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

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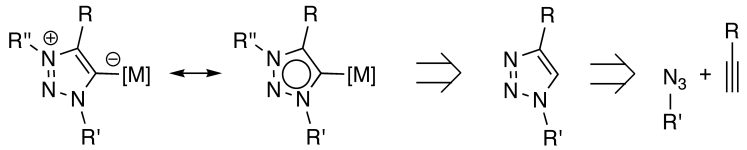
ABSTRACT. Palladation of N3-alkylated 1,2,3-triazolium salts with $Pd(OAc)_2$ afforded a μ^2–I_2 bridged bimetallic complex $[Pd(trz)I_2]_2$ and monometallic bis(carbene) complexes $Pd(trz)_2I_2$ as a mixture of *trans* and *cis* isomers (trz = 1,2,3-triazol-5-ylidene). Addition of excess halide or modification 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 δ_C and $^1J_{Rh–C}$, 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]



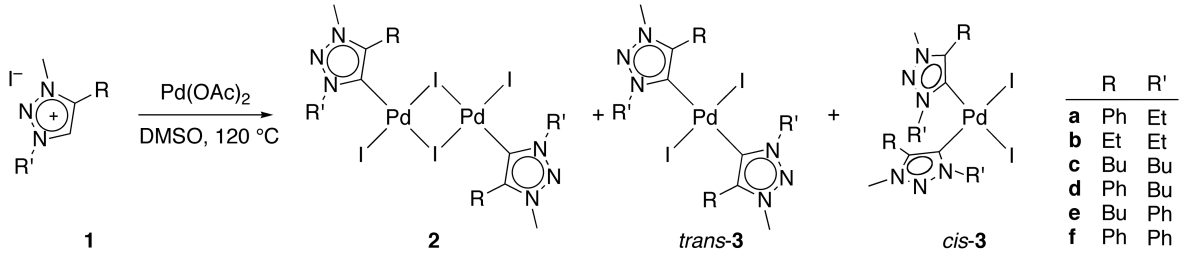
Scheme 1. Retrosynthetic approach towards triazolylidene metal complexes.

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_2Cl_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_2Cl_2 solution of **3a**.



	R	R'
a	Ph	Et
b	Et	Et
c	Bu	Bu
d	Ph	Bu
e	Bu	Ph
f	Ph	Ph

Scheme 2. Synthesis of complexes **2**, *trans*-**3**, and *cis*-**3** by direct metalation.

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.

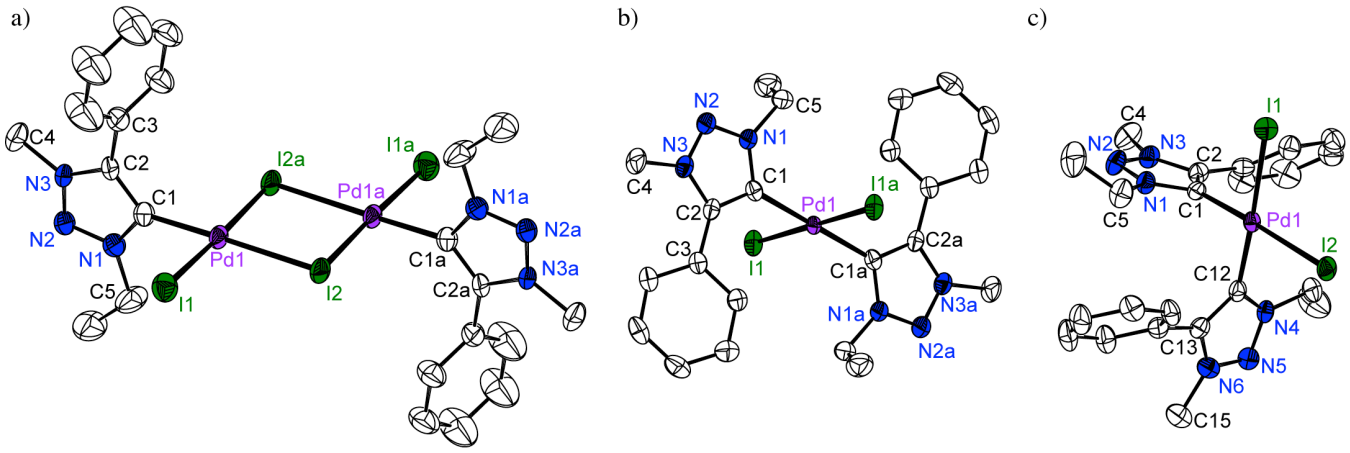


Figure 1. ORTEP drawings of complex **2a** (a; only one of the two crystallographically independent molecules is shown), *trans*-**3a** (b), and *cis*-**3a** (c; all structures at 50% probability level, hydrogen atoms and cocrystallized solvents omitted for clarity).

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

	2a [a]		*trans*–**3a** [b]	*cis*–**3a** [c]
	molecule 1	molecule 2		
Pd1–C1	1.967(6)	1.979(6)	2.049(3)	1.993(5)
Pd1–I1	2.5732(7)	2.5916(6)	2.6181(3)	2.6622(6)
Pd1–X1	2.6821(19)	2.6733(6)	2.049(3)	2.6506(5)
Pd1–X2	2.6369(19)	2.6195(6)	2.6181(3)	1.997(5)
C1–C2	1.402(9)	1.377(9)	1.394(4)	1.393(8)
C1–Pd1–I1	87.26(17)	86.98(15)	90.49(8)	89.50(16)
C1–Pd1–X2	90.02(18)	91.73(15)	89.51(8)	88.4(2)
C1–Pd1–X1	174.05(18)	177.55(16)	180	175.47(15)
I1–Pd1–X1	93.70(4)	94.16(2)	89.51(8)	94.54(2)
X1–Pd–X2	89.67(6)	87.20(2)	90.49(8)	87.67(16)
I1–Pd1–X2	173.01(4)	177.88(2)	180	177.24(15)
C2–C1–N1	104.4(5)	103.8(5)	103.3(3)	102.9(5)

a) X1 = I2, X2 = I2a; 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) X1 = C1a, X2 = I1a; c) X1 = I2, X2 = C12.

The availability of crystalline samples and structural evidence allowed for identifying the diagnostic ethyl group resonances of complex **2a** in solution, δ_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**.

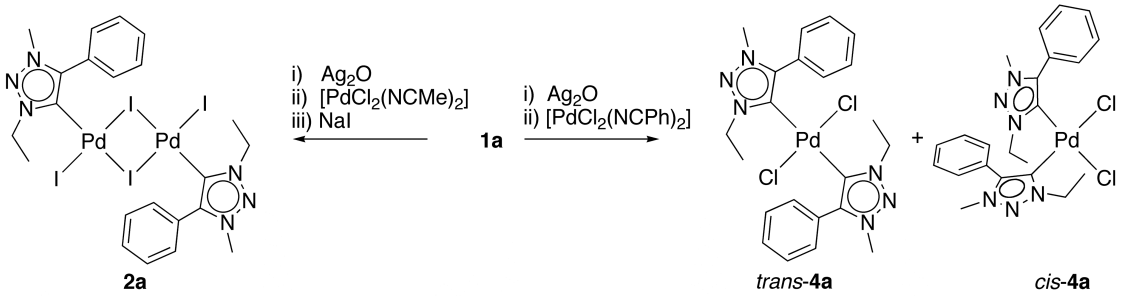
The most significant differences in the ^{13}C NMR spectra of the complexes comprises the palladium-bound carbene resonance, which appears at δ_C 128.5 in complex **2a**,[16] yet at substantially lower field (δ_C 154.6 and 154.0) for the *cis*/*trans* mixture of **3a**. This effect is much smaller for the phenyl-bound heterocyclic carbon which resonates at δ_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 μ^2 or κ^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 Ag_2O and the triazolium precursor,[8] followed by transmetalation with $PdCl_2(NCR)_2$ (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}H NMR spectrum in CD_3CN 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±0.8 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**.

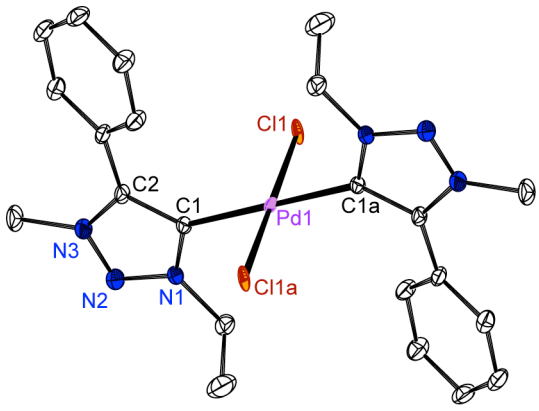


Figure 2. ORTEP representation of complex *trans*-**4a** (50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) are: Pd1–C1 2.037(3) Å; Pd1–Cl1 2.3534(8) Å; C1–Pd1–C1a 180°; C1–Pd1–Cl1 88.8(1)°.

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 ^{1}H and ^{13}C NMR spectra.

Purification of the mixtures by MeCN extraction and crystallization provided pure fractions of the dimetallic complexes **2b–2f**.[21] Analysis of their ^{13}C NMR spectra reveals a moderate correlation between δ_C and the electronic properties of the wingtip groups. The most shielded carbenes were observed for triazolylidenes possessing two alkyl wingtip groups (*cf* δ_C 126.0 and 126.4 for **2b** and **2c**, respectively), whereas introduction of a phenyl group shifts the resonance to lower field (*cf* δ_C 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 Pd_2I_2 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.[22] 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.

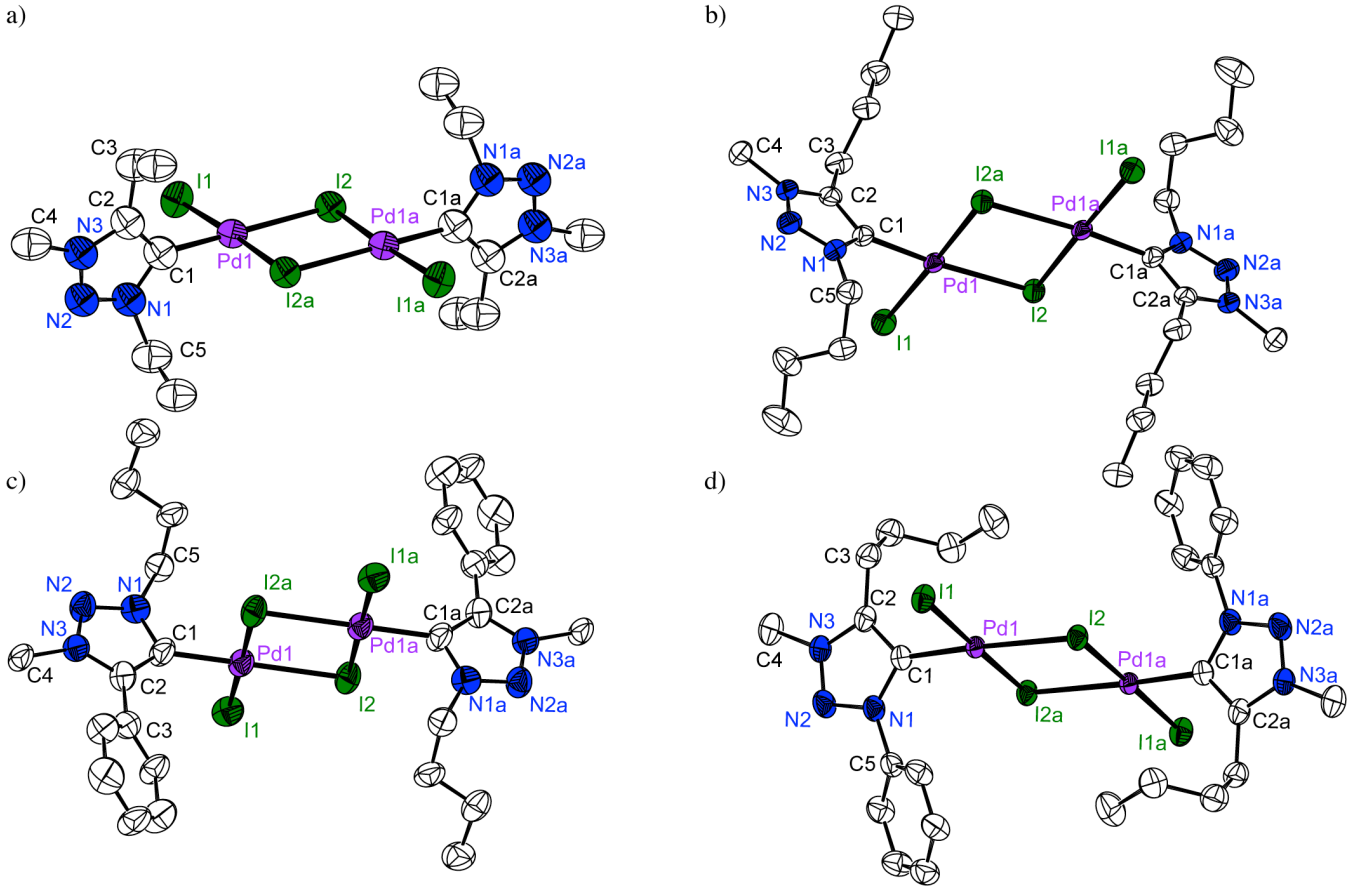
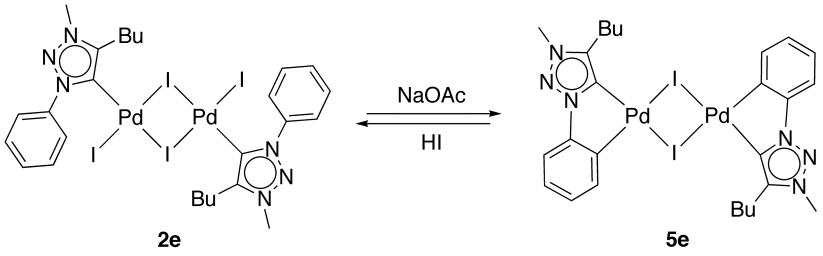


Figure 3. ORTEP drawings of complex **2b** (a; only one of the two crystallographically independent molecules shown), **2c** (b), **2d** (c), and **2e** (d; all structures at 50% probability level but **2b**, which is at 30% probability; hydrogen atoms and cocrystallized solvents in **2d** and **2e** omitted for clarity).

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

	2b	**2c**	**2d**	**2e**
Pd1–C1	1.96(3)	1.969(5)	1.977(13)	1.972(6)
Pd1–I1	2.587(2)	2.5876(5)	2.5918(15)	2.6039(6)
Pd1–I2	2.667(3)	2.6814(6)	2.6574(13)	2.6652(5)
Pd1–I2a	2.605(2)	2.6050(5)	2.6070(15)	2.6065(6)
C1–C2	1.38(4)	1.377(7)	1.366(18)	1.383(8)
C1–Pd1–I1	87.6(8)	88.98(16)	89.0(5)	88.84(18)
C1–Pd1–I2	178.6(8)	175.24(15)	178.2(5)	177.02(17)
C1–Pd1–I2a	90.7(8)	89.52(16)	90.3(5)	90.66(18)
I1–Pd1–I2	93.68(8)	94.67(2)	92.52(5)	93.770(18)
I1–Pd1–I2a	177.34(11)	178.49(2)	178.15(5)	178.33(2)
I2–Pd1–I2a	88.04(8)	86.84(2)	88.17(4)	86.766(17)
C2–C1–N1	100(3)	102.8(4)	103.2(11)	103.0(5)

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}C NMR signal at δ_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_2I_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.

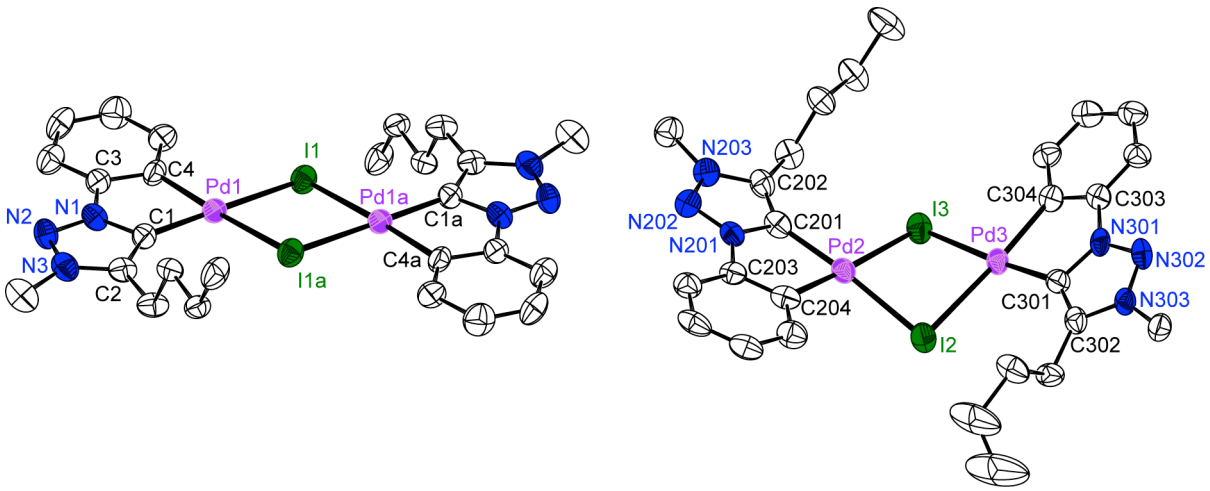


Figure 4. ORTEP drawings of the two crystallographically independent molecules of **5e** (50% probability, cocrystallized solvent molecules and hydrogen atoms omitted for clarity).

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

	molecule 1	molecule 2 (Pd2)	molecule 2 (Pd3)
Pd1–C1	1.983(8)	2.010(9)	1.979(8)
Pd1–C4	2.034(8)	2.047(8)	2.031(8)
Pd1–I1	2.6539(9)	2.6482(10)	2.6683(9)
Pd1–I1a	2.6842(8)	2.7045 (9)	2.6901(9)
C1–Pd1–C4	80.6(3)	80.7(3)	81.1(3)
C1–Pd1–I1	174.5(2)	175.1(2)	176.3(2)
C1–Pd1–I1a	97.6(2)	97.8(2)	96.8(2)
C4–Pd1–I1	95.7(2)	94.9(3)	95.3(3)
C4–Pd1–I1a	174.1(2)	176.1(2)	172.3(2)
I1–Pd1–I1a	86.50(3)	86.72(3)	86.61(3)

a) numbering scheme for molecule 2 adapted.

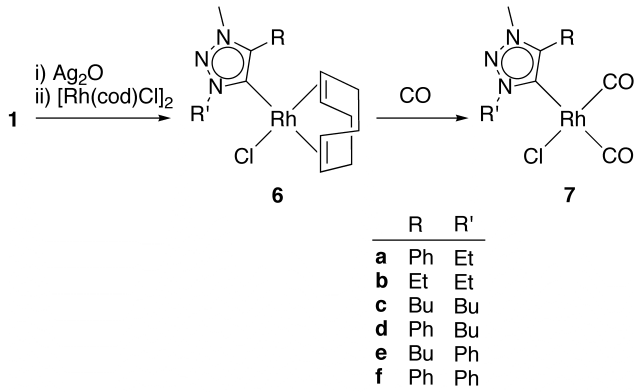
Investigation of the cyclopalladation revealed that heating of complex **2e** in DMSO to 120 °C for 3.5 h, *i.e.* conditions used for the preparation of **2**, did not induce any significant palladacycle formation. In the presence of a weak base such as acetate, several products yet no **5e** were formed 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.[25] Attempts to substitute acetate by NEt_3 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.[26]

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 ^{1}H 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.[14,27] 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[28] — have obvious implications when using this type of complexes in catalysis.[9a]

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),[29] 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 Ag_2O 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]



	R	R'
a	Ph	Et
b	Et	Et
c	Bu	Bu
d	Ph	Bu
e	Bu	Ph
f	Ph	Ph

Scheme 5. Synthesis of the rhodium complexes **6** and **7**.

The ^{13}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 ($^1J_{RhC}$ = 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–$C_{carbene}$ coupling constant is smaller in complexes **7** with $^1J_{RhC}$ = 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** ($^1J_{RhC}$ = 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

$^1J_{RhC}$ 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)]

	7a	**7b**	**7c**	**7d**	**7e**	**7f**
δ_C ($^1J_{RhC}$) $C_{carbene}$	161.2 (39.4)	159.8 (39.4)	160.4 (39.4)	161.3 (39.4)	161.8 (39.4)	162.6 (39.4)
δ_C ($^1J_{RhC}$) CO_{trans}	186.1 (54.1)	186.8 (53.4)	187.0 (53.4)	186.8 (54.2)	186.7 (54.9)	186.7 (54.8)
δ_C ($^1J_{RhC}$) CO_{cis}	183.5 (75.4)	184.3 (74.6)	184.4 (74.8)	183.9 (75.4)	183.8 (75.4)	183.7 (74.6)

a) in CD_2Cl_2, δ_C in ppm, $^1J_{RhC}$ 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** (ν_{CO} = 1988 and 2068 cm^{-1}). Depending on the applied linear regression,[33] 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.[34] Perhaps, steric effects may affect the Rh–CO_{cis} bond and may thus interfere with the electronic component exerted by the ligand. Such stereoelectronic perturbation has been noted before[5c,35] 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. CH_2Cl_2 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. ^{1}H and $^{13}C\{^{1}H\}$ 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 $SiMe_4$. 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 CH_2Cl_2, the solution was filtered through Celite, H_2O was added, and the solution was extracted with CH_2Cl_2. The organic phases were combined, washed

with H_2O and dried over Na_2SO_4 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 CH_2Cl_2 yielded the mono(carbene) species **3**. Further purification of the fractions was achieved by crystallization.

Method B: The triazolium salt (1 equiv.) and Ag_2O (1 equiv.) in CH_2Cl_2 were stirred at rt for 24 h. After filtration through Celite, $PdCl_2(NCMe)_2$ (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 H_2O, the residue was extracted with CH_2Cl_2. The combined organic phases were washed with H_2O then with a saturated aqueous solution of sodium pyrosulfite ($Na_2S_2O_5$), dried over Na_2SO_4 and evaporated to dryness.

Synthesis of 2a. According to method B, **1a** (0.237 g, 0.75 mmol) in CH_2Cl_2 (15 mL) were stirred at rt with Ag_2O (0.173 g, 0.75 mmol) for 24 h and $PdCl_2(MeCN)_2$ (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 CH_2Cl_2 solution.

^{1}H NMR (400 MHz, DMSO–D_6): δ 7.98–7.92 (m, 4H, H^{ortho}_{ph}), 7.63–7.52 (m, 6H, H^{meta}_{ph}, H^{para}_{ph}), 4.71 (q, $^3J_{HH}$ = 7.2 Hz, 4H, NCH_2CH$_3$), 4.06 (s, 6H, NCH$_3$), 1.63 (t, $^3J_{HH}$ = 7.2 Hz, 6H, NCH$_2$CH_3); ^{13}C{^{1}H} NMR (100 MHz, DMSO–D_6): δ 142.5 (C_{trz}), 130.0 (C^{ortho}_{ph}), 129.8 (C^{para}_{ph}), 128.5 (C^{meta}_{ph} + C_{trz}–Pd), 126.9 (C^{ipso}_{ph}), 50.8 (NCH$_2$CH$_3$), 38.1 (NCH$_3$), 14.2 (NCH$_2$$CH_3$); Anal. Found (calcd) for $C_{22}H_{26}I_4N_6Pd_2$ (1094.93) × 1/2 C_5H_{12}: 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 CH_2Cl_2 (10 mL), Ag_2O (0.090 g, 0.39 mmol), $PdCl_2(MeCN)_2$ (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, $^3J_{HH}$ = 7.3 Hz, 4H, NCH_2CH$_3$), 4.06 (s, 6H, NCH$_3$), 2.85 (q, $^3J_{HH}$ = 7.6 Hz, 4H, CCH_2CH$_3$), 1.54 (t, $^3J_{HH}$ = 7.3 Hz, 6H, NCH$_2$CH_3), 1.34 (t, $^3J_{HH}$ = 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_{trz}–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 $C_{14}H_{26}I_4N_6Pd_2$ (998.86): 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_2Cl_2 (15 mL), Ag_2O (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 recrystallistion by slow diffusion of pentane into CH_2Cl_2. This procedure gave off an analytically pure fraction of **2c** (0.137 g, 71%).

^{1}H NMR (500 MHz, DMSO–D_6): δ 4.52 (t, $^3J_{HH}$ = 7.2 Hz, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 4.04 (s, 6H, NCH$_3$), 2.84 (t, $^3J_{HH}$ = 7.9 Hz, 4H, CCH_2CH$_2$CH$_2$CH$_3$), 2.08 (quint, $^3J_{HH}$ = 7.2 Hz, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.85 (quint, $^3J_{HH}$ = 7.9 Hz, 4H, CCH$_2$CH_2CH$_2$CH$_3$), 1.37 (sext, $^3J_{HH}$ = 7.5 Hz, 4H, CCH$_2$CH$_2$CH_2CH$_3$), 1.30 (sext, $^3J_{HH}$ = 7.5 Hz, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 0.93 (q, $^3J_{HH}$ = 7.5 Hz, 12H, CCH$_2$CH$_2$CH$_2$CH_3, 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_{trz}–Pd), 54.6 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.6 (NCH$_3$), 29.9 (NCH$_2$$CH_2CH_2CH_3$), 29.2 (CCH$_2$$CH_2CH_2CH_3$), 24.5 (C$CH_2CH_2CH_2CH_3$), 21.9 (CCH$_2CH_2$$CH_2CH_3$), 19.0 (NCH$_2CH_2$$CH_2CH_3$), 13.7 (CCH$_2CH_2CH_2$$CH_3$), 13.3 (N$CH_2CH_2CH_2$$CH_3$); Anal. Found (calcd) for $C_{22}H_{42}I_4N_6Pd_2$ (1111.07): 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_2Cl_2 (15 mL), Ag_2O (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).

^{1}H NMR (500 MHz, DMSO–D_6): δ 7.97–7.94 (m, 4H, H^{ortho}_{ph}), 7.60–7.53 (m, 6H, H^{meta}_{ph}, H^{para}_{ph}), 4.66 (t, $^{3}J_{HH}$ = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 4.06 (s, 6H, NCH_3), 2.16 (quint, $^{3}J_{HH}$ = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 1.40 (sext, $^{3}J_{HH}$ = 7.4 Hz, 4H, $NCH_2CH_2CH_2CH_3$), 0.96 (t, $^{3}J_{HH}$ = 7.4 Hz, 6H, $NCH_2CH_2CH_2CH_3$); $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO–D_6): δ 142.6 (C_{trz}), 129.9 (C^{ortho}_{ph}), 129.7 (C^{para}_{ph}), 128.4 (C^{meta}_{ph}+ C_{trz}–Pd), 127.0 (C^{ipso}_{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).

^{1}H NMR (500 MHz, DMSO–D_6): δ 8.23 (d, $^{3}J_{HH}$ = 7.8 Hz, 4H, H^{ortho}_{ph}), 7.68–7.58 (m, 6H, H^{meta}_{ph}, H^{para}_{ph}), 4.18 (s, 3H, NCH_3), 2.98 (t, $^{3}J_{HH}$ = 7.8 Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.93 (quint, $^{3}J_{HH}$ = 7.8 Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.44 (sext, $^{3}J_{HH}$ = 7.4 Hz, 4H, $CH_2CH_2CH_2CH_3$), 0.97 (t, $^{3}J_{HH}$ = 7.4 Hz, 6H, $CH_2CH_2CH_2CH_3$); $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO–D_6): δ 144.2 (C_{trz}), 139.1 (C^{ipso}_{ph}), 130.0 (C^{para}_{ph}), 129.1 (C^{meta}_{ph} + C_{trz}–Pd), 124.4 (C^{ortho}_{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 NMR (500 MHz, DMSO–D_6): δ 8.34–8.31 (m, 4H, $H^{ortho}{}_{NPh}$), 8.04–8.02 (m, 4H, $H^{ortho}{}_{CPh}$), 7.72–7.68 (m, 4H, $H^{meta}{}_{NPh}$), 7.66–7.57 (m, 8H, $H^{meta}{}_{CPh}$, $H^{para}{}_{CPh}$, $H^{para}{}_{NPh}$), 4.17 (s, 6H, NCH_3); $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO–D_6): δ 143.3 (C_{trz}), 139.0 ($C^{ipso}{}_{NPh}$), 130.3 ($C^{para}{}_{NPh}$), 130.2 ($C^{ortho}{}_{CPh}$), 130.0 ($C^{para}{}_{CPh}$), 129.2 ($C^{meta}{}_{NPh}$), 128.5 ($C^{meta}{}_{CPh}$), 126.9 ($C^{ipso}{}_{CPh}$), 124.7 ($C^{ortho}{}_{NPh}$), 38.4 (NCH_3), C_{trz}–Pd not observed; Anal. Found (calcd) for $C_{30}H_{26}I_4N_6Pd_2$ (1191.02) × 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: ^{1}H NMR (400 MHz, DMSO–D_6): δ 8.13 (d, $^{3}J_{HH}$ = 7.3 Hz, 4H, $H^{ortho}{}_{ph}$), 7.58–7.49 (m, 6H, $H^{meta}{}_{ph}$, $H^{para}{}_{ph}$), 4.65 (q, $^{3}J_{HH}$ = 7.3 Hz, 4H, NCH_2), 4.09 (s, 6H, NCH_3), 1.56 (t, $^{3}J_{HH}$ = 7.3 Hz, 6H, NCH_2CH_3); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–D_6): δ 154.6 (C_{trz}–Pd), 144.1 (C_{trz}), 129.8 ($C^{ortho}{}_{ph}$), 128.3 ($C^{ipso}{}_{ph}$), 128.1 ($C^{meta}{}_{ph}$), $C^{para}{}_{ph}$ not observed, 49.6 (NCH_2), 37.5 (NCH_3), 14.9 (NCH_2CH_3).

Minor isomer: ^{1}H NMR (400 MHz, DMSO–D_6): δ 7.93 (d, $^{3}J_{HH}$ = 7.1 Hz, 4H, $H^{ortho}{}_{ph}$), 7.58–7.41 (m, 6H, $H^{meta}{}_{ph}$, $H^{para}{}_{ph}$), 4.85 (q, $^{3}J_{HH}$ = 7.2 Hz, 4H, NCH_2), 4.05 (s, 6H, NCH_3), 1.71 (t, $^{3}J_{HH}$ = 7.2 Hz, 6H, NCH_2CH_3); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–D_6): δ 154.0 (C_{trz}–Pd), 144.1 (C_{trz}), 129.6 ($C^{ortho}{}_{ph}$), 129.1 ($C^{meta}{}_{ph}$), 128.8 ($C^{para}{}_{ph}$), 127.9 ($C^{ipso}{}_{ph}$), 50.0 (NCH_2), 37.6 (NCH_3), 14.6 (NCH_2CH_3); Anal. Found (calcd) for $C_{22}H_{26}I_2N_6Pd$ (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_2O (490 mg, 2.1 mmol), and $PdCl_2(NCMe)_2$ (315 mg, 1.2 mmol) in CH_2Cl_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_2Cl_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_3CN, 348 K): δ 8.10 (br. s, 4H, H_{ar}), 7.55 (br. s, 6H, H_{ar}), 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_2CH_3). ^{13}C{^{1}H} NMR (125 MHz $CDCl_3$) major isomer: δ 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_2CH_3). ^{13}C{^{1}H} NMR (125 MHz $CDCl_3$) minor isomer: δ 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_2CH_3). Anal. Found (calcd) for $C_{22}H_{26}Cl_2N_6Pd$ (550.06) × 1/4 CH_2Cl_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): δ 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, $CH_2CH_2CH_2CH_3$), 1.60–1.57 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.47–1.40 (m, 4H, $CH_2CH_2CH_2CH_3$), 0.95 (t, $^3J_{HH}$ = 7.3 Hz, 6H, $CH_2CH_2CH_2CH_3$); ^{13}C{^{1}H} NMR (125 MHz, DMSO–D_6, 333 K): δ 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 ($CH_2CH_2CH_2CH_3$), 23.6 ($CH_2CH_2CH_2CH_3$), 21.5 ($CH_2CH_2CH_2CH_3$), 13.3 ($CCH_2CH_2CH_2CH_3$), 2 C_{ph} and C_{trz}–Pd not observed; Anal. Found (calcd) for $C_{26}H_{32}I_2N_6Pd_2$ (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_2Cl_2 and Ag_2O (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 CH_2Cl_2 and pentane.

Synthesis of 6b. According to the general method, **1b** (0.110 g, 0.41 mmol) in CH_2Cl_2 (10 mL) was stirred with Ag_2O (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%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.84–4.77 (m, 4H, NCH_2CH$_3$, CH_{COD}), 3.88 (s, 3H, NCH_3), 3.24 (br.s, 2H, CH_{COD}), 2.95 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CCH_2CH$_3$), 2.46–2.25 (br. m, 4H, $CH_{2\ COD}$), 1.97–1.81 (br. m, 4H, $CH_{2\ COD}$), 1.64 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH$_2$CH_3), 1.47 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CCH$_2$CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 168.5 (d, $^1J_{CRh}$ = 46.2 Hz, C_{trz}–Rh), 145.5 (d, $^2J_{CRh}$ = 2.8 Hz, C_{trz}), 96.6 (d, $^1J_{CRh}$ = 7.2 Hz, CH_{COD}), 96.2 (d, $^1J_{CRh}$ = 7.2 Hz, CH_{COD}), 68.3 (d, $^1J_{CRh}$ = 14.9 Hz, CH_{COD}), 67.9 (d, $^1J_{CRh}$ = 14.9 Hz, CH_{COD}), 50.6 (NCH_2CH$_3$), 36.2 (NCH_3), 33.8 ($CH_{2\ COD}$), 33.1 ($CH_{2\ COD}$), 29.6 ($CH_{2\ COD}$), 29.3 ($CH_{2\ COD}$), 19.3 (CCH_2CH$_3$), 16.0 (NCH$_2$CH_3), 14.5 (CCH$_2$CH_3); Anal. Found (calcd) for $C_{15}H_{25}ClN_3Rh$ (385.74) × 2/3 CH_2Cl_2: 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 CH_2Cl_2 (15 mL) was stirred with Ag_2O (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%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 4.88–4.79 (m, 3H, NCH_2CH$_2$CH$_2$CH$_3$, CH_{COD}), 4.67–4.57 (m, 1H, CH_{COD}), 3.87 (s, 1H, NCH_3), 3.33–3.17 (m, 2H, CH_{COD}), 2.88 (t, $^3J_{HH}$ = 8.1 Hz, 2H, CCH_2CH$_2$CH$_2$CH$_3$), 2.46–2.24 (m, 4H, $CH_{2\ COD}$), 2.22–1.97 (m, 4H, CCH$_2$CH_2CH$_2$CH$_3$, NCH$_2$CH_2CH$_2$CH$_3$), 1.95–1.73 (m, 4H, $CH_{2\ COD}$), 1.36 (m, 4H, CCH$_2$CH$_2$CH_2CH$_3$ NCH$_2$CH$_2$CH_2CH$_3$), 1.07–1.00 (m, 6H, CCH$_2$CH$_2$CH$_2$CH_3, NCH$_2$CH$_2$CH$_2$CH_3); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ 168.6 (d, $^1J_{CRh}$ = 46.7 Hz,

C_{trz}–Rh), 144.5 (d, $^2J_{CRh}$ = 2.8 Hz, C_{trz}), 96.4 (d, $^1J_{CRh}$ = 7.2 Hz, CH_{COD}), 96.1 (d, $^1J_{CRh}$ = 7.2 Hz, CH_{COD}), 68.1 (d, $^1J_{CRh}$ = 14.9 Hz, CH_{COD}), 67.8 (d, $^1J_{CRh}$ = 14.9 Hz, CH_{COD}), 55.1 ($NCH_2CH_2CH_2CH_3$), 36.3 (NCH_3), 33.9 ($CH_{2\ COD}$), 33.1 ($CH_{2\ COD}$), 32.5, 32.2 ($NCH_2CH_2CH_2CH_3$ + $CCH_2CH_2CH_2CH_3$), 29.7 ($CH_{2\ COD}$), 29.3 ($CH_{2\ COD}$), 25.6 ($CCH_2CH_2CH_2CH_3$), 23.3, 20.5 ($NCH_2CH_2CH_2CH_3$ + $CCH_2CH_2CH_2CH_3$)], 14.1, 14.0 ($CCH_2CH_2CH_2CH_3$ + $NCH_2CH_2CH_2CH_3$); Anal. Found (calcd) for $C_{19}H_{33}ClN_3Rh$ (441.84) × 1/4 CH_2Cl_2: 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 CH_2Cl_2 (15 mL) was stirred with Ag_2O (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, CD_2Cl_2): 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, $NCH_2CH_2CH_2CH_3$), 4.92–4.75 (m, 2H, CH_{COD}), 4.67–4.60 (m, 1H, $NCH_2CH_2CH_2CH_3$), 4.01 (s, 3H, NCH_3), 3.14 (br. s, 1H, CH_{COD}), 2.59 (br. s, 1H, CH_{COD}), 2.35–2.13 (m, 5H, $NCH_2CH_2CH_2CH_3$ + $CH_{2\ COD}$), 1.82–1.64 (m, 5H, $NCH_2CH_2CH_2CH_3$ + $CH_{2\ COD}$), 1.55–1.48 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.07 (t, $^3J_{HH}$ = 7.5 Hz, 3H, $NCH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 170.4 (d, $^1J_{CRh}$ = 46.8 Hz, C_{trz}–Rh), 144.3 (d, $^2J_{CRh}$ = 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 (CH_{COD}), 96.2 (CH_{COD}), 70.2 (d, $^1J_{CRh}$ = 13.9 Hz, CH_{COD}), 67.7 (d, $^1J_{CRh}$ = 14.7 Hz, CH_{COD}), 55.3 ($NCH_2CH_2CH_2CH_3$), 37.8 (NCH_3), 33.6 ($CH_{2\ COD}$), 32.7 ($CH_{2\ COD}$), 32.5, ($NCH_2CH_2CH_2CH_3$), 29.5 ($CH_{2\ COD}$), 29.4 ($CH_{2\ COD}$), 20.5 ($NCH_2CH_2CH_2CH_3$), 14.1 ($NCH_2CH_2CH_2CH_3$); Anal. Found (calcd) for $C_{21}H_{29}ClN_3Rh$ (461.83) × 1/8 CH_2Cl_2: 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 CH_2Cl_2 (10 mL) were stirred with Ag_2O (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_2Cl_2): δ 8.64–8.61(m, 2H, H^{ortho}_{ph}), 7.62–7.52 (m, 3H, H^{meta}_{ph}, H^{para}_{ph}), 4.94–4.80 (m, 2H, CH_{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_{COD}, 8H, $CH_{2\ COD}$, 2H, $CH_2CH_2CH_2CH_3$, 2H, $CH_2CH_2CH_2CH_3$, 2H, $CH_2CH_2CH_2CH_3$), 1.08 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $CH_2CH_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 170.4 (d, $^1J_{CRh}$ = 46.8 Hz, C_{trz}–Rh), 146.1 (d, $^2J_{CRh}$ = 1.5 Hz, C_{trz}), 140.6 (C^{ipso}_{ph}), 129.8 (C^{para}_{ph}), 129.2 (C^{meta}_{ph}), 124.6 (C^{ortho}_{ph}), 96.1 (d, $^1J_{CRh}$ = 7.3 Hz, CH_{COD}), 95.8 (d, $^1J_{CRh}$ = 7.3 Hz, CH_{COD}), 69.0 (d, $^1J_{CRh}$ = 14.6 Hz, CH_{COD}), 68.6 (d, $^1J_{CRh}$ = 14.6 Hz, CH_{COD}), 36.6 (NCH_3), 33.1, 33.0, 31.9, 29.7, 29.2, 26.3, 23.5, (4 × $CH_{2\ COD}$, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$), 14.3 ($CCH_2CH_2CH_2CH_3$); Anal. Found (calcd) for $C_{21}H_{29}ClN_3Rh$ (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_2Cl_2 (20 mL) was stirred with Ag_2O (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_2Cl_2): δ 8.84–8.80 (m, 2H, H^{ortho}_{Nph}), 8.22–8.19 (m, 2H, H^{ortho}_{Cph}), 7.66–7.54 (m, 6H, H^{meta}_{Cph}, H^{para}_{Cph}, H^{meta}_{Nph} H^{para}_{Nph}), 4.87–4.83 (m, 2H, CH_{COD}), 4.13 (s, 1H, NCH_3), 2.79–2.70 (m, 2H, CH_{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, $CH_{2\ COD}$); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 172.2 (d, $^1J_{CRh}$ = 46.8 Hz, C_{trz}–Rh), 145.1 (d, $^2J_{CRh}$ = 1.5 Hz, C_{trz}), 140.5 (C^{ipso}_{Nph}), 131.0 (C^{ortho}_{Cph}), 129.9 (C^{para}_{ph}), 129.3 (C^{meta}_{ph}), 129.1 (C^{ipso}_{ph}), 128.9 (C^{meta}_{ph}), 124.5 (C^{ortho}_{Nph}), 96.2 (d, $^1J_{CRh}$ = 8.1 Hz, CH_{COD}), 95.8 (d, $^1J_{CRh}$ = 7.3 Hz, CH_{COD}), 69.9 (d, $^1J_{CRh}$ = 14.6 Hz, CH_{COD}), 68.0 (d, $^1J_{CRh}$ = 14.6 Hz, CH_{COD}), 38.1 (NCH_3), 33.1 ($CH_{2\ COD}$), 32.7

($CH_{2\ COD}$), 29.4 ($CH_{2\ COD}$); Anal. Found (calcd) for $C_{23}H_{26}ClN_3Rh$ (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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Synthesis and Tunability of Abnormal 1,2,3-Triazolylidene Palladium and Rhodium Complexes

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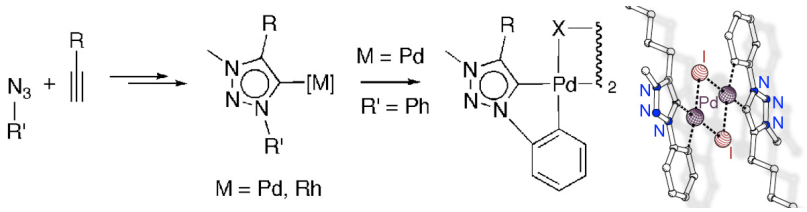

Triazolylium salts, readily available via 'click' chemistry and *N*-alkylation, react with $Pd(OAc)_2$ or with Ag_2O and subsequent transmetallation to give palladium and rhodium complexes. Variation of the reaction conditions induces product selectivity (mono- vs bimetallic complexes) while modification in the wingtip groups affects the donor ability of the triazolylidene ligand and its propensity to undergo cyclopalladation.