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N-Heterocyclic Carbenes

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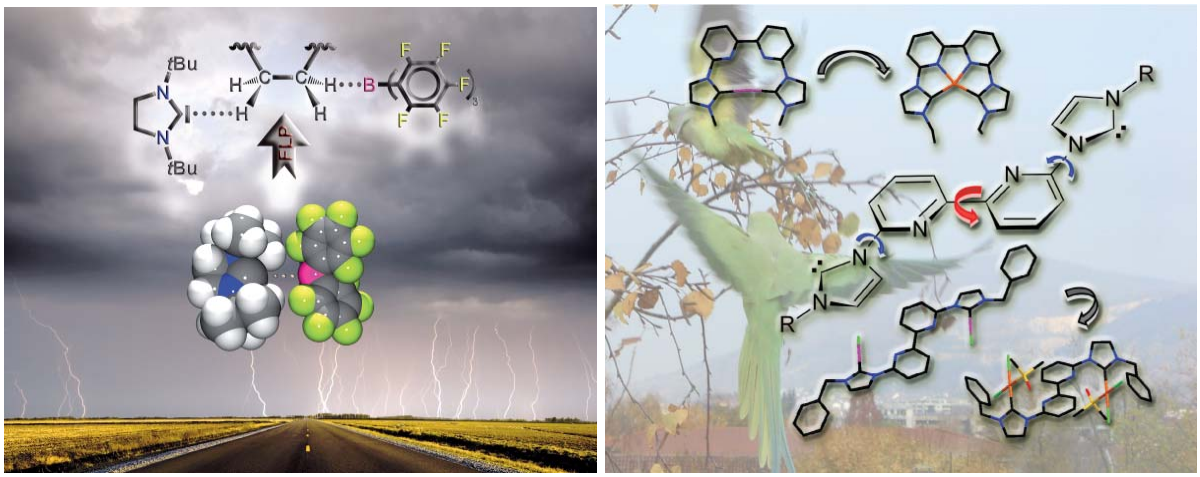

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Synthesis, structure and properties of [1,2,4]triazolo[4,3-*a*]pyridin-3-ylidene rhodium and palladium complexes†‡

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The reaction of [1,2,4]triazolo[4,3-*a*]pyridinium tetrafluoroborates with $[RhCl(COD)]_2$ and $[PdCl(allyl)]_2$ takes place under mild basic conditions (Et_3N, THF, room temperature) to afford the corresponding [RhCl(COD)(Tripy)] and [PdCl(allyl)(Tripy)] complexes, respectively (Tripy = [1,2,4]triazolo[4,3-*a*]pyridin-3-ylidene), and their structures were analysed by X-ray diffractometry and spectroscopic techniques. The σ-donor ability of the new ligands was estimated by comparative analysis of infrared ν_{CO} stretching frequencies of $[RhCl(CO)_2(Tripy)]$ complexes, and proved to be strongly dependent on the substitution pattern. Additionally, a first insight into the catalytic properties of the latter in the Suzuki–Miyaura cross coupling demonstrates a good catalytic activity that enables the coupling of aryl chlorides at room temperature.

Introduction

The design of new types of ligands has been one of the cornerstones that enabled the formidable development of homogeneous catalysis over the past decades. *N*-Heterocyclic carbenes (NHCs) have emerged as the younger family of widely used ligands in transition metals catalysis. The high relevance of these ligands is founded on the number and importance of the applications, in turn developed on the basis of their extraordinary characteristics.[1] In some aspects, these compounds can be viewed as phosphane surrogates, the σ-donor ability of NHC ligands matching or improving that of the most basic phosphines. To further exploit their potential as C-ligands, additional tools for the fine tuning of their electronic and steric properties are still required.

The main strategies used to tune the electronic properties of NHCs are the modification of the heterocycle core and their inclusion into bicyclic systems. Taking classic imidazole and dihydroimidazole derivatives **I** and **II** as the basic systems, structural variability according to the first group of modifications has been achieved by: (a) substitution of one N atom by other heteroatoms (*e.g.* thiazol-2-ylidenes **III**[2]), (b) inclusion of additional heteroatoms in the heterocyclic backbone (*e.g.* triazole-3-ylidenes **IV**),[3] (c) modification of the heterocycle ring size (*e.g.* four membered **V**),[4] six-membered tetrahydropyrimidin-2-ylidenes (**VI**),[5] and seven-membered 1,3-diazepan-2-ylidenes (**VII**),[6] (d) removal of one of the stabilizing N atoms, including not only structures such as pyrrolidin-2-ylidenes **VIII**,[7] but also the so-called 'abnormal' NHCs **IX**,[8] and the pyridine derivatives **X**[9] (Fig. 1).

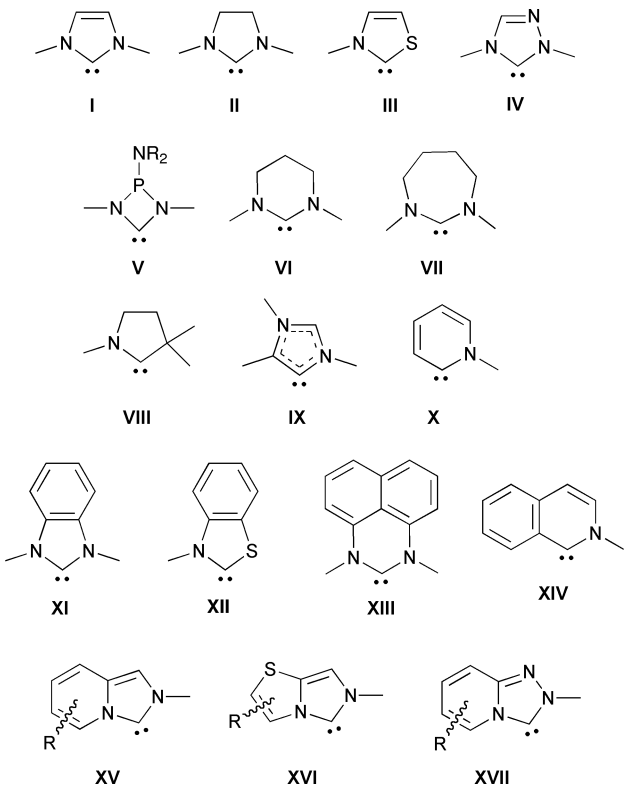

Fig. 1 Structural variation of NHC architectures.

On the other hand, the construction of bicyclic systems by annulation is another strategy that has been often applied to modulate the electronic and steric properties of NHC ligands. Thus, Hahn and co-workers have shown that benzimidazole-derived ligands **XI** exhibit modified properties with respect of

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† Dedicated to Professor Josep Font on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra for new compounds and crystallographic data for **10**, **11**, and **19**. CCDC reference numbers 727062–727064. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b907043e

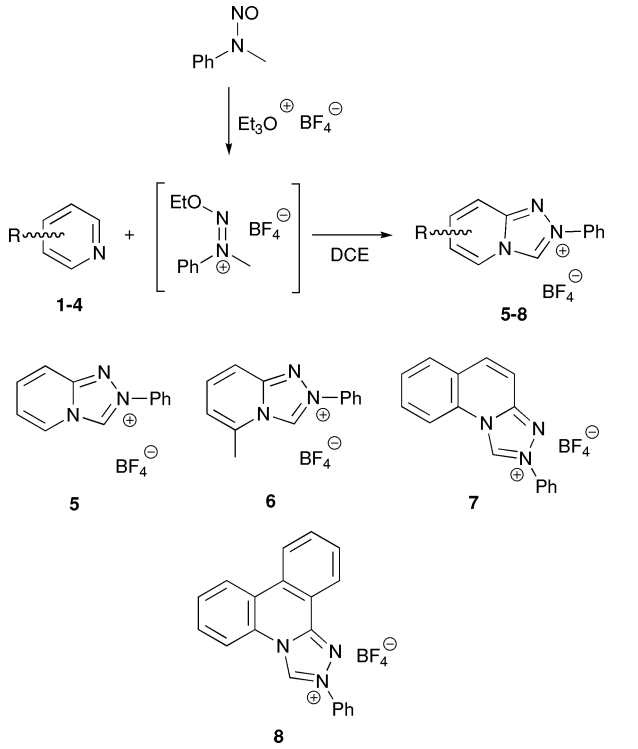
analogues **I**.[10] Selected additional examples where benzannulation at contiguous carbon centres have an impact in the properties of the NHC ligand include benzothiazole derivatives **XII**,[11] perimidine tricyclic derivative **XIII**,[12] and isoquinoline derived monoaminocarbenes **XIV**.[13]

More recently, our group[14] and Glorius *et al.*[15] independently developed pyrido-annulated bicyclic systems, namely imidazo[1,5-*a*]pyridin-3-ylidenes **XV**. This new NHC architecture is characterized by the inclusion of one of the N atoms as a bridge to the additional aromatic (pyridine) ring, and thereby offers interesting possibilities for the electronic modulation of the carbene ligand, even by using cross-talk communication between arenes in cyclophane-containing systems.[16] A similar annulation strategy has also been applied to the synthesis of thiazole-annelated imidazol-2-ylidenes **XVI**.[17]

The related [1,2,4]triazolo[4,3-*a*]pyridin-3-ylidenes **XVII** were first reported by Enders and co-workers as *in situ* prepared organocatalysts in the benzoin condensation.[18] Very recently You and co-workers[19] have expanded the study of this carbenes as organocatalysts, and described a silver complex thereof. The coordination chemistry of the new family of NHCs, however, remains unexplored.[20] We now wish to disclose our own results on the synthesis, structure and ligand properties of Rh(I) and Pd(II) complexes of [1,2,4]triazolo[4,3-*a*]pyridin-3-ylidenes **XVII**.

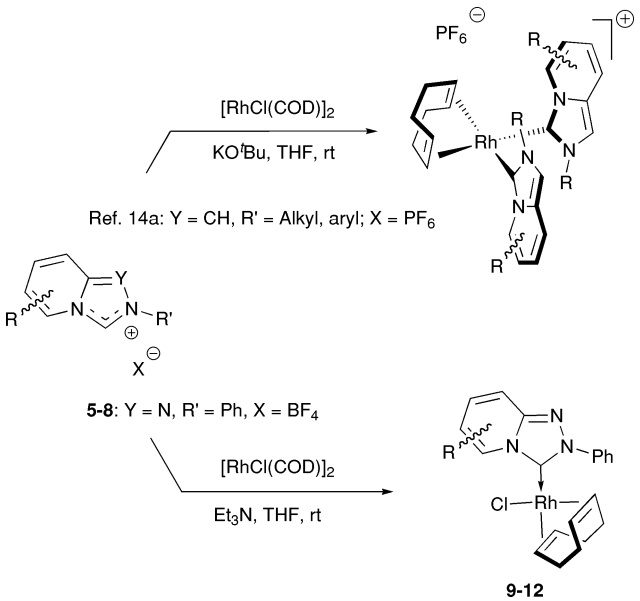
Results and discussion

The most common strategy to the synthesis of NHCs and their metal complexes require the synthesis of the corresponding azolium salts as the starting materials. The synthesis of the required [1,2,4]triazolo[4,3-*a*]pyridin-2-ium salts **5–8** was accomplished in a single step from substituted pyridines **1–4** according to a modification of the original procedure by Eicher and co-workers[21] (Scheme 1).



Scheme 1 Synthesis of triazolium salts **5–8**.

In order to have a first insight into the coordination properties of the [1,2,4]triazolo[4,3-*a*]pyridin-3-ylidenes (Tripys), we decide to prepare the corresponding Rh(I) compounds. Compared to the above-mentioned imidazopyridinium analogues,[14] the additional N-atom is expected to confer a relatively high acidity to the [1,2,4]triazolo[4,3-*a*]pyridin-2-ium salts, a difference that is also found between the monocyclic triazolium and imidazolium salts. In fact, this higher acidity makes possible their reaction with $[RhCl(COD)]_2$ at room temperature in the presence of a weak base as Et_3N. In this way, neutral [RhCl(COD)(Tripy)] complexes **9–12** were easily obtained in high (83–93%) yields as robust, bench-stable compounds, that resisted chromatographic purification on silica-gel (Scheme 2). Of interest, the slightly lower σ-donor ability of these carbenes results also in a different behaviour with respect to the imidazopyridine (Impy) analogues. Thus, starting from azolium salts with a non-coordinating counteranion (hexafluorophosphate), the latter afforded exclusively cationic bis-carbene $[Rh(ImPy)_2(COD)]^+$ complexes in their reaction with $[RhCl(COD)]_2$,[14a] even though the Rh : carbene precursor ratio was 1 : 1.



Scheme 2 Synthesis of [RhCl(COD)(Tripy)].

The structures of compounds **9–12** were assigned on the basis of their analytical and spectroscopic data. The ^{13}C NMR spectra showed the characteristic C(2) doublets at δ 180–183 ($^2J_{Rh,C}$ = 50–52 Hz). Additionally, good quality crystals of compounds **10** and **11** suitable for X-ray diffractometry were obtained by slow diffusion of hexane into a solution of the complexes in CH_2Cl_2 (Fig. 2 and 3). Both structures show the expected slightly distorted square-planar geometry at the Rh centres [C(1)–Rh(1)–Cl(1) = 87.9(3) and 85.56(9)°, respectively], with the heterocycle plane oriented near orthogonal to the coordination plane. This geometry enables Rh–H interactions with H(9) and H(7), respectively, that, according to the observed Rh–H bond distances (2.761 and 2.497 Å, respectively), C–H–Rh angles (112.1 and 141.3°, respectively) and ^1H chemical shifts [δ_H 9.31 ppm for H(9) in **10**;

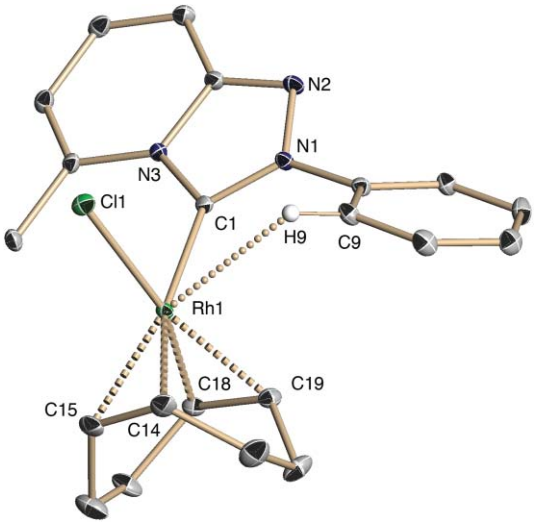


Fig. 2 ORTEP-like drawing of complex **10**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: Rh(1)–C(1) 2.041(10), N(1)–C(1) 1.349(13), N(3)–C(1) 1.377(14), N(1)–N(2), 1.370(12), Rh(1)–C(14) 2.180(11), Rh(1)–C(15) 2.186(10), Rh(1)–C(18) 2.104(11), Rh(1)–C(19) 2.119(12), Rh(1)–H(9) 2.761; C(1)–Rh(1)–Cl(1) 87.9(3), C(9)–H(9)–Rh(1) 112.05, N(1)–C(1)–N(3) 101.8(8), Cl(1)–Rh(1)–C(1)–N(1) –98.0(9), Cl(1)–Rh(1)–C(1)–N(3) 73.2(10).

δ_H 8.31 for H(7) in **11**] can be classified as anagostic interactions.§[22] The observed C(carbene)–Rh bond lengths [2.041(12) Å (**10**) and 2.019(3) Å (**11**)] are in the same range as those of related complexes based on diaminocarbenes [C(carbene)–Rh 2.00–2.06 Å]. In both structures, the mean Rh–C(COD) bonds *trans* to the carbene ligand are clearly longer (2.183 and 2.199 Å, respectively) than those *trans* to the Cl ligand (2.107 and 2.124 Å, respectively), reflecting a strong *trans* influence of the Tripy ligand.

We decided also to evaluate the effect of the annulation in the [1,2,4]triazolo[4,3-*a*]pyridin-3-ylidene ligand properties. One of the best established methods to evaluate the relative basicity of a given ligand is based on the analysis of the infrared ν_{CO} stretching frequencies of [M(ligand)X(CO)$_n$] complexes.[23] The availability of data for a number of [RhCl(NHC)(CO)$_2$] complexes prompted us to synthesize the [RhCl(Tripy)(CO)$_2$] derivatives **13–16**. These compounds were readily obtained from complexes **8–12** through a fast and quantitative COD to CO ligand exchange, smoothly performed by bubbling CO through a solution of the latter in $CHCl_3$ (Scheme 3).

The infrared spectra of **13–16** were recorded in solution and the observed ν_{CO} stretching frequencies are collected in Table 1. These values indicate a remarkable influence by the substitution pattern of the heterocycles in the σ-donor ability of some of the ligands. All of them exhibit a higher basicity than monocyclic triazole-3-ylidenes,[24,25] and, within the series, a higher aromaticity of the ring condensed with the triazole ring results in a better donor ability by the ligand (entries 2–4), approaching typical values of imidazol-2-ylidenes (Fig. 4).

§ Anagostic interactions, also termed "preagostic", "pregostic" or "pseudoagostic" interactions, are characterized by a M–H distance range of 2.3–2.9 Å, a M–H–C angle range of 110–170°, and chemical shifts typically observed downfield of the uncoordinated hydrogen atoms. See ref. 22 for pertinent discussions.

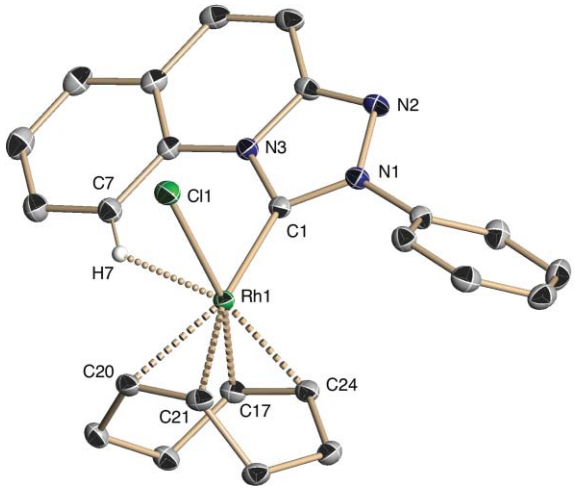
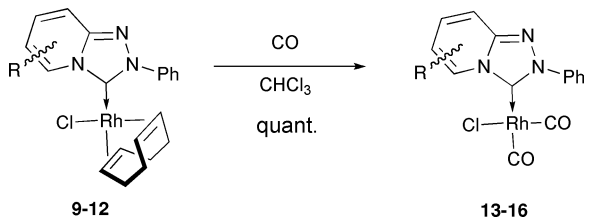


Fig. 3 ORTEP-like drawing of complex **11**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: Rh(1)–C(1) 2.019(3), N(1)–C(1) 1.344(4), N(3)–C(1) 1.380(4), N(1)–N(2), 1.382(4), Rh(1)–C(20) 2.188(3), Rh(1)–C(21) 2.210(3), Rh(1)–C(17) 2.125(3), Rh(1)–C(24) 2.123(3), Rh(1)–H(7) 2.497; C(1)–Rh(1)–Cl(1) 85.56(9), C(7)–H(7)–Rh(1) 141.313, N(1)–C(1)–N(3) 102.2(3), Cl(1)–Rh(1)–C(1)–N(1) 94.4(3), Cl(1)–Rh(1)–C(1)–N(3) –73.5(3).



Scheme 3 Synthesis of [RhCl(Tripy)(CO)$_2$] complexes.

Table 1 ν_{CO} stretching frequencies for complexes **13–16**

Entry	Compound	$\nu_{CO\ sym}$/cm^{-1}	$\nu_{CO\ asym}$/cm^{-1}	$\nu_{CO\ average}$/cm^{-1}
1	**13**	2083	2007	2045
2	**14**	2078	2004	2041
3	**15**	2088	2005	2046
4	**16**	2084	2010	2047

Taking into consideration the growing interest in palladium–NHC complexes as catalysts in cross-coupling reactions, we decided to prepare also a series of [PdCl(allyl)(Tripy)] complexes. Exploiting again their relatively high acidity, salts **6–8** were made to react with [PdCl(allyl)]$_2$ in the presence of Et_3N under mild conditions (Scheme 4). The expected products **17** and **18** were obtained in good yields (81 and 75%, respectively) but, in sharp contrast, the analogous complex **19** was isolated in very poor 16% yield under the same conditions.¶

¶ The steric properties of the carbene ligand in **19** are almost identical to those of **18**. On the other hand, the slight electronic difference (as measured in the IR data of the corresponding [RhCl(Tripy)(CO)$_2$] complexes **15** and **16**) can hardly be invoked as a possible reason to explain the marked difference in the observed behaviour of **19**. However, lower stability of the complex appears to be responsible for the much lower yield of the latter.

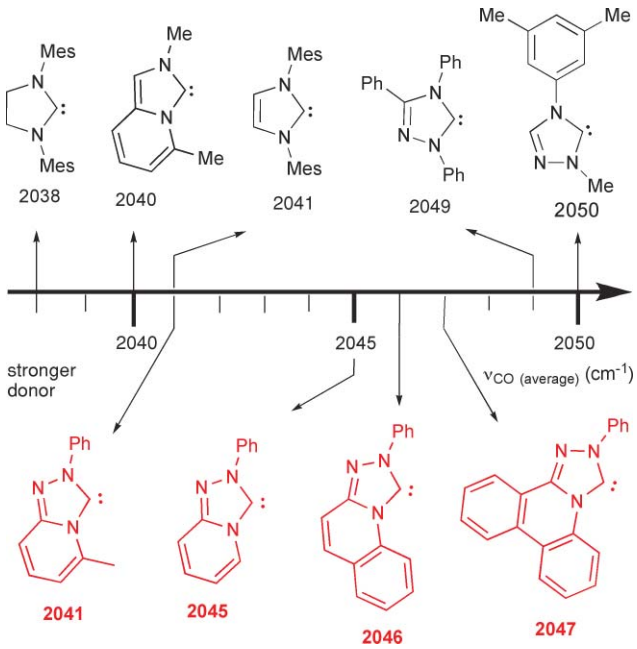
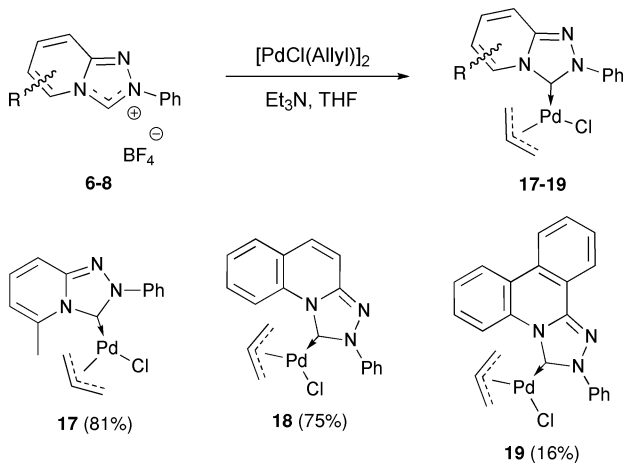


Fig. 4 Relative donor ability of Tripy ligands.



Scheme 4 Synthesis of [PdCl(allyl)(Tripy)] complexes.

The ^{1}H NMR spectra of these compounds indicated the presence of two sets of peaks which can be assigned to the mixture of diastereomers that result from the *exo* and *endo* orientation of the π-allyl ligand.

Suitable crystals of **19** for X-ray diffraction analysis were obtained by slow diffusion of hexane into a concentrated solution of the complex in CH_2Cl_2. The structure reveals the expected square-planar geometry at the Pd(II) centre and, as in the Rh(I) cases, the heterocycle plane is oriented near orthogonal to the coordination plane (Fig. 5), a geometry that enables Pd–H interactions with H(11) and H(20) that, can also be classified as anagostic interactions according to the observed distances [Pd(1)–H(11) 2.601 Å; Pd(1)–H(20) 2.792 Å] and angles [C(11)–H(11)–Pd(1) 142.6°; C(20)–H(20)–Pd(1) 104.2]. The Pd–C(allyl) distance *trans* to the carbene ligand [Pd(1)–C(21) 2.172(7)] is longer than that *trans* to the Cl ligand [Pd(1)–C(23) 2.115(6)], providing also evidence in this case of a strong *trans* influence of the Tripy ligand.

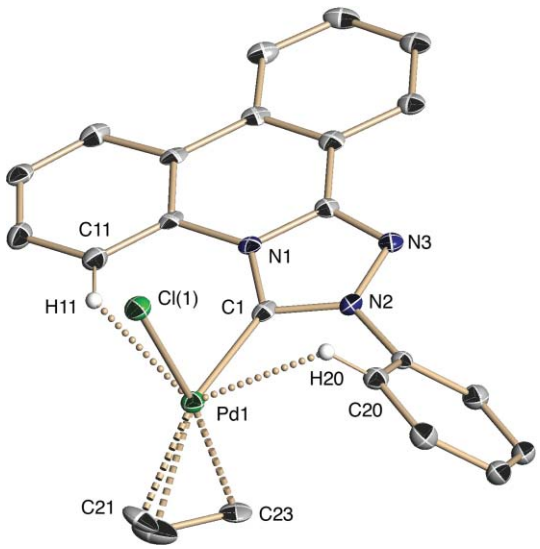
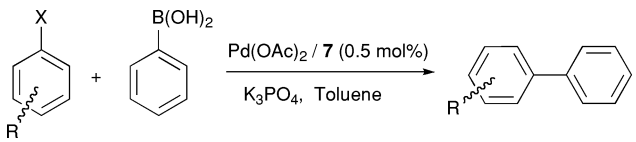


Fig. 5 ORTEP-like drawing of complex **19**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: Pd(1)–C(1) 2.031(6), N(1)–C(1) 1.386(7), N(2)–C(1) 1.360(7), N(2)–N(3) 1.376(6), Pd(1)–C(23) 2.115(6), Pd(1)–C(21) 2.172(7); Pd(1)–H(11) 2.601, Pd(1)–H(20) 2.792, C(1)–Pd(1)–Cl(1) 95.17(16), N(2)–C(1)–N(1) 100.4(5), Cl(1)–Pd(1)–C(1)–N(1) −79.5(6), Cl(1)–Pd(1)–C(1)–N(2) 102.4(4).

A preliminary evaluation of the catalytic activity of complexes **17–19** was attained from the Suzuki–Miyaura cross coupling of a series of aryl halides with phenyl boronic acid. Similar results were obtained with catalysts formed *in situ* from $Pd(OAc)_2$ and salts **6–8** as the ligand precursor in the presence of K_3PO_4 as the base (Scheme 5). The results collected by using $Pd(OAc)_2$/**7** as a representative example are summarized in Table 2. Excellent yields of the coupling products were observed not only for aryl bromides (entries 1, 2, 5, 6), but also for less reactive chlorides (entries 3, 4), even with a low catalyst loading (0.5 mol%) and at relatively low reaction temperatures.



Scheme 5 Suzuki–Miyaura cross-coupling with Tripy ligands.

Table 2 Cross-coupling of aryl halides with phenyl boronic acid

Entry	Starting material	*T*/°C	*t*/min	Isolated yield (%)
1	4-Bromotoluene	25	75	96
2	2-Bromotoluene	25	75	97
3	4-Chlorotoluene	25	75	97
4	Methyl 4-chlorobenzoate	25	75	99
5	1-Bromonaphthalene	25	1800	58
6	1-Bromonaphthalene	65	120	96

Conclusions

In summary, the synthesis of Rh(I) and Pd(II) complexes based on [1,2,4]triazolo[4,3-*a*]pyridin-3-ylidene ligands has been

accomplished in only two steps from commercially available pyridine derivatives. The analysis of infrared ν_{CO} stretching frequencies in [RhCl(Tripy)$(CO)_2$] complexes reveals that the σ-donor ability in these new bicyclic NHCs is dependent on the substitution pattern of the heterocycle. From this study it was also concluded that the benzannulation of the triazole-5-ylidene system results in a higher basicity of the NHC ligand.

Experimental

General methods

Solvents were purified and dried by standard procedures. Flash chromatography was carried out on silica-gel (0.040–0.063 mm or 0.015–0.040 mm). Melting points were recorded in a metal block and are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz or 500 MHz; ^{13}C NMR spectra were recorded at 75 MHz or 125 MHz, with the solvent peak used as the internal reference. *J* values are given in Hz.

General procedure for the preparation of 2-phenyl[1,2,4]triazolo[4,3-*a*]pyridin-2-ium salts 5–8

A Schlenk tube was charged with triethyloxonium tetrafluoroborate (431 mg, 2.2 mmol) under an argon atmosphere and a solution of *N*-methyl-*N*-nitrosoaniline (300 mg, 2.2 mmol) in dry dichloroethane (1.5 mL) was added. The reaction mixture was stirred at room temperature for 1 h and then cooled to 0–5 °C. A solution of the corresponding pyridine derivative (2.6 mmol) in dry dichloroethane (1.0 mL) was added dropwise and the mixture stirred for 2 h. The reaction mixture is then warmed up to room temperature and stirred for 15 h. The solvent was removed *in vacuo* and cold CH_2Cl_2 was added to the residue. The corresponding triazolium salts were isolated by filtration. Starting materials, yields and spectral and analytical data for compounds **5–8** are as follows:

2-Phenyl[1,2,4]triazolo[4,3-*a*]pyridinium tetrafluoroborate (5). From pyridine (**1**, 213 μL, 2.6 mmol), **5** (268 mg, 43%) was obtained as a light brown solid; mp 203–205 °C; ν_{max}(film)/cm^{-1} 3449, 3005, 1713, 1635, 1497, 1363, 1225, 1187 and 1092; δ_H[300 MHz; $(CD_3)_2SO$]: 6.61 (1 H, t, *J* 7.0, py), 6.79–6.88 (3 H, m, Ph), 7.03 (1 H, t, *J* 7.0, py), 7.16 (2 H, d, *J* 7.7, Ph), 7.29 (1 H, d, *J* 7.0, py), 7.94 (1 H, d, *J* 7.0, py) and 10.52 (1 H, s, 3-H); δ_C[75 MHz; $(CD_3)_2SO$] 120.1, 127.5, 128.8, 130.4, 134.6, 143.1, 147.0, 148.6, 149.1 and 150.6; *m*/*z* (CI) 196.0874 (M$^+$, $C_{12}H_{10}N_3$ requires 196.0872), 108 (11) and 80 (100%)

5-Methyl-2-phenyl[1,2,4]triazolo[4,3-*a*]pyridinium tetrafluoroborate (6). From 2-methylpyridine (**2**, 267 μL, 2.6 mmol), **6** (248 mg, 38%) was obtained as a white solid; mp 226–228 °C; ν_{max}(film)/cm^{-1} 3153, 3126, 2344, 1656, 1540, 1506, 1420, 1287, 1053, 1028, 917, 783, 762 and 682; δ_H[300 MHz; $(CD_3)_2CO$] 2.82 (3 H, s, Me), 7.48 (1 H, d, *J* 6.9, py), 7.78–7.82 (3 H, m, Ph, py), 7.97–8.10 (2 H, m, Ph), 8.23–8.26 (2 H, m, Ph) and 11.23 (1 H, s, 3-H); δ_C[75 MHz; $(CD_3)_2CO$] 17.2, 112.8, 117.8, 122.0, 130.4, 131.6, 132.3, 135.0, 135.9, 136.9 and 148.6; *m*/*z* (CI) 210.1036 (M$^+$, $C_{13}H_{12}N_3$ requires 210.1031), 209 (63) and 80 (49%).

2-Phenyl[1,2,4]triazolo[4,3-*a*]quinolinium tetrafluoroborate (7). From quinoline (**3**, 315 μL, 2.6 mmol), **7** (308 mg, 42%) was obtained as a light brown solid; mp 214–216 °C; ν_{max}(film)/cm^{-1} 3118, 2925, 1739, 1629, 1442, 1226, 1056, 1033, 810 and 764; δ_H[300 MHz; $(CD_3)_2CO$] 7.73–7.83 (3 H, m, Ar), 7.91–7.96 (1 H, m, Ar), 8.00–8.09 (2 H, m, Ar), 8.24–8.30 (3 H, m, Ar), 8.44 (1 H, d, *J* 9.9, Ar), 8.74 (1 H, d, *J* 8.4, Ar) and 11.74 (1 H, s, 3-H); δ_C[75 MHz; $(CD_3)_2CO$] 112.1, 117.8, 121.7, 124.3, 129.8, 130.4, 131.5, 132.0, 134.0, 135.8, 136.4 and 147.6; *m*/*z* (CI) 246.1038 (M$^+$, $C_{16}H_{12}N_3$ requires 246.1031), 245 (49), 220 (11) and 128 (8%).

2-Phenyl[1,2,4]triazolo[4,3-*f*]phenanthridinium tetrafluoroborate (8). From phenanthridine (**4**, 466 mg, 2.6 mmol), **8** (431 mg, 56%) was obtained as a light brown solid; mp 256–258 °C; ν_{max}(film)/cm^{-1} 1618, 1571, 1468, 1440, 1239, 1029, 970, 834, 757, 715 and 685; δ_H[300 MHz; $(CD_3)_2SO$] 7.67–7.83 (6 H, m, Ar), 7.89 (1 H, t, *J* 7.8, Ar), 8.05 (2 H, d, *J* 7.2, Ar), 8.29 (1 H, d, *J* 7.8, Ar), 8.45–8.57 (3 H, m, Ar) and 11.71 (1 H, s, 3-H); δ_C[75 MHz; $(CD_3)_2SO$] 116.9, 118.3, 121.6, 122.6, 124.1, 125.2, 125.3, 127.3, 129.6, 130.3, 130.5, 130.8, 131.1, 131.8, 134.1, 135.1, 135.3 and 146.9; *m*/*z* (CI) 296.1180 (M$^+$, $C_{20}H_{14}N_3$ requires 296.1187), 295 (47), 271 (14), 195 (26), 194 (22), 178 (17) and 104 (11%).

General procedure for the synthesis of RhCl(COD)(2-phenyl[1,2,4]triazolo[4,3-*a*]pyridin-3-ylidene) complexes 9–12

To a suspension of 2-phenyl[1,2,4]triazolo[4,3-*a*]pyridin-2-ium salts **5–8** (0.13 mmol) and $[RhCl(COD)]_2$ (33.2 mg, 0.065 mmol) in dry THF (1 mL) under Ar was added Et_3N (21 μL, 0.143 mmol) and the mixture was stirred for 4 h at rt. The solvent was removed *in vacuo* and the residue purified by flash chromatography (2 : 1 CH_2Cl_2–hexane → CH_2Cl_2 → 100 : 1 CH_2Cl_2–MeOH). Starting materials, yields and spectral and analytical data for compounds **9–12** are as follows:

Rhodium(I) complex 9. From **5** (37 mg, 0.13 mmol), flash chromatography afforded **9** (51 mg, 89%) as a yellow solid; mp 222–224 °C; ν_{max}(film)/cm^{-1} 2918, 2890, 2827, 1643, 1578, 1493, 1342, 1280, 1056, 798 and 730; δ_H(500 MHz; C_6D_6) 1.68–1.84 (4 H, m, 2 × $CH_{2(COD)}$), 2.17–2.30 (4 H, m, 2 × $CH_{2(COD)}$), 2.83–2.86 (1 H, m, $CH_{(COD)}$), 3.02–3.06 (1 H, m, $CH_{(COD)}$), 5.58–5.62 (1 H, m, $CH_{(COD)}$), 5.68–5.72 (1 H, m, $CH_{(COD)}$), 6.04 (1 H, t, *J* 7.0, Ar), 6.37 (1 H, td, *J* 7.0, *J* 2.2, Ar), 6.79 (1 H, d, *J* 7.0, Ar), 7.11 (1 H, t, *J* 7.5, Ph), 7.23 (2 H, t, *J* 7.5, Ph), 8.95 (2 H, d, *J* 7.5, Ph) and 9.31 (1 H, d, *J* 7.0, Ar); δ_C(125 MHz; C_6D_6) 28.8, 29.2, 32.1, 33.2, 68.6 (d, $J_{Rh,C}$ 13.8), 69.2 (d, $J_{Rh,C}$ 12.5), 99.1 (d, $J_{Rh,C}$ 6.3), 99.7 (d, $J_{Rh,C}$ 7.5), 112.9, 114.4, 124.3, 128.5, 128.6, 130.5, 130.7, 140.5, 148.2 and 181.3 (d, $J_{Rh,C}$ 52.0); *m*/*z* (CI) 441.0048 (M$^+$, $C_{20}H_{21}N_3ClRh$ requires 441.0036), 406 (96, M − Cl), 196 (48) and 195 (10%, M − RhClCOD).

Rhodium(I) complex 10. From **6** (40 mg, 0.13 mmol), flash chromatography afforded **10** (51 mg, 86%) as a yellow solid. X-Ray quality crystals were grown by slow diffusion of hexane into a solution of **10** in CH_2Cl_2; mp 208 °C (decomp.); ν_{max}(film)/cm^{-1} 2919, 2897, 1652, 1543, 1496, 1413, 1335, 1091 and 764; δ_H(500 MHz; C_6D_6) 1.54–1.70 (4 H, m, 2 × $CH_{2(COD)}$), 2.07–2.22 (4 H, m, 2 × $CH_{2(COD)}$), 2.67–2.70 (1 H, m, $CH_{(COD)}$), 2.89–2.93 (1 H, m, $CH_{(COD)}$), 3.82 (3 H, s, Me), 5.38–5.43 (1 H, m, $CH_{(COD)}$), 5.59–5.64 (1 H, m, $CH_{(COD)}$), 5.83 (1 H, d, *J* 6.7, Ar), 6.37 (1 H, dd, *J* 9.0, 8.0, Ar), 6.83 (1 H, d, *J* 9.0, Ar), 7.12 (1 H, t, *J* 7.6, Ph), 7.24 (2 H, t, *J* 7.6, Ph) and 8.91 (2 H, d, *J* 7.6, Ph); δ_C(125 MHz; C_6D_6) 23.9, 29.0, 29.1, 32.1, 33.2, 67.5 (d, $J_{Rh,C}$ 13.9), 70.4 (d, $J_{Rh,C}$ 14.3), 96.3 (d, $J_{Rh,C}$ 7.5),

98.1 (d, $J_{Rh,C}$ 7.6), 112.8, 113.5, 126.3, 128.6, 128.9, 130.2, 140.5, 142.3, 150.1 and 180.0 (d, $J_{Rh,C}$ 52.0); *m/z* (CI) 455.0662 (M^+, $C_{21}H_{23}N_3ClRh$ requires 455.0636), 420 (100, M – Cl), 312 (5, M – COD), 210 (38), 209 (7, M – RhClCOD), 75 (58) and 61 (100%).

Crystal structure determination of complex 10.

Crystal data. $C_{21}H_{23}ClN_3Rh$, $M = 455.78$, monoclinic, space group $C2/c$ (no. 15), $a = 23.5474(17)$, $b = 16.3564(12)$, $c = 9.7329(7)$ Å, $\beta = 91.310(3)°$, $V = 3747.7(5)$ Å^3, $T = 100(2)$ K, $Z = 8$, 39366 reflections measured, 5734 unique ($R_{int} = 0.0487$). The final $wR(F^2)$ was 0.1781 (all data).

Rhodium(I) complex 11. From **7** (43 mg, 0.13 mmol), flash chromatography afforded **11** (59 mg, 93%) as a yellow solid. X-Ray quality crystals were grown by slow diffusion of hexane into a solution of **11** in CH_2Cl_2; mp 232–234 °C; ν_{max}(film)/cm^{-1} 3343, 2917, 2880, 2833, 1630, 1595, 1561, 1497, 1450, 1356, 1333, 1252, 1064, 863, 804, 758, 729 and 690; δ_H(500 MHz; $CDCl_3$) 1.59–1.68 (2 H, m, $CH_{2(COD)}$), 1.87–1.98 (3 H, m, $CH_{2(COD)}$), 2.19–2.27 (1 H, m, $CH_{2(COD)}$), 2.34–2.42 (1 H, m, $CH_{2(COD)}$), 2.47–2.54 (1 H, m, $CH_{2(COD)}$), 2.74–2.76 (1 H, m, $CH_{(COD)}$), 3.17 (1 H, t, *J* 7.0, $CH_{(COD)}$), 5.29–5.34 (2 H, m, $CH_{(COD)}$), 7.39 (1 H, d, *J* 9.5, Ar), 7.57 (1 H, t, *J* 7.0, Ar), 7.62–7.68 (4 H, m, Ar), 7.77 (1 H, dd, *J* 8.0, *J* 1.0, Ar), 7.94 (1 H, td, *J* 8.0, *J* 1.0, Ar), 8.74 (2 H, d, *J* 8.5, Ar) and 11.67 (1 H, d, *J* 8.0, Ar); δ_C(125 MHz; $CDCl_3$) 28.7, 29.1, 31.5, 33.2, 69.2 (d, $J_{Rh,C}$ 13.8), 71.2 (d, $J_{Rh,C}$ 13.8), 97.5 (d, $J_{Rh,C}$ 7.5), 98.9 (d, $J_{Rh,C}$ 7.5), 112.9, 121.5, 125.3, 127.1, 128.7, 128.9, 129.0, 130.1, 133.1, 124.1, 133.7, 141.2, 148.4 and 181.3 (d, $J_{Rh,C}$ 52.0); *m/z* (CI) 491.0667 (M^+, $C_{24}H_{23}N_3ClRh$ requires 491.0636), 456 (100, M – Cl), 246 (41), 245 (38, M – RhClCOD) and 67 (63%).

Crystal structure determination of complex 11.

Crystal data. $C_{25}H_{25}Cl_3N_3Rh$ [$C_{24}H_{23}ClN_3Rh{\cdot}CH_2Cl_2$], $M = 576.74$, orthorhombic, space group *Pbca* (no. 61), $a = 11.2461(5)$, $b = 20.3332(9)$, $c = 20.7475(9)$ Å, $V = 4744.3(4)$ Å^3, $T = 100(2)$ K, $Z = 8$, 32732 reflections measured, 7229 unique ($R_{int} = 0.0358$). The final $wR(F^2)$ was 0.1397 (all data).

Rhodium(I) complex 12. From **8** (50 mg, 0.13 mmol), flash chromatography afforded **12** (58 mg, 83%) as a yellow solid; mp 244 °C (decomp.); ν_{max}(film)/cm^{-1} 2935, 2879, 2831, 1619, 1598, 1565, 1496, 1462, 1444, 1377, 1306, 1250, 972, 754, 734 and 717; δ_H(500 MHz; $CDCl_3$) 1.60–1.68 (2 H, m, $CH_{2(COD)}$), 1.88–1.98 (3 H, m, $CH_{2(COD)}$), 2.18–2.27 (1 H, m, $CH_{2(COD)}$), 2.36–2.43 (1 H, m, $CH_{2(COD)}$), 2.50–2.55 (1 H, m, $CH_{2(COD)}$), 2.76–2.78 (1 H, m, $CH_{(COD)}$), 3.19 (1 H, t, *J* 7.0, $CH_{(COD)}$), 5.30–5.33 (2 H, m, $CH_{(COD)}$), 7.57–7.70 (2 H, m, Ar), 7.74–7.77 (3 H, m, Ar), 7.91 (1 H, t, *J* 7.8, Ar), 8.37 (1 H, d, *J* 8.0, Ar), 8.41 (1 H, d, *J* 8.0, Ar), 8.47 (1 H, d, *J* 7.5, Ar), 8.77 (2 H, d, *J* 8.0, Ar) and 11.75 (1 H, dd, *J* 8.0, 1.0, Ar); δ_C(125 MHz; $CDCl_3$) 28.7, 29.1, 31.5, 33.1, 69.3 (d, $J_{Rh,C}$ 14.0), 71.2 (d, $J_{Rh,C}$ 14.1), 97.3 (d, $J_{Rh,C}$ 7.4), 98.8 (d, $J_{Rh,C}$ 7.4), 119.5, 122.3, 122.7, 123.5, 124.9, 125.4, 127.4, 128.7, 128.8, 128.9, 129.2, 129.7, 131.6, 131.9, 141.3, 148.1 and 182.4; *m/z* (CI) 541.0818 (M^+, $C_{28}H_{25}N_3ClRh$ requires 541.0792), 506 (94, M – Cl), 457 (33), 296 (44), 295 (7, M – RhClCOD), 195 (46) and 67 (100%).

General procedure for the synthesis of dicarbonyl rhodium complexes 13–16

CO was bubbled through a solution of **9–12** (0.05 mmol) in $CDCl_3$ (0.5 mL) for 15 min. The solvent was then concentrated and the residue was dried in vacuum to give the dicarbonyl complexes in quantitative yields. Spectral and analytical data for compounds **13–16** are as follows:

Complex 13. ν_{max}(film)/cm^{-1} 2910, 2083, 2007, 1648, 1540, 1500, 1280, 910 and 871; δ_H(400 MHz; $CDCl_3$) 6.99 (1H, t, *J* 7.2, Ar), 7.49–7.67 (5H, m, Ar), 8.22 (1H, d, *J* 7.2, Ar), 8.72 (1H, d, *J* 7.2, Ar) and 9.06 (1H, d, *J* 7.2, Ar); δ_C(100 MHz; $CDCl_3$) 114.8, 115.0, 124.8 (2C), 125.5, 129.1 (2C), 130.0, 131.9, 139.3, 148.9 (Ar), 170.8 (d, J_{Rh-C} 43.5, C-3), 181.2 (d, J_{Rh-C} 72.8, CO) and 184.5 (d, J_{Rh-C} 55.5, CO); *m/z* (CI) 391.6226 (M^+, $C_{14}H_{11}N_3ClRhO_2$ requires 391.6221), 328 (100%, M^+ – Cl – CO).

Complex 14. ν_{max}(film)/cm^{-1} 2924, 2078, 2004, 1650, 1539, 1497, 1290, 1151 and 911; δ_H(300 MHz; $CDCl_3$) 3.44 (3H, s, Me), 6.77 (1H, d, *J* 6.7, py), 7.41 (1H, dd, *J* 9.3, 6.7, py), 7.56–7.61 (4H, m, H-8, py, Ar) and 8.14–8.18 (2H, m, Ar); δ_C(75 MHz; $CDCl_3$) 24.7 (CH_3), 113.1, 115.0, 126.1 (2C), 129.0 (2C), 130.0, 131.5, 139.6, 140.6, 150.2 (Ar), 169.6 (d, J_{Rh-C} 44.5, C-3), 181.6 (d, J_{Rh-C} 73.9, CO) and 184.9 (d, J_{Rh-C} 56.5, CO); *m/z* (CI) 403.6406 (M^+, $C_{15}H_{11}N_3ClRhO_2$ requires 403.6394), 340 (100%, M^+ – Cl – CO).

Complex 15. ν_{max}(film)/cm^{-1} 3442, 2088, 2005, 1629, 1560, 815 and 763; δ_H(300 MHz; $CDCl_3$) 7.51–7.68 (5H, m, Ar), 7.78–7.86 (3H, m, Ar), 8.19–8.24 (2H, m, Ar) and 10.49 (1H, d, *J* 8.4, Ar); δ_C(75 MHz; $CDCl_3$) 112.7, 121.0, 124.2, 125.9 (2C), 127.8, 129.1 (2C), 129.3, 130.0, 130.3, 133.1, 133.9, 140.6, 148.8 (Ar), 172.1 (d, J_{Rh-C} 43.8, C-3), 181.3 (d, J_{Rh-C} 73.9, CO), 185.0 (d, J_{Rh-C} 56.2, CO); *m/z* (CI) 439.6720 (M^+, $C_{18}H_{11}N_3RhClO_2$ requires 439.6727), 376 (100%, M – Cl – CO).

Complex 16. ν_{max}(film)/cm^{-1} 3433, 2084, 2047, 2010, 1650, 1628, 1558, 1529, 846 and 751; δ_H(400 MHz; $CDCl_3$) 7.58–7.69 (5H, m, Ar), 7.74–7.81 (2H, m, Ar), 8.25 (2H, d, *J* 8.2, Ar), 8.39 (1H, d, *J* 8.2, Ar), 8.42 (1H, d, *J* 8.2, Ar), 8.51 (1H, d, *J* 7.2, Ar) and 10.52 (1H, d, *J* 8.2, Ar); δ_C(100 MHz; $CDCl_3$) 119.0, 121.7, 122.6, 123.8, 125.1, 126.0 (2C), 128.0, 129.1 (2C), 129.2, 129.3, 129.7, 129.9, 131.3, 132.2, 140.7, 148.6 (Ar), 173.2 (d, J_{Rh-C} 43.7, C-3), 181.3 (d, J_{Rh-C} 73.7, CO), 185.0 (d, J_{Rh-C} 55.8, CO); *m/z* (CI) 491.7436 (M^+, $C_{22}H_{15}N_3RhClO_2$ requires 491.7432), 428 (100%, M – Cl – CO).

General procedure for the synthesis of PdCl(allyl)(2-phenyl[1,2,4]triazolo[4,3-*a*]pyridin-3-ylidene) complexes 17–19

To a suspension of salts **6–8** (0.1 mmol) and $[PdCl(allyl)]_2$ (17 mg, 0.05 mmol) in dry THF (1 mL) under Ar was slowly added Et_3N (14 μL, 0.11 mmol) and the mixture was stirred for 1 h at rt. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (2 : 1 EtOAc–hexane). Starting materials, yields and spectral and analytical data for compounds **17–19** are as follows:

Monocarbene palladium complex 17. From **6** (29 mg, 0.1 mmol), flash chromatography afforded **17** (30 mg, 81%) as a light brown solid; δ_H(300 MHz; $CDCl_3$) 1.82 (0.55 H, d, *J* 12.0,

anti C*H*H, allyl), 2.32 (0.45 H, d, *J* 12.0, *anti* C*H*H, allyl), 3.05 (0.45, H, d, *J* 6.9, *syn* C*H*H, allyl), 3.22 (0.55 H, d, *J* 13.2, *anti* C*H*H, allyl), 3.24 (1.65 H, s, CH_3), 3.30–3.34 (1 H, m, C*H*H, allyl), 3.53 (1.35 H, s, CH_3), 4.31 (1 H, td, *J* 7.2, 2.4, *syn* C*H*H, allyl), 4.91–5.04 (0.45 H, m, central C*H*, allyl), 5.22–5.35 (0.55 H, m, central C*H*, allyl), 6.65 (0.55 H, d, *J* 6.6, CH_{Arom}), 6.72 (0.45 H, d, *J* 6.9, CH_{Arom}), 7.35 (1 H, dd, *J* 15.6, 9.0, CH_{Arom}), 7.45–7.59 (4 H, m, CH_{Arom}), 8.17 (0.9 H, d, *J* 8.1, CH_{Arom}) and 8.39 (1.1 H, d, *J* 8.1, CH_{Arom}); δ_C(75 MHz; $CDCl_3$) 22.8, 51.3, 51.8, 71.2, 113.0, 113.0, 113.6, 114.0, 114.1, 114.8, 125.1, 125.3, 128.9, 128.9, 129.2, 129.4, 131.1, 140.1, 140.8, 141.1, 150.1 and 175.6; *m*/*z* (CI) 356.0403 (M^+ – Cl, $C_{16}H_{16}N_3Pd$ requires 356.0379) and 210 (100%).

Monocarbene palladium complex 18. From **7** (54 mg, 0.1 mmol), flash chromatography afforded **18** (51 mg, 75%) as a white solid; δ_H(500 MHz; $CDCl_3$) 1.83 (0.67 H, d, *J* 12.0, *anti* C*H*H, allyl), 2.41 (0.33 H, d, *J* 11.5, *anti* C*H*H, allyl), 3.05 (0.41 H, d, *J* 6.0 Hz, *syn* C*H*H, allyl), 3.29–3.33 (1.14 H, m, C*H*H, allyl), 3.51 (0.45 H, d, *J* 13.0, *anti* C*H*H, allyl), 4.43 (1 H, d, *J* 7.0, *syn* C*H*H, allyl), 5.00–5.08 (0.41 H, m, central C*H*, allyl), 5.35–5.47 (0.59 H, m, central C*H*, allyl), 7.47–7.61 (5 H, m, CH_{Arom}), 7.69–7.79 (3 H, m, CH_{Arom}), 8.22 (0.89 H, d, *J* 7.5, CH_{Arom}), 8.42 (1.11 H, d, *J* 7.5, CH_{Arom}), 10.00 (0.56 H, d, *J* 8.5, CH_{Arom}) and 10.33 (0.44 H, d, *J* 8.5, CH_{Arom}); δ_C(125 MHz; $CDCl_3$) 51.4, 51.6, 71.8, 72.0, 77.2, 112.6, 112.7, 114.3, 115.3, 119.2, 119.4, 123.9, 124.0, 124.7, 125.0, 127.2, 127.2, 128.9, 129.0, 129.1, 129.1, 129.3, 130.4, 130.5, 133.4, 133.6, 148.6 and 177.6; *m*/*z* (FAB) 387 (14, M – allyl), 237 (100), 173 (31), 153 (31) and 131 (69%).

Monocarbene palladium complex 19. From **8** (38 mg, 0.1 mmol), flash chromatography afforded **19** (15 mg, 16%) as a white solid; δ_H(500 MHz; $CDCl_3$) 1.88 (d, *J* 12.5, *anti* C*H*H, allyl), 2.47–2.27 (m, *anti* C*H*H, allyl), 3.07 (0.43H, d, *J* 6.7, *syn* C*H*H, allyl), 3.33–3.29 (1.14H, m, *syn* C*H*H + *anti* C*H*H, allyl), 3.51 (0.43H, d, *J* 13.0, *anti* C*H*H, allyl), 4.44 (1H, m, *anti* C*H*H, allyl), 5.10–4.95 (0.43H, m, central C*H*, allyl), 5.44–5.34 (0.57H, m, central C*H*, allyl), 8.54–87.36 (12H, m, CH_{Arom}), 10.07 (0.57H, dd, *J* 8.2, *J* 0.9, CH_{Arom}) and 10.41 (0.43H, d, *J* 8.1, CH_{Arom}); δ_C(125 MHz; $CDCl_3$) 51.5, 51.6, 71.7, 72.0, 77.4, 114.4, 115.3, 119.3, 120.0, 120.1, 123.7, 123.9, 124.9, 125.1, 127.5, 129,0, 129,3, 129,5, 129.7, 131,8, 141,0, 141.1, 148.4 and 179.0.

Crystal structure determination of complex 19.

Crystal data. $C_{23}H_{18}ClN_3Pd$, $M = 478.25$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.5846(6)$, $b = 30.038(2)$, $c = 7.0204(5)$ Å, $\beta = 108.420(3)°$, $V = 1917.6(2)$ Å^3, $T = 100(2)$ K, $Z = 4$, 15674 reflections measured, 3931 unique ($R_{int} = 0.0739$). The final $wR(F^2)$ was 0.1274 (all data).

General procedure for Suzuki–Miyaura cross-coupling

A solution of **7** (0.5 mol%, 0.002 mmol) in toluene (1 mL) was added to a mixture of the aryl halide (0.4 mmol), phenyl boronic acid (0.6 mmol) and K_3PO_4 (170 mg, 0.8 mmol). A solution of $Pd(OAc)_2$ (0.002 mmol) in toluene (1 mL) was then added and the mixture was stirred until consumption of the starting halide (TLC monitoring). The resulting residue was purified by flash chromatography using hexane as eluent.

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