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N-Heterotricyclic cationic carbene ligands. Synthesis, reactivity and coordination chemistry

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The direct dialkylation of triazolo[4,3-*b*]isoquinolin-3-ylidene structures readily afford dicationic N-heterotricyclic azolium salts. These are suitable starting materials for the synthesis of transition metal complexes containing N-heterotricyclic, cationic ligands characterized by extended charge delocalization. Silver and gold complexes as well as mono- and dicationic rhodium(I) complexes have been prepared and characterized, and the electronic properties of the ligand have been evaluated by using the TEP parameter and by comparison with a non-cationic analogue. X-Ray diffraction analysis of several carbene-metal complexes show a negligible effect of the charge in the structures of the complexes. The catalytic activity of a tricationic gold complex has been evaluated in the intramolecular hydroarylation of a terminal alkyne.

Introduction

Chiral N-heterocyclic carbenes (NHCs) constitute not only a privileged type of ligands in transition-metal catalysis,[1] but also a useful class of Lewis bases with a plethora of applications in asymmetric organocatalysis.[2] Although research on metal NHC complexes has focused primarily on their excellent σ-donor properties, recent examples of ligands with increased π-acceptor character have been reported.[3] Transition metal complexes based on these π-acidic NHCs exhibit enhanced Lewis acidity, consequently performing a superior catalytic activity in π-acid-catalyzed reactions. For instance, Fürstner and co-workers reported different reactions pathways in cycloisomerization reactions using various NHC-gold complexes and rationalized a correlation of the reaction fate with the π-accepting properties of the ligands.[4] Commonly, the π-accepting ability of NHCs has been modulated by modifying the backbone structures and N-substituents, usually with the introduction of electron-withdrawing groups.[3c,5] While the introduction of remote anionic moieties into the NHC backbone has emerged as an efficient strategy to increase the electron-donating properties and reveal new reactivities,[6] the introduction of cationic charges into the carbene moiety should efficiently provide more π-acidic NHC ligands. However, cationic ligands with a positive charge on (or adjacent to) the coordinating atom are rare, as its coordination ability is logically compromised. Nevertheless, metal species with cationic ligands have been synthesized and have shown their superior activity in a number of challenging processes such as the electrophilic C-H bond activation of hydrocarbons and electrophilic cyclizations of unsaturated systems.[7] There are examples in literature that include nitrenium cations,[8] α-cationic phosphines[9] and pyridiniophosphines[10] but examples with NHCs have been scarce. In the last years, however, a handful of reports dealing with cationic NHCs have appeared (Figure 1). For example, Ganter has described cationic NHCs with an attached Cp*Ru$^+$ fragment[11] or a fused pyridinium moiety.[12] These carbenes showed attenuated donor properties with enhanced π-accepting character. Recently, César[13] and Weigand[14] have reported cationic imidazol-ylidenes NHCs with an ammonium and a phosphonium substituent, respectively, in an imidazolium scaffold. Finally, the electronic properties of a known triazoliumylidene have also been very recently reported by Ganter and co–workers.[15]

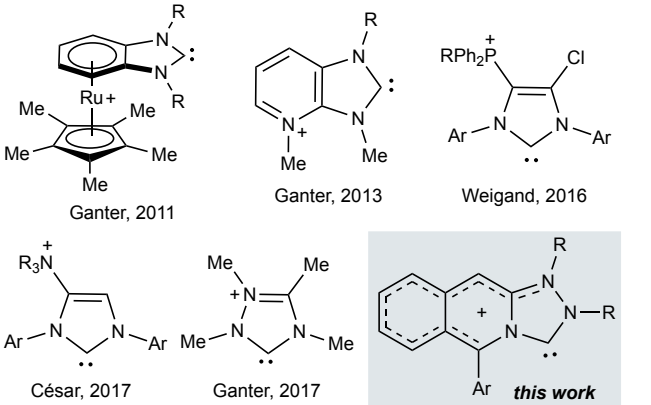

Figure 1 Selected examples of cationic N-heterocyclic carbenes.

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Electronic Supplementary Information (ESI) available: NMR spectra for new compounds and crystallographic data for compounds **8**, **12**, **13** and **22-25**. See DOI: 10.1039/x0xx00000x

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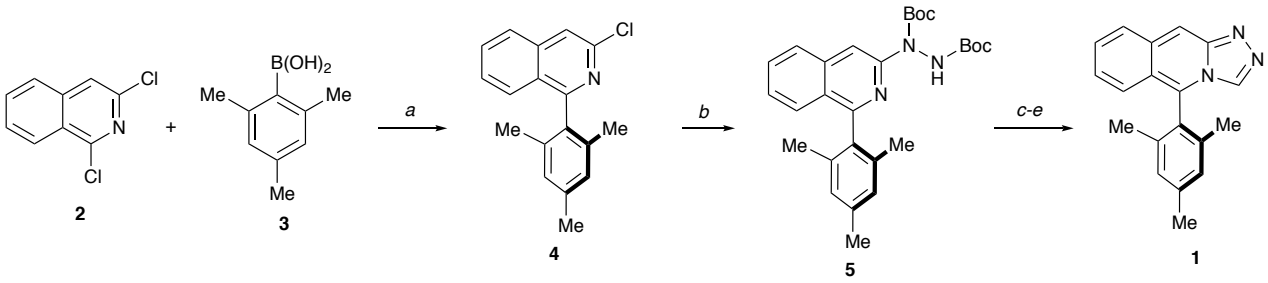


Scheme 1 Synthesis of **1**. Reagents and conditions: (a) $Pd(PPh_3)_4$, CsF, DME, reflux, 24 h, 78%; (b) BocNHNHBoc, $Pd_2(dba)_3$, dppf, Cs_2CO_3, toluene, reflux, 24 h, 92%; (c) HCl 2M dioxane, rt, 12 h; (d) HCOOH, reflux, 24h; (e) $POCl_3$, toluene, reflux, 24 h, 62% overall.

During the last years our group has been involved in the design, synthesis and applications of new families of N-heterocyclic carbenes, focusing in particular in NHCs fused in heterobicyclic systems like imidazopyridines[16] or triazolopyridines,[17] as well as larger tricyclic systems such as imidazoloisoquinolinylidene structures.[18] More recently, we have been also interested in the development of applications for these type of ligands in Au(I)-catalysed asymmetric transformations.[19] During these investigations it became evident that the activation of the substrate is the rate determining step in many cases[20] and, therefore, more π-acidic ligands should provide superior catalytic activities. In this context, we envisaged a new strategy based on the synthesis of dicationic salts as direct precursors of cationic N(1),N(2)-dialkylated triazolo[4,3-*b*]isoquinolin-3-ylidene structures. In this article we report our results on the synthesis, structure, and electronic properties of these new type of ligands.

Results and discussion

On the light of the above-mentioned antecedents, we anticipated that triazoisoquinoline derivative **1** could be a particularly well suited model system for double alkylations leading to the required dicationic azolium salts. The choice of this particular system was made on the basis of the following considerations:

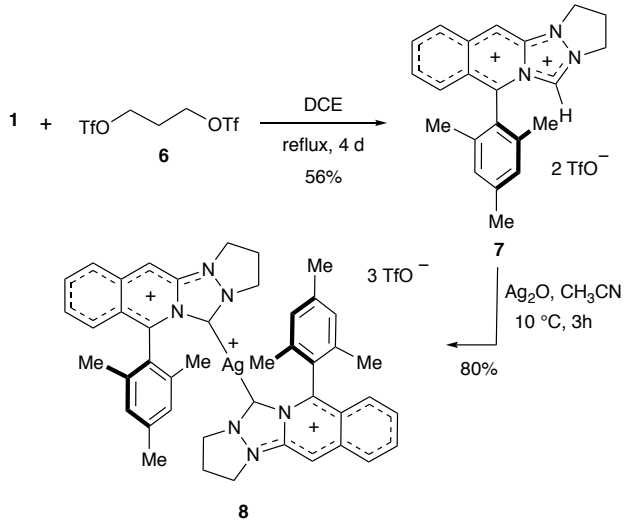
1. The corresponding carbene has the advantage of a considerable steric protection.

2. It is a good model for future work in asymmetric catalysis: a desymmetrization of the aromatic substituent in C5 would easily incorporate axial chirality in the resulting cationic NHC ligands.

3. A particularly low-lying LUMO energy is expected as a consequence of very efficient charge delocalization in the heterotricyclic scaffold.

The synthesis of **1** was readily accomplished according to the reaction sequence indicated in the Scheme 1. The process involves a selective Suzuki coupling between 1,3-dichloroisoquinoline **2** and mesityl boronic acid **3**, followed by Buchwald-Hartwig amination of the resulting product **4** with BocNHNHBoc to yield hydrazine **5**. Finally, a 'one pot' deprotection/formylation/cyclization protocol using HCl, formic acid and $POCl_3$ as reagents yielded the desired triazoisoquinoline **1**.

Our first approach consisted on a dialkylation reaction using 1,3-bis(trifluoromethanesulfonyloxy)propane **6** to obtain azolium salt **7** (Scheme 2). We initially assumed that the second intramolecular alkylation would be favoured in relative terms by entropic factors. However, this proved to be a very challenging reaction; most tested conditions led to a mixture



Scheme 2 Synthesis of dicationic salt **7** and tricationic silver complex **8**.

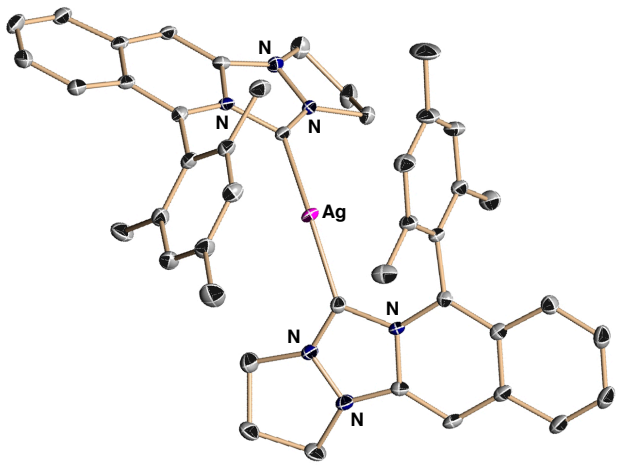


Figure 2 X-Ray structure of silver complex **8**. Triflate anions and H atoms are omitted for clarity.

of compounds resulting from intermolecular dialkylation of **6**. Finally, slow addition of a 1,2-dichloroethane solution of compound **1** to bis-triflate **6** led to the desired salt **7** after 4 days at reflux. This salt proved to be very sensitive to ring-opening nucleophilic attacks at the N^+-CH_2 methylene carbons, thereby relaxing the charge concentration in the heterocycle. Nevertheless, a careful manipulation under inert atmosphere in the absence of nucleophilic solvents allowed its isolation in a reasonable 56% yield. Treatment of this salt with Ag_2O in CH_3CN led to the corresponding tricationic, silver tris-triflate complex **8** in excellent yield (80%). The structure of this complex was unequivocally determined by single-crystal X-ray diffraction (Figure 2). As the most remarkable feature, the C–Ag–C angle shows a record deviation from linearity [158.28(11)°] for dicoordinated complexes of this type. Experiments performed in the presence of NaI, aimed to obtain the monocarbene NHC-AgI complex, were unsuccessful. In order to obtain a similar tricationic gold complex, salt **7** was treated with Ag_2O and the crude product was transmetallated with AuI, leading to a very unstable compound that decomposed rapidly in solution.

Aiming to overcome these stability problems, we considered the synthesis of dicationic salts lacking the strained aliphatic cyclic moiety. Interestingly, azolium salt **9** (a direct precursor of the alternative carbene **10**) could be easily prepared in quantitative yield from cyclic compound **1** and methyl triflate (Scheme 3). The corresponding silver complex was prepared again with Ag_2O in CH_3CN. In this case, however, the analysis of NMR spectra (^1H, ^{13}C, HSQC and DOSY experiments) indicated a 1:2.2 mixture of two different NHC-Ag species: the expected tricationic silver complex **11** and a second silver complex **12**. Crystallization of the latter could be accomplished by slow diffusion of pentane into a saturated acetone solution of the above mixture, and the single-crystal X-ray diffraction analysis showed a dicationic silver monocarbene complex with solvent acetonitrile as ligand (Figure 3). Attempts to obtain exclusively the NHC-silver

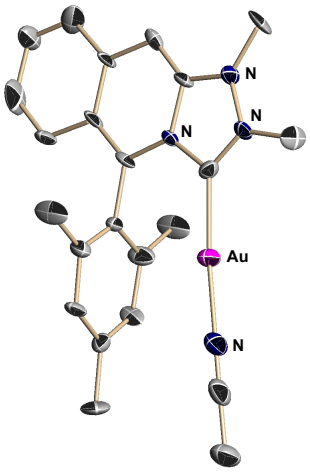
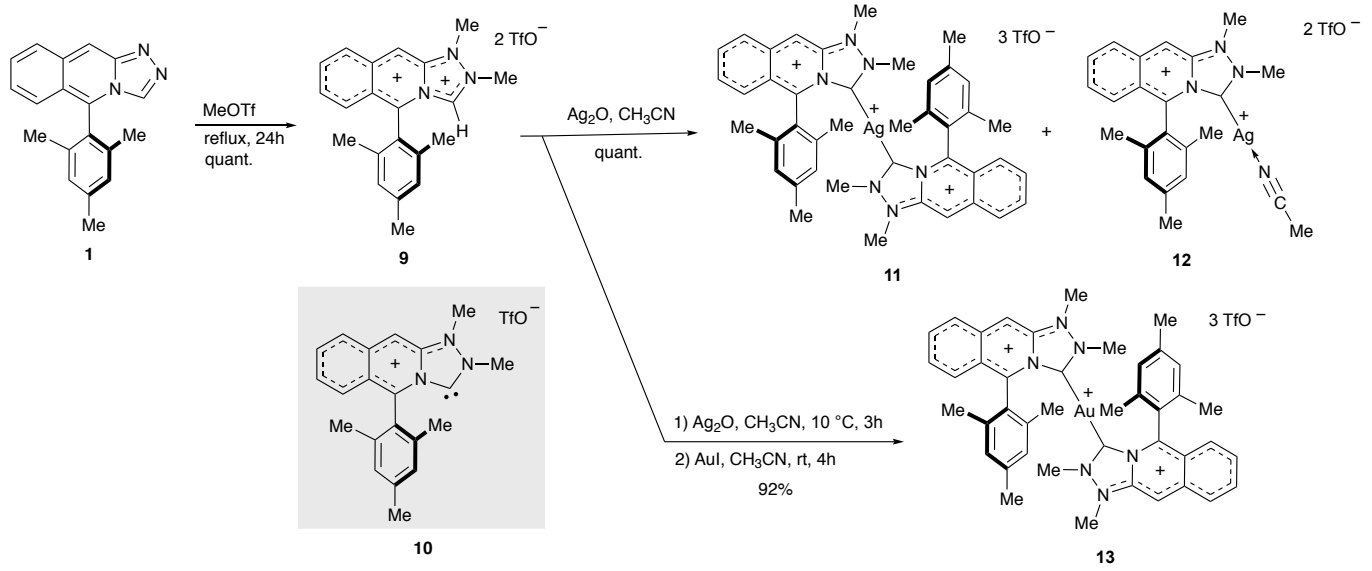


Figure 3 ORTEP drawing of NHC-Ag complex **12**. Triflate anions and H atoms are omitted for clarity.



Scheme 3 Synthesis of dicationic salt **9** and derivative complexes **11-13**.

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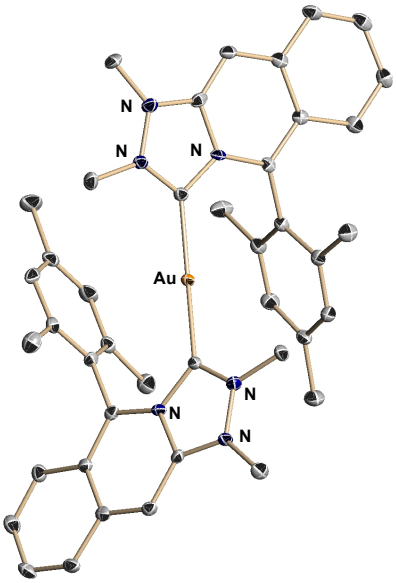
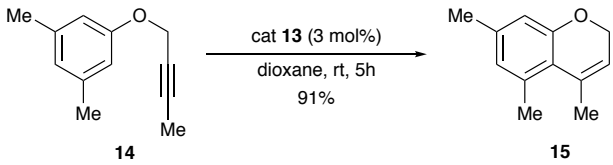


Figure 4 X-Ray structure of gold complex **13**. Triflate anions and H atoms are omitted for clarity.

complex **11** using non-coordinating solvents failed for the poor solubility of the triazolium ditriflate **9** in such media. However, *in situ* treatment of this mixture with AuI in acetonitrile led exclusively to the corresponding tricationic gold complex **13** in excellent yield. As anticipated, this complex exhibited a much higher stability and could be fully characterized. Moreover, crystals of **13** suitable for X-ray diffraction analysis were grown by slow diffusion of pentane into a saturated acetone solution of this complex (Figure 4).

The intramolecular hydroarylation of propargyl aryl ether **14** was used as a model system for a preliminary evaluation of the potential of this type of complexes in catalysis. Thus, the reaction carried out using a 3 mol% of **13** in dioxane at room temperature led to the corresponding chromene **15** in an excellent 91% yield in 5 h (Scheme 4). This result compares well with previously reported Pt^{II} or Au^{I} catalysts.[21] Remarkably, bulky, neutral Au^{I}(NHC) complexes such as [IMes(NCMe)]SbF_6 or [IPrAu(NCMe)]SbF_6 show a relatively poor performance in the hydroarylation reaction.[22]

We were next interested in the quantification of the electronic properties of the new cationic NHC ligand **10**, and perform a comparative analysis with a similar non-cationic system. We considered N-heterocyclic carbene **16** as a suitable reference for comparison purposes (Figure 5). Azolium salt **17**, direct precursor of **16**, was prepared in excellent yield from cyclic compound **1** by regioselective alkylation with adamantyl bromide (Scheme 5). This monocationic salt showed high



Scheme 4 Hydroarylation of propargyl aryl ether **14**.

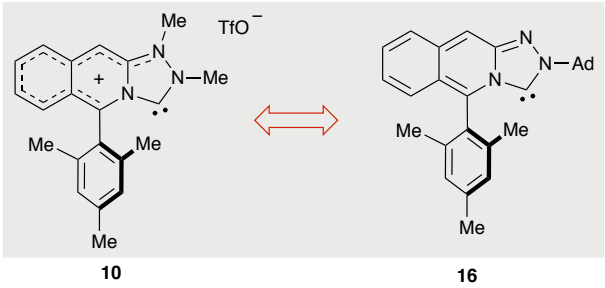
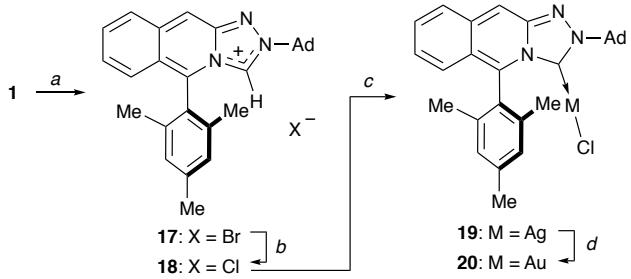


Figure 5 Comparison of cationic and non-cationic NHCs.

solubility in chlorinated solvents in clear contrast with the triazolium ditriflate **9**. In addition, the chemical shift of the C5 proton at the triazolium ring appears at δ 10.15 ppm, whereas the second positive charge in salt **9** induced a stronger deshielding to this proton (δ 11.07 ppm). Silver and gold complexes were easily obtained from **17**: after anion exchange, metallation of the chloride salt **18** with Ag_2O (→**19**) followed by transmetallation with AuCl·Me_2S gave the desired gold complex **20** in good yield.

On the other hand, azolium salt **18** was deprotonated with potassium *tert*-butoxide and treated with $[Rh(COD)Cl]_2$ in dry THF to give the corresponding Rh(NHC)(COD)Cl complex **21** in 61% yield (Scheme 6). The preparation of a similar complex from dicationic salt **9**, however, was a challenging reaction. Direct deprotonation by KO^{t}Bu, NaH or KHMDS led to decomposition of the starting material. On the other hand,



Scheme 5 Synthesis of monocationic salt **17** and complexes **19** and **20**. Reaction conditions: (a) AdBr, AcOH, reflux, 48 h, 88%; (b) Dowex 22 (Cl), quantitative; (c) Ag_2O, $CHCl_3$, MS 4Å, quantitative; (d) AuCl·Me_2S, toluene 86% (overall from **18**).

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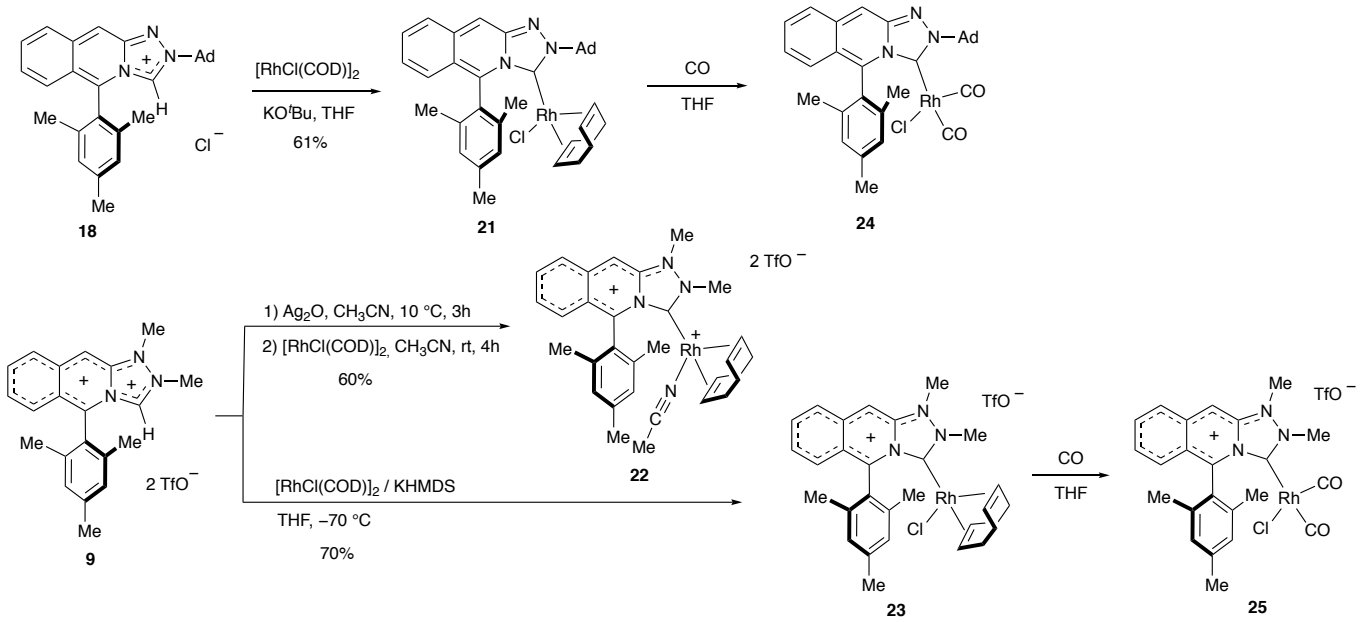

Scheme 6 Synthesis of rhodium complexes **21-25**.

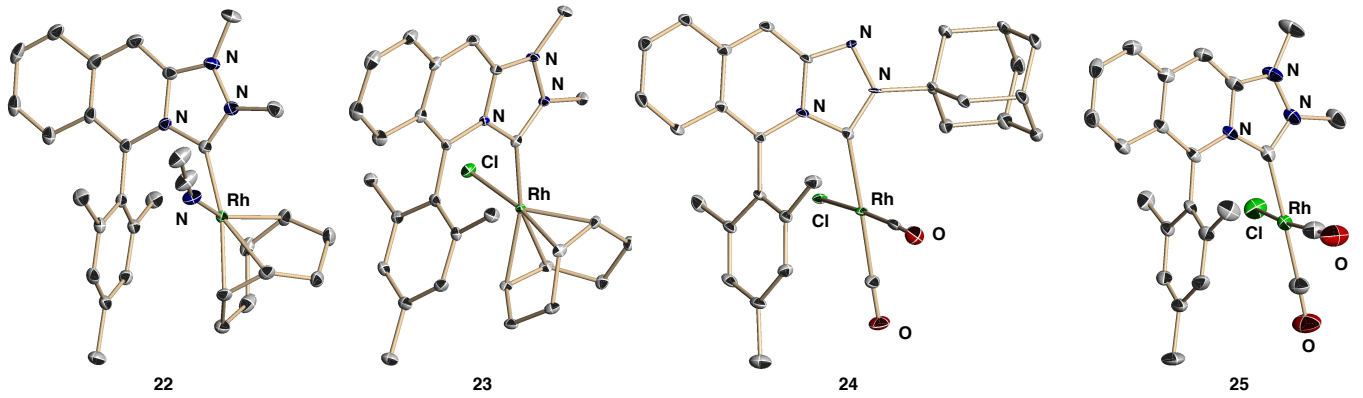

Figure 6 X-Ray structure of rhodium complexes **22-25**. H atoms and triflate anions are omitted for clarity.

transmetallation from the silver complex in acetonitrile was used to access dicationic rhodium complex **22** as the main product. Again, the poor solubility of **9** prevented the use of non–coordinating solvents in this reaction. Finally, treatment of ditriflate **9** with 0.5 mol equivalents of *in situ* generated $\{Rh[N(SiMe_3)_2](COD)\}_2$ led to the formation of the monocationic rhodium complex **23** in good yield (70%). This complex has been fully characterized by spectroscopic and analytical techniques. The coordinated carbene carbon resonates at δ 185.3 ppm (J_{Rh-C} 54.3 Hz) in the ^{13}C NMR spectrum, which is significantly shifted to low field in comparison to the corresponding carbene signal in the neutral complex (δ 175.2 ppm, J_{Rh-C} 51.6 Hz). Crystals suitable for X-ray diffraction analysis of **22** were grown by slow diffusion of diethyl ether into a solution of the complex in acetonitrile. Similarly, crystallization of **23** was accomplished by slow diffusion of pentane into a solution of the complex in acetone. Very similar bond lengths and angles, corresponding to nearly perfect planar geometries, were observed for both complexes. Additionally, dicarbonyl complexes **24** and **25** were

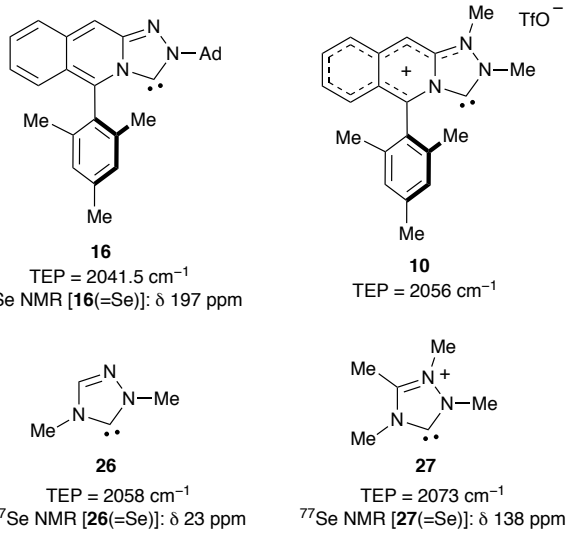

Figure 7 Electronic parameters for neutral and cationic, tricyclic and monocyclic 1,2,4-triazolylidene-based ligands.

quantitatively obtained by bubbling a slow CO stream through a THF solution of the corresponding Rh(NHC)(COD)Cl complexes **21** and **23**. Crystals of both dicarbonyl complexes were also grown by slow diffusion of pentane into acetone solutions of the complexes. X–Ray diffraction analysis (Figure 6) of both structures showed that the delocalized charge in the latter has no significant influence on the structure of these complexes. On the other hand, IR spectra of both complexes were recorded and the CO stretching vibrations were used to calculate their corresponding TEP values[23] according to the linear regression established by Plenio and Nolan[24] (Figure 7). As expected, the introduction of a positive charge in the heterocyclic system modifies significantly the σ-donation ability of the carbene. A shift of approximately 15 cm^{-1} towards a higher frequency is observed for the cationic ligand **10** (TEP = 2056 cm^{-1}) with respect of the neutral analogue **16** (TEP = 2041.5 cm^{-1}). Nevertheless, the donor ability of the cationic ligand remains relatively good, in particular compared with the monocyclic cationic NHC ligand **27** recently described by Ganter, with a record TEP of 2073 cm^{-1} [Δ(TEP) = –17 cm^{-1}]. The effect of the inclusion of the carbene into a heterotricyclic system is quantitatively very similar in the neutral series: the TEP for the monocyclic ligand **26** of 2058 cm^{-1} is 16.5 cm^{-1} higher than the tricyclic derivative **16**, suggesting that the donation ability is markedly improved by the inclusion of the NHC in the fused tricyclic system.§ On the other hand, the use of ^{77}Se NMR chemical shifts in their corresponding NHC(=Se) adducts was envisaged as a convenient method to assess the π-accepting ability of these ligands.[25] It was anticipated that the extended π system in ligands **16** and **10** should result in a marked lowering of the LUMO with respect of the monocyclic derivatives. In fact, the δ(^{77}Se) value of 197 ppm in **16**(=Se) is strongly shifted with respect to the monocyclic species [δ(^{77}Se) = 23 ppm in **26**(=Se)]. Unfortunately, any attempts to synthesize the cationic adduct **10**(=Se) were unsuccessful and the comparative analysis with **16**(=Se) and **27**(=Se) could not be performed, although an even better acceptor ability of **10** is logically inferred from the available data.

Conclusions

In summary, dicationic [1,2,4]triazolo[4,3-*b*]isoquinoline-1,2-diium salt **9**, readily available by double methylation of 5-mesityl-[1,2,4]triazolo[4,3-*b*]isoquinoline **1**, can be used as a precursor of cationic N-heterotricyclic carbene ligands in silver, gold and rhodium complexes. Cationic [Rh(NHC)$(CO)_2$] complexes have been prepared and used to calculate the TEP parameter of the ligand, and the comparison with neutral and monocyclic analogues indicate a relatively good donation ability at the level of a neutral monocyclic 1,2,4-triazol-2-ylidene. However, ^{77}Se NMR data recorded for the neutral, tricyclic NHC(=Se) adduct show a remarkable acidity that, arguably, must be even higher in the cationic analogue. Modifications of the model system to obtain axially chiral analogues and their application in asymmetric metal-catalyzed reactions are currently under investigation in our laboratory.

Experimental

General information. Solvents were purified and dried by standard procedures. Flash chromatography was carried out on silica-gel (Merck Kiesegel 40-60). Melting points were recorded in a metal block and are uncorrected. The NMR spectra were recorded on a Bruker Avance 300, Bruker Avance III 300, Bruker Avance 500, and a Bruker Avance III 700. All ^{1}H and ^{13}C NMR spectra are referenced to the chemical shifts of residual solvent signal: $\delta_{1H}(CDCl_3)$ = 7.26 ppm, $\delta_{13C}(CDCl_3)$ = 77.00 ppm, $\delta_{1H}((CD_3)_2CO)$ = 2.05 ppm, δ_{13C} $((CD_3)_2CO)$ = 29.84 ppm, $\delta_{1H}(CD_3CN)$ = 1.94 ppm, *J* values are given in Hz. ^{77}Se chemical shifts were referenced indirectly[26] using the signal of TMS as the reference frequency (Ξ =19.071513 for ^{77}Se). NMR samples of all cationic complexes have been prepared under inert atmosphere. Mass spectra were recorded on an Orbitrap ELITE (ESI) and DFS (CI or EI) mass spectrometers. X-Ray crystal structure data were collected on a Bruker Kappa APEX DUO diffractometer. 1,3-Dichloroisoquinoline (**2**)[27] and 1,3-*bis*(trifluoromethanesulfonyloxy)propane (**6**)[28] were prepared following previously described procedures.

Synthesis of 3-chloro-1-mesitylisoquinoline (4).

A round-bottom flask was charged with 1,3-dichloroisoquinoline **2** (5.50 g, 27.7 mmol), mesitylboronic acid **3** (5.00 g, 30.5 mmol), $Pd(PPh_3)_4$ (1.60 g, 5 mmol%) and CsF (9.40 g, 60.9 mmol) and dry 1,2-dimethoxyethane (55 mL) under an argon atmosphere. The mixture was deoxygenated and heated under reflux for 24 h. Et_2O was added (100 mL) and the mixture was filtered through a celite pad. The organic layer was washed with brine (2 × 40 mL), dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (1:3 EtOAc–cyclohexane).

Yield 6.01 g, 78%. White solid. Mp 108–110 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, d, *J* = 7.6 Hz), 7.72 (1H, d, *J* = 0.9 Hz), 7.68 (1H, ddd, *J* = 7.9, 6.9, 1.5 Hz), 7.55–7.52 (1H, m), 7.44 (1H, ddd, *J* = 7.9, 6.7, 1.2 Hz), 6.97 (2H, d, *J* = 0.6 Hz), 2.36 (3H, s, CH_3), 1.88 (6H, s, 2CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6, 145.0, 138.3, 138.1, 136.1, 134.3, 131.1, 128.3, 127.5, 127.0, 126.5, 126.2, 118.6, 21.1, 19.8.

m/z (ESI) 284 (32%, M^++1, ^{37}Cl), 282 (100, M^++1, ^{35}Cl), 214 (7). HRMS *m/z* calcd for $C_{18}H_{17}NCl$ 282.1044, found 282.1035.

Synthesis of di-*tert*-butyl-1-(1-mesitylisoquinolin-3-yl)hydrazine-1,2-dicarboxylate (5).

3-Chloro-1-mesitylisoquinoline **4** (3.73 g, 13.3 mmol), di-*tert*-butylhydrazine-1,2-dicarboxylate (9.53 g, 39.8 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.82 g, 1.99 mmol, 15 mmol%), 1,1'-bis(diphenylphosphino)ferrocene (1.47 g, 2.65 mmol, 20 mmol%) and cesium carbonate (10.8 g, 33.2 mmol) were solved in dry toluene (65 mL) under an argon atmosphere. The mixture was deoxygenated and then heated under reflux overnight. Ethyl acetate was added and the reaction mixture was filtered through a celite pad. The organic layer was washed with brine (2 × 60 mL), dried ($MgSO_4$), filtered and concentrated to dryness. The residue was purified by flash chromatography (100:3:1 CH_2Cl_2–cyclohexane–diethylether→ CH_2Cl_2).

Yield 5.82 g, 92%. Yellow solid. Mp 82–84 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (1H, br s), 7.88 (1H, d, *J* = 8.3 Hz), 7.62 (1H, t, *J* = 7.5 Hz), 7.48 (1H, d, *J* = 8.3 Hz), 7.38 (1H, t, *J* = 7.5 Hz), 7.24 (1H, br s), 6.99 (2H, s), 2.37 (3H, s, CH_3), 1.87 (6H, s, 2CH_3), 1.53 (9H, s, ^{t}Bu), 1.42 (9H, s, ^{t}Bu).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 154.9, 153.8, 147.8, 137.9, 137.9, 136.3, 135.0, 130.3, 128.3, 127.5, 126.8, 126.6, 126.1, 114.2, 82.2, 81.1, 28.2, 28.1, 21.1, 19.8.

m/z (ESI) 478 (100%, M^++1), 304 (46), 282 (8), 183 (22). HRMS *m/z* calcd for $C_{28}H_{36}O_4N_3$ 478.2700, found 478.2700.

Synthesis of 5-mesityl[1,2,4]triazolo[4,3-*b*]isoquinoline (1).

4.0 M HCl in dioxane (29 mL) was added to a solution of **5** (4.0 g, 8.4 mmol) in dioxane (29 mL) under an argon atmosphere and the mixture was stirred at rt overnight. The mixture was concentrated to dryness and the residue was solved in HCOOH (42 mL) and refluxed under argon for 24 h. The mixture was concentrated and the resulting residue was solved in dry toluene (72 mL). $POCl_3$ (2.40 mL, 25.1 mmol) was added and the mixture was heated under reflux for 24 h. The solvent was removed in vacuo and the residue was solved in EtOAc, washed with 2M NaOH (3 × 50 mL), and brine (50 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated to dryness. The residue was purified by flash chromatography (2:1 EtOAc–cyclohexane).

Yield 1.50 g, 62%. Yellow solid. Mp 202–203 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (1H, s), 8.29 (1H, s), 7.76 (1H, d, *J* = 8.9 Hz), 7.32–7.29 (1H, m), 7.18–7.12 (4H, m), 2.43 (3H, s, CH_3), 1.80 (6H, s, 2CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 140.7, 137.4, 133.0, 132.7, 132.6, 129.3, 128.1, 128.0, 126.7, 126.5, 124.5, 120.9, 110.0, 21.3, 19.1.

m/z (ESI) 288 (100%, M^++1), 214 (5). HRMS *m/z* calcd for $C_{19}H_{18}N_3$ 288.1495, found 288.1486.

Synthesis of dicationic salt 7.

Neutral heterocycle **1** (210 mg, 0.730 mmol) was solved in dry 1,2-dichloroethane (10 mL) and was added slowly (0.6 mL/h) to 1,3-*bis*(trifluoromethanesulfonyloxy)propane **6** (620 mg, 1.83 mmol). Next, dry 1,2-dichloroethane (6 mL) was added and the reaction was stirred under reflux for 4 days. Then, the mixture was concentrated *in vacuo* and the residue was washed with dry diethylether.

Yield 257 mg, 56%. Yellow solid.

^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 10.91 (1H, d, *J* = 1.1 Hz), 9.37 (1H, s), 8.52 (1H, d, *J* = 9.1 Hz), 8.23–8.18 (1H, m), 7.95 (1H, ddd, *J* = 9.0, 6.6, 1.0 Hz), 7.80 (1H, dq, *J* = 9.0, 1.0 Hz), 7.32 (2H, br s), 5.48 (2H, td, *J* = 7.6, 1.2 Hz, NCH_2), 5.39 (2H, t, *J* = 7.2 Hz, NCH_2), 3.52 (2H, m, *J* = 7.3 Hz, $CH_2CH_2CH_2$), 2.48 (3H, s, CH_3), 1.96 (6H, s, 2CH_3).

Synthesis of tricationic silver complex 8.

Triazolium salt **7** (50 mg, 0.080 mmol), Ag_2O (18 mg, 0.080 mmol) and 3Å molecular sieves were suspended in dry CH_3CN (1 mL) under an argon atmosphere and in darkness. The mixture was stirred at 10 °C for 3 h, filtered under argon via cannula and the concentrated to dryness.

Yield 38 mg, 80%. Yellow solid.

^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 9.00 (2H, s), 8.33 (2H, d, *J* = 8.9 Hz), 8.04–7.99 (2H, m), 7.72 (2H, ddd, *J* = 9.0, 6.6, 0.9 Hz), 7.49–7.46 (6H, m), 5.15 (8H, br t, *J* = 7.2 Hz, 4NCH_2), 3.35 (4H, quintet, *J* = 7.2 Hz, 2$CH_2CH_2CH_2$), 2.30 (6H, s, 2CH_3), 1.99 (12H, s, 4CH_3).

^{13}C NMR (75 MHz, $(CD_3)_2CO$) δ 170.5 (2 d, $J_{C,Ag}$ = 236.1 and 204.3 Hz, *C*–Ag), 145.5, 143.9, 140.8, 138.9, 137.9, 136.0, 130.9, 130.7, 129.1, 128.6, 127.1, 126.3, 124.5, 122.0 (q, $J_{C,F}$ = 321.3 Hz, *C*F_3), 117.7, 106.7, 52.7, 49.6, 21.6, 20.3.

Synthesis of 5-mesityl-1,2-dimethyl-[1,2,4]triazolo[4,3-*b*]isoquinolin-1,2-diium bis(triflate) (9).

1 (600 mg, 2.09 mmol) was solved, under an argon atmosphere, in methyltrifluoromethanesulfonate (31.0 mmol, 3.50 mL) and heated at 110 °C for 15 h. The mixture was concentrated in vacuo and the residue was washed with dry Et_2O.

Yield 1.29 g, quant. Yellow solid.

^{1}H NMR (700 MHz, $(CD_3)_2CO$) δ 11.07 (1H, s), 9.44 (1H, s), 8.46 (1H, d, *J* = 8.8 Hz), 8.17–8.15 (1H, m), 7.93–7.91 (1H, m), 7.76 (1H, d, *J* = 9.0 Hz), 7.31 (2H, br s), 4.91 (3H, s, NCH_3), 4.86 (3H, s, NCH_3), 2.47 (3H, s, CH_3), 1.95 (6H, s, 2CH_3).

^{13}C NMR (175 MHz, $(CD_3)_2CO$) δ 144.0, 142.6, 141.9, 140.7, 139.7, 137.6, 135.9, 132.8, 130.6, 129.0, 127.2, 126.2, 123.1, 107.3, 40.2, 36.1, 21.4, 19.7.

HRMS (ESI) *m/z* calcd for $[C_{21}H_{23}N_3]^{2+}$ 158.5941, found 158.5940.

Synthesis of silver complexes 11 and 12.

Triazolium salt **9** (300 mg, 0.500 mmol), Ag_2O (113 mg, 0.500 mmol) and 3Å molecular sieves were suspended in dry CH_3CN (1.5 mL) under an argon atmosphere and in darkness. The mixture was stirred at 10 °C for 4 h and then filtered under argon via cannula. The solvent was evaporated and the resulting oil was solidified by treatment with dry Et_2O. Removal of the solvent via cannula yielded complexes **11** and **12** as a yellow solid (ratio 1:2.2) in quantitative combined yield (341 mg). Complex **12** was recrystallized from a pentane–acetone mixture.

^{1}H NMR data of complex **12** from recrystallizated product (500 MHz, $(CD_3)_2CO$) δ 9.09 (1H, s), 8.34 (1H, d, *J* = 8.8 Hz), 8.04–8.01 (1H, m), 7.73 (1H, dd, *J* = 8.3, 6.7 Hz), 7.47–7.45 (3H, m), 4.69 (3H, s, NCH_3), 4.67 (3H, s, NCH_3), 2.28 (3H, s, CH_3), 1.99 (6H, s, CH_3).

^{1}H NMR data of complex **11** from mixture of **11** and **12** (500 MHz, $(CD_3)_2CO$) δ 9.06 (2H, s), 8.33–8.30 (2H, m), 8.01–7.96 (2H, m), 7.73–7.68 (2H, m), 7.51 (2H, d, *J* = 8.8 Hz), 7.33 (4H, s), 4.72 (6H, s, 2 NCH_3), 4.66 (6H, s, 2 NCH_3), 2.49 (6H, s, 2CH_3), 1.90 (12H, s, 4CH_3).

^{13}C NMR (125 MHz, $(CD_3)_2CO$) data of **11** and **12** δ 176.0 (2 d, $J_{C,Ag}$ = 238.1 and 206.2 Hz, C–Ag), 145.3, 144.6, 144.0, 143.3, 141.5, 141.1, 139.0, 138.9, 136.1, 135.9, 131.1, 130.9, 130.7, 130.6, 128.6, 128.5, 127.0, 126.9, 125.9, 124.8, 124.7, 122.0 (q, $J_{C,F}$ = 321.4 Hz, CF_3), 118.4, 106.6, 106.0, 42.0, 40.8, 35.8, 35.4, 21.5, 21.2, 20.4, 19.9, 1.4.

Synthesis of gold complex 13.

A mixture of complexes **11** and **12** (ratio 1:2.2, from 0.50 mmol of salt **9**), AuI (81 mg, 1.0 mmol) and 3Å molecular sieves were suspended in dry CH_3CN (1.5 mL) under an argon atmosphere and in darkness. The mixture was stirred at rt for 4 h and then filtered under argon via cannula. The solvent was evaporated and the resulting oil was solidified by treatment with dry Et_2O. Removal of the solvent via cannula led to gold complex **13**.

Yield 290 mg, 92% from salt **9**. Yellow solid.

^{1}H NMR (700 MHz, $(CD_3)_2CO$) δ 9.17 (2H, s), 8.35 (2H, d, *J* = 9.1 Hz), 8.07 (2H, dd, *J* = 8.7, 6.6 Hz), 7.77 (2H, ddd, *J* = 9.0, 6.6, 0.9 Hz), 7.44 (2H, dd, *J* = 9.0, 0.9 Hz), 7.40 (4H, s), 4.75 (12H, s, 4 NCH_3), 2.25 (s, 6H, 2CH_3), 1.97 (12H, s, 4CH_3).

^{13}C NMR (175 MHz, $(CD_3)_2CO$) δ 177.8, 144.6, 143.8, 141.7, 141.3, 139.3, 136.7, 131.7, 130.8, 128.6, 127.1, 126.4, 125.4, 106.9, 42.3, 36.1, 21.5, 20.5.

HRMS (ESI) *m/z* calcd for $[C_{42}H_{44}N_6Au]^{3+}$ 276.4426, found 276.4418.

Synthesis of 2-(adamantan-1-yl)-5-mesityl-[1,2,4]triazolo[4,3-*b*]isoquinolin-2-ium bromide (17).

Neutral heterocycle **1** (100 mg, 0.350 mmol) and 1-bromoadamantane (227 mg, 1.05 mmol) were solved in acetic acid (1.5 mL) under an argon atmosphere and the mixture was stirred at reflux for 2 days. The mixture was concentrated and the residue was purified by flash chromatography (CH_2Cl_2 → 97:3 CH_2Cl_2–MeOH).

Yield 154 mg, 88%. Yellow solid. Mp 170 °C (desc.).

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.15 (1H, d, *J* = 0.8 Hz), 8.37 (1H, s), 7.89 (1H, d, *J* = 8.9 Hz), 7.51 (1H, ddd, *J* = 8.7, 6.0, 1.4 Hz), 7.32–7.27 (2H, m), 7.15 (2H, s), 2.56–2.55 (6H, m, 6H_{Ad}), 2.42 (3H, s, CH_3), 2.31 (3H, br s, 3H_{Ad}), 1.92 (6H, s, 2CH_3), 1.87–1.73 (6H, m, 6H_{Ad}).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 142.1, 137.8, 136.7, 136.2, 131.0, 130.0, 129.2, 128.9, 127.6, 124.9, 124.0, 123.6, 110.3, 66.7, 41.7, 35.3, 29.5, 21.4, 20.1.

m/z (ESI) 422 (100%, M^+). HRMS *m/z* calcd for $C_{29}H_{32}N_3$ 422.2591, found 422.2587.

Synthesis of 2-(adamantan-1-yl)-5-mesityl-[1,2,4]triazolo[4,3-*b*]isoquinolin-2-ium chloride (18).

Bromide **17** (154 mg, 0.310 mmol) was eluted through a Dowex 22 anion exchange resin column using methanol as eluant. The solvent was removed in vacuo and the residue was solved in CH_2Cl_2, dried ($MgSO_4$) and concentrated.

Yield 142 mg, quantitative. Yellow solid. Mp 180-183 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.39 (1H, s), 8.34 (1H, s), 7.87 (1H, d, *J* = 9.0 Hz), 7.51 (1H, ddd, *J* = 8.7, 5.8, 1.6 Hz), 7.31–7.26 (2H, m), 7.15 (2H, s), 2.56–2.55 (6H, m, 6H_{Ad}), 2.41 (3H, s, CH_3), 2.31 (3H, br s, 3H_{Ad}), 1.91 (6H, s, 2CH_3), 1.87–1.72 (m, 6H, 6H_{Ad}).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 142.0, 137.8, 136.9, 136.2, 130.9, 129.9, 129.7, 128.8, 127.5, 124.9, 124.1, 123.5, 110.1, 66.7, 41.7, 35.4, 29.5, 21.4, 19.9.

Synthesis of silver complex 19.

Triazolium salt **18** (106 mg, 0.230 mmol), Ag_2O (35 mg, 0.15 mmol) and 4Å molecular sieves were suspended in dry $CHCl_3$ (1.5 mL) under an argon atmosphere and in darkness. The mixture was stirred at rt for 12 h and then filtered through a celite pad and concentrated to dryness.

Yield 130 mg, quantitative. Yellow foam.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (1H, s), 7.67 (1H, d, *J* = 8.9 Hz), 7.34–7.28 (1H, m), 7.18 (2H, s), 7.09 (2H, br s), 2.55–2.54 (6H, m, 6H_{Ad}), 2.50 (3H, br s, CH_3), 2.29 (3H, br s, 3H_{Ad}), 1.79–1.78 (12H, m, 2CH_3 + 6H_{Ad}).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 145.6, 145.5, 139.3, 136.5, 135.2, 130.0, 129.4, 127.2, 126.9, 126.5, 125.3, 121.7, 109.3, 63.7, 44.3, 35.8, 29.8, 21.6, 19.7.

Synthesis of gold complex 20.

A solution of silver complex **19** (130 mg, 0.230 mmol) and AuCl·Me_2S (88 mg, 0.30 mmol) in dry toluene (0.7 mL) was stirred at rt in darkness for 12 h. The mixture was filtered through a celite pad and concentrated to dryness. The residue was purified by flash chromatography (45:45:10 EtOAc–cyclohexane–CH_2Cl_2).

Yield 130 mg, 86%. Yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (1H, s), 7.67 (1H, d, *J* = 9.0 Hz), 7.33–7.30 (1H, m), 7.13 (2H, br s), 7.11–7.09 (2H, m),

2.76–2.75 (6H, m, 6H_{Ad}), 2.50 (3H, s, CH_3), 2.29 (3H, br s, 3H_{Ad}), 1.83–1.75 (12H, m, 2CH_3 + 6H_{Ad}).

^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1 (*C*–Au), 144.9, 141.8, 139.2, 137.1, 135.1, 129.5, 129.4, 127.8, 127.1, 126.7, 125.5, 122.2, 109.6, 65.1, 44.0, 35.8, 30.1, 21.6, 19.8.

HRMS (ESI) *m/z* calcd for $C_{29}H_{31}AuClN_3Na$ 676.1764, found 676.1753.

Synthesis of rhodium complex 21.

A solution of triazolium chloride **18** (54 mg, 0.12 mmol), $[RhCl(COD)]_2$ (35 mg, 0.070 mmol) and ^{t}BuOK (15 mg, 0.13 mmol) in dry THF (1 mL) was stirred at rt under an argon atmosphere for 4 h. The mixture was concentrated and the residue was purified by flash chromatography (CH_2Cl_2→ 99:1 CH_2Cl_2–MeOH).

Yield 48 mg, 61%. Yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (1H, s), 7.49 (1H, d, *J* = 8.9 Hz), 7.19 (1H, s), 7.18 (1H, s), 7.14 (1H, dd, *J* = 8.8, 6.2 Hz), 6.90 (1H, dd, *J* = 8.6, 6.3 Hz), 6.74 (1H, d, *J* = 8.9 Hz), 4.90 (1H, q, *J* = 7.5 Hz, CH_{COD}), 4.28 (1H, t, *J* = 7.5 Hz, CH_{COD}), 3.18–3.07 (7H, m, 6H_{Ad}+CH_{COD}), 2.85–2.84 (1H, m, CH_{COD}), 2.61–2.54 (1H, m, C$H_{2\ COD}$), 2.50 (3H, s, CH_3), 2.40 (3H, br s, 3H_{Ad}), 2.12 (3H, s, CH_3), 2.10–2.03 (2H, m, C$H_{2\ COD}$), 1.96–1.73 (8H, m, 6H_{Ad} + C$H_{2\ COD}$), 1.86 (3H, s, CH_3), 1.70–1.65 (1H, m, C$H_{2\ COD}$), 1.40–1.36 (1H, m, C$H_{2\ COD}$), 1.25–1.19 (1H, m, C$H_{2\ COD}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2 (d, J_{CRh} = 51.6 Hz, N*C*N), 146.9, 140.9, 140.6, 139.6, 137.3, 134.6, 130.0, 129.8, 128.6, 128.5, 126.9, 126.5, 125.7, 121.6, 109.8, 94.8 (d, J_{CRh} = 7.8 Hz, *C*H$_{COD}$), 93.5 (d, J_{CRh} = 8.5 Hz, *C*H$_{COD}$), 70.7 (d, J_{CRh} = 14.8 Hz, *C*H$_{COD}$), 66.5 (C$_{Ad}$), 65.2 (d, J_{CRh} = 14.8 Hz, *C*H$_{COD}$), 44.2 (C$_{Ad}$), 36.2 (*C*$_{Ad}$), 34.3 (*C*H$_{2\ COD}$), 30.4 (*C*$_{Ad}$), 30.0 (*C*H$_{2\ COD}$), 28.5 (*C*H$_{2\ COD}$), 27.0 (*C*H$_{2\ COD}$), 21.9 (*C*H$_3$), 21.4 (*C*H$_3$), 21.2 (*C*H$_3$).

Synthesis of rhodium complex 22.

A mixture of complexes **11** and **12** (ratio 1:2.2, from 0.070 mmol of salt **9**), $[RhCl(COD)]_2$ (35 mg, 0.070 mmol) and 3Å molecular sieves were suspended in dry CH_3CN (1.0 mL) under an argon atmosphere and in darkness. The mixture was stirred at rt for 4 h and then filtered under argon via cannula. The solvent was evaporated and the resulting residue was treated with dry Et_2O. Removal of the solvent via cannula and recrystallization of the precipitate from acetonitrile/Et_2O led to the corresponding rhodium complex.

Yield 36 mg, 60% from salt **9**. Yellow solid.

^{1}H NMR (300 MHz, CD_3CN) δ 8.50 (1H, s), 8.12 (1H, d, *J* = 8.9 Hz), 7.92–7.87 (1H, m), 7.57 (1H, ddd, *J* = 9.1, 6.6, 1.1 Hz), 7.49 (1H, br s), 7.35 (1H, br s), 7.27 (1H, dd, *J* = 9.1, 0.9 Hz), 5.04 (3H, s, NCH_3), 5.00–4.95 (1H, m, CH_{COD}), 4.35 (3H, s, NCH_3), 4.27–4.22 (1H, m, CH_{COD}), 4.15–4.11 (1H, m, CH_{COD}), 3.28–3.22 (1H, m, CH_{COD}), 2.81–2.67 (1H, m, C$H_{2\ COD}$), 2.60 (s, 3H, CH_3), 2.26–1.89 (5H, m, C$H_{2\ COD}$), 2.05 (s, 3H, CH_3), 1.72–1.55 (2H, m, C$H_{2\ COD}$), 1.65 (3H, s, CH_3).

^{13}C NMR (175 MHz, CD_3CN) δ 179.3 (d, J_{CRh} = 52.9 Hz, N*C*N), 145.9, 143.4, 141.7, 141.0, 139.6, 139.5, 138.9, 136.4, 131.0, 130.9, 130.6, 128.1, 127.7, 127.5, 125.0, 122.0 (q, J_{CF} = 320.6 Hz, *C*F$_3$), 105.6, 102.5 (d, J_{CRh} = 8.4 Hz, *C*H$_{COD}$), 98.3 (d, J_{CRh} = 6.9 Hz, *C*H$_{COD}$), 86.3 (d, J_{CRh} = 13.7 Hz, *C*H$_{COD}$), 73.7 (d, J_{CRh} = 12.2 Hz, *C*H$_{COD}$), 41.6 (N*C*H$_3$), 35.8, 35.6 (N*C*H$_3$+*C*H$_{2\ COD}$), 29.0 (*C*H$_{2\ COD}$), 28.9 (*C*H$_{2\ COD}$), 27.9 (*C*H$_{2\ COD}$), 21.7 (*C*H$_3$), 20.9 (*C*H$_3$), 20.8 (*C*H$_3$).

Synthesis of rhodium complex 23.

A solution of KHMDS (0.50 M in toluene, 0.28 mL, 0.14 mmol, 1.05 equiv) was added dropwise to a solution of $[RhCl(COD)]_2$ (35 mg, 0.07 mmol, 0.5 equiv) in dry 1:1 THF–toluene (1 mL) at –80 °C. After 30 min, solid bis(triflate) **9** (82 mg, 0.13 mmol, 1.0 equiv) was added and the solution stirred at rt overnight. The solvent was evaporated and the resulting oil was solidified by treatment with dry Et_2O. Removal of the solvent via cannula led to rhodium complex **23**.

Yield 66 mg, 70%. Yellow solid.

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 8.88 (1H, s), 8.21 (1H, d, *J* = 8.7 Hz), 7.94–7.91 (1H, m), 7.61 (1H, dd, *J* = 9.1, 6.5 Hz), 7.37 (1H, s), 7.32 (1H, s), 7.26 (1H, d, *J* = 9.1 Hz), 5.28 (3H, s, NCH_3), 5.01 (1H, q, *J* = 8.1 Hz, CH_{COD}), 4.62 (3H, s, NCH_3), 4.49 (1H, t, *J* = 7.6 Hz, CH_{COD}), 3.97 (1H, t, *J* = 6.8 Hz, CH_{COD}), 3.05–3.03 (1H, m, CH_{COD}), 2.79–2.76 (1H, m, C$H_{2\ COD}$), 2.60 (3H, s, CH_3), 2.18–2.17 (1H, m, C$H_{2\ COD}$), 2.01–1.88 (2H, m, C$H_{2\ COD}$), 1.98 (3H, s, CH_3), 1.93 (3H, s, CH_3), 1.81–1.74 (1H, m, C$H_{2\ COD}$), 1.60–1.40 (2H, m, C$H_{2\ COD}$), 1.16–1.14 (1H, m, C$H_{2\ COD}$).

^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 185.3 (d, J_{CRh} = 54.3 Hz, N*C*N), 147.1, 142.4, 142.0, 140.8, 140.4, 139.4, 135.7, 130.4, 130.3, 129.8, 128.2, 128.1, 127.7, 124.8, 122.2 (q, J_{CF} = 321.4 Hz, *C*F$_3$), 105.8, 100.7 (d, J_{CRh} = 8.3 Hz, *C*H$_{COD}$), 98.5 (d, J_{CRh} = 7.0 Hz, *C*H$_{COD}$), 75.4 (d, J_{CRh} = 14.2 Hz, *C*H$_{COD}$), 67.2 (d, J_{CRh} = 13.5 Hz, *C*H$_{COD}$), 41.4 (N*C*H$_3$), 36.4 (*C*H$_{2\ COD}$), 35.3 (N*C*H$_3$), 29.4 (*C*H$_{2\ COD}$), 29.3 (*C*H$_{2\ COD}$), 27.0 (*C*H$_{2\ COD}$), 22.1 (*C*H$_3$), 21.6 (*C*H$_3$), 20.8 (*C*H$_3$).

General procedure for the synthesis of dicarbonyl rhodium complexes 24-25.

CO gas was bubbled into a solution of the corresponding rhodium complex (0.07 mmol) in dry CH_2Cl_2 (1 mL) for 10 min, during which time the colour changed from bright yellow to pale yellow. After 30 min, all volatiles were removed under vacuum to obtain the corresponding dicarbonyl rhodium complexes in quantitative yield.

Rhodium complex 24.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (1H, s), 7.61 (1H, d, *J* = 8.9 Hz), 7.27–7.24 (1H, m), 7.20 (1H, s), 7.08 (1H, s), 7.04–6.99 (2H, m), 2.80–2.71 (6H, m, 6H_{Ad}), 2.46 (3H, s, CH_3), 2.32 (3H, br s, 3H_{Ad}), 2.02 (3H, s, CH_3), 1.85–1.76 (6H, m, 6H_{Ad}), 1.73 (3H, s, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 185.2 (d, J_{CRh} = 57.4 Hz, N*C*N), 182.6 (d, J_{CRh} = 76.0 Hz, Rh–*C*O), 166.4 (d, J_{CRh} = 44.2 Hz, Rh–*C*O), 146.7, 140.6, 139.8, 139.6, 138.2, 134.9, 129.6, 129.2, 129.0, 128.2, 127.0, 126.4, 125.8, 122.1, 109.8, 65.2, 44.2, 35.9, 30.1, 21.5, 21.3, 20.2.

IR (CH_2Cl_2) ν_{CO} 1987, 2068 cm^{-1}.

m/z (ESI) 580 (100%, M^+–Cl), 552 (98, M^+–Cl–CO), 524 (8, M^+–Cl–2CO). HRMS *m/z* calcd for $C_{31}H_{31}O_2N_3ClRhNa$ 638.1052, found 638.1053.

Rhodium complex 25.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (1H, s), 8.00 (1H, d, *J* = 8.9 Hz), 7.70–7.67 (1H, m), 7.49–7.44 (2H, m), 7.24 (1H, s), 7.22 (1H, s), 4.75 (3H, s, NCH_3), 4.56 (3H, s, NCH_3), 2.51 (3H, s, CH_3), 1.95 (3H, s, CH_3), 1.88 (3H, s, CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 183.6 (d, J_{CRh} = 58.3 Hz, N*C*N), 179.6 (d, J_{CRh} = 73.6 Hz, Rh–*C*O), 177.7 (d, J_{CRh} = 46.9 Hz, Rh–*C*O), 146.4, 142.3, 140.5, 140.3, 139.3, 138.5, 134.9, 130.1, 129.5, 129.1, 128.7, 127.6, 126.9, 125.6, 124.4, 120.3 (q, J_{CF} = 319.6 Hz, *C*F_3), 104.7, 41.2, 35.2, 21.4, 21.1, 20.1.

IR (CH_2Cl_2) ν_{CO} 2011, 2083 cm^{-1}.

Synthesis of 2-(adamantan-1-yl)-5-mesityl[1,2,4]triazolo[4,3-*b*]isoquinoline-3(2H)-selenone [(16(=Se)].

A mixture of triazolium chloride **18** (50 mg, 0.11 mmol) and Se (13 mg, 0.16 mmol) were suspended in dry THF (1 mL) under an argon atmosphere. A solution of KHMDS (0.50 M in toluene, 0.26 mL, 0.13 mmol) was added. The mixture was stirred at rt for 5 h. The solvent was evaporated and the residue was purified by flash chromatography (CH_2Cl_2-cyclohexane 1:1).

Yield 44 mg, 81%. Pink solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (1H, s), 7.47 (1H, d, *J* = 8.8 Hz), 7.13 (1H, t, *J* = 6.4 Hz), 7.00 (1H, d, *J* = 9.2 Hz), 6.94-6.91 (3H, m), 2.92 (6H, s, 2CH_3), 2.41 (3H, s, CH_3), 2.29 (3H, br s, 3H_{Ad}), 1.85–1.71 (12H, m, 12H_{Ad}).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 145.3, 139.9, 139.4, 138.3, 135.2, 129.1, 128.1, 127.4, 126.7, 125.9, 125.8, 121.9, 110.0, 66.6 (C_{Ad}), 39.1(C_{Ad}), 36.1 (C_{Ad}), 30.2 (C_{Ad}), 21.4 (CH_3), 20.8 (2CH_3).

^{77}Se NMR (96 MHz, $CDCl_3$) δ 197.0.

m/z (ESI) 502 (1%, M^++1), 422 (100, M^+–Se). HRMS (ESI) *m/z* calcd for $C_{29}H_{32}N_3Se$ 502.1744, found 502.1756.

Gold(I)-catalyzed intramolecular hydroarylation reaccion.

Catalyst **13** (3 mmol%) was added to a solution of 1,3-dimethyl-5-(prop-2-yn-1-yloxy)benzene **14** (30 mg, 0.17 mmol) in dry dioxane (0.15 M) under nitrogen atmosphere. The mixture was stirred at rt for 5 h and then filtered over celite. The solvent was evaporated and the residue was purified by flash chromatography (2:1 cyclohexane–CH_2Cl_2) to yield 5,7-dimethyl-2H-chromene **15**. The NMR data was in complete agreement with those reported in literature.[21a]

Yield 25 mg, 91% (mixed with 9% of unreacted starting material).

Conflicts of interest

There are no conflicts to declare.

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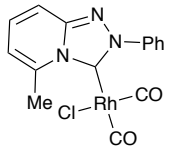
Notes and references

§ Noteworthy, heterobicyclic [1,2,4]triazolo[4,3-*a*]pyridin-3-ylidenes also follow this trend. For instance, a TEP of 2051 was calculated by linear regression from the IR data for the 5-methyl-2-phenyl derivative shown bellow. See ref. 17.



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