Chiral Palladium Bis(acyclic diaminocarbene) Complexes as Enantioselective Catalysts for the Aza-Claisen Rearrangement

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Received October 14, 2007

Summary: Palladium complexes of chiral bis(acyclic diaminocarbene) ligands with seven-membered chelate rings catalyze the aza-Claisen rearrangement of an allylic benzimidate to an allylic amide with moderate yields and enantioselectivities of 30–59% ee. The promotion of electrophilic catalysis by complexes of these ligands highlights their distinct stereoelectronic properties relative to those of common bis(N-heterocyclic carbenes).

Cyclic diaminocarbenes, commonly known as N-heterocyclic carbenes or NHCs, promote a growing number of transition-metal-catalyzed reactions with activity superior to that of the more traditional phosphine ligands.[1] This is generally believed to result from stronger σ-donation by NHCs relative to phosphines, a view that is supported by calorimetric studies,[2] CO stretching frequencies,[3,4] and theoretical pK_a values.[5] Thus, attention has focused on catalytic reactions in which stable ligation of electron-rich, coordinatively unsaturated metal intermediates is important, such as Pd-catalyzed cross-coupling[6,7] and Ru-catalyzed olefin metathesis.[8] Notably, several studies have indicated that commonly employed NHCs show little variation of donor ability with changing N-substituents[4,9] or backbone saturation,[5,10] implying that steric factors may be primarily responsible for observed differences in catalyst activity.[11] Although a few examples of NHCs with tunable donicity have appeared, including Bertrand's borazine-derived NHCs[12] and a recently reported series of NHCs bearing electron-withdrawing aryl groups,[13] NHCs cannot yet match the diversity of donor abilities available in phosphine ligands.[14] In order to extend the utility of ancillary carbene ligands to new areas of catalysis, access to carbenes that combine a wider range of donor properties with the advantages of NHCs (e.g., ease of synthesis and robustness) is an important goal.

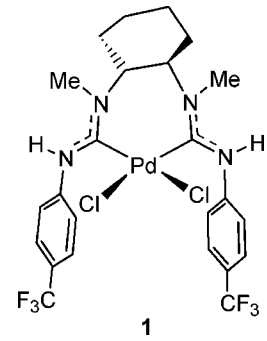

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Figure 1. Previously reported chiral bis(ADC) complex.

Although they possess electronic stabilization similar to that of NHCs,[15] acyclic diaminocarbenes (ADCs)[16] have only begun to be investigated in catalysis.[17,18] The available evidence suggests that ADCs are stronger donors than the corresponding NHCs.[5,19] However, the increased reactivity of the free carbenes[20] has hindered development of their coordination chemistry.[21] In spite of this, a few recent reports have demonstrated that ADCs effectively promote several Pd-catalyzed cross-coupling reactions,[17,18] in some cases with activities comparable to those of NHCs.[18] We have been investigating routes to chelating bis(ADC) ligands,[17] including the first chiral example (**1**; Figure 1),[22] that utilize the facile addition of diamines to

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10.1021/om701029j CCC: $40.75
Publication on Web 12/13/2007

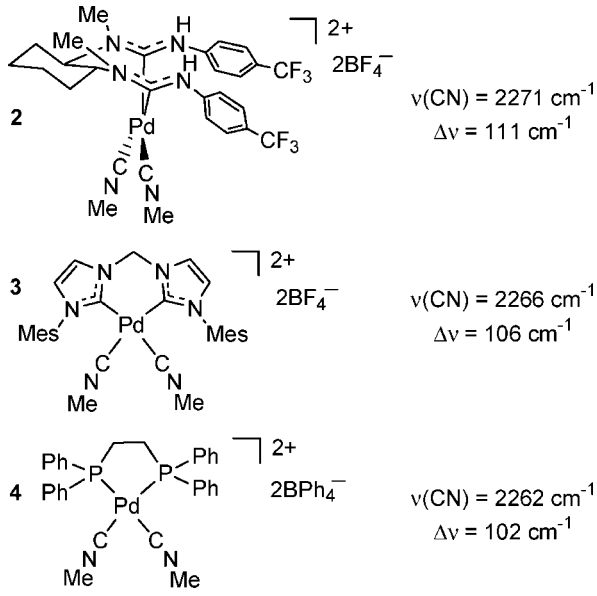

Figure 2. Evaluation of chelating ligand donor properties using MeNC as a probe ligand. $\Delta\nu$ is reported relative to the IR stretch of free MeNC (ν 2160 cm^{-1}).

coordinated isocyanides[23] to circumvent formation of the free ADC. Herein we report enantioselective catalysis of the aza-Claisen rearrangement using chiral palladium bis(ADC) complexes as precatalysts. This is an unusual example of electrophilic catalysis supported by a diaminocarbene ligand[24] as well as the first example of enantioselective catalysis by a chiral ADC complex.

This study began with efforts to evaluate the donor ability of the previously reported[22] chiral palladium bis(ADC) complex **1** using methyl isocyanide as a probe ligand. Because isocyanides are stronger σ-donors and weaker π-acceptors than CO,[25] we viewed this as a useful method for assessing relative σ-donor strengths of different ligands without interference from π-effects. The bis(methyl isocyanide) adduct **2** (Figure 2) was prepared by treating the chiral Pd bis(ADC) complex **1** with excess MeNC and $AgBF_4$ in acetonitrile. For comparison, analogous adducts were prepared of a bis(NHC) having the most common chelate structure (**3**)[6,26] and the widely used bis(phosphine) DPPE (**4**). In all cases, the higher ν(CN) value relative to that of free MeNC indicates strong donation to Pd from the weakly σ* HOMO with negligible π-back-bonding.[25] Complex **2** shows the highest $\Delta\nu$ value of 111 cm^{-1}, indicating that the bis(ADC) is the weakest donor in the series: MeNC is able to donate more strongly due to the weaker trans influence of the chelate ligand. Strikingly, both the bis(ADC) of **2** and the bis(NHC) of **3** appear to be weaker donors than the bis(phosphine) of **4** by this analysis. Although the CF_3-substituted aryl groups give the bis(ADC) of **2** a substitution pattern very different from those of common ADCs or NHCs, it is unclear to what extent the high $\Delta\nu$ value reflects a weaker intrinsic σ-donor ability relative to NHCs or phosphines. Another consideration is that the seven-membered chelate ring of the bis(ADC) may result in nonideal overlap of the ADC donors with metal orbitals (C−Pd−C angle 82.3(2)°)[22] whereas the respective six-membered and five-membered chelates of the bis(NHC) and DPPE should permit bite angles closer to 90°. This chelate effect on donicity is the subject of ongoing work that will be reported in due course. What is apparent at this point is that the *effective* donor strength of the bis(ADC) as transmitted to the trans coordination site is lower than those of the most common bis(NHC) and bis(phosphine) ligand types.

These results suggested that bis(ADC) ligands with seven-membered chelates could support electrophilic reactivity at the Pd center. To test this hypothesis, we examined the aza-Claisen [3,3]-sigmatropic rearrangement of allylic imidates to allylic amides (Table 1), a reaction developed primarily by Overman and co-workers.[27,28] This reaction is potentially synthetically useful because it creates a new chiral center,[29] but only a limited number of ligands have been reported to promote effective Pd catalysis, due to the stringent stereoelectronic demands of the reaction.[27–29] Moderate Lewis acidity is considered key: the Pd center must be electrophilic enough to activate the olefin toward attack by the imidate nitrogen, but it should not strongly bind the imidate nitrogen, or side reactions will occur.[27] There are also strict steric requirements for high enantioselectivity, with only a few complexes−all nitrogen-containing palladacycles−reported to give a high percent ee.[30,31]

The rearrangement of benzimidate **5** (Table 1), a benchmark aza-Claisen substrate,[29,30] was examined to test the activity of bis(ADC) Pd catalysts. Upon activation with 1 equiv of $AgBAr^F_4$,[32] the racemic bis(ADC) palladium complex **1** catalyzed the conversion of **5** to the desired allylic amide **6** in 70% yield in CD_2Cl_2 at 40 °C over 2 days, as judged by ^{19}F NMR (Table 1, entry 3).[33,34] The noncoordinating $[BAr^F_4]^-$ anion was essential for catalysis: coordinating triflate anion resulted in no conversion of **5** (entry 1), and even BF_4^- provided only a trace of the desired product (entry 2). Reactions run in THF also showed no conversion, indicating that coordinating solvents inhibit catalytic activity (entry 4). As observed in other systems,[29] the [1,3]-rearrangement product **7** and amide elimination product **8** appeared as significant side products (10–15%). When 2 equiv of $AgBAr^F_4$ was used per Pd, the [1,3]-

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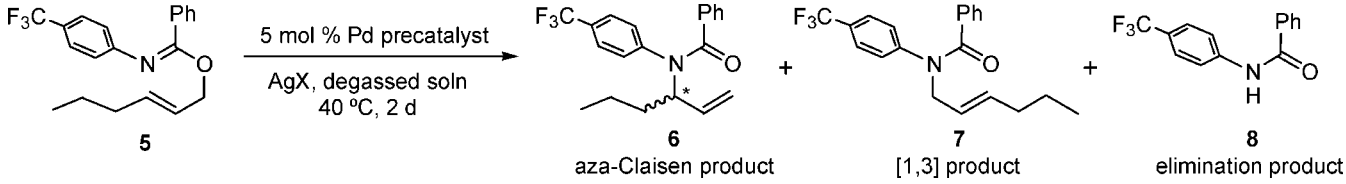
(33) Typical catalytic procedure: Complex **1** (5 mg, 7.5 μmol), $AgBAr^F_4$ (7 mg, 7.5 μmol), and benzimidate **5** (52 mg, 0.15 mmol) were placed in a J. Young NMR tube. The tube was evacuated, and 0.6 mL of dry CD_2Cl_2 was added by vacuum transfer. The tube was sealed and heated to 40 °C for 2 days. Yields were determined by ^{19}F NMR analysis of the reaction mixture (see the Supporting Information).

(34) Although **1** is susceptible to aerobic oxidation to a bis(amidine) complex, previous studies established that it is thermally stable up to 80 °C in degassed solutions.[22]

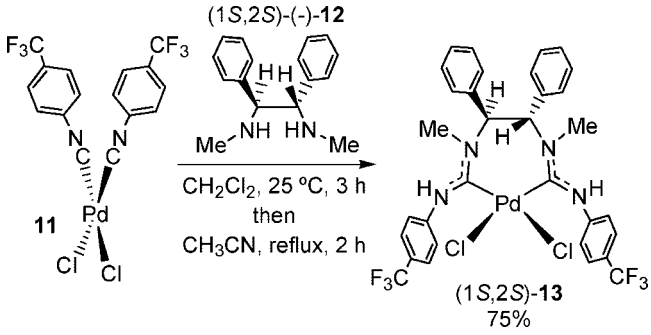
Table 1. Palladium-Catalyzed Aza-Claisen rearrangement of Benzimidate 5[a]



entry	catalyst	AgX	solvent	yield (%)[b] 6	7	8
1	(±)-**1**	5 mol % AgOTf	CD_2Cl_2	0	0	0
2	(±)-**1**	5 mol % $AgBF_4$	CD_2Cl_2	2	11	12[c]
3	(±)-**1**	5 mol % $AgBAr^F{}_4$[d]	CD_2Cl_2	70 (54)[e]	14	12[c]
4	(±)-**1**	5 mol % $AgBAr^F{}_4$[d]	THF-d_8	0	0	0
5	(±)-**1**	10 mol % $AgBAr^F{}_4$[d]	CD_2Cl_2	6	51	9[c]
6	$(DIMes^{Me})PdBr_2$ (**9**)[f]	5 mol % $AgBAr^F{}_4$[d]	CD_2Cl_2	6	28	2
7	$(DPPE)PdCl_2$ (**10**)[g]	5 mol % $AgBAr^F{}_4$[d]	CD_2Cl_2	75	10	7[c]
8	(1*R*,2*R*)-**1**	5 mol % $AgBAr^F{}_4$[d]	CD_2Cl_2	50 (41),[e] 30% ee (*S*)-(+)	14 (12)[e]	20[c]
9	(1*S*,2*S*)-**1**	5 mol % $AgBAr^F{}_4$[d]	CD_2Cl_2	36 (24),[e] 32% ee (*R*)-(−)	14	13[c]
10	(1*S*,2*S*)-**13**	5 mol % $AgBAr^F{}_4$[d]	CD_2Cl_2	34 (33),[e] 59% ee (*S*)-(+)	11	15[c]

[a] Reaction conditions: 0.15 mmol of **5**, 5 mol % of catalyst, 0.6 mL of dry degassed solvent in a J. Young NMR tube, 40 °C, 2 days. [b] Yield determined by ^{19}F NMR. [c] A small crystalline precipitate of amide **8** also formed in these reactions; thus, yields are underestimated. [d] $[BAr^F{}_4]^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. [e] Isolated yields in parentheses, determined from larger scale reactions (0.44 mmol of **5**; see the Supporting Information). Isolated **6** typically contained 5–8% **7** due to difficulties in chromatographic separation. [f] $DIMes^{Me}$ = 1,1′-dimesityl-3,3′-methylenediimidazol-2,2′-diylidene; see compound **3**. [g] DPPE = 1,2-bis(diphenylphosphino)ethane; see compound **4**.

Scheme 1. Synthesis of a New Chiral Palladium Bis(ADC) Complex



rearrangement product **7** dominated (51%) with very little allylic amide **6** formed (entry 5). This is consistent with previous proposals that increased charge at palladium favors side reactions.[27] To compare the activity of the bis(ADC) complex with those of precatalysts containing other chelate ligands, $(DIMes^{Me})PdBr_2$ (**9**), containing the same bis(NHC) ligand as complex **3**, and $(DPPE)PdCl_2$ (**10**) were screened under identical conditions. The bis(NHC) complex **9** gave only a 6% yield of the desired product, with the [1,3]-rearrangement product predominant (28%, entry 6). In contrast to an earlier report that bis(phosphine)palladium complexes are ineffective for aza-Claisen rearrangements,[35] complex **10** provided a moderate yield of **6** (75%), indicating activity comparable to that of the bis(ADC) complex **1**. We postulate that the noncoordinating $[BAr^F{}_4]^-$ anion unlocks previously unrecognized reactivity of Pd phosphine complexes in this reaction. The lack of correlation of catalytic activity of **1**, **9**, and **10** with relative ligand donor ability, as gauged by the MeNC probe studies (Figure 2), suggests that the steric environment about the metal is of equal or greater importance than the ligand donor strength for efficient catalysis of this rearrangement.

Enantiomerically pure samples of the palladium bis(ADC) complex **1** were prepared in order to examine their effectiveness

(35) Footnote 10 in ref 29 stated "catalysts of composition $PdCl_2$.(diphosphine) are inactive, while catalysts prepared from the reaction of diphosphines (1 equiv) with $Pd(MeCN)_4(BF_4)_2$ promoted elimination of allylic imidates".

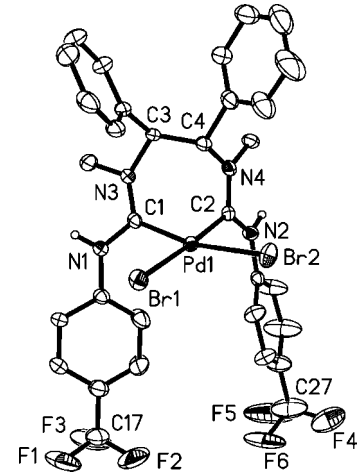


Figure 3. ORTEP view of **14**, the dibromide derivative of **13**. Thermal ellipsoids are drawn at the 50% probability level, and non-NH hydrogen atoms have been removed for clarity. Selected distances (Å) and angles (deg): Pd1−C1 = 2.011(3), Pd1−C2 = 1.987(3), Pd1−Br1 = 2.4929(5), Pd1−Br2 = 2.5238(5), C1−N1 = 1.356(3), C1−N3 = 1.335(4), C2−N2 = 1.351(4), C2−N4 = 1.327(4); C1−Pd1−C2 = 86.55(10).

as enantioselective catalysts for the aza-Claisen rearrangement of benzimidate **5** (Table 1). Two enantiomers of **1** provided the rearrangement product with equal and opposite enantioselectivities: (1*R*,2*R*)-**1** yielded (*S*)-(+)-**6** in 30% ee, and (1*S*,2*S*)-**1** afforded (*R*)-(−)-**6** in 32% ee (entries 8 and 9). However, yields of **6** (36–50%) were noticeably lower than for reactions catalyzed by (±)-**1**. Our working hypothesis to explain this result is that a catalyst monomer–dimer equilibrium plays an important role in the catalytic cycle, consistent with the dimeric nature of known Pd catalysts for aza-Claisen rearrangements.[29–31] For the racemic catalyst, the mixed (*R*,*R*)-(*S*,*S*) dimer can form, perturbing the equilibrium relative to reactions of enantiomerically pure **1**, in which only one diastereomer can form.

We sought to improve upon the poor enantioselectivity displayed by **1** by fashioning a bis(ADC) ligand with more pronounced chirality. By the same one-step protocol used to prepare **1**,[22] the palladium isocyanide precursor **11** was treated

with commercially available (1*S*,2*S*)-(−)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine (**12**) to give the new enantiopure palladium bis(ADC) complex **13** (Scheme 1). An X-ray structure of the dibromide derivative **14**, obtained by treating **13** with aqueous NaBr, displayed the same seven-membered bis(ADC) chelate ring present in **1**,[22] but with a more asymmetric coordination environment by virtue of the phenyl group on C3, which leans toward the Pd center (Figure 3). X-ray anomalous dispersion effects confirmed the (*S*,*S*)-configuration of the ligand of **14**.[36] As expected, a higher ee of 59% (*S*)-(+) for the allylic amide **6** was obtained in the rearrangement of **5** using **13** as a precatalyst, although the yield was poor (34%). However, this result demonstrates that systematic improvements in percent ee are possible.

This study places chiral bis(ADCs) among the small number of ligands that have been reported to promote enantioselective aza-Claisen rearrangements. Although significantly lower activities and percent ee values for rearrangement of **5** are obtained in comparison with those of the best palladacycle systems,[30] these bis(ADC) Pd catalysts are comparable to the first generation of enantioselective aza-Claisen catalysts reported by Overman.[29] Notably, the bis(ADC)s in this study are significantly better suited for this catalytic rearrangement than a bis(NHC), highlighting their distinct stereoelectronic properties. The facile synthesis of the Pd bis(ADC) precatalysts should permit systematic tuning of the ligand electronic properties and chirality by variation of the aryl isocyanide and chiral diamine, respectively, potentially leading to effective catalysts for a range of substrates and related reactions. This aza-Claisen study represents a rare example of a diaminocarbene ligand supporting a catalytic reaction in which the primary role of the metal is as an electrophile.[24]

Acknowledgment. We thank the National Science Foundation (CAREER Award CHE-0645438) for funding. The Oklahoma State Regents for Higher Education provided funds for purchase of the APEX II diffractometer.

Supporting Information Available: Text giving detailed experimental procedures, figures showing chiral HPLC traces for enantioselective reactions, and a CIF file giving crystallographic data for **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Crystal data for **14**: $C_{32}H_{28}Br_2F_6N_4Pd \cdot 2CH_3OH$, $M_r = 912.89$, orthorhombic, space group $P2_12_12_1$, $a = 8.8307(11)$ Å, $b = 13.1779(15)$ Å, $c = 30.571(4)$ Å, $U = 3557.6(8)$ Å^3, $Z = 4$, μ(Mo Kα) = 2.836 mm^{-1}, $T = 115(2)$ K, $2\theta_{max} = 61.0°$, 85 137 total reflections, 10 870 independent ($R_{int} = 0.053$), 9988 observed ($I > 2\sigma(I)$) (Friedel pairs not merged). Final R1 ($I > 2\sigma(I)$) = 0.0324, wR2 (all data) = 0.0766, Flack $x = 0.013(6)$. For refinement as the inverted (1*R*,2*R*) structure: Flack $x = 1.000(12)$, R1 ($I > 2\sigma(I)$) = 0.0640, wR2 (all data) = 0.1549.