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Palladium complexes of bis(acyclic diaminocarbene) ligands with chiral N-substituents and 8-membered chelate rings

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ABSTRACT

Reaction of *cis*-dichloridobis(*p*-trifluoromethylphenylisocyanide)palladium(II) with *N*,*N*′-bis[(*R*)-1-phenylethyl]-1,3-diaminopropane afforded an enantiomerically pure, C_1-symmetric bis(acyclic diaminocarbene)$PdCl_2$ complex in 41% yield. The X-ray crystal structure of the complex revealed that three of the four carbene nitrogens are twisted out of conjugation with the carbene units, apparently as a result of steric interactions between one phenyl group and the propylene backbone of the chelate. A similar reaction with *N*,*N*′-bis[(*R*)-1-(1-naphthyl)ethyl]-1,3-diaminopropane did not lead to an isolable bis(carbene) complex, instead forming significant amounts of bis(ammonium) salt as a decomposition product. However, reaction of the same palladium isocyanide precursor with a mixture of all diastereomers of *N*,*N*′-bis[1-(1-naphthyl)ethyl]-1,3-diaminopropane provided an achiral, C_s-symmetric palladium bis(acyclic diaminocarbene) complex derived exclusively from the (*R*,*S*) diamine in 20% yield. An X-ray structure showed that the (*R*,*S*) stereochemistry allows the bulky naphthyl groups to adopt an orientation that avoids steric interactions with the backbone that likely lead to the instability of the homochiral analogue. The two palladium carbene complexes catalyzed the aza-Claisen rearrangement of an allylic imidate to an allylic amide in 24–34% yield, with an enantiomeric excess of 8% ee for the [(*R*)-1-phenylethyl]-substituted complex.

1. Introduction

Cyclic diaminocarbene ligands, more commonly known as N-heterocyclic carbenes (NHCs), are now firmly established as one of the most important classes of ancillary ligands in transition metal coordination chemistry [1] and catalysis [2]. The ability of NHCs to boost the activities of organometallic catalysts relative to the corresponding phosphine-ligated systems [3] has been frequently attributed to the higher σ-donating abilities of the NHCs [4], although there is growing recognition that NHCs may not act as stronger donors than phosphines under all circumstances [5,6]. Whereas a large and growing literature documents the organometallic chemistry of the imidazolium-derived imidazolin-2-ylidenes and their backbone-saturated analogues [7], which represent the most popular classes of NHCs, the related acyclic diaminocarbenes (ADCs) [8] have been largely neglected as ancillary ligands. The presence of two nitrogen substituents on the carbene carbon atoms of ADCs should provide them with electronic stabilization similar to that of NHCs [9], in accordance with Alder's seminal work demonstrating the stability of free bis(diisopropylamino)carbene (**A**, Fig. 1) [10]. The limited amount of ADC coordination chemistry that has appeared following Alder's work [11–15] points out some ligand properties of ADCs that could potentially provide certain advantages over NHCs: ADCs can act as stronger σ-donors than NHCs [11,16], their larger N–C–N angles can place steric bulk or chiral substituents nearer to the metal center [11,12,15], and hindered rotation about the carbene C–N bonds [10,17] provides conformational flexibility [15] that could lead to "flexible steric bulk [18]." Investigations of ADCs as ancillary ligands in catalysis have been very few [14,19,20], but they have been shown to provide comparable or better activity relative to analogous NHC systems in certain types of Pd-catalyzed coupling reactions [14,20]. Related acyclic alkylaminocarbenes have also shown promise in catalysis [21].

Reports of ADC coordination chemistry since Alder's work have largely utilized synthetic routes involving the free carbenes [11–15], which creates limitations on the types of ADCs that can be used. In contrast to imidazolium-derived NHCs [22], free ADCs are thermodynamically inclined to dimerize to enetetramines [23], although sufficient steric bulk as in **A** can prevent this [10]. In order to expand the range of available ADC structures, we sought routes to these ligands that avoid free carbene generation. We turned to the well-established, but recently little-studied, reaction of protic amines with coordinated isocyanides [24] as a one-step, metal-templated route to coordinated ADCs [25]. This chemistry was inadvertently discovered by Chugaev as early as 1915 in the synthesis of the first known carbene complex, a chelated platinum

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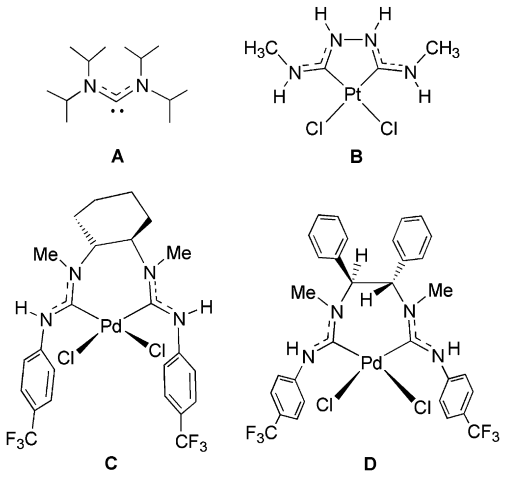


Fig. 1. Representative free ADC (**A**) and bis(ADC) complexes (**B**–**D**).

bis(ADC) complex resulting from nucleophilic addition of hydrazine to *cis* methylisocyanide ligands (**B**, Fig. 1) [26]. Complex **B** was not recognized as a carbene complex until 1970, when its structure was elucidated by Rouschias and Shaw [27] and Burke et al. [28].

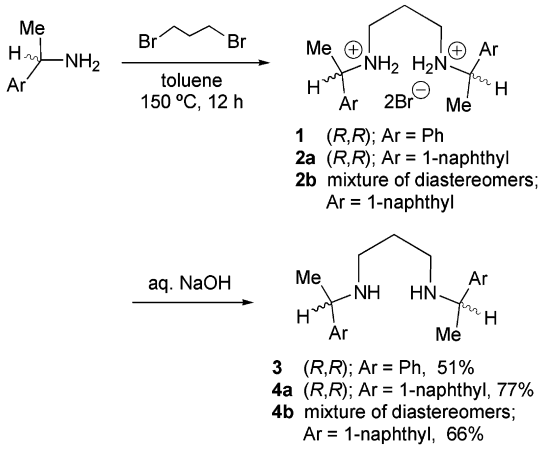
Our earlier work has shown that a small "library" of palladium complexes containing variants of the Chugaev-type bis(ADC) can be prepared by a common synthetic procedure and screened to identify an air-stable, moderately active Suzuki–Miyaura cross coupling catalyst [19]. Subsequently, we extended this synthetic approach to chiral bis(ADC) palladium complexes **C** and **D** (Fig. 1) by reaction of arylisocyanide complexes with chiral secondary diamines [6,29]. In addition to providing the first chiral ADC ligands, this one-step synthetic route provides a strategy for systematically varying the chiral structure and chelate ring size. The 7-membered chelate rings of **C** and **D** were found to engender non-ideal C–Pd–C bite angles of 82–87°, which we viewed as a likely cause of the lower effective donor abilities of these ligands relative to common bis(NHC) or bis(phosphine) ligands [6]. This allowed the use of **C** and **D** as electrophilic catalysts for aza-Claisen rearrangement reactions [6], an unusual departure from the prevailing use of NHCs and ADCs to stabilize electron-rich metal centers. In addition, the 7-membered chelate structure constrains the bis(ADCs) of **C** and **D** to C_1-symmetric conformations with the chiral elements relatively remote from the metal center. While the influence of the chiral backbone on the metal coordination sphere was sufficient to provide modest enantiomeric excesses of 30–59% ee in aza-Claisen rearrangement reactions [6], the need for highly enantioselective catalysts led us to pursue other ligand architectures that might provide enhanced chiral environments about the metal. The development of structurally diverse chiral bis(ADC) ligands is particularly important given that reported examples of chiral bis(NHC) ligands are still relatively scarce [30]. Herein we report extension of the isocyanide-based synthetic route to a novel chiral bis(ADC) architecture based on diamines with chiral N-substituents and flexible, achiral backbones that form 8-membered chelate rings. While this strategy does not place the chiral centers in closer proximity to the metal compared with chiral backbone-containing complexes **C** and **D**, we hypothesized that the achiral chelate backbone might engender enough flexibility to create a dynamic chiral environment in which chiral groups approach the metal center during conformational changes. Although bis(ADC) complexes with enhanced chiral coordination environments and utility as enantioselective catalysts did not result from this work, it did provide important insights into how structural features of the diamine precursor influence the preferred geometry of the bis(ADC) chelates formed in these one-step ligand assembly processes.

2. Results and discussion

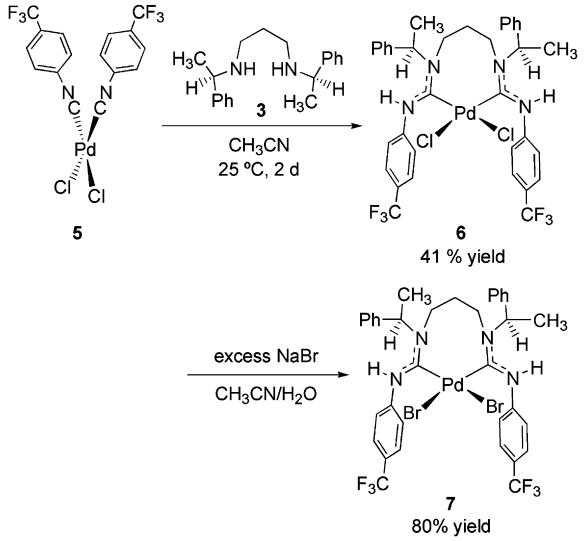
2.1. Synthesis of chiral diamines

Our motivation for this study was to examine how the use of diamines with bulky, chiral N-substituents and a flexible hydrocarbon tether would influence the chelate structures of bis(ADC) ligands formed upon reaction with *cis*-coordinated isocyanide ligands. A propylene linker was chosen for the initial studies, because the resulting 8-membered bis(ADC) chelate ring should have greater conformational flexibility compared to the 7-membered chelate structures previously reported by us (**C** and **D**, Fig. 1) [6,29], thus potentially allowing the chiral groups to approach the metal in some ligand conformations. The chiral N-substituents chosen were 1-phenylethyl and 1-(1-naphthyl)ethyl groups, providing two bis(ADC) precursors with different amounts of steric bulk. Palladium complexes of chelating imidazole-based bis(NHC) ligands containing these same chiral N-substituents have recently been reported by Herrmann and co-workers [31], although no examples containing three-carbon linkers were prepared. The need to prepare the chiral imidazole precursors in a low-yielding reaction (~33%) is one disadvantage of this previous work that is avoided in the approach to bis(carbene) ligands reported here.

The chiral diamine precursors were prepared by a modification of a procedure reported by Horner and Dickerhof [32] and Feringa and co-workers [33], with 1,3-dibromopropane used in place of the dichloroalkane. Heating 1,3-dibromopropane with 2 equiv of either 1-phenylethylamine or 1-(1-naphthyl)ethylamine at 150 °C in toluene for 12 h, followed by cooling to room temperature, led to isolation of the bis(dialkylammonium) dibromide salts **1** and **2** as intermediates that could be washed with solvents to provide cleaner products in the subsequent step (Scheme 1). The bis(ammonium) salts were characterized by two inequivalent ^{1}H NMR signals for the diastereotopic $RR'NH_2^+$ groups. Treatment of **1** and **2** with aqueous NaOH provided the corresponding diamines **3** and **4** in 51–77% overall yields. The same procedure was used for the enantiomerically pure diamines (**3**, **4a**) and a diastereomeric mixture (**4b**). The (*S*,*S*) isomer of *N*,*N*′-bis[1-phenylethyl]-1,3-diaminopropane (**3**) was previously synthesized and characterized by Feringa and co-workers [33]. Reactions of the (*S*,*S*) isomer of *N*,*N*′-bis[1-(1-naphthyl)ethyl]-1,3-diaminopropane (**4**) have been reported by Equey and Alexakis, but no details of synthesis and characterization were provided [34].



Scheme 1. Synthesis of chiral diamines used to construct bis(ADC) ligands.



Scheme 2. Synthesis of enantiomerically pure palladium bis(ADC) complexes with homochiral N-substituents.

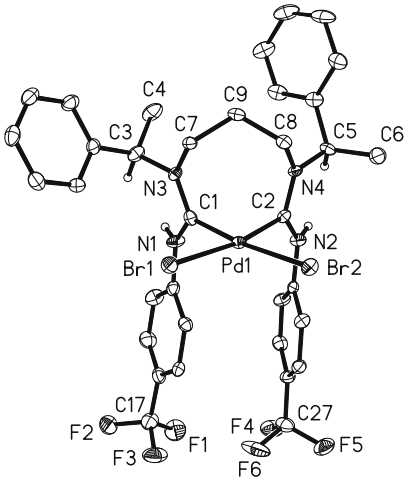


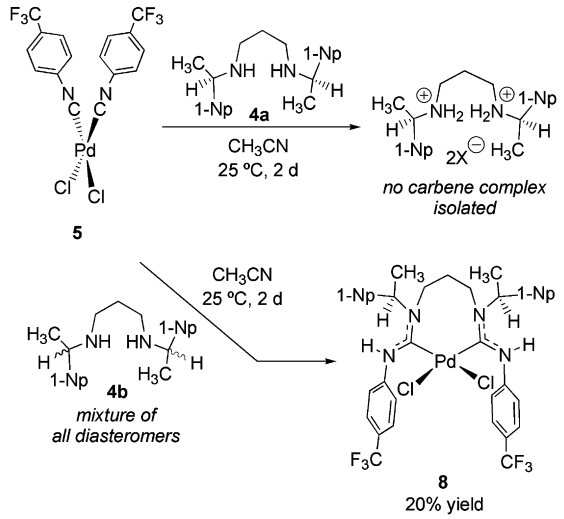
Fig. 2. Molecular structure of complex **7**, with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms have been removed for clarity, except for those on N1, N2, C3, and C5. Selected bond lengths (Å), angles (°), and torsion angles (°): Pd1–C1 1.981(4), Pd1–C2 2.012(3), C1–N1 1.347(4), C1–N3 1.335(4), C2–N2 1.338(4), C2–N4 1.330(4), N1–C1–N3 116.6(3), N2–C2–N4 118.9(3), C1–N3–C3 125.3(3), C1–N3–C7 119.6(3), C3–N3–C7 113.5(3), C2–N4–C5 123.1(3), C2–N4–C8 120.0(3), C5–N4–C8 115.4(3), C1–Pd–C2 84.06(13), N1–C1–N3–C3 14.1(5), N1–C1–N3–C7 178.7(3), N2–C2–N4–C5 −9.0(5), N2–C2–N4–C8 −174.0(3).

2.2. Synthesis and structural analysis of palladium bis(ADC) complexes

Bis(*p*-trifluoromethylphenylisocyanide) palladium complex **5** (Scheme 2) was chosen as a bis(ADC) synthon because it has previously been shown to react with structurally diverse diamines to give stable bis(ADC) complexes [6,29], including one exhibiting substantial steric strain [35]. Stirring a dichloromethane solution of **5** with *N*,*N*′-bis[(*R*)-1-phenylethyl]-1,3-diaminopropane (**3**) led to very slow formation of a white, microcrystalline precipitate, requiring 2 d of reaction to obtain reasonable yields. This is in contrast to the much faster formation of the 7-membered chelate bis(ADC) complexes **C** and **D** (Fig. 1), which occurred within 2 h [6,29]. The ^{1}H NMR spectrum of the complex in DMSO-d_6 exhibits two inequivalent NH resonances at 9.63 and 9.56 ppm, two inequivalent Ph(CH$_3$)C*H* quartets at 5.88 and 5.71 ppm, and an overlapped pair of Ph(C*H*$_3$)CH doublets at 1.43 ppm. These data are consistent with a chelating bis(ADC)PdCl$_2$ complex **6** possessing C_1 symmetry (Scheme 2), with the two chiral N-substituents occupying stereochemically distinct environments. In addition, each of the six protons on the propylene linker gives rise to a unique multiplet, with chemical shifts ranging from 5.62 to 0.72 ppm. This suggests that the propylene backbone of the chelate ring is conformationally rigid in solution. Because bis(ADC)PdCl$_2$ **6** was not sufficiently soluble in DMSO-d_6 to obtain a ^{13}C NMR spectrum, it was converted to the more soluble bis(ADC)PdBr$_2$ analogue **7** by treatment with excess NaBr in aqueous CH$_3$CN, following a procedure reported previously by us (Scheme 2) [6]. The ^{13}C NMR spectrum of **7** revealed two inequivalent carbene resonances at 193.6 and 191.6 ppm, slightly downfield of the range of 184–190 ppm seen for the analogous 7-membered chelate bis(ADC) complexes **C** and **D** [6,29].

An X-ray crystallographic analysis of a crystal of **7** obtained by slow evaporation of an acetonitrile solution of the complex confirmed a C_1-symmetric conformation of the chiral bis(ADC) ligand (Fig. 2). The complex crystallized in the chiral orthorhombic space group $P2_12_12_1$, and X-ray anomalous dispersion effects substantiated the (*R*,*R*) stereochemistry of the ligand. The two (*R*)-1-phenylethyl N-substituents both adopt the same orientation relative to the nitrogen to which they are attached, apparently to avoid steric interactions of the phenyl groups with each other or with the propylene linker. This results in the two phenyl groups pointing to different parts of the molecule, with the one attached to C5 oriented toward the back of the chelate ring and the one attached to C3 obliquely facing the coordination plane. The 8-membered chelate ring is chair-like, with C9 of the propylene linker folded away from the Pd atom. The need to avoid steric interactions of the CH$_2$ units of C7 and C8 with the bulky N-substituents explains why the chelate is locked into this conformation in solution rather than interconverting with the boat conformer. The ligand geometry does not appear to provide a substantially asymmetric coordination environment at the palladium center: the phenyl group on C3 is too distant from the coordination sphere to exert significant steric influence, and the propylene backbone presents no appreciable asymmetry to the coordination sphere. However, there are two indications of potential strain in the bis(ADC) ligand caused by the steric influence of the chiral N-substituents. First, the hydrogen atoms on C3 and C5 are forced into close proximity with the neighboring N–H hydrogens (1.86 and 1.85 Å, respectively), presumably to avoid worse steric interactions between the chiral groups and the propylene tether that would otherwise arise. Second, the substituents on the carbene nitrogens are twisted substantially out of the NCN planes, disrupting the favorable π-conjugation of the ADC moieties. This is most evident in the torsion angles between the NCN planes and the α-carbons of the chiral N-substituents: the N1–C1–N3–C3 torsion angle is 14.1(5)°, and the N2–C2–N4–C5 torsion angle is −9.0(5)°. The N2–C2–N4–C8 torsion angle of −174.0(3) also indicates a substantial deviation from co-planarity at the end of the propylene linker that is closest to a phenyl ring of the N-substituents, suggesting that steric repulsions are occurring. The Pd–C$_{carbene}$ distances of 1.981(4) and 2.012(3) Å are similar to values observed in the related 7-membered chelate bis(ADC) complexes **C** and **D** (Fig. 1) [6,29].

We anticipated that using *N*,*N*′-bis[(*R*)-1-(1-naphthyl)ethyl]-1,3-diaminopropane (**4a**) to construct a bis(ADC) ligand could lead to a more asymmetric environment at the metal center by virtue of the significantly bulkier naphthyl group. However, reaction of **4a** with palladium arylisocyanide synthon **5** under identical conditions to those used with diamine **3** (Scheme 3) resulted in formation of a yellow precipitate whose ^{1}H NMR spectrum matched that of the bis(ammonium) salt **2a**. Further stirring did not afford any isolable metal complex, and the use of rigorously dried



Scheme 3. Formation of an achiral, C_s-symmetric palladium bis(ADC) complex by reaction of palladium arylisocyanide precursor **5** with a diastereomeric mixture of diamines (1-Np = 1-naphthyl).

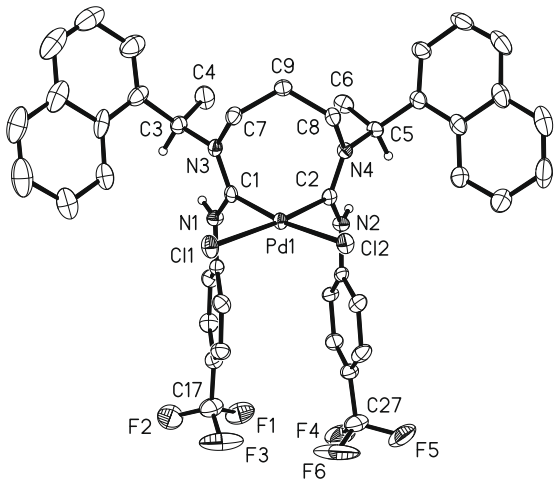


Fig. 3. Molecular structure of complex **8**, with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms have been removed for clarity, except for those on N1, N2, C3, and C5. Selected bond lengths (Å), angles (°), and torsion angles (°): Pd1–C1 1.993(3), Pd1–C2 2.000(3), C1–N1 1.350(4), C1–N3 1.331(4), C2–N2 1.348(4), C2–N4 1.330(4), N1–C1–N3 117.6(3), N2–C2–N4 118.3(3), C1–N3–C3 123.5(3), C1–N3–C7 119.8(2), C3–N3–C7 116.7(2), C2–N4–C5 123.8(2), C2–N4–C8 119.4(2), C5–N4–C8 116.8(2), C1–Pd–C2 84.4(1), N1–C1–N3–C3 4.1(4), N1–C1–N3–C7 −177.6(3), N2–C2–N4–C5 −1.8(4), N2–C2–N4–C8 −179.3(2).

acetonitrile under a dry nitrogen atmosphere gave the same result. We postulated that a bis(ADC) complex may have formed and rapidly decomposed (vide infra).

The apparent inability to form a stable bis(ADC) complex from the (*R*,*R*) naphthyl diamine **4a** raised the question of whether such a complex could be prepared from the corresponding (*R*,*S*) diamine. Lacking a readily available means of resolving the (*R*,*S*)-*meso* diamine from the (*R*,*R*)/(*S*,*S*) racemate, we decided to examine the reaction of palladium arylisocyanide synthon **5** with the unresolved diastereomeric mixture **4b**. As in the reaction of enantiomerically pure **4a**, the solid initially formed upon treatment of palladium isocyanide precursor **5** with the diastereomeric mixture of diamines **4b** in acetonitrile was identified as a bis(ammonium) salt by ^{1}H NMR. However, removal of this solid by filtration after 3 h followed by continued stirring of the clear filtrate for 2 d at 25 °C afforded a white precipitate in poor yield (20% relative to Pd) whose ^{1}H and ^{13}C NMR spectra were consistent with bis(ADC)$PdCl_2$ complex **8** (Scheme 3). In contrast to complexes **6** and **7**, the NMR spectral data indicate twofold symmetry in the bis(ADC) ligand of **8**. Only one NH resonance is visible at 9.73 ppm in the ^{1}H NMR spectrum. A single set of resonances is present for the 1-(1-naphthyl)ethyl N-substituents, with a Np(CH_3)C*H* quartet at 6.28 ppm and a Np(C*H*$_3$)CH doublet at 1.92 ppm. Four distinct multiplets are present for the propylene linker, indicating a symmetric but conformationally rigid tether in the bis(ADC) backbone. The ^{13}C NMR spectrum of **8** contains a single carbene resonance at 191.3 ppm as well as one set of peaks for the 1-(1-naphthyl)ethyl N-substituents and the CF_3–Ph group.

A crystal of **8** suitable for X-ray crystallographic analysis was obtained by slow evaporation of a DMSO solution of the complex. The X-ray structure revealed that the complex has C_s symmetry, with the two halves of the bis(ADC) ligand related by a (non-crystallographic) mirror plane (Fig. 3). The 8-membered chelate ring of **8** adopts a chair-like conformation similar to that seen in **7**. The 1-(1-naphthyl)ethyl N-substituents have (*R*) and (*S*) stereochemistry at C3 and C5, respectively, confirming that the complex itself is achiral and derived from the *meso* diamine. This stereochemical arrangement allows both bulky naphthyl groups to orient themselves toward the outside of the complex, avoiding any steric interactions with the propylene linker. Instead, the much less sterically demanding methyl groups are directed toward the back of linker. This appears to result in significantly less strained carbene units compared with chiral complex **7**. The substituents on N3 and N4 of the carbene moieties are nearly co-planar with the NCN units, with the NCN–C_{linker} and NCN–$C_{N\text{-}subst}$ torsion angles showing deviations from planarity of 0.7(2)–4.1(4)°. This is in contrast to the deviations of 1.3(3)–14.1(5)° observed in complex **7**. One notable similarity to **7** is that the methine C–H groups of **8** are in close proximity to the N–H hydrogens, with respective H···H distances of 1.82 and 1.87 Å.

A comparison of the structures of **7** and **8** with those of related palladium bis(ADC) complexes is instructive. The respective C–Pd–C bite angles of 84.06(13)° and 84.41(11)° for **7** and **8** are little changed compared with the 7-membered chelate bis(ADC) complexes **C** and **D** (Fig. 1), which exhibited respective C–Pd–C angles of 82.3(2)° and 86.6(1)° [6,29]. Differences are apparent, however, in the dihedral angles between the carbene NCN planes and the PdC_2X_2 planes. The average dihedral angles of 87.7° and 85.6° observed for **7** and **8**, respectively, are significantly larger than the average dihedral angles of 77.8° in **C** and 69.0° in **D**. Thus, the use of a longer linker results in no significant change in the bis(ADC) bite angle, but instead permits the carbene units to rotate to a near-perpendicular arrangement. The carbene N–C–N angles of **7** and **8** (average angles 117.8° and 118.0°, respectively) are not significantly different from those of **C** (average 116.8°) and **D** (average 115.6°), indicating little difference in the amount of strain within the carbene units.

A structural comparison of **7** and **8** with reported examples of bis(NHC) palladium complexes having 8-membered chelate rings is also informative [36]. The three structurally characterized examples of such complexes are shown in Fig. 4 [37–39]. Similarly to **7** and **8**, these all contain saturated three-carbon tethers. The C–Pd–C bite angles are quite similar to those seen in bis(ADC) complexes **7** and **8**: 84.8(2)° in **E** [37], 85.0(2)° in **F** [38], and 87.6(1)° in **G** [39]. However, the dihedral angles between the carbene NCN planes and the PdC_2X_2 planes are significantly smaller, averaging 83.2° for **E**, 81.0° for **F**, and 73.8° for **G**, in comparison with respective values of 87.7° and 85.6° for **7** and **8**. The smaller dihedral angles for the bis(NHC) ligands relative to the bis(ADC) ligands having the same chelate ring size can be explained as a result of the smaller carbene NCN angles of ~107° inherent to imidazole-derived carbene ligands, in contrast to the larger NCN angles of ~118° found in the

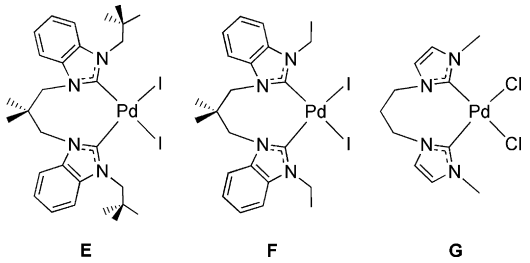
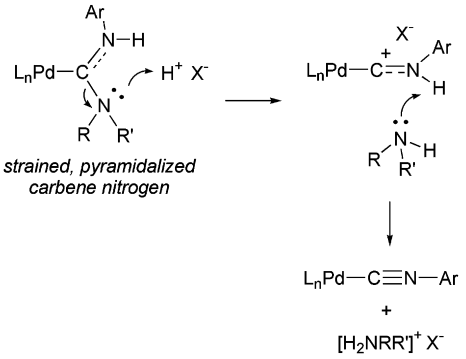


Fig. 4. Structurally characterized palladium complexes of bis(NHC) ligands with 8-membered chelate rings.



Scheme 4. Proposed mechanism for the decomposition of a strained ADC ligand to generate an ammonium salt.

acyclic carbene moieties of **7** and **8**. Assuming identical bite angles and perpendicular dihedral angles, the smaller NCN angles in a bis(NHC) complex would result in a greater distance between the two nitrogen atoms connected to the three-carbon tether in comparison to an analogous bis(ADC) complex (Fig. 5), creating additional strain in the chelate ring of the bis(NHC) ligand. This would be relieved by rotation of the carbene units away from a perpendicular arrangement, which would bring the tethered nitrogen atoms closer together. It is notable that the dimethyl substitution on the tethers of **E** and **F** may result in more rigid linkers that could affect the ability of the NHC rings to attain optimal dihedral angles. Thus, complex **G**, which exhibits the smallest NCN– PdC_2X_2 dihedral angles, is probably the best comparison to use for analyzing bis(NHC) versus bis(ADC) ligand geometries.

2.3. Discussion of the effect of ligand structure on complex stability

A comparison of the structures of **7** and **8** provides a rationale for the inability to form a stable bis(ADC) complex from enantiomerically pure (*R*,*R*) naphthyl diamine **4a** (Scheme 3). The 1-arylethyl N-substituents in both structures adopt an orientation with the methine C–H pointing toward the neighboring N–H group, and the aryl and methyl groups pointing either behind the chelate ring or toward the outside of the complex. Steric strain leading to deviations from substituent co-planarity at the "upper" carbene nitrogens N3 and N4 is minimized if the larger aryl groups face the outside of the complex, as observed in the (*R*,*S*) naphthyl complex **8**. When both 1-arylethyl groups have the same stereochemical configuration as in complex **7**, one aryl group must point toward the back of the chelate ring, where steric interactions with the propylene tether and possibly the methyl group of the other N-substituent are significant. A homochiral naphthyl analogue of complex **7** would likely display even greater deviations from planarity at N3 and N4 due to the greater bulk of a naphthyl group relative to a phenyl group, thus rendering the carbene units unstable. It is also interesting to note that another, stereochemically inequivalent isomer of complex **8** could form from the *meso* diamine, with (*S*) stereochemistry at C3 and (*R*) stereochemistry at C5. However, this isomer is not observed. The arguments given above predict that this isomer would have both bulky naphthyl groups oriented toward the back of the chelate ring, resulting in highly strained and unstable diaminocarbene moieties.

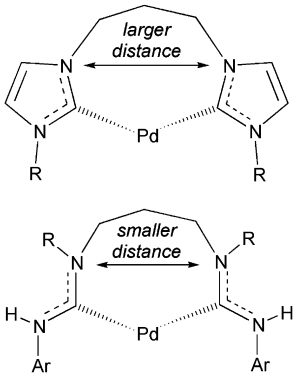
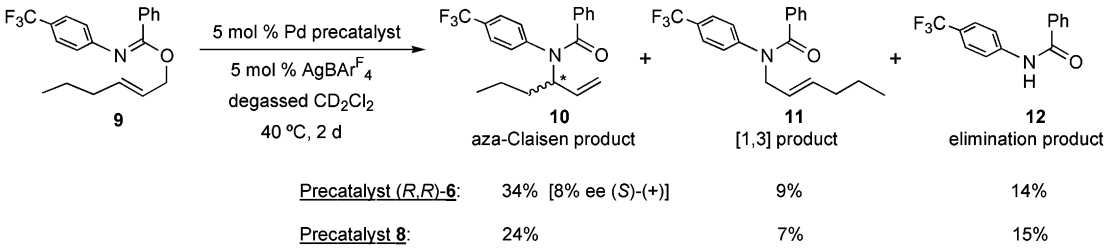


Fig. 5. Rationale for the smaller NCN–PdC_2X_2 dihedral angles observed in bis(NHC) versus bis(ADC) chelates with three-carbon linkers.

A further question is whether the bis(ADC) ligands predicted to be unstable by the above arguments actually form and then decompose during the reactions of the diamines with palladium isocyanide precursor **5**. We have previously reported one example of a strained, tetrasubstituted Chugaev-type bis(ADC) complex formed from **5** in which the chelate-forming 1,2 addition of an N–H group across the isocyanide CN bond was observed to be reversible in solution [35]. However, the isolation of bis(ammonium) salts from reactions of **4a** and **4b** with **5** suggests that a different process is occurring. A proposed pathway to the bis(ammonium) salt decomposition product is shown in Scheme 4. A carbene nitrogen is twisted out of conjugation with the NCN unit due to steric strain, causing it to pyramidalize. This renders the nitrogen susceptible to attack by small traces of H_2O or acid in the acetonitrile solvent, affording a free secondary amine and an N-protonated isocyanide ligand. The latter species is rapidly deprotonated by the liberated amine to generate the ammonium salt. In principle, this process regenerates the isocyanide complex, which may react with an amine in a more favorable conformation to give a stable bis(ADC) palladium complex. However, the low yield obtained in the formation of **8** (20% per Pd) suggests that other decomposition processes may be operating as well.

2.4. Catalytic studies

We have previously reported that palladium complexes **C** and **D** (Fig. 1), which have chiral bis(ADC) ligands with 7-membered chelate rings, act as precatalysts in the enantioselective aza-Claisen rearrangement of an allylic imidate to an allylic amide, providing up to 70% yield and enantiomeric excesses of 30–59% ee [6]. We wished to examine how the activity and enantioselectivity of this reaction would compare when the 8-membered chelate bis(ADC) complexes **6** and **8** were utilized. An identical protocol to that reported previously by us was followed: the precatalyst was activated with one equiv of $AgBAr^F_4$ ($[BAr^F_4]^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) in dichloromethane solution in the presence of the benchmark benzimidate substrate **9** [40,41], followed by heating at 40 °C for 2 d (Scheme 5). The enantiomerically pure precatalyst (*R*,*R*)-**6** provided the desired [3,3]-rearrangement product **10** in 34% yield, with the undesired [1,3]-rearrangement product **11** and the amide elimination product **12** also obtained in 9% and 14% yields,



Scheme 5. Aza-Claisen rearrangements of benzimidate **9** catalyzed by 8-membered chelated palladium bis(ADC) complexes.

respectively. This product distribution is comparable to those obtained with enantiomerically pure samples of precatalysts **C** and **D** [6]. However, the measured enantiomeric excess was only 8% ee of the (*S*)-(+) isomer of **10**, making **6** a significantly less enantioselective precatalyst than either of the 7-membered chelate palladium bis(ADC) complexes. Achiral naphthyl-substituted bis(ADC) complex **8** provided an even poorer yield of 24% of the desired product **10**, as well as side products **11** and **12** in respective yields of 7% and 14%. Thus, neither of the 8-membered chelate complexes provides an advantage over the previously studied bis(ADC) complexes in the yield of the [3,3]-rearrangement product.

3. Conclusion

The one-step assembly of chelating bis(ADC) ligands by reaction of diamines with palladium bis(isocyanide) synthons has been extended to examples containing achiral propylene linkers and chiral 1-arylethyl N-substituents. Use of enantiomerically pure *N*,*N*′-bis[(*R*)-1-phenylethyl]-1,3-diaminopropane (**3**) provided a C_1-symmetric, chiral bis(ADC) complex with slightly strained diaminocarbene moieties as judged by the structure of **7**. No stable bis(ADC) complex could be obtained from homochiral *N*,*N*′-bis[(*R*)-1-(1-naphthyl)ethyl]-1,3-diaminopropane, but reaction of palladium arylisocyanide precursor **5** with a mixture of diastereomers of the same naphthyl-substituted diamine afforded an achiral, C_s-symmetric bis(ADC) complex **8**. The favored bis(ADC) conformations in both complexes appear to minimize steric interactions between aryl groups and the propylene linker which might disrupt the π-conjugation within the carbene moieties. The propylene linkers in these complexes are surprisingly rigid in solution, precluding the conformational flexibility that would be required to bring the chiral N-substituents in close proximity to the palladium center. The formation of a single stable bis(ADC) complex **8** from a diastereomeric mixture of the diamine is particularly interesting, because it suggests that reactions of metal isocyanide precursors with diastereomeric mixtures might be utilized in future work to select the most stable chelate structure obtainable from a given diamine without the need to resolve the diamine into its *meso* and homochiral components. Finally, the new bis(ADC) complexes gave unimpressive yields in the catalytic aza-Claisen rearrangement of an allylic imidate, as well as poor enantioselectivity (8% ee) in the case of (*R*,*R*)-**6**. These results indicate that this particular bis(ADC) ligand design, incorporating chiral N-substituents and rigid 8-membered chelate rings, does not provide the electronic or asymmetric properties needed for effective enantioselective electrophilic palladium catalysis. Similar bis(ADC) designs with longer, more flexible achiral backbones are a worthy target for future studies.

4. Experimental

4.1. General procedures

All manipulations were performed under air unless otherwise noted. Acetonitrile (Pharmco) was pre-dried over $CaCl_2$, then boiled over and distilled from CaH_2 before use. Dichloromethane (Pharmco) was washed with concentrated H_2SO_4, water, aqueous $NaHCO_3$, and again water, and then distilled from P_2O_5 prior to use. Hexanes (Pharmco), toluene (Pharmco) and diethyl ether (Acros) were dried over and distilled from Na/benzophenone ketyl prior to use. DMSO for crystal growth (Acros, reagent grade) was used as received. Water was purified by an E-pure system (Barnstead) and had a resistivity of $\geqslant$17.6 MΩ cm. NMR solvents were purchased from Cambridge Isotopes Laboratories. C_6D_6 and DMSO-d_6 were dried by stirring over activated 4 Å molecular sieves followed by vacuum distillation at room temperature and were stored in a nitrogen glove box before use. CD_2Cl_2 was dried by a similar procedure and then stored over and distilled from P_2O_5 prior to use. (*R*)-(+)-1-Phenylethylamine (99+%), (*R*)-(+)-1-(1-naphthyl)ethylamine (99+%), and 1,3-dibromopropane (98%) were purchased from Acros. (±)-1-(1-Naphthyl)ethylamine (98%) was purchased from Aldrich. Bis(*p*-trifluoromethylphenylisocyanide)$PdCl_2$ (**5**) was prepared as previously reported [29]. Silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($AgBAr^F_4$) [42] and (*E*)-2-hexenyl-*N*-[4-(trifluoromethyl)phenyl]benzimidate (**9**) [40] were prepared by literature procedures. All other materials were purchased from Acros and used as received.

NMR spectra were recorded on Varian Unity INOVA 400 MHz and 600 MHz spectrometers. Reported chemical shifts are referenced to residual solvent peaks (^{13}C, ^1H). Elemental analyses were performed by Desert Analytics (Tucson, Arizona) or Midwest Microlab (Indianapolis, Indiana).

4.2. Syntheses

4.2.1. *N*,*N*′-Bis[(*R*)-1-phenylethyl]-1,3-diaminopropane (**3**)

(*R*)-(+)-1-Phenylethylamine (0.10 mL, 0.78 mmol) and 1,3-dibromopropane (0.040 mL, 0.39 mmol) were dissolved in toluene (5 mL) in a sealable glass vessel. The sealed vessel was placed in an oil bath at 150 °C, and the reaction mixture was stirred for 12 h. Upon cooling to room temperature, white needle-shaped crystals precipitated from the reaction mixture. The precipitate was filtered, washed with toluene and diethyl ether, and dried in vacuo. The ^1H NMR spectrum of this solid characterized it as the bis(dialkylammonium) dibromide salt **1**. Yield: 102 mg, 59%. ^1H NMR (400 MHz, DMSO-d_6): δ 9.18 (br s, 2 H, NH_2), 9.02 (br s, 2 H, NH_2), 7.53–7.38 (m, 10 H, Ar), 4.36 (s, 2 H, PhCH), 2.90 (br s, 2 H, NCH_2), 2.63 (br s, 2 H, NCH_2), 1.99 (unresolved m, 2 H, CH_2), 1.55 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, CH_3). The bis(ammonium) salt was dissolved in dichloromethane (20 mL), and 20 mL of a 20% (w/v) aqueous solution of NaOH was added. The mixture was placed in a separatory funnel, and the organic layer was separated. The aqueous layer was extracted twice more with 20 mL of distilled dichloromethane, and the combined organic layers were dried over anhydrous Na_2SO_4. Removal of solvent on a rotary evaporator followed by drying in vacuo yielded **2** as yellow oil. Yield: 56 mg, 51% overall. NMR spectral data matched those previously reported by Feringa et al. for the (*S*,*S*) isomer [33].

4.2.2. N,N′-Bis[1-(1-naphthyl)ethyl]-1,3-diaminopropane, diastereomeric mixture (**4b**)

The same procedure employed for diamine **3** was followed, starting with 0.10 mL (0.62 mmol) of (±)-1-(1-naphthylethylamine) and 0.032 mL (0.31 mmol) of 1,3-dibromopropane to yield the bis(ammonium) dibromide salt **2b** as an intermediate in 71% yield (0.12 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.41 (br s, 2 H, NH_2), 9.13 (br s, 2 H, NH_2), 8.22 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, naphthyl), 8.05–7.93 (m, 4 H, naphthyl), 7.86 (br s, 2 H, naphthyl), 7.68–7.53 (m, 6 H, naphthyl), 5.27 (s, 2 H, NpCH), 3.06 (br s, 2 H, NCH_2), 2.82 (br s, 2 H, NCH_2), 2.07 (br s, 2 H, CH_2), 1.63 (br s, 6 H, CH_3). After deprotonation with NaOH, the diastereomeric mixture of diamines **4b** was obtained in 66% overall yield (0.078 g). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.24–8.10 (m, 2 H, naphthyl), 7.88–7.80 (m, 2 H, naphthyl), 7.74 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, naphthyl), 7.64 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, naphthyl), 7.49–7.34 (m, 6 H, naphthyl), 4.48 (q, $^3J_{H,H}$ = 6.3 Hz, 2H, NpCH), 2.51–2.30 (m, 4 H, NCH_2), 2.06 (br s, 2 H, NH), 1.60–1.48 (m, 2 H, CH_2), 1.33 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH_3). ^{13}C NMR (101 MHz, C_6D_6): δ 142.2 (2 s overlapped, naphthyl *ipso*), 134.6 (naphthyl), 132.0 (naphthyl), 129.3 (naphthyl), 128.2 (2 s overlapped, naphthyl), 128.0 (2 s overlapped, naphthyl), 127.8 (2 s overlapped, naphthyl), 127.4 (naphthyl), 126.0 (2 s overlapped, naphthyl), 125.8 (naphthyl), 125.5 (naphthyl), 123.6 (2 s overlapped, naphthyl), 123.3 (2 s overlapped, naphthyl), 54.7 (NCMe), 54.6 (NCMe), 46.9 (NCH_2), 46.6 (NCH_2), 31.3 (NCH_2CH_2), 31.2 (NCH_2CH_2), 24.1 (CH_3), 24.0 (CH_3). HRMS (ESI), *m/z*: 383.25 $[M+H]^+$, 405.25 $[M+Na]^+$. Homochiral *N,N′*-bis[(*R*)-1-(1-naphthyl)ethyl]-1,3-diaminopropane **4a** was prepared similarly from 1,3-dibromopropane (0.16 mL, 1.6 mmol) and (*R*)-(+)-1-(1-naphthyl)ethylamine (0.50 mL, 3.1 mmol), affording the bis(ammonium) dibromide salt **2a** in 92% yield (0.75 g) and then the diamine in 77% overall yield (0.45 g). ^{1}H NMR spectral data of **4a** were identical to those of the diastereomeric mixture **4b**, but with sharper peaks.

4.2.3. N,N′-Bis[(R)-1-phenylethyl]-bis(ADC) palladium dichloride complex (**6**)

A solution of *N,N′*-bis[(*R*)-1-phenylethyl]-1,3-diaminopropane **3** (30 mg, 0.11 mmol) in 4 mL of acetonitrile was added dropwise into a solution of bis(*p*-trifluoromethylphenylisocyanide)$PdCl_2$ **5** (60 mg, 0.11 mmol) in 22 mL of acetonitrile while the latter was stirred. The reaction mixture was stirred for 2 d at 25 °C, during which time bis(ADC) complex **6** precipitated as a white, microcrystalline solid. The solid was collected by filtration, washed with acetonitrile and dichloromethane, and dried in vacuo overnight. Yield: 34 mg, 41%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.63 (s, 1 H, NH), 9.56 (s, 1 H, NH), 8.15 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, CF_3–Ph), 8.02 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, CF_3–Ph), 7.57–7.42 (m, 6 H, Ar), 7.30–7.15 (m, 8 H, Ar), 5.88 (q, $^3J_{H,H}$ = 6.4 Hz, 1 H, PhCH), 5.71 (q, $^3J_{H,H}$ = 6.4 Hz, 1 H, PhCH), 5.62 (m, 1 H, CH_2), 5.54 (m, 1 H, CH_2), 3.85 (m, 1 H, CH_2), 3.29 (m, 1 H, CH_2), 1.56 (m, 1 H, CH_2), 1.43 (2d unresolved, 6 H, CH_3), 0.72 (m, 1 H, CH_2). Anal. Calc. for $C_{35}H_{34}Cl_2F_6N_4Pd$: C, 52.42; H, 4.27; N, 6.99. Found: C, 52.13; H, 4.12; N, 6.91%.

4.2.4. N,N′-Bis[(R)-1-phenylethyl]-bis(ADC) palladium dibromide complex (**7**)

Bis(ADC)$PdCl_2$ complex **6** (95 mg, 0.12 mmol) was suspended in acetonitrile (60 mL) in a round bottomed flask. NaBr (512 mg, 5 mmol) and 2.0 mL of deionized water were added. The flask was sealed with a polyethylene stopper, and the mixture was stirred for 12 h at 25 °C. The resultant turbid solution was filtered through a sintered glass frit, and the filtrate was concentrated to 2 mL under reduced pressure without applying heat. Deionized water (10 mL) was added, resulting in formation of a grey precipitate that floated on the liquid surface. The solid was collected by suction filtration, washed with deionized water (20 mL) and diethyl ether (5 mL), and dried in vacuo overnight. Yield: 85 mg (0.095 mmol), 80%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.64 (s, 1 H, NH), 9.58 (s, 1 H, NH), 8.23 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, CF_3–Ph), 8.05 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, CF_3–Ph), 7.65–7.43 (m, 6 H, Ar), 7.35–7.13 (m, 8 H, Ar), 5.92 (q, $^3J_{H,H}$ = 6.4 Hz, 1 H, PhCH), 5.74 (q, $^3J_{H,H}$ = 6.4 Hz, 1 H, PhCH), 5.64 (m, 1 H, CH_2), 5.49 (m, 1 H, CH_2), 3.82 (m, 1 H, CH_2), 3.28 (m, 1 H, CH_2), 1.54 (m, 1 H, CH_2), 1.43 (2d unresolved, 6 H, CH_3), 0.76 (m, 1 H, CH_2). ^{13}C NMR (101 MHz, DMSO-d_6): δ 193.6 (carbene), 191.6 (carbene), 143.8 (CF_3–Ph *ipso*), 143.7 (CF_3–Ph *ipso*), 138.4 (Ph *ipso*), 137.8 (Ph *ipso*), 128.9 (Ph), 128.7 (Ph), 128.6 (Ph), 128.4 (Ph), 127.4 (Ph), 126.5 (Ph), 124.9 (CF_3–Ph *meta*), 124.8 (CF_3–Ph *meta*), 124.1 (2 q overlapped, $^2J_{C,F}$ = 30 Hz, CF_3–Ph *para*), 124.1 (2 q overlapped, $^1J_{C,F}$ = 272 Hz, CF_3), 122.3 (CF_3–Ph *ortho*), 121.7 (CF_3–Ph *ortho*), 56.6 (NCMe), 55.8 (NCMe), 54.3 (NCH_2), 53.5 (NCH_2), 29.2 (NCH_2CH_2), 18.0 (CH_3), 15.4 (CH_3). Anal. Calc. for $C_{35}H_{34}Br_2F_6N_4Pd$: C, 47.19; H, 3.85; N, 6.29. Found: C, 47.20; H, 3.90; N, 6.40%.

4.2.5. N,N′-Bis[1-(1-naphthyl)ethyl]-bis(ADC) palladium dichloride complex (**8**)

Under a nitrogen atmosphere, a solution of *N,N′*-Bis[1-(1-naphthyl)ethyl]-1,3-diaminopropane **4b** (67 mg, 0.18 mmol; mixture of all diastereomers) in 4 mL of acetonitrile was added dropwise into a solution of bis(*p*-trifluoromethylphenylisocyanide)$PdCl_2$ **5** (91 mg, 0.18 mmol) in 30 mL of acetonitrile while the latter was stirred. Over the next 3 h a yellow precipitate, identified by ^{1}H NMR as a bis(ammonium) salt of the diamine, formed in the reaction mixture. The precipitate was removed by filtration through a fine frit, and the clear filtrate was stirred for an additional 2 d at 25 °C. During this time, bis(ADC) complex **8** precipitated as a white solid. The solid was collected by filtration in air, washed with acetonitrile and dichloromethane, and dried in vacuo overnight. Yield: 33 mg, 0.037 mmol, 20%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.73 (s, 2 H, NH), 8.17 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, CF_3–Ph), 7.92 (d, $^3J_{H,H}$ = 8.2 Hz, 4 H, CF_3–Ph), 7.79 (d, 2 H, $^3J_{H,H}$ = 7.2 Hz, naphthyl), 7.60–7.54 (m, 4 H, naphthyl), 7.52–7.45 (m, 2 H, naphthyl), 7.47–7.32 (m, 2 H, naphthyl), 7.28 (d, 4H, $^3J_{H,H}$ = 8.8 Hz, naphthyl), 6.28 (q, $^3J_{H,H}$ = 6.2 Hz, 2 H, NpCH), 5.48 (m, 2 H, CH_2), 3.44 (m, 2 H, CH_2), 2.19 (m, 1 H, CH_2), 1.92 (d, $^3J_{H,H}$ = 6.2 Hz, 6 H, CH_3), 1.90 (m, 1 H, CH_2). ^{13}C NMR (151 MHz, DMSO-d_6): δ 191.3 (carbene), 144.0 (CF_3–Ph *ipso*), 133.5 (naphthyl), 133.4 (naphthyl), 130.7 (naphthyl), 129.2 (naphthyl), 128.7 (naphthyl), 127.0 (naphthyl), 126.2 (naphthyl), 125.4 (naphthyl), 125.2 (naphthyl), 125.0 (CF_3–Ph *meta*), 124.5 (q, $^2J_{C,F}$ = 33 Hz, CF_3–Ph *para*), 124.2 (q, $^1J_{C,F}$ = 272 Hz, CF_3), 123.2 (naphthyl), 122.5 (CF_3–Ph *ortho*), 54.3 (NCMe), 53.8 (NCH_2), 30.3 (NCH_2CH_2), 19.2 (CH_3). Anal. Calc. for $C_{35}H_{34}Cl_2F_6N_4Pd$: C, 57.25; H, 4.25; N, 6.21. Found: C, 57.49; H, 4.36; N, 6.49%.

4.3. X-ray crystallography

4.3.1. General crystallographic procedures

X-ray diffraction data were collected on a Bruker SMART APEX II diffractometer with a CCD detector using a combination of ϕ and ω scans. The crystal-to-detector distance was 6.0 cm. A Bruker Kryoflex liquid nitrogen cooling device was used for low-temperature data collections. Unit cell determination and data collection utilized the Bruker APEX2 software package [43]. Data integration employed SAINT [44]. Multiscan absorption corrections were implemented using SADABS [45]. X-ray diffraction experiments employed graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software suite [46]. Non-hydrogen atoms were assigned anisotropic temperature factors, with hydrogen atoms included in calculated positions (riding model) except as indicated. Further details of the structural determinations are presented in Table 1 and in the text below.

Table 1
Details of X-ray crystallographic structural determinations of palladium bis(ADC) complexes **7** and **8**.

	7	**8**·DMSO
Formula	$C_{35}H_{34}Br_2F_6N_4Pd$	$C_{43}H_{38}Cl_2F_6N_4Pd{\cdot}C_2H_6OS$
M_r	890.88	980.20
T (K)	115(2)	125(2)
Crystal size (mm)	0.33 × 0.07 × 0.04	0.19 × 0.17 × 0.02
Color, habit	Colorless rod	Colorless plate
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	7.3123(1)	13.6755(6)
b (Å)	17.5737(2)	24.5368(11)
c (Å)	26.6940(3)	14.0915(6)
β (°)	90	114.997(1)
V (Å^3)	3430.29(7)	4285.5(3)
Z	4	4
$d_{calcd.}$ (g cm^{-3})	1.725	1.519
μ (mm^{-1})	2.935	0.672
F(0 0 0)	1768	2000
θ Range (°)	1.53–25.63	1.64–28.28
Index ranges	$-8 \leqslant h \leqslant 8$	$-18 \leqslant h \leqslant 18$
	$-21 \leqslant k \leqslant 21$	$-32 \leqslant k \leqslant 32$
	$-32 \leqslant l \leqslant 32$	$-18 \leqslant l \leqslant 18$
Reflections measured	26 414	55 796
Reflections unique [R_{int}]	6452 [0.048]	10 627 [0.067]
Reflections observed [$I > 2\sigma(I)$]	5906	7726
R_1, wR_2 [$I>2\sigma(I)$]	0.0265, 0.0538	0.0432, 0.0925
R_1, wR_2 (all data)	0.0323, 0.0557	0.0720, 0.1048
Goodness of fit (GoF) on F^2	1.016	1.010
Peak/hole (e Å^{-3})	0.516/−0.354	1.248/−1.094
Absolute structure parameter	0.005(6)	–

*4.3.2. X-ray crystallographic analysis of complex **7***

Data were collected in 50 s scans, with a target data redundancy of 4.0 including 75% of Friedel pairs. Friedel opposites were not merged in the final reflection data used for structure solution and refinement, in order to allow absolute structure determination by anomalous dispersion effects. The N–H hydrogen atoms attached to N1 and N2 were restrained to a distance of 0.88 Å, with other positional parameters of these atoms allowed to refine freely. For refinement as the (*R*,*R*) enantiomer, Flack $x = 0.005(6)$, R_1 [$I > 2\sigma(I)$] = 0.0265, and wR_2 (all data) = 0.0557. For refinement as the (*S*,*S*) enantiomer, Flack $x = 0.99(1)$, R_1 [$I > 2\sigma(I)$] = 0.0571, and wR_2 (all data) = 0.1343.

*4.3.3. X-ray crystallographic analysis of complex **8***

Data were collected in 30 s scans with use of a Monocap collimator to boost X-ray intensity. One molecule of DMSO was located in the difference Fourier map and refined as a part of the structural model.

4.4. Catalytic aza-Claisen rearrangements

Pd precatalyst (7.5 μmol), $AgBAr^F_4$ [42] (7.5–15 μmol), and (*E*)-2-hexenyl-*N*-[4-(trifluoromethyl)phenyl]benzimidate **9** [40] (52 mg, 0.15 mmol) were added to a sealable J Young NMR tube under nitrogen. The tube was evacuated on a vacuum line, and 0.6 mL of dry CD_2Cl_2 was added by vacuum distillation. The NMR tube was kept in a constant temperature water bath for 2 d at 40 °C. To determine yields, 30 μL of *p*-fluoronitrobenzene was added to the tube as an internal standard, and the mixture was analyzed by ^{1}H and ^{19}F NMR spectroscopy. Product identities were assigned based on previously reported ^{1}H NMR data for aza-Claisen rearrangements of **9** [40]. NMR yields were determined from integrations of ^{19}F NMR signals of the products and the internal standard. The rearrangement products and side products appeared with the following chemical shifts: [3,3] product **10** −62.82 ppm; [1,3] product **11** −62.75 ppm, amide **12** −62.36 ppm. These values were determined from samples of each product purified by flash chromatography using a 10:90 mixture of ethyl acetate and hexanes.

For determination of enantiomeric excess, a 2 mg sample of purified allylic amide **10** was dissolved in 2 mL of 95:5 *n*-hexane/EtOH to make a solution of roughly 1000 ppm concentration. An aliquot of this solution was diluted to 30–50 ppm to be used for HPLC analysis. Enantiomeric excess was determined using a Beckman System Gold HPLC equipped with a 25 cm Chiralpak AD–H column (Chiral Technologies Inc.) and a UV detector (254 nm). Sample injection volume was 20 μL, and a Shimadzu CR501 Chromatopac integrator was used to determine the enantiomeric ratio. Test runs of a racemic mixture of **10** were performed before the % ee measurement to ensure baseline separation and reliable integrated peak ratios. The absolute configuration was determined as previously described [6].

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Appendix A. Supplementary material

CCDC 711505 and 711254 contain the supplementary crystallographic data for complexes **7** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.007.

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