M]^+$ calcd for $C_{45}H_{38}N_3S^+$ 652.2786 found 652.2726.

1-(Benzo[*d*]thiazol-2-yl)-3-(2,6-dibenzhydryl-4-methoxyphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium Chloride (3b). *New compound.* The product was obtained in 73% yield (0.29 g, 0.41 mmol) as beige powder of mp 258 - 260 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.50 (dd, *J* = 11.8, 4.7 Hz, 1H), 7.26 – 7.23 (m, 14H), 7.16 – 7.14 (m, 2H), 7.01 (d, *J* = 6.4 Hz, 4H), 6.45 (s, 2H), 5.39 (s, 2H), 3.53 (s, 3H), 2.49 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.98, 153.28, 149.72, 144.17, 140.73, 140.69, 139.83, 134.41, 129.68, 129.41, 129.07, 128.85, 127.37, 127.33, 127.19, 127.11, 123.80, 123.52, 122.45, 115.50, 55.33, 52.44, 11.03, 7.99. HRMS (ESI/Q-TOF) m/z (%) $[M]^+$ calcd for $C_{45}H_{38}N_3OS^+$ 668.2735 found 668.2691.

6-Chloro-1-(Benzothiazol-2-yl)-3-(2,6-dibenzhydryl-4-methylphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium Chloride (3c). *New compound.* The product was obtained in 89% yield (0.20 g, 0.27 mmol) as beige powder of mp 248 - 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.22 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.57 (dd, *J* = 8.7 Hz, 2.0 Hz, 1H), 7.27 – 7.20 (m, 14H), 7.16 (d, *J* =7.1 Hz, 2H), 6.99 (d, *J* = 6.4 Hz, 4H), 6.76 (s, 2H), 5.38 (s, 2H), 3.53 (s, 3H), 2.21 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.72, 148.17, 142.12, 141.66, 140.97, 140.86, 139.74, 135.56, 133.10, 130.67, 129.74, 129.46, 129.03, 128.83, 128.43, 128.35, 127.27, 124.62, 121.97, 52.19, 22.03, 11.04, 7.88. HRMS (ESI/Q-TOF)_m/z (%) $[M]^+$ calcd for $C_{45}H_{37}ClN_3S^+$ 686.2396 found 686.2434.

6-Bromo-1-(Benzothiazol-2-yl)-3-(2,6-dibenzhydryl-4-methylphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium Chloride (3d). *New compound.* The product was obtained in 84% yield (0.20 g, 0.26 mmol) as off-white powder of mp 257 - 259 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.38 (s, 1H), 8.04 (d, *J* = 1.7 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.67 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.27 – 7.21 (m, 14H), 7.15 (d, *J* = 7.0 Hz, 2H), 6.99 (d, *J* = 6.4 Hz, 4H), 6.75 (s, 2H), 5.38 (s, 2H), 2.48 (s, 3H), 2.21 (s, 3H), 1.31 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 153.76, 148.48, 142.08, 141.61, 140.91, 140.86, 139.91, 135.92, 131.01, 130.65, 129.70, 129.46, 129.00, 128.81, 128.41, 127.25, 124.91, 124.84, 120.70, 52.20, 22.01, 11.04, 7.87. HRMS (ESI/Q-TOF)_m/z (%) $[M]^+$ calcd for $C_{45}H_{37}BrN_3S^+$ 730.1891 found 730.1921.

6-(Oxidaneyl)diazenyl-1-(Benzothiazol-2-yl)-3-(2,6-dibenzhydryl-4-methylphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium Chloride (3e). *New compound.* A mixture of 1-Arylimidazole (**2a**) and 2-chloro-6-nitrobenzothiazole was kept neat at 170 °C for 12 h. After cooling, the formed solid was purified by repetitive precipitation from CH_2Cl_2–Et_2O mixtures and the resulting product dried in vacuo. The product was obtained in 70% yield (0.16 g, 0.22 mmol) as pale yellow powder of mp 180 - 182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.65 (s, 1H) 8.86 (d, *J* = 2.1 Hz, 1H), 8.43 (dd, *J* = 9.0, 2.2 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 7.27 – 7.22 (m, 14H), 7.16 (t, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 6.3 Hz, 4H), 6.76 (s, 2H), 5.42 (s, 2H), 2.51 (s, 3H), 2.22 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.26, 153.25, 146.09, 142.09, 141.80, 140.90, 140.82, 140.77, 134.83, 130.72, 129.75, 129.49, 129.08, 128.87, 128.80, 128.32, 127.32, 124.24, 119.10, 52.21, 22.05, 11.20, 7.83. HRMS (ESI/Q-TOF)_m/z (%) $[M]^+$ calcd for $C_{45}H_{37}N_5OS^+$ 695.2719 found 695.2662.

5-Carbonitrile-1-(thiazol-2-yl)-3-(2,6-dibenzhydryl-4-methylphenyl)-4,5-dimethyl-1*H*-imidazol-3-ium Chloride (3f). *New compound.* The imidazole salt was synthesized according to the literature procedure using 1-arylimidazole (**2a**) and 2-chlorothiazole-5-carbonitrile in toluene, then the mixture was refluxed overnight. During the reaction, a precipitate formed which, after cooling, was washed twice with Et_2O and then the formed solid was purified by repeated precipitation from CH_2Cl_2-Et_2O mixtures, and the obtained product was dried in vacuum to obtain the desired imidazolium salt. The product was obtained in 58% yield (0.12 g, 0.18 mmol) as off-white powder of mp 233 - 235 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.15 (s, 1H), 7.26 (d, *J* = 7.7 Hz, 10H), 7.18 (d, *J* = 5.9 Hz, 6H), 7.01 (s, 4H), 6.77 (s, 2H), 5.45 (s, 2H), 2.36 (s, 3H), 2.22 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.04, 148.94, 142.22, 141.83, 140.92, 140.04, 130.70, 129.74, 129.43, 129.07, 128.86, 128.24, 127.31, 127.27, 110.56, 108.94, 51.98, 22.04, 10.71, 7.79. HRMS (ESI/Q-TOF)_m/z (%) $[M]^+$ calcd for $C_{42}H_{35}N_4S^+$ 627.2582 found 627.2605.

General Procedure for the Synthesis of [Ag(NHC)Cl] Complexes. Ag(I)–NHC complexes were synthesized according to a modified literature procedure.[18] A mixture of imidazolium salt (**3a** or **3b**) (1 equiv.) and $AgNO_3$ (1 equiv.) in dichloromethane was stirred for 2 min and then K_2CO_3 (17 equiv.) was added. After 24 h, the mixture was filtered through Celite and the solvent was removed in vacuo until 2 mL (c.a.). The product was precipitated with ether and washed to give a white solid.

[Ag(IPr*^{Thiaz})Cl] (4a). *New compound.* The product was obtained in 76% yield (0.47 g, 0.59 mmol) as beige solid. Single crystals of 4a were obtained by slow evaporation of a saturated solution in CH_2Cl_2/Et_2O at room temperature, yielding suitable crystals for X-ray diffraction studies. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.14 (m, 12H), 7.04 (d, *J* = 7.4 Hz, 4H), 6.95 (d, *J* = 6.7 Hz, 4H), 6.81 (s, 2H), 5.21 (s, 2H), 2.50 (s, 3H,), 2.26 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.57, 185.39, 183.07, 182.89, 158.87, 150.32, 142.27, 141.47, 141.13, 140.21, 133.29, 133.01, 130.30, 129.81, 129.32, 129.29, 128.63, 127.20, 127.07, 126.58, 126.52, 126.35, 123.31, 122.10, 52.11, 22.00, 11.50, 8.36. Anal. Calcd for $C_{45}H_{37}AgClN_3S$ (795.19): C, 67.97; H, 4.69; N, 5.28; S, 4.03. found: C, 67.82; H, 4.67; N, 5.22; S, 3.97.

[Ag(IPr*^{MeThiaz})Cl] (4b). *New compound.* The product was obtained in 73% yield (0.11 g, 0.14 mmol) as beige solid. Single crystals of 4a were obtained by slow evaporation of a saturated solution in CH_2Cl_2/Et_2O at room temperature, yielding suitable crystals for X-ray diffraction studies. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 1H), 7.27 (dd, *J* = 26.0, 8.2 Hz, 12H), 7.05 (d, *J* = 7.3 Hz, 4H), 6.96 (d, *J* = 6.5 Hz, 4H), 6.51 (s, 2H), 5.21 (s, 2H), 3.61 (s, 3H), 2.49 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 187.85, 187.47, 186.49, 186.05, 160.11,

150.36, 144.19, 141.20, 140.94, 133.04, 129.79, 129.38, 129.31, 129.03, 128.70, 127.35, 127.20, 127.07, 126.53, 126.47, 126.38, 123.33, 122.14, 115.12, 55.37, 52.39, 11.55, 8.38. Anal. Calc for $C_{45}H_{37}AgClN_3OS$ (811.19): C, 66.63; H, 4.60; N, 5.18; S, 3.95. Found: C, 66.59; H, 4.71; N, 5.20; S, 3.90.

General Procedure for the Synthesis of [Pd(NHC)Cl$_2$] Complexes. Palladium complexes were synthesized according to a modified literature procedure.[20] [$PdCl_2$(1,5-COD)] (1 equiv.) was added to a solution of Ag(I)–NHC complex (4a or 4b) (1 equiv.) in CH_2Cl_2 with exclusion of light. The mixture became cloudy immediately. After one night at room temperature, the solution was filtered through Celite. The solvent was removed in vacuo**.**

[Pd(IPr*^{Thiaz})Cl$_2$] (5a). *New compound.* The product was obtained in 95% yield (0.20 g, 0.25 mmol) as yellow solid. Single crystals of 5a were obtained by slow evaporation of a saturated solution in CH_2Cl_2/Hex at room temperature, yielding suitable crystals for X-ray diffraction studies. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 7.9 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 4H), 7.46 (dd, *J* = 25.0, 7.5 Hz, 12H), 7.22 (d, *J* = 6.9 Hz, 4H), 7.06 (s, 2H), 5.78 (s, 2H), 2.50 (s, 3H), 2.43 (s, 3H), 0.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.64, 155.64, 147.44, 142.31, 141.47, 140.49, 139.69, 133.36, 132.71, 130.13, 130.00, 128.95, 128.46, 128.34, 127.19, 127.00, 126.57, 124.93, 121.94, 121.37, 117.04, 52.15, 22.11, 9.85, 7.18. Anal. calcd for $C_{45}H_{37}Cl_2N_3PdS$ (829.19): C, 65.18; H, 4.50; N, 5.07; S, 3.87. Found: C, 65.10; H, 4.46; N, 4.95; S, 3.77.

[Pd(IPr*^{MeThiaz})Cl$_2$] (5b). *New compound.* The product was obtained in 92% yield (0.19 g, 0.23 mmol) as yellow solid. Single crystals of 5a were obtained by slow evaporation of a saturated solution in CH_2Cl_2/Hex at room temperature, yielding suitable crystals for X-ray diffraction studies. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.46 (d, *J* = 8.5 Hz, 1H), 8.46 (dd, *J* = 8.1, 0.8 Hz, 1H), 8.18 – 8.14 (m, 1H), 8.09 – 8.05 (m, 1H), 7.85 (d, *J* = 7.4 Hz, 4H), 7.77 (t, *J* = 7.6 Hz, 4H), 7.70 – 7.66 (m, 8H), 7.51 – 7.47 (m, 4H), 7.01 (s, 2H), 6.01 (s, 2H), 4.09 (s, 3H), 2.68 (s, 3H), 0.43 (s, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 162.10, 159.79, 147.38, 143.27, 142.17, 139.97, 133.29, 129.90, 129.80, 129.17, 129.09, 128.65, 128.54, 128.40, 128.22, 128.15, 127.03, 126.93, 126.58, 124.31, 121.98, 121.59, 114.42, 55.14, 52.17, 9.54, 6.82. Anal. calcd for $C_{45}H_{37}Cl_2N_3OPdS$ (845.19): C, 63.95; H, 4.41; N, 4.97; S, 3.79. Found: C, 63.70; H, 4.55; N, 4.93; S, 3.67.

General Procedure for the Synthesis of [Se(NHC)] Complexes. Selenium complex was synthesized according to a modified literature procedure.[25] A 7-mL screwcap vial equipped with a septum cap and a stirring bar was charged with imidazolium salt (3a) (0.16 g, 0.235 mmol, 1 equiv.), Se (0.02 g, 1.1 equiv.) and acetone (1 mL). The mixture was stirred at 40 °C for 15 min. NEt_3 (0.1 mL, 3 equiv.) was then added in one portion and the mixture was stirred overnight at 60 °C. Afterwards, the mixture was filtered through a plug silica gel and washed with DCM (20 mL). All volatiles were then removed under vacuum. The product was obtained as a yellow microcrystalline material.

[(IPr*^{Thiaz})Se] (6a). *New compound.* The product was obtained in 67% yield (0.28 g, 0.39 mmol) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.52 (s, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 4H), 7.22 – 7.19 (m, 8H), 7.16 (d, *J* = 7.0 Hz, 4H), 7.05 (d, *J* = 7.1 Hz, 4H), 6.87 (s, 2H), 5.33 (s, 2H), 2.25 (s, 3H), 2.17 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.90, 157.18, 148.86, 143.10, 143.07, 140.76, 139.39, 134.58, 132.56, 130.50, 130.05, 129.73, 128.55, 128.46, 128.28, 126.80, 126.50, 126.41, 125.94, 124.72, 123.23, 121.70, 52.14, 22.03, 11.74, 7.38. ^{77}Se NMR (114 MHz, $CDCl_3$) δ 151.94, Anal. Calc for $C_{45}H_{37}N_3SSe$ (730.83): C, 73.96; H, 5.10; N, 5.75; S, 4.39. Found: C, 73.90; H, 5.05; N, 5.65; S, 4.31.

[(IPr*^{MeOThia})Se] (6b). *New compound.* The product was obtained in 89% yield (0.18 g, 0.24 mmol) as yellow solid. Single crystals of 6b were obtained by slow evaporation of a saturated solution in CH_2Cl_2/Et_2O at -20 °C, yielding suitable crystals for X-ray diffraction studies. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 4H), 7.22 (d, *J* = 7.5 Hz, 8H), 7.19 – 7.15 (m, 4H), 7.08 (d, *J* = 7.1 Hz, 4H), 6.60 (s, 2H), 5.36 (s, 2H), 3.62 (s, 3H), 2.19 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.76, 159.41, 157.23, 148.90, 144.90, 142.87, 140.56, 134.6, 130.01, 129.71, 128.72, 128.49, 128.33, 128.03, 126.88, 126.64, 126.41, 125.94, 124.63, 123.24, 121.71, 115.28, 55.32, 52.37, 11.75, 7.41. ^{77}Se NMR (95 MHz, $CDCl_3$) δ 153.50, Anal. Calc for $C_{45}H_{37}N_3SSe$ (746.83): C, 72.37; H, 4.99; N, 5.63; S, 4.29. Found: C, 72.36; H, 5.00; N, 5.62; S, 4.27.

General Procedure for the Synthesis of [Rh(NHC)(CO)Cl] Complexes. Rhodium complex was synthesized according to a modified literature procedure.[26] Solid Rh(acac)$(CO)_2$ (0.05 g, 0.194 mmol, 1 equiv.) and imidazolium salt (3a) (0.05 g, 0.194 mmol, 1 equiv.) were weighed in a Schlenk tube in a glovebox. THF (10 mL) was then added, and the colour of the solution immediately turned yellow. After stirring for 2 h at room temperature, the solvent was removed in vacuo, and the crude product was twice washed with Et_2O, giving the rhodium complex as a yellow solid.

[Rh(IPr*^{Thiaz})(CO)Cl] (7a). *New compound.* The product was obtained in 70% yield (0.17 g, 0.21 mmol) as orange solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.34 – 7.28 (m, 10H), 7.20 – 7.18 (m, 6H), 7.02 – 6.99 (m, 4H), 6.94 (s, 2H), 5.60 (s, 2H), 2.29 (s, 3H), 2.20 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.72, 184.54, 161.69, 148.99, 142.35, 142.21, 141.12, 140.44, 133.01, 131.16, 130.48, 129.95, 129.79, 129.22, 128.60, 128.44, 126.87, 126.76, 126.05, 124.68, 121.27, 119.35, 51.84, 22.13, 9.99, 7.37. FT-IR (KBr): 1995 cm^{-1} ($\nu_{(C=O)}$). Anal. Calc for $C_{46}H_{37}ClN_3ORhS$ (818.24): C, 67.52; H, 4.56; N, 5.14; S, 3.92. Found: C, 63.12; H, 4.76; N, 5.01; S, 3.82

General Procedure for the Three-Component Coupling Reaction. Previously reported procedure was followed.[21a,27] Prepared according to the procedure using catalyst **4a** or **4b** (2 mol%), aldehyde (0.5 mmol), amine (0.55 mmol), alkyne (0.55 mmol) and MeOH (0.25 mL) at room temperature for 1 hour. After the desired time, the conversion was determined by ^{1}H NMR or GC analysis. The mixture was diluted with Et_2O and filtered over a pad of silica.

1-(1-Cyclohexyl-3-phenyl-2-propynyl)piperidine. The product was obtained in 77% yield (108.35 mg, 0.5 mmol) as a yellow liquid. Purification by flash chromatography (petroleum ether/AcOEt = 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.32 – 7.25 (m, 3H), 3.10 (d, *J* = 9.9 Hz, 1H), 2.63 (ddd, *J* = 10.8, 7.1, 3.5 Hz, 2H), 2.40 (dd, *J* = 8.8, 5.1 Hz, 2H), 2.10 (dd, *J* = 12.8, 1.6 Hz, 1H), 2.03 (d, *J* = 13.3 Hz, 1H), 1.79 – 1.71 (m, 2H), 1.68 – 1.51 (m, 6H), 1.44 (dd, *J* = 11.2, 5.4 Hz, 2H), 1.29 – 1.14 (m, 3H), 1.05 – 0.88 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.87, 128.34, 127.77, 123.95, 87.95, 86.27, 64.54, 39.73, 31.50, 30.60, 26.97, 26.46, 26,28, 24.89.

General Procedure for the Alkynylation. Previously reported procedure was followed.[21b] Prepared according to the procedure using, N-benzylisatine (0.5 mmol), catalyst **4a** or **4b** (5 mol%) in water (2 ml) were added phenylacetylene (1.0 mmol) and DIPEA (10 mol%). The reaction mixture was stirred for 24 hours at 60 °C and extracted with DCM (2 x 15 mL). After the desired time, the conversion was determined by ^{1}H NMR or GC analysis. The mixture was diluted with DCM and filtered over a pad of silica.

1-Benzyl-3-hydroxy-3-(phenylethynyl)indolin-2-one. The product was obtained in 99% yield (96.89 mg, 0.25 mmol) as a yellow liquid. Purification by flash chromatography (petroleum ether/AcOEt = 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.61 (m, 1H), 7.45 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.32 – 7.23 (m, 9H), 7.15 – 7.10 (m, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 4.94 (s, 2H), 3.88 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.39, 142.32, 135.14, 132.25, 130.52, 129.24, 129.10, 128.35, 127.61, 127.33, 124.06, 123.40, 121.72, 110.13, 86.78, 85.56, 69.80, 44.23

General Procedure for the Heck Cross-Coupling Reaction. Previously reported procedure was followed.[1c] According to the procedure, catalyst **5a** or **5b** (0.2 mol%), base (1.50 mmol), and Bu_4NBr (0.2 mmol) were placed in a Schlenk tube containing a small stirring bar. The Schlenk tube was subjected to evacuation/backfilling cycles with argon, styrene (2.0 mmol), di(ethylene glycol) dibutyl ether (0.50 mmol), DMA (2.5 mL), and the haloarene (1.0 mmol) were added. The mixture was then heated at 135 °C for 2-24 h. After the desired time, the conversion was determined by ^{1}H NMR or GC analysis. The mixture was diluted with Et_2O and filtered over a pad of silica.

(*E*)-1-(4-Styrylphenyl)ethenone. The product was obtained in 85% yield (94.47 mg, 0.5 mmol) as a yellow liquid. Purification by flash chromatography (Hexane /AcOEt = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.22 (s, 1H), 7.14 (d, *J* = 16.4 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.69, 142.16, 136.84, 136.08, 131.61, 129.05, 128.97, 128.49, 127.59, 126.98, 126.66, 26.79**(*E*)-1-Methoxy-4-styrylbenzene.** The product was obtained in 89% yield (93.57 mg, 0.5 mmol) as a yellow liquid. Purification by flash chromatography (Hexane/ AcOEt = 10/1)**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 13.5, 8.2 Hz, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 6.2 Hz, 1H), 7.11 – 6.97 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.45, 137.80, 130.29, 128.82, 128.36, 127.89, 127.39, 126.76, 126.42, 114.29, 55.50.

General Procedure for Hydrosilylation Reaction. Previously reported procedure was followed.[26] According to the procedure, in a Schlenk tube, a solution of complex **7a** (0.005 mmol) in dry toluene (1.5 mL) was prepared, phenylacetylene (0.5 mmol), and triethylsilane (0.55 mmol), and *n*-dodecane (100 µL) were added in quick succession via syringe. The bright yellow reaction mixture was stirred at 100 °C for 24 h. The crude mixture was filtered through alumina and analyzed by GC-MS. The solvent was evaporated, the products were purified by flash chromatography through a short plug of silica and analyzed by ^{1}H NMR spectroscopy. The three reaction products were determined on the basis of the olefinic coupling constants in the ^{1}H NMR (400 MHz, $CDCl_3$) spectra: β-*(Z)*-isomer: 7.44 (d, *J* = 9.2 Hz), 5.76 (d, *J* = 15.2 Hz), β-(*E*)-isomer: 6.89 (d, *J* = 19.4 Hz), 6.43 (d, *J* = 19.3 Hz), α-isomer: ^{1}H NMR 5.87 (d, *J* = 3.1 Hz), 5.57 (d, *J* = 3.1 Hz).

Conflicts of interest

There are no conflicts to declare.

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Data Availability Statement

The authors confirm that the data supporting this article have been included as part of the Supplementary Information. Crystallographic data for the structures reported in this manuscript have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers: CCDC 2354247, CCDC 2354248, CCDC 2354249, CCDC 2354250, CCDC 2372438.

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