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<th>Synthesis and Tunability of Abnormal 1,2,3-Triazolylidene Palladium and Rhodium Complexes</th>
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<td>Authors(s)</td>
<td>Poulain, Aurélie; Canseco-Gonzalez, Daniel; Hynes-Roche, Rachel; Müller-Bunz, Helge; Albrecht, Martin; et al.</td>
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Synthesis and Tunability of Abnormal 1,2,3-
Triazolylidene Palladium and Rhodium Complexes

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ABSTRACT. Palladation of N3-alkylated 1,2,3-triazolium salts with Pd(OAc)$_2$ afforded a $\mu^2$–I$_2$ bridged bimetallic complex [Pd(trz)I$_2$]$_2$ and monometallic bis(carbene) complexes Pd(trz)I$_2$ as a mixture of trans and cis isomers (trz = 1,2,3-triazol-5-ylidene). Addition of excess halide or modification of the palladation procedure from direct functionalization to a transmetalation sequence involving a silver intermediate allowed for chemoselective formation of the bis(carbene) complex, while subsequent anion metathesis with NaI produced the monometallic bis(carbene) complexes exclusively. Modification of the wingtip group had little influence on the metalation to palladium or rhodium(I) via transmetalation. According to NMR analysis using $\delta_C$ and $^{1}J_{Rh-C}$, subtle but noticeable tunability of the metal electronic properties were identified. In addition, phenyl wingtip groups as N-substituents in the triazolylidene ligands were susceptible to cyclopalladation in the presence of NaOAc and are thus not chemically inert.
Introduction

The enormous impact of N-heterocyclic carbenes as spectator ligands in all areas of transition metal chemistry\(^1\) — and in catalysis in particular\(^2\) — has stimulated significant research interest in developing NHC-type scaffolds that allow for substantial modification of steric and electronic properties. Such modification include, for example, expansion of the heterocyclic ring from classic 5-membered imidazol-derived structures to 6- and 7-membered heterocycles,\(^3\) or the displacement of one or both carbene-stabilizing heteroatoms into more remote positions.\(^4\) Depending on the location of the heteroatoms, a neutral resonance structure is not conceivable anymore and mesoionic resonance structures become largely dominant.\(^5\) A pronounced mesoionic character may be an attractive feature, for example in redox catalysis,\(^6\) and has been exploited recently in a variety of carbene-type scaffold (abnormal carbenes).\(^7\)

In this context, 1,3-disubstituted 1,2,3-triazolylidenes constitute a particularly attractive class of ligands (Scheme 1).\(^8\),\(^9\) The heterocyclic ligand precursor is accessible via a synthetically highly versatile ‘click reaction’ involving a copper-catalyzed [3+2] cycloaddition of azides and alkynes (Scheme 1).\(^10\) This click reaction tolerates a wide variety of functional groups both in the azide and in the alkyne reactant,\(^11\) and hence allows for synthetic variation of wingtip groups that may not be (easily) conceivable in NHC chemistry relying on imidazole-derived heterocycles. Unlike their much more investigated 1,2,4-triazolylidene homologues,\(^12\) 1,2,3-triazolylidenes have a strong mesoionic character, as demonstrated in elegant work by Bertrand and coworkers on the free carbene ligand.\(^13\)

![Scheme 1](image)

Scheme 1. Retrosynthetic approach towards triazolylidene metal complexes.

Following our initial studies,\(^8\) we report here on a detailed investigation of the factors that influence the metalation of triazolium salts with palladium and rhodium. Wingtip modification has been probed as
a methodology for tuning the stability and the donor ability of the ligand. Specifically, \(N\)-bound phenyl groups were observed to undergo facile cyclopalladation.

**Results and discussion**

**Synthesis of palladium complexes.** Direct palladation of the triazolium salt 1a was accomplished thermally by stirring the ligand precursor and Pd(OAc)\(_2\) in DMSO at 120°C.\(^{14}\) Analysis of the crude reaction mixture revealed three separate sets of signals for the ethyl group in the \(^1\)H NMR spectrum, while the aromatic region was more complex. Sequential extraction with MeCN and CH\(_2\)Cl\(_2\) and fractional crystallization allowed for isolating the three major compounds, *i.e.*, dimeric complex 2a and the monomeric complex 3a as a mixture of *trans* and *cis* isomers, *i.e.*, *trans*-3a and *cis*-3a (Scheme 2).\(^{15}\) Specifically, the bimetallic complex 2a is soluble in MeCN, while 3a is only sparingly, thus allowing for separating the red complex 2a from the two yellow bis(carbene) palladium complexes *trans*-3a and *cis*-3a by a straightforward consecutive extractions. The residual *cis/trans* mixture of 3a was further purified by fractional crystallization by slow diffusion of pentane into a CH\(_2\)Cl\(_2\) solution of 3a.

![Scheme 2. Synthesis of complexes 2, trans-3, and cis-3 by direct metalation.](image)

The molecular structures of complexes 2a, *trans*-3a and *cis*-3a are depicted in Fig. 1. The unit cell of the dimeric complex 2a consists of two crystallographically independent centrosymmetric binuclear molecules. In all three complexes the palladium constitutes the center of a distorted square plane with the triazole rings oriented essentially perpendicular with respect to the metal coordination plane. The C2–C1–Pd1–I1 torsion angles are 88.5(5)°, 98.7(5)°, and 77.9(3)° for 2a, *trans*-3a, and *cis*-3a,
respectively. The Pd–C_{carbene} bond is slightly shorter in the dimeric structure 2a (1.967(6) Å, 1.979(6) Å) than in monomeric species cis-3a (1.993(5) Å and 1.997(5) Å), and significantly shorter than in trans-3a (2.049(3) Å), reflecting the expected increase of the trans influence from µ^2-I to terminal I to carbene (Table 1). The same conclusions can be drawn when comparing the Pd–I distances in the three complexes. No significant perturbation of the bond lengths in the heterocycles were noted, the C–C bond is in all complexes in the range of conjugated C=C bonds.

![Figure 1](image.png)

**Figure 1.** ORTEP drawings of complex 2a (a; only one of the two crystallographically independent molecules is shown), trans-3a (b), and cis-3a (c; all structures at 50% probability level, hydrogen atoms and cocrystallized solvents omitted for clarity).

**Table 1.** Selected bond lengths (Å) and angles (°) for 2a, trans-3a, and cis-3a

<table>
<thead>
<tr>
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<th>2a</th>
<th>trans-3a</th>
<th>cis-3a</th>
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<td></td>
<td>molecule 1</td>
<td>molecule 2</td>
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<td>Pd1–C1</td>
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<td>2.5916(6)</td>
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<td>94.16(2)</td>
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<td>103.8(5)</td>
<td>103.3(3)</td>
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a) $X_1 = I_2, X_2 = I_2a$; in molecule 1, the iodide was found to be disordered over two positions (occupancies 0.7/0.3), only the major component is considered here; labeling scheme adapted for molecule 2; b) $X_1 = C_1a, X_2 = I_1a$; c) $X_1 = I_2, X_2 = C_12$.

The availability of crystalline samples and structural evidence allowed for identifying the diagnostic ethyl group resonances of complex 2a in solution, $\delta_H 4.71$ and $1.63$. Attempts to collect sufficient crystalline material of 3a always resulted in a mixture of trans and cis isomers, as indicated by two sets of resonances at 4.65 ppm and 1.56 ppm, and at 4.85 ppm and 1.71 ppm. Therefore, NMR spectroscopy did not allow cis and trans configurations to be unequivocally distinguished. Steric consideration suggest that the former set, which is the major one in the crude reaction mixture, is due to trans-3a. The trans configuration is expected to alleviate steric congestion around the metal coordination sphere and may therefore be more easily accessible than cis-3a.

The most significant differences in the $^{13}$C NMR spectra of the complexes comprises the palladium-bound carbene resonance, which appears at $\delta_C 128.5$ in complex 2a, yet at substantially lower field ($\delta_C 154.6$ and $154.0$) for the cis/trans mixture of 3a. This effect is much smaller for the phenyl-bound heterocyclic carbon which resonates at $\delta_C 142.5$ in 2a and at 144.1 in 3a. No difference between the cis and trans isomers was detected for this nucleus. All other $^{13}$C NMR signal differ by less than 1 ppm in the three sets and hence do not allow for an unambiguous distinction between the three structures.

**Factors affecting product selectivity.** Upon repeating the palladation reaction, the dimetallic complex 2a and monomeric 3a were obtained invariably in an approximate 1:1 ratio, with a 5:2 trans/cis isomeric distribution in the latter. When the metalation was carried out with excess KI (4 molequiv.) and under otherwise identical conditions, complex 2a became the major product (ca. 8:1 ratio) as deduced from the crude $^1$H NMR spectra. This preference is in agreement with the asymmetric halide/carbene stoichiometry in the dimetallic product. Replacing KI by KCl (2 molequiv) similarly favored the production of the dimetallic complex (5:1 ratio obtained after stirring the product mixture with NaI in order to convert the initial chloropalladium products into their iodide analogues). Likewise,
using NaOAc as an additive increased the ratio of the dimetallic complex (ca. 4:1), thus demonstrating that large and potentially \( \mu^2 \) or \( \kappa^2 \) coordinating anions favor the formation of complex 2a comprising a 1:1 palladium to carbene ratio.

Attempts to favor the formation of the bis(carbene) complex 3a initially focused on the modification of the ligand/palladium stoichiometry in the reaction mixture. However, even in the presence of a four-fold excess of triazolium salt, the product distribution remained at an approximate 1:1 ratio. This observation may suggest that species such as 2a are poor substrates for the second Pd–carbene bond formation. Utilization of a transmetalation protocol was more successful.\(^{17}\) Formation of the silver intermediate from \( \text{Ag}_2\text{O} \) and the triazolium precursor,\(^8\) followed by transmetalation with \( \text{PdCl}_2(\text{NCR})_2 \) (R = Me, Ph) at room temperature and subsequent stirring of the product in the presence of NaI produced the bimetallic complex 2a only.\(^{18}\) Most remarkably, slight modification in this procedure, viz. omitting NaI for anion metathesis inverted the selectivity and afforded the monometallic bis(carbene) complex 4a containing chloride anions as the exclusive product (Scheme 3). Again a mixture of cis and trans isomers were formed (1:6 ratio). The room temperature \(^1\text{H} \)NMR spectrum in CD\(_3\)CN featured broad signals, indicating a dynamic behavior. The spectrum recorded at +75 °C showed sharp signals for a single species and is in agreement with fast cis-trans isomerization at this temperature.\(^{19}\) At the slow exchange limit (–20 °C), four sets of signals were well resolved and were assigned to syn and anti conformations of the trans and cis isomers of 4a (relative distribution of the sets was 52%, 32%, 11% and 5%). Variable temperature NMR spectroscopy revealed a coalescence of the multiplets at around 20 °C for the two major components (\( \Delta G^\ddagger = 58.7\pm0.8 \text{ kJ mol}^{-1} \)), while the other pair of signals was still sharp. Coalescence of this set required warming to 60 °C (\( \Delta G^\ddagger \) ca. 67 kJ mol\(^{-1}\)). This coalescence was complicated by the fact that the two pairs of sets coalesce at only slightly higher temperature (ca. 65 °C). Tentatively, we have assigned the more hindered rotation about the C–Pd bond (syn-anti isomerization) to the sterically congested cis isomer, while the same type of rotation is expected to be comparably facile in trans-4a. In line with this model, the syn-anti isomerization process in the cis
isomer should have a similar activation barrier as the *cis-trans* interconversion, in particular in coordinating solvents such as MeCN. Accordingly, the activation barrier for *cis-trans* isomerization is around 70 kJ mol\(^{-1}\).

**Scheme 3.** Selective synthesis of either dimetallic complex 2 or monometallic bis(carbene) complex 4.

**Figure 2.** ORTEP representation of complex *trans*-4a (50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) are: Pd1–C1 2.037(3) Å; Pd1–Cl1 2.3534(8) Å; C1–Pd1–C1a 180°; C1–Pd1–Cl1 88.8(1)°.

**Variation of the wingtip groups.** In an effort to evaluate the influence of the ortho substituents (wingtip groups), a series of triazolium salts 1b–1f were synthesized in good to excellent yields by established [3+2] cycloaddition protocols using the corresponding azides and alkynes,\(^{20}\) and subsequent alkylation with MeI. Selective N3-methylation was unambiguously confirmed by NOE and long range CH cross correlation experiments. Direct palladation using Pd(OAc)_2 as described above again provided a mixture of complexes 2, *cis*-3, and *trans*-3 (*cf* Scheme 2). The 2:3 ratio showed a moderate dependence on the wingtip group pattern. While for the dialkylated systems 2b and 2c, about equimolar
quantities of monomeric species (3b and 3c, respectively) were formed, the dimetallic complex 2d was slightly more preferred over the corresponding monometallic complex (1.25:1). Swapping the phenyl and butyl substituents resulted in an inversion of the selectivity, with the monometallic species favored (ratio 2e/3e approximately 0.5:1). With two phenyl wingtip groups, the ratio could not be determined unambiguously due to considerable signal overlap both in the ¹H and ¹³C NMR spectra.

Purification of the mixtures by MeCN extraction and crystallization provided pure fractions of the dimetallic complexes 2b–2f. Analysis of their ¹³C NMR spectra reveals a moderate correlation between δC and the electronic properties of the wingtip groups. The most shielded carbenes were observed for triazolylidenes possessing two alkyl wingtip groups (cf δC 126.0 and 126.4 for 2b and 2c, respectively), whereas introduction of a phenyl group shifts the resonance to lower field (cf δC 128.5, 128.4, and 129.1 for 2a, 2d, and 2e, respectively). The carbene signal for the supposedly most deshielded carbene in 2f was not resolved.

Complexes 2b–e were investigated in the solid state by X-ray diffraction analysis (Fig. 3). The global structure of all dimeric compounds is identical to that of 2a (cf Fig. 1a) and comprises two palladium centers, two bridging iodides, and at each metal center one triazolylidene and one iodide ligand. In all complexes the center of the Pd₂I₂ square is a crystallographic inversion center. As a consequence, the wingtip groups in complexes 2d and 2e adopt a mutual anti conformation. The Pd–C bond lengths in all complexes are identical within esd’s and average to 1.97(1) Å. This distance is in the range generally observed for abnormal palladium carbene complexes. Further bond lengths and angles are similar to those of 2a (Table 2). Again, the triazolylidene ring is oriented almost perpendicular to the palladium square plane, with dihedral angles between 71° (2e) and 88° (2b). The Pd1–I2 bond trans to the carbene ligand is slightly shorter in the phenyl-substituted triazolylidene complexes than in the complexes comprising exclusively alkyl wingtip groups. These observations may point to a moderate tunability of the trans influence of the triazolylidene ligand via wingtip group modification.
Figure 3. ORTEP drawings of complex 2b (a; only one of the two crystallographically independent molecules shown), 2c (b), 2d (c), and 2e (d; all structures at 50% probability level but 2b, which is at 30% probability; hydrogen atoms and cocrystallized solvents in 2d and 2e omitted for clarity).

Table 2. Selected bond lengths (Å) and angles (°) for complexes 2b–2e

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<th>2b</th>
<th>2c</th>
<th>2d</th>
<th>2e</th>
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<tr>
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<td>2.6814(6)</td>
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<td>Pd1–I2a</td>
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<td>2.6070(15)</td>
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<td>C1–C2</td>
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<td>C1–Pd1–I1</td>
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<td>C1–Pd1–I2</td>
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Upon crystallization of complex \(2e\), a smooth color change from orange to yellow was noted in some cases. Analysis of this yellow fraction gave broad NMR resonances in the aromatic region. Measurements at 60 °C revealed four distinct resonances between 7 and 8 ppm. Desymmetrization of the phenyl ring and loss of one proton resonance is indicative for orthopalladation and the formation of the palladacycle \(5e\) (Scheme 4). The presence of a Pd–C\(_{aryl}\) bond was also supported by a low-field \(^{13}\text{C}\) NMR signal at \(\delta_c\) 144.6. Related cyclopalladation was also observed in imidazolium-derived N-heterocyclic carbenes.\(^{23}\) Unambiguous evidence for the formation of a cyclopalladated product was provided by X-ray diffraction analysis (Fig. 4). Crystals of \(5e\) contained two crystallographically independent molecules, which differed considerably in their global structure. One molecule is located on a crystallographic inversion center and features a planar Pd\(_2\)I\(_2\) core, thus resulting in a co-planar arrangement of the two metalacycles. In contrast the second molecule is characterized by an open book-type arrangement, with the metalacycles mutually tilted.\(^{24}\) Despite this different arrangement, bond lengths and angles in both molecules are highly similar. The Pd–C\(_{carbene}\) bonds are longer than in the monodentate complexes \(2\) and only slightly shorter than the Pd–C\(_{aryl}\) bonds (Table 3).

Scheme 4. Reversible cyclopalladation of triazolylidenes comprising N-phenyl wingtip groups.
Figure 4. ORTEP drawings of the two crystallographically independent molecules of 5e (50% probability, cocrystallized solvent molecules and hydrogen atoms omitted for clarity).

Table 3. Selected bond lengths (Å) and angles (°) for 5e a)

<table>
<thead>
<tr>
<th></th>
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<th>molecule 2 (Pd2)</th>
<th>molecule 2 (Pd3)</th>
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a) numbering scheme for molecule 2 adapted.

Investigation of the cyclopalladation revealed that heating of complex 2e in DMSO to 120 °C for 3.5 h, i.e. conditions used for the preparation of 2, did not induce any significant palladacycle formation. In the presence of a weak base such as acetate, several products yet no 5e were formed at room temperature, perhaps originating from anion metathesis due to the coordination ability of acetate. A similar outcome was noted when the reaction mixture was heated to 50°C. Further elevation of the temperature to 80°C induced formation of 5e albeit incomplete after 3 h. Cyclopalladation was
essentially quantitative, however, when 2e and an excess NaOAc were kept at 120 °C for 2 h. Longer reaction times led to significant decomposition as indicated by the formation of a black precipitate. Acetate seems to be a privileged base in this cyclometalation process. Attempts to substitute acetate by NEt₃ were unsuccessful and gave either no reaction at all (room temperature) or decomposition products only (3 h at 80 °C). Moreover, only N-bound phenyl wingtip groups were observed to undergo cyclopalladation. For example, complex 2f underwent C–H activation in the presence of acetate to give the cyclopalladated complex 5f. In this complex, the N-bound phenyl was palladated exclusively and neither activation of the C-bound phenyl group in 2f nor isomerization of the palladacycle in 5f was observed. Along the same lines, complex 2a and 2d, both featuring only a C-bound phenyl wingtip group were inert under the conditions used for cyclopalladation of complex 2e. Apparently, the electron-releasing character of nitrogen is beneficial to aryl functionalization, which is in line with an electrophilic mechanism for this cyclopalladation.

Metalacycle formation is fully reversible. When exposing complex 5a to excess HI, complex 2e is recovered in high yields. Cleavage of the metalacycle was indicated macroscopically by the instantaneous color change from yellow to orange, and microscopically by the pertinent ¹H NMR data, which were identical to those of the parent complex 2e. Exposure of 2e to HI for several days did not induce any complex degradation and hence demonstrates a remarkable resistance of the palladium-carbene bond towards acidolysis. Both, the stability of the Pd–C_carbene bond towards acids and bases as well as the sensitivity of N-bound phenyl groups towards cyclopalladation under basic conditions — typical conditions for example in cross-coupling reactions — have obvious implications when using this type of complexes in catalysis.

Synthesis of rhodium complexes. Ligand complexation to rhodium provides a useful probe for evaluating ligand effects, first by measuring the CO stretch vibration in the corresponding rhodium carbonyl complexes (translating into Tolman electronic parameters, TEPs), and second by NMR spectroscopy due to the I = 1/2 spin of $^{103}$Rh. Therefore, the rhodium complexes 6 were prepared using
classical transmetalation procedures involving Ag₂O as a basic silver salt and [Rh(cod)Cl]₂ as transmetalating agent (Scheme 5). Exposure of complexes 6 to a CO-saturated environment afforded the corresponding carbonyl analogues 7 in essentially quantitative yield.³⁰

\[
\text{Scheme 5. Synthesis of the rhodium complexes 6 and 7.}
\]

The \(^{13}\text{C}\) NMR chemical shift of the rhodium-bound triazolylidene carbon shows an apparent correlation with the nature of the wingtip group. With alkyl wingtip groups, the doublet (\(^1J_{\text{RhC}} = 46.5±3\) Hz for all complexes) appeared at highest field (δ \(_C\) 168.5 and 168.6 for 6b and 6c, respectively), while the presence of one phenyl group as in 6d and 6e induces a downfield shift (δ \(_C\) 170.4 for both complexes). When incorporating a second phenyl group (6f), the resonance is shifted by another 2 ppm to lower field (δ \(_C\) 172.2). A similar trend was observed when comparing the carbene resonance of the carbonyl complexes 7, although the effect is more gradual and not additive as in complexes 6 (Table 4). In agreement with the stronger trans influence of CO as opposed to olefins, the Rh–C\(_{\text{carbene}}\) coupling constant is smaller in complexes 7 with \(^1J_{\text{RhC}} = 39.1±4\). When considering the NMR characteristics of the CO ligand trans to the carbene,³¹ an increase of the coupling constant was observed upon reducing the wingtip donation. Thus, the lowest coupling constant was noted for the alkyl substituted carbene complexes 7b and 7c (\(^1J_{\text{RhC}} = 53.4\)), and this value increases upon replacing electron releasing alkyl groups with electron withdrawing phenyl wingtips. The trend is not rigid (cf 7e and 7f). Since larger coupling constants may be attributed to weaker ligand donor properties in trans position,³² this trend in
$^{1}J_{\text{RhC}}$ and chemical shift analyses are both in line with a soft yet noticeable tunability of electronic properties via wingtip group modifications.

**Table 4.** Selected spectroscopic data for complexes 7a–f $^{a)}$

<table>
<thead>
<tr>
<th></th>
<th>7a</th>
<th>7b</th>
<th>7c</th>
<th>7d</th>
<th>7e</th>
<th>7f</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_C$ ($^{1}J_{\text{RhC}}$) $C_{\text{carbene}}$</td>
<td>161.2 (39.4)</td>
<td>159.8 (39.4)</td>
<td>160.4 (39.4)</td>
<td>161.3 (39.4)</td>
<td>161.8 (39.4)</td>
<td>162.6 (39.4)</td>
</tr>
<tr>
<td>$\delta_C$ ($^{1}J_{\text{RhC}}$) $C_O^{\text{trans}}$</td>
<td>186.1 (54.1)</td>
<td>186.8 (53.4)</td>
<td>187.0 (53.4)</td>
<td>186.8 (54.2)</td>
<td>186.7 (54.9)</td>
<td>186.7 (54.8)</td>
</tr>
<tr>
<td>$\delta_C$ ($^{1}J_{\text{RhC}}$) $C_O^{\text{cis}}$</td>
<td>183.5 (75.4)</td>
<td>184.3 (74.6)</td>
<td>184.4 (74.8)</td>
<td>183.9 (75.4)</td>
<td>183.8 (75.4)</td>
<td>183.7 (74.6)</td>
</tr>
</tbody>
</table>

$a)$ in CD$_2$Cl$_2$, $\delta_C$ in ppm, $^{1}J_{\text{RhC}}$ in Hz, trans refers to the carbene position; data for 7a from ref 8.

The CO stretch vibrations occur in the IR spectrum at 1983 and 2065 cm$^{-1}$ for all complexes except for 7f ($\nu_{CO} = 1988$ and 2068 cm$^{-1}$). Depending on the applied linear regression, these values translate into a TEP in the range of 2035 to 2042 cm$^{-1}$. Because of the identical CO absorption energies, the calculated TEPs for the triazolylidene ligands in complexes 7b–7e are obviously the same, which may indicate some limitation of this method for evaluating ligand donor properties. Perhaps, steric effects may affect the Rh–CO$_{\text{cis}}$ bond and may thus interfere with the electronic component exerted by the ligand. Such stereoelectronic perturbation has been noted before and may, in the complexes investigated here, compensate the moderate donor differences due to wingtip modifications.

**Conclusions**

Palladation of triazolium salts afforded different types of complexes, including monometallic bis(carbene) species and bimetallic complexes with 1:1 metal carbene stoichiometry. Careful choice of reaction conditions and work-up procedures provide access to pure materials. Variation of the wingtip groups has distinct implications on the properties of the triazolylidene ligand. Accordingly, swapping from an alkyl to an aryl substituent reduces the electron density at the metal center. The arrangement of the substituents (e.g. C-bound vs N-bound phenyl as in 6d and 6e) appears to play no significant role for tuning the electronic properties of the metal center. This wingtip arrangement strongly affects, however,
the stability of the corresponding palladium complexes, since N-bound phenyl groups tend to
cyclopalladate, while the C-bound analogue resists such processes. Ligand tunability and stability will
have profound implications for applying this class of complexes in catalysis. Investigations along these
lines are currently in progress and will be subject of a forthcoming report.

**Experimental Section**

**General comments.** Air sensitive reactions were carried out under Ar using schlenk techniques.
CH₂Cl₂ was dried by passage through solvent purification column. The preparation of the triazolium
salts is detailed in the supporting information. All other chemicals were commercially available and
were used as received. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker spectrometers at room
temperature, unless stated otherwise, and were referenced to the protio signal of the solvent and are
reported downfield from SiMe₄. Chemical shifts (δ) are given in ppm; coupling constants J are given in
Hz. NMR assignments are based on distortionless enhancement of polarization transfer (DEPT)
experiments or on homo- and heteronuclear shift correlation spectroscopy. Elemental analysis were
performed by the Microanalytical Laboratory of the ETH Zürich (Switzerland). Mass spectra were
measured by electrospray ionization (ESI–MS) in MeCN on a Bruker 4.7 BioAPEX II instrument and
infrared spectra on a Bruker Tensor 27 using a Golden Gate ATR. Details on crystallographic structure
determination and refinement of the complexes are compiled in the supporting information. CCDC
800720–800720 contain the supplementary crystallographic data for this paper. These data can be
obtained free of charge from the Cambridge Crystallographic Data Centre via
www.ccdc.cam.ac.uk/data_request/cif.

**Palladation reactions.** Method A: A solution of triazolium salt and Pd(OAc)₂ (1 equiv.) in DMSO
was stirred at 120 °C for 3.5 h. After addition of CH₂Cl₂, the solution was filtered through Celite, H₂O
was added, and the solution was extracted with CH₂Cl₂. The organic phases were combined, washed
with H₂O and dried over Na₂SO₄ and all volatiles were evaporated, yielding a mixture of 2 and 3. Repeated extraction of this mixture with small portions of MeCN gave complex 2 in almost pure form, while subsequent extraction of the residue with CH₂Cl₂ yielded the mono(carbene) species 3. Further purification of the fractions was achieved by crystallization.

**Method B:** The triazolium salt (1 equiv.) and Ag₂O (1 equiv.) in CH₂Cl₂ were stirred at rt for 24 h. After filtration through Celite, PdCl₂(MeCN)₂ (1 equiv.) was added and the solution was stirred at rt during 4 h. The solution was filtered through Celite and a solution of NaI (6 equiv.) in acetone was added and stirred at rt for another hour. After evaporation of volatiles and addition of H₂O, the residue was extracted with CH₂Cl₂. The combined organic phases were washed with H₂O then with a saturated aqueous solution of sodium pyrosulfite (Na₂S₂O₅), dried over Na₂SO₄ and evaporated to dryness.

**Synthesis of 2a.** According to method B, 1a (0.237 g, 0.75 mmol) in CH₂Cl₂ (15 mL) were stirred at rt with Ag₂O (0.173 g, 0.75 mmol) for 24 h and PdCl₂(MeCN)₂ (0.196 g, 0.75 mmol) was then added. After filtration through celite, NaI (0.668 g, 4.46 mmol) dissolved in acetone (25 mL) was added and the mixture was stirred for 1.5 h. All volatiles were evaporated and the residue was extracted to yield a red powder (0.313 g, 76%). Analytically pure 2a was obtained after recrystallization by slow diffusion of pentane into a saturated CH₂Cl₂ solution.

**1H NMR (400 MHz, DMSO–D₆):** δ 7.98–7.92 (m, 4H, H₉ortho), 7.63–7.52 (m, 6H, H₉meta, H₉para), 4.71 (q, JHH = 7.2 Hz, 4H, NC₃H₇CH₃), 4.06 (s, 6H, NCH₃), 1.63 (t, JHH = 7.2 Hz, 6H, NCH₂C₃H₃); **13C{¹H} NMR (100 MHz, DMSO–D₆):** δ 142.5 (C₉trz), 130.0 (C₉ortho), 129.8 (C₉para), 128.5 (C₉meta + C₉trz–Pd), 126.9 (C₉ipso), 50.8 (NCH₂CH₃), 38.1 (NCH₃), 14.2 (NCH₂CH₃); Anal. Found (calcd) for C₂₂H₂₆I₄N₆Pd₂ (1094.93) × 1/2 C₅H₁₂: C 26.17 (26.02), H 2.60 (2.85), N 7.85 (7.43).

**Synthesis of 2b.** According to method B, starting from 1b (0.104 g, 0.39 mmol) in CH₂Cl₂ (10 mL), Ag₂O (0.090 g, 0.39 mmol), PdCl₂(MeCN)₂ (0.101 g, 0.39 mmol). After stirring for 20 h, Celite
filtration, addition of NaI (0.359 g, 2.39 mmol) dissolved in acetone (20 mL) and purification gave 2b as a red solid (0.084 g, 43%).

$^1$H NMR (500 MHz, DMSO–D$_6$): δ 4.56 (q, $^3$J$_{HH} = 7.3$ Hz, 4H, NCH$_2$CH$_3$), 4.06 (s, 6H, NCH$_3$), 2.85 (q, $^3$J$_{HH} = 7.6$ Hz, 4H, CCH$_2$CH$_3$), 1.54 (t, $^3$J$_{HH} = 7.3$ Hz, 6H, NCH$_2$CH$_3$), 1.34 (t, $^3$J$_{HH} = 7.6$ Hz, 6H, CCH$_2$CH$_3$); $^{13}$C{${^1}$H} NMR (125 MHz, DMSO–D$_6$): δ 144.1 (C$_{trz}$), 126.0 (C$_{uz}$–Pd), 50.3 (NCH$_2$CH$_3$), 36.6 (NCH$_3$), 18.1 (CCH$_2$CH$_3$), 14.2 (NCH$_2$CH$_3$), 12.0 (CCH$_2$CH$_3$); Anal. Found (calcd) for C$_{14}$H$_{26}$I$_4$N$_6$Pd$_2$: C 16.76 (16.83), H 2.55 (2.62), N 8.09 (8.41).

**Synthesis of 2c.** According to method B, starting from 1c (0.113 g, 0.35 mmol) in CH$_2$Cl$_2$ (15 mL), Ag$_2$O (0.082 g, 0.35 mmol), PdCl$_2$(MeCN)$_2$ (0.092 g, 0.35 mmol). Stirring for 5 h, Celite filtration and addition of NaI (0.202 g, 1.35 mmol) in acetone (15 mL) was followed by an extraction and recrystallization by slow diffusion of pentane into CH$_2$Cl$_2$. This procedure gave an analytically pure fraction of 2c (0.137 g, 71%).

$^1$H NMR (500 MHz, DMSO–D$_6$): δ 4.52 (t, $^3$J$_{HH} = 7.2$ Hz, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$), 4.04 (s, 6H, NCH$_3$), 2.84 (t, $^3$J$_{HH} = 7.9$ Hz, 4H, CCH$_2$CH$_2$CH$_2$CH$_3$), 2.08 (quint, $^3$J$_{HH} = 7.2$ Hz, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.85 (quint,$^3$J$_{HH} = 7.9$ Hz, 4H, CCH$_2$CH$_2$CH$_2$CH$_3$), 1.37 (sext, $^3$J$_{HH} = 7.5$ Hz, 4H, CCH$_2$CH$_2$CH$_2$CH$_3$), 1.30 (sext, $^3$J$_{HH} = 7.5$ Hz, 4H, NCH$_2$CH$_2$CH$_2$CH$_3$), 0.93 (q, $^3$J$_{HH} = 7.5$ Hz, 12H, CCH$_2$CH$_2$CH$_2$CH$_3$), 0.93 (q, $^3$J$_{HH} = 7.5$ Hz, 12H, NCH$_2$CH$_2$CH$_2$CH$_3$); $^{13}$C{${^1}$H} NMR (125 MHz, DMSO–D$_6$): δ 143.5 (C$_{trz}$), 126.4 (C$_{uz}$–Pd), 54.6 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.6 (NCH$_3$), 29.9 (NCH$_2$CH$_2$CH$_2$CH$_3$), 29.2 (CCH$_2$CH$_2$CH$_2$CH$_3$), 24.5 (CCH$_2$CH$_2$CH$_2$CH$_3$), 21.9 (CCH$_2$CH$_2$CH$_2$CH$_3$), 19.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.7 (CCH$_2$CH$_2$CH$_2$CH$_3$), 13.3 (NCH$_2$CH$_2$CH$_2$CH$_3$); Anal. Found (calcd) for C$_{22}$H$_{44}$I$_4$N$_6$Pd$_2$: C 23.70 (23.78), H 3.82 (3.81), N 7.42 (7.56).

**Synthesis of 2d.** According to method B, starting from 1d (0.150 g, 0.44 mmol) in CH$_2$Cl$_2$ (15 mL), Ag$_2$O (0.100 g, 0.43 mmol), PdCl$_2$(MeCN)$_2$ (0.115 g, 0.44 mmol) After stirring for 4 h, filtration
through Celite, addition of NaI (0.399 g, 2.66 mmol) dissolved in acetone (20 mL) followed by
evaporation of volatiles and extraction. Recrystallization allowed for obtaining an analytically pure
fraction of 2d (0.189 g, 75% yield).

\[ ^1H \text{NMR (500 MHz, DMSO–D}_6\]): \delta 7.97–7.94 (m, 4H, H_{ortho}^\text{ph}), 7.60–7.53 (m, 6H, H_{meta}^\text{ph}, H_{para}^\text{ph}), 4.66 (t, 3J_{HH} = 7.4 Hz, 4H, NCH}_2CH_2CH_2CH_3), 4.06 (s, 6H, NCH_3), 2.16 (quint, 3J_{HH} = 7.4 Hz, 4H, NCH}_2CH_2CH_2CH_3), 1.40 (sext, 3J_{HH} = 7.4 Hz, 4H, CH}_2CH_2CH_2CH_3), 0.96 (t, 3J_{HH} = 7.4 Hz, 6H, NCH}_2CH_2CH_2CH_3); ^13C{^1H} \text{NMR (125 MHz, DMSO–D}_6\): \delta 142.6 (C_{trz}), 129.9 (C_{ortho}^\text{ph}), 129.7 (C_{para}^\text{ph}), 128.4 (C_{meta}^\text{ph}+ C_{trz–Pd}), 127.0 (C_{ipso}^\text{ph}), 54.9 (NCH}_2CH_2CH_2CH_3), 38.0 (NCH_3), 29.9 (NCH}_2CH_2CH_2CH_3), 19.0 (NCH}_2CH_2CH_2CH_3), 13.4 (NCH}_2CH_2CH_2CH_3); Anal. Found (calcd) for C_{26}H_{34}I_4N_6Pd_2 (1151.05): C 27.07 (27.13), H 2.98 (2.98), N 7.21 (7.30).

**Synthesis of 2e.** According to method B, starting from 1e (0.073 g, 0.21 mmol) in CH_2Cl_2 (10 mL),
Ag_2O (0.050 g, 0.21 mmol), PdCl_2(MeCN)_2 (0.056 g, 0.21 mmol). After stirring for 20 h, filtration
through celite, NaI (0.194 g, 1.29 mmol) dissolved in acetone (20 mL), evaporation of volatiles and
extraction, an analytically pure fraction of 2e was obtained (0.106 g, 87% yield).

\[ ^1H \text{NMR (500 MHz, DMSO–D}_6\): \delta 8.23 (d, 3J_{HH} = 7.8 Hz, 4H, H_{ortho}^\text{ph}), 7.68–7.58 (m, 6H, H_{meta}^\text{ph}, \text{H}_{para}^\text{ph}), 4.18 (s, 3H, NCH_3), 2.98 (t, 3J_{HH} = 7.8 Hz, 4H, CH}_2CH_2CH_2CH_3), 1.93 (quint, 3J_{HH} = 7.8 Hz, 4H, CH}_2CH_2CH_2CH_3), 1.44 (sext, 3J_{HH} = 7.4 Hz, 4H, CH}_2CH_2CH_2CH_3), 0.97 (t, 3J_{HH} = 7.4 Hz, 6H, CH}_2CH_2CH_2CH_3); ^13C{^1H} \text{NMR (75 MHz, DMSO–D}_6\): \delta 144.2 (C_{trz}), 139.1 (C_{ipso}^\text{ph}), 130.0 (C_{para}^\text{ph}), 129.1 (C_{meta}^\text{ph}+ C_{trz–Pd}), 124.4 (C_{ortho}^\text{ph}), 37.0 (NCH_3), 29.0 (CH}_2CH_2CH_2CH_3), 24.8 (CH}_2CH_2CH_2CH_3), 21.9 (CH}_2CH_2CH_2CH_3), 13.6 (CCH}_2CH_2CH_2CH_3); Anal. Found (calcd) for C_{26}H_{34}I_4N_6Pd_2 (1151.05): C 27.35 (27.13), H 3.10 (2.98), N 7.25 (7.30).

**Synthesis of 2f.** According to method B, starting from 1f (0.105 g, 0.29 mmol) in CH_2Cl_2 (20 mL),
Ag_2O (0.065 g, 0.28 mmol), PdCl_2(MeCN)_2 (0.074 g, 0.29 mmol). Stirring for 6 h, Celite filtration,
addition of NaI (0.260 g, 1.73 mmol) dissolved in acetone (25 mL) was followed by evaporation of volatiles and extraction (0.091 g, 53% yield).

\[ 1^H \text{NMR (500 MHz, DMSO-}D_6\text{): } \delta \ 8.34-8.31 \ (m, 4H, H^\text{ortho}_\text{NPh}), \ 8.04-8.02 \ (m, 4H, H^\text{ortho}_\text{CPh}), \ 7.72-7.68 \ (m, 4H, H^\text{meta}_\text{NPh}), \ 7.66-7.57 \ (m, 8H, H^\text{meta}_\text{CPh}, H^\text{para}_\text{CPh}, H^\text{para}_\text{NPh}), \ 4.17 \ (s, 6H, NCH}_3 \text{);} \]

\[ 1^H \text{NMR (400 MHz, DMSO-}D_6\text{): } \delta \ 8.13 \ (d, \ ^3J_{HH} = 7.3 \ Hz, 4H, H^\text{ortho}_\text{ph}), \ 7.58-7.49 \ (m, 6H, H^\text{meta}_\text{ph}, H^\text{para}_\text{ph}), \ 4.65 \ (q, \ ^3J_{HH} = 7.3 \ Hz, 4H, NCH}_2 \text{);} \]

\[ 1^H \text{NMR (400 MHz, DMSO-}D_6\text{): } \delta \ 7.93 \ (d, \ ^3J_{HH} = 7.1 \ Hz, 4H, H^\text{ortho}_\text{ph}), \ 7.58-7.41 \ (m, 6H, H^\text{meta}_\text{ph}, H^\text{para}_\text{ph}), \ 4.85 \ (q, \ ^3J_{HH} = 7.2 \ Hz, 4H, NCH}_2 \text{);} \]

\[ 1^H \text{NMR (500 MHz, DMSO-}D_6\text{): } \delta \ 143.3 \ (C^\text{trz}), \ 139.0 \ (C^\text{ipso}_\text{NPh}), \ 130.3 \ (C^\text{para}_\text{NPh}), \ 130.2 \ (C^\text{ortho}_\text{CPh}), \ 130.0 \ (C^\text{para}_\text{CPh}), \ 129.2 \ (C^\text{meta}_\text{NPh}), \ 128.5 \ (C^\text{meta}_\text{CPh}), \ 126.9 \ (C^\text{ipso}_\text{CPh}), \ 124.7 \ (C^\text{ortho}_\text{NPh}), \ 38.4 \ (NCH}_3 \text{); C^\text{trz-Pd} \text{ not observed; Anal. Found (calcd) for C}_{31}H_{28}I_4N_6Pd_2 (1191.02) \times 1/2 CH}_2Cl_2: C \ 28.73 (29.18), H \ 2.15 (2.21), N \ 6.65 (6.59).} \]

**Synthesis of 3a.** According to method A, 1a (0.301 g, 0.95 mmol) in DMSO (25 mL) were heated with Pd(OAc)$_2$ (0.214 g, 0.95 mmol). After extraction 0.315 g of mixture of 2a and 3a was obtained. This mixture was washed with MeCN and the residue was dried in vacuo, thus giving 3a (0.091 g, 26%) as an analytically pure cis/trans mixture (1:2.5 ratio).

**Major isomer:** 1H NMR (400 MHz, DMSO–D$_6$): $\delta$ 8.13 (d, $^3J_{HH} = 7.3$ Hz, 4H, H$^\text{ortho}_\text{ph}$), 7.58–7.49 (m, 6H, H$^\text{meta}_\text{ph}$, H$^\text{para}_\text{ph}$), 4.65 (q, $^3J_{HH} = 7.3$ Hz, 4H, NCH$_2$), 4.09 (s, 6H, NCH$_3$), 1.56 (t, $^3J_{HH} = 7.3$ Hz, 6H, NCH$_2$C$_3$H$_2$); $^{13}$C{$^1$H} NMR (100 MHz, DMSO–D$_6$): $\delta$ 154.6 (C$_{trz}$–Pd), 144.1 (C$_{trz}$), 129.8 (C$_{ortho}_\text{ph}$), 128.3 (C$^\text{ipso}_\text{ph}$), 128.1 (C$^\text{meta}_\text{ph}$), C$_{para}_\text{ph}$ not observed, 49.6 (NCH$_2$), 37.5 (NCH$_3$), 14.9 (NCH$_2$CH$_3$).

**Minor isomer:** 1H NMR (400 MHz, DMSO–D$_6$): $\delta$ 7.93 (d, $^3J_{HH} = 7.1$ Hz, 4H, H$^\text{ortho}_\text{ph}$), 7.58–7.41 (m, 6H, H$^\text{meta}_\text{ph}$, H$^\text{para}_\text{ph}$), 4.85 (q, $^3J_{HH} = 7.2$ Hz, 4H, NCH$_2$), 4.05 (s, 6H, NCH$_3$), 1.71 (t, $^3J_{HH} = 7.2$ Hz, 6H, NCH$_2$CH$_3$); $^{13}$C{$^1$H} NMR (100 MHz, DMSO–D$_6$): $\delta$ 154.0 (C$_{trz}$–Pd), 144.1 (C$_{trz}$), 129.6 (C$_{ortho}_\text{ph}$), 129.1 (C$^\text{meta}_\text{ph}$), 128.8 (C$_{para}_\text{ph}$), 127.9 (C$^\text{ipso}_\text{ph}$), 50.0 (NCH$_2$), 37.6 (NCH$_3$), 14.6 (NCH$_2$CH$_3$); Anal. Found (calcd) for C$_{32}$H$_{26}$I$_4$N$_6$Pd (734.72): C 35.54 (35.96), H 3.49 (3.57), N 11.13 (11.44).

**Synthesis of 4a.** According to method B starting from 1a (400 mg, 1.27 mmol), Ag$_2$O (490 mg, 2.1 mmol), and PdCl$_2$(NCMe)$_2$ (315 mg, 1.2 mmol) in CH$_2$Cl$_2$ (20 mL) at rt during 2 h. After filtration
through Celite, the mixture was eluted from a short pad of SiO$_2$ by using CH$_2$Cl$_2$. After evaporation of all volatiles, the residue was washed with pentane (3 × 20 mL) to afford 4a as a yellow solid (334 mg, 96%).

$^1$H NMR (500 MHz, CD$_3$CN, 348 K): $\delta$ 8.10 (br. s, 4H, H$_{ar}$), 7.55 (br. s, 6H, H$_{ir}$), 4.92 (q, $^3J_{HH} = 7.1$ Hz, 4H, NCH$_2$), 4.02 (s, 6H, NCH$_3$), 1.76 (t, $^3J_{HH} = 7.1$ Hz, 6H, NCH$_2$C$_3$H$_7$).

$^{13}$C{$^1$H} NMR (125 MHz CDCl$_3$) major isomer: $\delta$ 159.0 (C$_{trz}$–Pd), 144.5 (C$_{trz}$), 132.3 (C$_{ipso}$ ph), 130.3 (C$_{meta}$ ph), 129.0 (C$_{para}$ ph), 128.4 (C$_{ortho}$ ph), 49.7 (NCH$_2$), 36.9 (NCH$_3$), 15.5 (NCH$_2$C$_3$H$_7$).

$^{13}$C{$^1$H} NMR (125 MHz CDCl$_3$) minor isomer: $\delta$ 158.1 (C$_{trz}$–Pd), 144.8 (C$_{trz}$), 132.7 (C$_{ipso}$ ph), 130.4 (C$_{meta}$ ph), 129.2 (C$_{para}$ ph), 128.3 (C$_{ortho}$ ph), 50.0 (NCH$_2$), 36.8 (NCH$_3$), 15.2 (NCH$_2$C$_3$H$_7$). Anal. Found (calcd) for C$_{22}$H$_{26}$Cl$_2$N$_6$Pd (550.06) × 1/4 CH$_2$Cl$_2$: C 46.51 (46.64); H, 4.50 (4.66); N, 14.54 (14.67).

**Synthesis of complex 5e.** The title complex was obtained upon recrystallization of a solution of 2e by slow evaporation of a warm MeCN solution.

$^1$H NMR (500 MHz, DMSO–D$_6$, 333 K): $\delta$ 7.89 (br. s, 2H, H$_{ph}$), 7.38 (d, $^3J_{HH} = 7.5$ Hz, 2H, H$_{ph}$), 7.15 (d, $^3J_{HH} = 7.5$ Hz, 2H, H$_{para}$ ph), 7.08–7.05 (m, 2H, H$_{ph}$), 4.14 (s, 6H, NCH$_3$), 3.12–3.11 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_3$), 1.60–1.57 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_3$), 1.47–1.40 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_3$), 0.95 (t, $^3J_{HH} = 7.3$ Hz, 6H, CH$_2$CH$_2$CH$_2$CH$_3$); $^{13}$C{$^1$H} NMR (125 MHz, DMSO–D$_6$, 333 K): $\delta$ 146.3 (C$_{trz}$), 144.6 (C$_{ph}$), 127.2 (CH$_{ph}$), 124.5 (CH$_{ph}$), 112.7 (CH$_{ph}$), 36.1 (NCH$_3$), 30.6 (CH$_2$CH$_2$CH$_2$CH$_3$), 23.6 (CH$_2$CH$_2$CH$_2$CH$_3$), 21.5 (CH$_2$CH$_2$CH$_2$CH$_3$), 13.3 (CCH$_2$CH$_2$CH$_2$CH$_3$), 2 C$_{ph}$ and C$_{trz}$–Pd not observed; Anal. Found (calcd) for C$_{26}$H$_{32}$I$_2$N$_6$Pd$_2$ (895.22): C 35.19 (34.88), H 3.77 (3.60), N 9.46 (9.39).

**General procedure for the synthesis of rhodium complexes 6.** General method: A flask, protected against light, containing 1 (1 equiv.) in CH$_2$Cl$_2$ and Ag$_2$O (1 equiv.) was stirred at r.t. during 24 h. After filtration through Celite, [Rh(COD)Cl]$_2$ (0.5 equiv) was added and the solution was stirred for the time
indicated and then filtered through Celite to give complex 6. Analytically pure samples were typically obtained by precipitation from CH₂Cl₂ and pentane.

**Synthesis of 6b.** According to the general method, 1b (0.110 g, 0.41 mmol) in CH₂Cl₂ (10 mL) was stirred with Ag₂O (0.095 g, 0.41 mmol). After filtration through Celite, [Rh(COD)Cl]₂ (0.091 g, 0.18 mmol) was added and the solution was stirred and, after 3 h, filtrated through Celite to give complex 6b (0.14 g, 88%).

**1H NMR (300 MHz, CD₂Cl₂):** δ 4.84–4.77 (m, 4H, NCH₂CH₃, CH COD), 3.88 (s, 3H, NCH₃), 3.24 (br.s, 2H, CH₂COD), 2.95 (q, 3JHH = 7.6 Hz, 2H, CCH₂CH₃), 2.46–2.25 (br. m, 4H, CH₂COD), 1.64 (t, 3JHH = 7.3 Hz, 3H, NCH₂CH₃), 1.47 (t, 3JHH = 7.6 Hz, 3H, CCH₂CH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ 168.5 (d, ¹JCₚₗₗₗ = 46.2 Hz, C trz–Rh), 145.5 (d, ²JCₚₗₗₗ = 2.8 Hz, C trz), 96.6 (d, ¹JCₚₗₗₗ = 7.2 Hz, CH COD), 96.2 (d, ¹JCₚₗₗₗ = 7.2 Hz, CH COD), 68.3 (d, ¹JCₚₗₗₗ = 14.9 Hz, CH COD), 67.9 (d, ¹JCₚₗₗₗ = 14.9 Hz, CH COD), 50.6 (NCH₂CH₃), 36.2 (NCH₃), 33.8 (CH₂ COD), 33.1 (CH₂ COD), 29.6 (CH₂ COD), 29.3 (CH₂ COD), 19.3 (CCH₂CH₃), 16.0 (NCH₂CH₃), 14.5 (CCH₂CH₃); Anal. Found (calcd) for C₁₅H₂₅ClN₃Rh (385.74) × 2/3 CH₂Cl₂: C 42.83 (42.54), H 5.93 (6.00), N 9.18 (9.50).

**Synthesis of 6c.** According to the general method, 1c (0.103 g, 0.32 mmol) in CH₂Cl₂ (15 mL) was stirred with Ag₂O (0.074 g, 0.32 mmol). After filtration through Celite, [Rh(COD)Cl]₂ (0.077 g, 0.16 mmol) was added and the solution was stirred and, after 8 h, filtrated through Celite to give complex 6c as a dark yellow oil (0.140 g, 99%).

**1H NMR (300 MHz, CD₂Cl₂):** δ 4.88–4.79 (m, 3H, NCH₂CH₂CH₂CH₃, CH COD), 4.67–4.57 (m, 1H, CH COD), 3.87 (s, 1H, NCH₃), 3.33–3.17 (m, 2H, CH COD), 2.88 (t, ³JHH = 8.1 Hz, 2H, CCH₂CH₂CH₂CH₃), 2.46–2.24 (m, 4H, CH₂ COD), 2.22–1.97 (m, 4H, CCH₂CH₂CH₂CH₃, NCH₂CH₂CH₂CH₃), 1.95–1.73 (m, 4H, CH₂ COD), 1.36 (m, 4H, CCH₂CH₂CH₂CH₃, NCH₂CH₂CH₂CH₃); ¹³C{¹H} NMR (75 MHz, CD₂Cl₂): δ 168.6 (d, ¹JCₚₗₗₗ = 46.7 Hz,
C_{trz}–Rh), 144.5 (d, $^2J_{\text{CRh}} = 2.8$ Hz, C_{trz}), 96.4 (d, $^1J_{\text{CRh}} = 7.2$ Hz, CH_{COD}), 96.1 (d, $^1J_{\text{CRh}} = 7.2$ Hz, CH_{COD}), 68.1 (d, $^1J_{\text{CRh}} = 14.9$ Hz, CH_{COD}), 67.8 (d, $^1J_{\text{CRh}} = 14.9$ Hz, CH_{COD}), 55.1 (NCH₂CH₂CH₂CH₃), 36.3 (NCH₃), 33.9 (CH₂COD), 33.1 (CH₂COD), 32.5, 32.2 (NCH₂CH₂CH₂CH₃ + CCH₂CH₂CH₂CH₃), 29.7 (CH₂COD), 29.3 (CH₂COD), 25.6 (CCH₂CH₂CH₂CH₃), 23.3, 20.5 (NCH₂CH₂CH₂CH₃ + CCH₂CH₂CH₂CH₃), 14.1, 14.0 (CCH₂CH₂CH₂CH₃ + NCH₂CH₂CH₂CH₃); Anal. Found (calcd) for C₁₉H₂₃ClN₃Rh (441.84) × 1/4 CH₂Cl₂: C 49.97 (49.93), H 7.25 (7.29), N 9.04 (9.07).

**Synthesis of 6d.** According to the general method, 1d (0.114 g, 0.33 mmol) in CH₂Cl₂ (15 mL) was stirred with Ag₂O (0.077 g, 0.33 mmol). After filtration through Celite, [Rh(COD)Cl]₂ (0.074 g, 0.15 mmol) was added and, after stirring 6 h, the solution was filtrated through Celite to afford 6d as a dark yellow solid (0.12 g, 77%).

$^1$H NMR (400 MHz, CD₂Cl₂): δ 8.09–8.07 (m, 2H, H^ortho_ph), 7.60–7.50 (m, 3H, H^meta_ph, H^para_ph), 5.09–5.02 (m, 1H, NCH₂CH₂CH₂CH₃), 4.92–4.75 (m, 2H, CH_{COD}), 4.67–4.60 (m, 1H, NCH₂CH₂CH₂CH₃), 4.01 (s, 3H, NCH₃), 3.14 (br. s, 1H, CH_{COD}), 2.59 (br. s, 1H, CH_{COD}), 2.35–2.13 (m, 5H, NCH₂CH₂CH₂CH₃ + CH₂COD), 1.82–1.64 (m, 5H, NCH₂CH₂CH₂CH₃ + CH₂COD), 1.55–1.48 (m, 2H, NCH₂CH₂CH₂CH₃), 1.07 (t, $^3J_{\text{HH}} = 7.5$ Hz, 3H, NCH₂CH₂CH₂CH₃); $^{13}$C($^1$H) NMR (100 MHz, CD₂Cl₂): δ 170.4 (d, $^1J_{\text{CRh}} = 46.8$ Hz, C_{trz}–Rh), 144.3 (d, $^2J_{\text{CRh}} = 2.2$ Hz, C_{trz}), 130.6 (C^ortho_ph), 129.7 (C^para_ph), 129.0 (C^{ipso_ph}), 128.8 (C^{meta_ph}), 96.3 (CH₃COD), 96.2 (CH_{COD}), 70.2 (d, $^1J_{\text{CRh}} = 13.9$ Hz, CH_{COD}), 67.7 (d, $^1J_{\text{CRh}} = 14.7$ Hz, CH_{COD}), 55.3 (NCH₂CH₂CH₂CH₃), 37.8 (NCH₃), 33.6 (CH₂COD), 32.7 (CH₂COD), 32.5, (NCH₂CH₂CH₂CH₃), 29.5 (CH₂COD), 29.4 (CH₂COD), 20.5 (NCH₂CH₂CH₂CH₃), 14.1 (NCH₂CH₂CH₂CH₃); Anal. Found (calcd) for C₂₁H₂₉ClN₃Rh (461.83) × 1/8 CH₂Cl₂: C 53.64 (53.70), H 6.13 (6.24), N 8.66 (8.89).

**Synthesis of 6e.** According to the general method, 1e (0.061 g, 0.17 mmol) in CH₂Cl₂ (10 mL) were stirred with Ag₂O (0.042 g, 0.18 mmol) for 20 h. After filtration through Celite, [Rh(COD)Cl]₂ (0.044 g,
0.09 mmol) was added and the solution was stirred and, after 5 h filtrated through Celite, to give complex 6e (0.078 g, quantitative).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 8.64–8.61 (m, 2H, H$_{\text{ortho ph}}$), 7.62–7.52 (m, 3H, H$_{\text{meta ph}}$, H$_{\text{para ph}}$), 4.94–4.80 (m, 2H, CH$_{\text{COD}}$), 4.02 (s, 3H, NCH$_3$), 3.27–3.19 (1H), 3.16–3.10 (1H), 3.00–3.92 (1H), 2.63–2.58 (1H), 2.41–2.26 (2H), 2.20–1.93 (3H), 1.91–1.82 (1H), 1.80–1.69 (3H), 1.62–1.51 (3H) (2H, CH$_{\text{COD}}$, 8H, CH$_2$COD, 2H, CH$_2$CH$_2$CH$_2$CH$_3$, 2H, CH$_2$CH$_2$CH$_2$CH$_3$, 2H, CH$_2$CH$_2$CH$_2$CH$_3$), 1.08 (t, $^3$J$_{\text{HH}}$ = 7.3 Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_3$); $^{13}$C{($^1$H)} NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 170.4 (d, $^1$J$_{\text{CRh}}$ = 46.8 Hz, C$_{\text{trz}}$–Rh), 146.1 (d, $^2$J$_{\text{CRh}}$ = 1.5 Hz, C$_{\text{trz}}$), 140.6 (C$_{\text{ipso ph}}$), 129.8 (C$_{\text{para ph}}$), 129.2 (C$_{\text{meta ph}}$), 124.6 (C$_{\text{ortho ph}}$), 96.1 (d, $^1$J$_{\text{CRh}}$ = 7.3 Hz, CH$_{\text{COD}}$), 95.8 (d, $^1$J$_{\text{CRh}}$ = 7.3 Hz, CH$_{\text{COD}}$), 69.0 (d, $^1$J$_{\text{CRh}}$ = 14.6 Hz, CH$_{\text{COD}}$), 68.6 (d, $^1$J$_{\text{CRh}}$ = 14.6 Hz, CH$_{\text{COD}}$), 36.6 (NCH$_3$), 33.1, 33.0, 31.9, 29.7, 29.2, 26.3, 23.5, (4 × CH$_2$COD, CH$_2$CH$_2$CH$_2$CH$_3$, CH$_2$CH$_2$CH$_2$CH$_3$, CH$_2$CH$_2$CH$_2$CH$_3$, CH$_2$CH$_2$CH$_2$CH$_3$), 14.3 (CCH$_2$CH$_2$CH$_2$CH$_3$); Anal. Found (calcd) for C$_{21}$H$_{29}$ClN$_3$Rh (461.84): C 54.86 (54.61), H 6.13 (6.33), N 9.05 (9.10).

**Synthesis of 6f.** According to the general method, 1f (0.052 g, 0.14 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred with Ag$_2$O (0.033 g, 0.14 mmol). After filtration through Celite, [Rh(COD)Cl]$_2$ (0.035 g, 0.07 mmol) was added and the solution was stirred and, after 6h, filtrated through Celite to give 1f as a yellow powder (0.037 g, 55%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 8.84–8.80 (m, 2H, H$_{\text{ortho ph}}$), 8.22–8.19 (m, 2H, H$_{\text{ortho Cph}}$), 7.66–7.54 (m, 6H, H$_{\text{meta Cph}}$, H$_{\text{para Cph}}$, H$_{\text{meta Nph}}$, H$_{\text{para Nph}}$), 4.87–4.83 (m, 2H, CH$_{\text{COD}}$), 4.13 (s, 1H, NCH$_3$), 2.79–2.70 (m, 2H, CH$_{\text{COD}}$), 2.19–2.02 (m, 2H, CH$_2$COD), 1.91–1.82 (m, 1H, CH$_2$COD), 1.76–1.66 (m, 3H, CH$_2$COD), 1.64–1.50 (m, 2H, CH$_2$COD); $^{13}$C{($^1$H)} NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 172.2 (d, $^1$J$_{\text{CRh}}$ = 46.8 Hz, C$_{\text{trz}}$–Rh), 145.1 (d, $^2$J$_{\text{CRh}}$ = 1.5 Hz, C$_{\text{trz}}$), 140.5 (C$_{\text{ipso ph}}$), 131.0 (C$_{\text{ortho ph}}$), 129.9 (C$_{\text{para ph}}$), 129.3 (C$_{\text{meta ph}}$), 129.1 (C$_{\text{ipso ph}}$), 128.9 (C$_{\text{meta ph}}$), 124.5 (C$_{\text{ortho ph}}$), 96.2 (d, $^1$J$_{\text{CRh}}$ = 8.1 Hz, CH$_{\text{COD}}$), 95.8 (d, $^1$J$_{\text{CRh}}$ = 7.3 Hz, CH$_{\text{COD}}$), 69.9 (d, $^1$J$_{\text{CRh}}$ = 14.6 Hz, CH$_{\text{COD}}$), 68.0 (d, $^1$J$_{\text{CRh}}$ = 14.6 Hz, CH$_{\text{COD}}$), 38.1 (NCH$_3$), 33.1 (CH$_2$COD), 32.7
(CH$_2$)$_{2}$COD), 29.4 (CH$_2$)$_{2}$COD); Anal. Found (calcd) for C$_{23}$H$_{26}$ClN$_3$Rh (482.84): C 57.21 (57.12), H 5.55 (5.43), N 8.61 (8.70).

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**Supporting Information Available:** Synthetic details for the triazolium salts 1 and for the rhodium complexes 7, a crystallographic analysis of a pseudo-polymorph of cis-3a and complex 5f, and crystallographic details for complexes 2a–e, trans-3a, cis-3a, trans-4a, 5e, and 5f in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) See the supporting information for representations and crystallographic details.


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Synthesis and Tunability of Abnormal 1,2,3-Triazolylidene Palladium and Rhodium Complexes

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Triazolylidium salts, readily available via ‘click’ chemistry and N-alkylation, react with Pd(OAc)$_2$ or with Ag$_2$O and subsequent transmetallation to give palladium and rhodium complexes. Variation of the reaction conditions induces product selectivity (mono- vs bimetallic complexes) while modification in the wingtip groups affects the donor ability of the triazolylidene ligand and its propensity to undergo cyclopalladation.