Synthesis and Stereochemistry of the First Chiral (Imidazolinylidene)- and (Triazolinylidene)palladium(II) Complexes

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The reaction of three equiv. of a chiral imidazolium or triazolium perchlorate with one equiv. of $Pd(OAc)_2$, an excess of NaI and a base leads to the corresponding chiral dicarbenediiodopalladium(II) complexes in chemical yields up to 98% and with the *trans* isomer as the major product (**1**, **2**). If only one equiv. of the imidazolium or triazolium perchlorate is used, then dinuclear complexes with bridging iodine atoms are formed (**3**, **4**, chemical yield 92–94%). The latter can add Lewis basic ligands, e.g. amines, phosphanes or other carbenes, to give mononuclear complexes with one carbene ligand coordinated to the PdI_2 fragment (**5**, **6**). Preliminary test experiments with these Pd(II) complexes as catalysts for an enantioselective Heck-type reaction have been carried out.

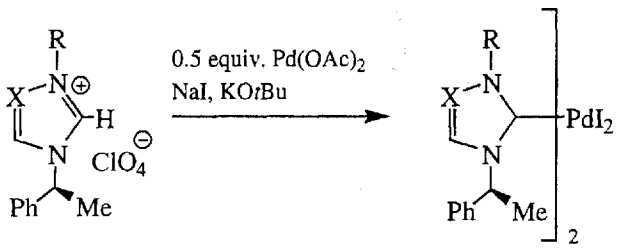
Introduction

Carbenes are usually reactive and electrophilic intermediates which cannot be isolated. After the discovery of nucleophilic carbenes by Wanzlick in the 1960s[1], the isolation and characterization of stable imidazolinylidenes in 1991 and later imidazolidinylidenes by Arduengo et al.[2] led to a renaissance of carbene chemistry. In 1995 we reported on a stable triazolinylidene[3], and recently Alder et al. published the first acyclic stable carbene[4].

These nucleophilic carbenes can be used as prebuilt ligands in organometallic chemistry. Since the preparation of the first complexes with nucleophilic carbenes as ligands, such as the Hg(II) complexes by Wanzlick et al.[5], the Cr(0)- and Fe(0) complexes by Öfele[6], the Ru(II) complexes by Taube et al.[7] and the complexes of various transition metals by Lappert et al.[8], numerous further complexes, e.g. of Cu(I), Ag(I)[9], Ni(0), Pt(0)[10], Cr(0), Mo(0), W(0), Fe(0), Ni(0)[11,12], Sm(II), Yb(II)[13], Pd(II), Rh(I), Ir(I), Os(II), and Ru(II)[14] have been published[15]. The first and up to now only chiral carbene complexes, i.e. Co and Rh complexes with chiral imidazolinylidene ligands, were investigated by Lappert et al. as early as 1983[16]. However, an enantioselective synthesis using these chiral carbene complexes as catalysts has not yet been published. We now report on the synthesis of chiral (imidazolinylidene)- and (triazolinylidene)palladium(II) complexes as possible catalysts for enantioselective synthesis.

Results and Discussion

The reaction of three equiv. of an imidazolium or triazolium perchlorate with one equiv. of $Pd(OAc)_2$, an excess of NaI and $KOtBu$ leads to dicarbenediiodopalladium(II) complexes, air- and water-stable pale yellow solids, in chemical yields of 90–98% (cf. Table 1). In both cases, *trans* and *cis* isomers are obtained, the former being the major product. This result is in contrast to that of Herrmann et al. whose achiral diimidazolinylidenediiodopalladium(II) complexes were reported to exist only in the *cis* form[14].



1 X = CH; R = (*S*)-1-phenylethyl
2 X = N; R = phenyl

Table 1. Chemical yields of the preparation of dicarbenediiodopalladium(II) complexes **1** and **2**

	yield (*trans* product)	yield (*cis* product)
1	89%	9%
2	82%	8%

The *trans* and *cis* complexes can be separated by column chromatography (silica gel, Et_2O/hexane, 1:1). Upon heating in DMF at 100°C for 0.5 h, the *cis* isomer is completely transformed into the *trans* isomer. Both isomers show

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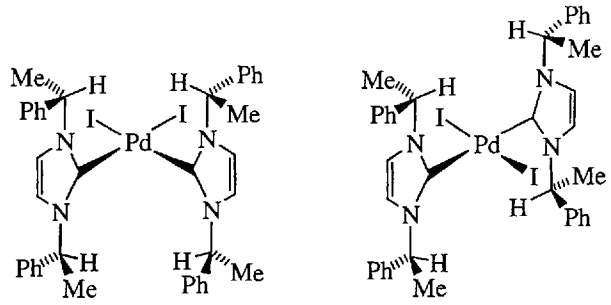
nearly identical mass and IR spectra and elemental analyses, but different NMR spectra.

For the diimidazolinylidenediiodopalladium(II) complex *trans*-**1**, the four 1-phenylethyl groups in one molecule cannot be distinguished. For *cis*-**1**, two different 1-phenylethyl groups were found in the ^{1}H- and ^{13}C-NMR spectra. With the ligands perpendicular to the square plane of the complex, the lower and upper halves of each ligand are diastereotopic to each other. Thus, a coupling constant of 2.14 Hz for the olefinic protons was found. By NOE investigations, the two different 1-phenylethyl groups and their conformation in solution can be assigned: the protons point at the palladium atom, and the phenyl group inside the molecule causes a ring-current effect on the proton and the methyl group of the other 1-phenylethyl group which leads to a high-field shift of $\delta = 1.5-2$ in the ^{1}H-NMR spectrum.

Figure 1. *cis* and *trans* isomers of complex **1**

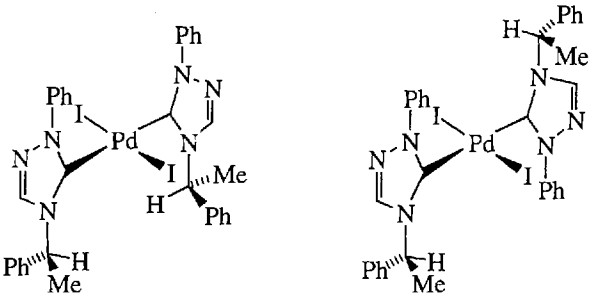


cis-**1** *trans*-**1**

With the non-symmetric triazolinylidene ligand, the number of possible isomers increases. For the *trans* complex as well as for the *cis* complex, different rotamers (or diastereomers) can be formed which have not yet been fully described.

In the *trans* isomer, the two 1-phenylethyl groups can either point in the same direction (we have named this isomer the *trans-syn* compound) or in different directions (*trans-anti*). These two atropisomers can be separated by their solubility; *trans-anti*-**2** is soluble in ether, whereas only traces of *trans-syn*-**2** are dissolved, and the *anti*/*syn* ratio is 2.6:1 (cf. Table 2).

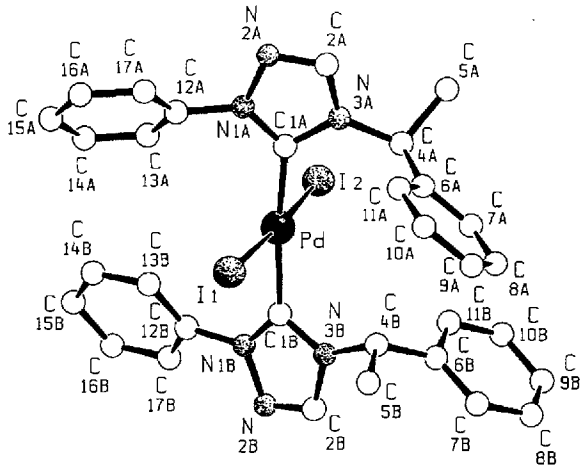
Figure 2. *trans-syn* and *trans-anti* isomers of complex **2**



trans-syn-**2** *trans-anti*-**2**

For *trans-anti*-**2**, an NOE between the phenyl group of one ligand and the 1-phenylethyl group of the other ligand was detected; for *trans-syn*-**2**, no NOE between the different parts of the molecule was observed. The *trans-syn* complex was crystallized and its structure in the solid-state was determined[17,18].

Figure 3. SCHAKAL plot of *trans-syn*-**2**[a]



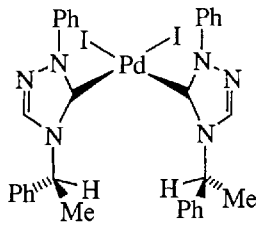
[a] Selected bond lengths [Å] and angles [°]: Pd–C1A 2.018(7), Pd–C1B 2.042(7), Pd–I1 2.5924(9), Pd–I2 2.6251(9), C1A–Pd–I1 89.4(2), C1A–Pd–I2 90.7(2). C1B–Pd–I1 89.1(2), C1B–Pd–I2 91.4(2).

The X-ray structure shows a slightly distorted square-planar Pd center. The triazolinylidene ligands are planar and the interatomic distances within these rings are similar to those obtained for the free carbene described in ref.[3]. As expected after the NOE investigations, the two 1-phenylethyl groups of the triazolinylidenes point in the same direction of the molecule, and the protons point at the palladium atom. The Pd–C bond lengths amount to 2.018(7) Å and 2.042(7) Å and are therefore comparable to other carbene-palladium bonds (1.948–2.074 Å)[20]. The striking distortion of one triazolinylidene unit in contrast to the other one oriented nearly perpendicular to the square plane of the complex leads to an angle of 32.4(3)° between the planes of the two triazolinylidene units.

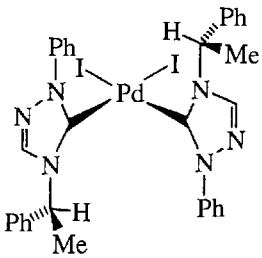
For the *cis* compound *cis*-**2** also, both *syn* and *anti* isomers are formed. The *anti* isomer exists as two diastereomers whereas only one *syn* isomer is possible (*meso* form). A separation of these three *cis* isomers has not been possible up to now. For the *syn* rotamer, two diastereotopic 1-phenylethyl groups can be observed in the ^{1}H-NMR spectrum (high-field shift of one of the groups because of a ring-current effect, cf. *cis*-**1**), whereas the 1-phenylethyl groups of each of the *anti* rotamers can be transformed into each other by means of rotation around a C_2 axis and are therefore identical. In this way, the diastereomeric excess (de = 39%) and the *syn*/*anti* ratio (7:1) can be determined (cf. Table 2).

Due to the existence of two diastereomers and one *meso* form, there must be two chiral elements within the molecule. There has already been an attempt to characterize the stereochemistry of the two enantiomers of square-planar *cis*-bis(guanosine)platinum(II) complexes by expanding the complex to a virtual octahedron and describing the helicity

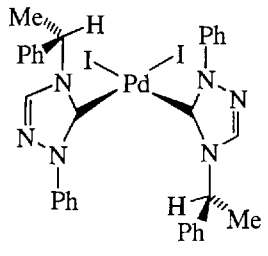
Figure 4. *cis-syn* and *cis-anti* isomers of complex **2**



cis-syn-(R_a,S_a)-**2**



cis-anti-(R_a,R_a)-**2**



cis-anti-(S_a,S_a)-**2**

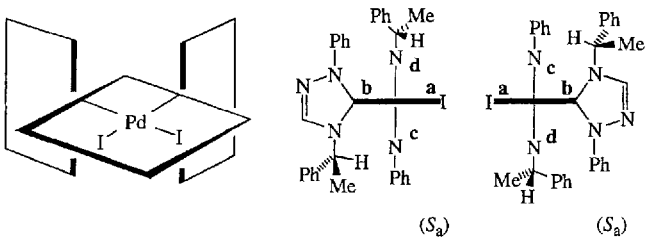
Table 2. Distribution of isomers of *trans*-**2** and *cis*-**2**

	syn product	*anti* product
trans-**2**	28%	72%
cis-**2**	12%	88%[a]

[a] de (*cis-anti*-**2**) = 39%.

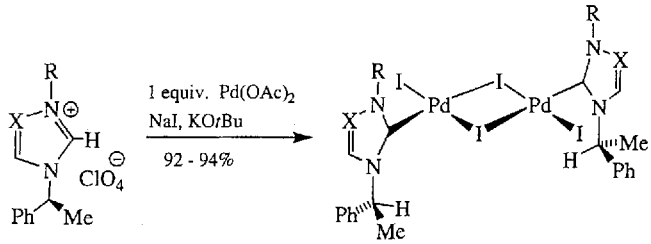
of two skew lines (Δ,Λ-nomenclature)[21]. This proposal does not take account of the *meso* form or complexes with only one or more than two of these non-symmetric ligands. We propose a comprehensive nomenclature that describes the stereochemistry of the square-planar complexes *cis*-**2** by means of two equal axes of chirality: There are three perpendicular planes within the molecule (cf. Figure 5). The two perpendicular planes representing one axis are the square plane of the complex and the plane of one of the planar triazolinylidenes. One iodine atom and the carbene carbon atom at the opposite side of the molecule are the substituents of the first plane; the two nitrogen atoms neighboring the other carbene carbon are the substituents of the other plane. The priorities of the different substituents (**a**–**d**) can be assigned according to the CIP rules[22] (cf. Figure 5).

Figure 5. Nomenclature for *cis-anti*-(S_a,S_a)-**2**



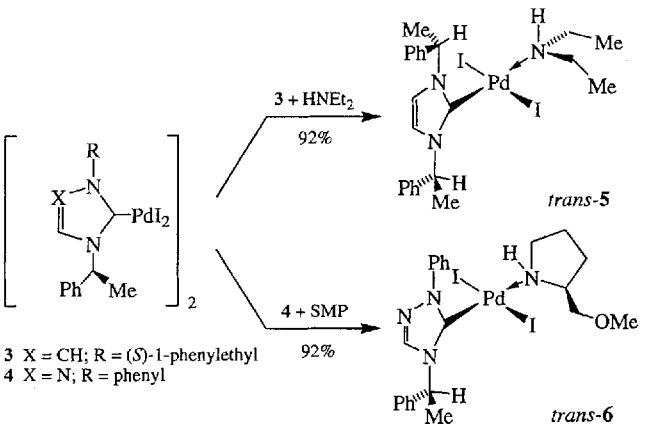
(S_a) (S_a)

If, in contrast to the aforementioned reaction, only one equiv. of the imidazolium or triazolium perchlorate is used, then Pd complexes with only one triazolinylidene ligand per palladium atom are formed as dark red solids. They are probably dinuclear complexes[23], examples of which with bridging halogen atoms and phosphane ligands instead of the carbenes are known in the literature[24].



3 X = CH; R = (*S*)-1-phenylethyl
4 X = N; R = phenyl

Lewis basic ligands, e.g. amines, phosphanes or other carbenes, can be added to these complexes[25]. Thus, the reaction of **3** and **4** with $HNEt_2$ and (*S*)-2-methoxymethylpyrrolidine (SMP), respectively, leads to the mononuclear (amino)(carbene)diiodopalladium(II) complexes *trans*-**5** and *trans*-**6** with chemical yields of 92%. Thereby further chirality information can be introduced by using a chiral amine, e.g. SMP in *trans*-**6**. Thus, the directed synthesis of catalysts with two different ligands can be performed.



3 X = CH; R = (*S*)-1-phenylethyl
4 X = N; R = phenyl

At the moment, we are investigating an enantioselective Heck-type reaction with the Pd(II) complexes as catalysts. However, only low asymmetric inductions have been realized so far (ee <8%). While usually the reduction to a Pd(0) species and the formation of elemental Pd are observed during the Heck reaction[26], it is possible to recycle the catalysts **1** and **2** after the reaction is completed. There might be a Pd(IV) intermediate involved in the catalytic cycle[27].

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Experimental

General: All solvents were dried and distilled before use. The imidazolium and triazolium perchlorates[3,28] and SMP[29] were prepared according to literature procedures. – Column chromatography: Merck silica gel 60, 0.040–0.063 mm (230–400 mesh) (flash). – Optical rotation value: Perkin-Elmer P 241, solvent UVASOL-quality. – Melting points (uncorrected): Büchi 510. – IR: Perkin-Elmer FT 1750. – NMR: Varian VXR 300 and Gemini 300 (300 and 75 MHz for ^1H and ^{13}C, respectively), Varian Unity 500 (500 MHz for ^1H), $CDCl_3$ as solvent, TMS as internal standard. – MS: Finnigan MAT (70 eV) and Finnigan SSQ 7000 (70 eV). – Elemental analyses (C, H, N): elementar vario EL.

1. General Procedure for the Preparation of the Dicarbenediiodopalladium(II) Complexes **1**, **2**: $Pd(OAc)_2$ (56 mg, 0.25 mmol), NaI (150 mg, 1.00 mmol), KO*t*Bu (87 mg, 0.80 mmol), and 0.75 mmol of the imidazolium perchlorate (283 mg) or triazolium perchlorate (262 mg) were dissolved in 20 ml of THF and the solution was stirred at room temperature for 1–5 h. The solution was evaporated to dryness in vacuo and the products were separated and purified by column chromatography (silica gel, Et_2O/hexane, 1:1).

(S)-Bis[1,3-bis(1-phenylethyl)-2,3-dihydro-1H-imidazol-2-ylidene]diiodopalladium(II) (**1**): After column chromatography, 203 mg (89%) of *trans*-**1** and 21 mg (9%) of *cis*-**1** were obtained.

trans-**1**: $[\alpha]_D^{25} = -206$ (0.10, $CHCl_3$). – M.p. 96°C. – IR (KBr): $\tilde{\nu} = 3060\ cm^{-1}$, 3020 (w), 2980, 2940 (m), 1600 (w), 1500 (m), 1450, 1420 (s), 1410, 1380 (m), 760 (w), 700 (s). – ^1H NMR (300 MHz): $\delta = 1.93$ (d, $^3J = 7.03$ Hz, 12H, $CHCH_3$), 6.61 (q, $^3J = 7.05$ Hz, 4H, $CHCH_3$), 6.60 (s, 4H, NCH), 7.26–7.40 (m, 12H, C_6H_5), 7.66 (m, 8H, C_6H_5). – ^{13}C NMR: $\delta = 20.2$ ($CHCH_3$), 58.5 ($CHCH_3$), 118.8 (NCH), 128.0, 128.6 (C_5H_5CR), 140.1 (C_5H_5CR), 166.8 (NCPd). – MS (70 eV); *m/z* (%): 912 (1.0) [M^+], 785 (7.5) [M^+ – I], 657 (2.5) [M^+ – 2 I], 381 (4.8), 277 (36.6); 171 (37.9), 105 (100.0). – $C_{38}H_{40}I_2N_4Pd$ (912.99): calcd. C 49.99, H 4.42, N 6.14; found C 49.89, H 4.55, N 5.89.

cis-**1**: $[\alpha]_D^{25} = -164$ (0.16, $CHCl_3$). – M.p. >220°C. – IR (KBr): $\tilde{\nu} = 3160\ cm^{-1}$, 3120, 3100, 3060 (w), 3020, 2980, 2930 (m), 1600, 1570 (w), 1500 (m), 1450, 1420, 1400, 1380 (s), 760 (m), 710, 700, 680 (s). – ^1H NMR (500 MHz): $\delta = 0.22$ (d, $^3J = 7.02$ Hz, 6H, $CHCH_3$), 1.74 (d, $^3J = 7.02$ Hz, 6H, $CHCH_3$), 5.23 (q, $^3J = 7.02$ Hz, 2H, $CHCH_3$), 6.49 (d, $^3J = 2.14$ Hz, 2H, NCH), 6.86 (m, 6H, C_6H_5), 7.11 (q, $^3J = 7.02$ Hz, 2H, $CHCH_3$), 7.25–7.31 (m, 10H, C_6H_5), 7.38 (d, $^3J = 2.13$ Hz, 2H, NCH), 7.53 (m, 4H, C_6H_5). – ^{13}C NMR: $\delta = 17.5$, 24.3 ($CHCH_3$), 57.9, 62.4 ($CHCH_3$), 118.6, 120.7 (NCH), 127.2, 127.8, 127.9, 128.0, 128.4, 128.9 (C_5H_5CR), 138.9, 140.4 (C_5H_5CR), 162.1 (NCPd). – MS (70 eV); *m/z* (%): 912 (1.0) [M^+], 785 (5.2) [M^+ – I], 657 (1.6) [M^+ – 2 I], 381 (4.0), 277 (27.6), 171 (36.3), 105 (100.0), 77 (20.2). – HR-MS; *m/z*: $C_{38}H_{40}IN_4Pd$ [M^+ – I]: calcd. 785.13317; found 758.13326. – $C_{38}H_{40}I_2N_4Pd$ (912.99): calcd. C 49.99, H 4.42, N 6.14; found C 49.42, H 4.52, N 5.84.

(S)-Bis[1-phenyl-4-(1-phenylethyl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene]diiodopalladium(II) (**2**): After column chromatography, 176 mg (82%) of *trans*-**2** and 17 mg (8%) of *cis*-**2** were obtained. *trans-anti*-**2** could be dissolved in Et_2O whereas *trans-syn*-**2** was not soluble in this solvent (*anti*/*syn*, 2.6:1). *trans-syn*-**2** was crystallized from a hexane/CH_2Cl_2 mixture. The three *cis* isomers could not be separated (*anti a*/*anti b*/*syn* 5:2.2:1, de (*anti*): 39%).

trans-syn-**2**: $[\alpha]_D^{25} = -76$ (0.11, $CHCl_3$). – M.p. >220°C. – IR (KBr): $\tilde{\nu} = 3120\ cm^{-1}$, 3060, 2980, 2940, 2880 (w), 1600 (m), 1540, 1500 (s), 1450, 1410 (m), 1380, 1350, 760, 710, 700 (s). – ^1H NMR (300 MHz): $\delta = 2.05$ (d, $^3J = 7.14$ Hz, 6H, $CHCH_3$), 6.75 (q, $^3J = 7.23$ Hz, 2H, $CHCH_3$), 7.36–7.50 (m, 12H, C_6H_5), 7.67 (m, 4H, C_6H_5), 7.82 (s, 2H, NCH), 8.00 (m, 4H, C_6H_5). – ^{13}C NMR: $\delta = 20.4$ ($CHCH_3$), 58.0 ($CHCH_3$), 124.9, 127.8, 128.5, 129.0, 129.1, 129.2 (C_5H_5CR), 138.3 (C_5H_5CR), 141.1 (NCH), 170.3 (NCPd). – MS (70 eV); *m/z* (%): 858 (<0.1) [M^+], 731 (0.6) [M^+ – I], 603 (0.3) [M^+ – 2 I], 354 (0.3), 105 (54.4), 103 (100.0), 77 (52.8). – HR-MS; *m/z*: $C_{32}H_{30}I_2N_6Pd$ [M^+]: calcd. 857.96554; found 857.96511. – $C_{32}H_{30}I_2N_6Pd$ (858.86): calcd. C 44.75, H 3.52, N 9.79; found C 44.70, H 3.58, N 9.78.

trans-anti-**2**: $[\alpha]_D^{25} = -130$ (0.11, $CHCl_3$). – M.p. 105°C. – IR (KBr): $\tilde{\nu} = 3120\ cm^{-1}$, 3050, 2970, 2930, 2880 (w), 1600, 1570 (m), 1500 (s), 1450, 1420, 1380, 1350 (m), 760, 710, 700 (s). – ^1H NMR (500 MHz): $\delta = 1.96$ (d, $^3J = 7.14$ Hz, 6H, $CHCH_3$), 6.45 (q, $^3J = 7.14$ Hz, 2H, $CHCH_3$), 7.30–7.50 (m, 12H, C_6H_5), 7.68 (m, 4H, C_6H_5), 7.80 (s, 2H, NCH), 8.22 (m, 4H, C_6H_5). – ^{13}C NMR: $\delta = 20.1$ ($CHCH_3$), 57.8 ($CHCH_3$), 125.2, 128.0, 128.5, 128.8, 129.0, 129.2 (C_5H_5CR), 138.0, 140.0 (C_5H_5CR), 141.1 (NCH), 171.0 (NCPd). – MS (70 eV); *m/z* (%): 858 (0.5) [M^+], 731 (4.9) [M^+ – I], 603 (2.7) [M^+ – 2 I], 354 (3.5), 249 (4.7), 248 (6.6), 145 (38.7), 105 (100.0), 77 (42.7). – $C_{32}H_{30}I_2N_6Pd$ (858.86): calcd. C 44.75, H 3.52, N 9.79; found C 44.54, H 3.59, N 9.71.

cis-**2**: $[\alpha]_D^{25} = -138$ (0.11, $CHCl_3$). – M.p. 64°C. – IR ($CHCl_3$): $\tilde{\nu} = 3120\ cm^{-1}$, 3060, 2980, 2940 (m), 1600, 1550, 1500, 1450, 1410, 1380, 1350, 760, 710, 700, 660 (s). – ^1H NMR (300 MHz): $\delta = 0.49$ (d, $^3J = 7.14$ Hz, 3H, $CHCH_3$ *syn*), 0.95 (d, $^3J = 7.14$ Hz, 6H, $CHCH_3$ *anti b*), 1.91 (d, $^3J = 7.14$ Hz, 6H, $CHCH_3$ *anti a*), 1.99 (d, $^3J = 7.14$ Hz, 3H, $CHCH_3$ *syn*), 3.75 (q, $^3J = 7.14$ Hz, 1H, CH_3CH *syn*), 5.56 (q, $^3J = 7.14$ Hz, 1H, CH_3CH *syn*), 5.67 (q, $^3J = 7.14$ Hz, 2H, CH_3CH *anti a*), 5.92 (q, $^3J = 7.14$ Hz, 2H, CH_3CH *anti b*), 6.51 (m, 4H, C_6H_5 *anti a*), 7.0–7.7 (m, C_6H_5 *anti*/*syn*), 7.77 (s, 2H, NCH *anti a*), 7.96 (s, 1H, NCH *syn*), 8.05 (s, 2H, NCH *anti b*), 8.45 (m, 4H, C_6H_5 *anti a*), 8.61 (s, 1H, NCH *syn*), 8.93 (m, 2H, C_6H_5 *anti a*). – ^{13}C NMR: $\delta = 19.6$ ($CHCH_3$ *anti a*), 20.8, 22.2 ($CHCH_3$ *anti b*, *syn*), 57.5 ($CHCH_3$ *anti a*), 58.8 ($CHCH_3$ *anti b*), 60.0 ($CHCH_3$ *syn*), 123.0, 123.7 (*anti a*), 124.2, 125.7 (*anti a*), 127.6, 128.5 (*anti a*), 128.6, 128.8, 128.9 (*anti a*), 129.1, 129.3, 129.5 (C_5H_5CR), 138.5, 138.8 (C_5H_5CR *anti a*), 141.6 (NCH *anti b*), 141.8 (NCH *anti a*), 167.9 (NCPd *anti a*). – MS (70 eV); *m/z* (%): 858 (0.5) [M^+], 731 (1.5) [M^+ – I], 603 (0.9) [M^+ – 2 I], 354 (4.0), 105 (100.0). – HR-MS; *m/z*: $C_{32}H_{30}IN_6Pd$ [M^+ – I]: calcd. 731.06106; found 731.06190. – $C_{32}H_{30}I_2N_6Pd$ (858.86): calcd. C 44.75, H 3.52, N 9.79; found C 44.61, H 3.57, N 9.69.

2. General Procedure for the Preparation of Dicarbenediiodo-μμ'-diiododipalladium(II) Complexes **3**, **4**: $Pd(OAc)_2$ (56 mg, 0.25 mmol), NaI (150 mg, 1.00 mmol), KO*t*Bu (33 mg, 0.30 mmol), and 0.25 mmol of the imidazolium perchlorate (94 mg) or triazolium perchlorate (87 mg) were dissolved in 20 ml of THF and the solution was stirred at room temperature for 1–5 h. It was evaporated to dryness in vacuo and the product was purified by column chromatography (silica gel, Et_2O/hexane, 1:1).

(S)-Bis[1,3-bis(1-phenylethyl)-2,3-dihydro-1H-imidazol-2-ylidene]diiodo-μμ'-diiododipalladium(II) (**3**): Yield: 149 mg (94%). – $[\alpha]_D^{25} = -230$ (0.09, $CHCl_3$). – M.p. 130°C. – IR (KBr): $\tilde{\nu} = 3160\ cm^{-1}$, 3140, 3080, 3060, 3020 (w), 2980, 2940 (m), 1600, 1560 (w), 1500, 1450, 1420, 1410, 1380 (s), 760 (m), 700, 680 (s). – ^1H NMR (300 MHz): $\delta = 1.92$ (br. d, $^3J = 7.05$ Hz, 12H, $CHCH_3$), 6.66 (br. d, $^3J = 2$ Hz, 2H, NCH), 6.74 (br. d, $^3J = 2$ Hz, 2H, NCH), 6.74 (q, $^3J = 7.39$ Hz, 2H, $CHCH_3$), 6.78 (q, $^3J = 6.72$ Hz, 2H, $CHCH_3$), 7.30–7.43 (m, 12H, C_6H_5), 7.52 (m, 4H, C_6H_5), 7.62 (m, 4H, C_6H_5). – ^{13}C NMR: $\delta = 20.3$, 20.6 ($CHCH_3$), 58.9, 59.4 ($CHCH_3$), 120.1, 120.3 (NCH), 127.6, 128.0, 128.3, 128.4, 128.6, 128.9 (C_5H_5CR), 138.9, 139.3 (C_5H_5CR), 152.7 (NCPd). –

$C_{38}H_{40}I_4N_4Pd_2$ (1273.22): calcd. C 35.85, H 3.17, N 4.40; found C 36.04, H 3.39, N 4.37.

(S)-Bis[1-phenyl-4-(1-phenylethyl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene]diiodo-μμ'-diiododipalladium(II) (**4**): Yield: 140 mg (92%). – $[\alpha]_D^{25} = -172$ (0.10, $CHCl_3$). – M.p. 120–122°C. – IR (KBr): $\tilde{\nu} = 3120\ cm^{-1}$, 3060, 3030, 2960, 2870 (w), 1600, 1530 (m), 1500 (s), 1450, 1380 (m), 760, 700 (s). – ^1H NMR (300 MHz): δ = 2.04 (br. d, $^3J = 6.86$ Hz, 3H, $CHCH_3$), 2.08 (br. d, $^3J = 7.14$ Hz, 3H, $CHCH_3$), 6.60–6.90 (m, 2H, $CHCH_3$), 7.40–7.60 (m, 16H, C_6H_5), 7.66–7.80 (m, 2H, NCH), 8.00–8.30 (m, 4H, C_6H_5). – ^{13}C NMR: δ = 20.6 ($CHCH_3$), 58.5, 59.4 ($CHCH_3$), 124.4–129.2 (C_5H_5CR), 138.9 (C_5H_5CR), 141.5, 142.0 (NCH), 161.7 (NCPd). – $C_{32}H_{30}I_4N_6Pd_2$ (1219.08): calcd. C 31.52, H 2.48, N 6.89; found C 31.18, H 2.46, N 6.79.

3. General Procedure for the Preparation of the (Amino)(carbene)-diiodopalladium(II) Complexes **5**, **6**: 0.1 mmol of **3** (127 mg) or **4** (122 mg) was dissolved in 10 ml of THF, and 0.12 mmol of the amine (9 mg, $HNEt_2$, 14 mg SMP) was added to the solution. This was stirred for 15 min at room temperature, then evaporated to dryness in vacuo and the product was purified by column chromatography (silica gel, Et_2O/hexane, 1:1).

trans-(S)-[1,3-Bis(1-phenylethyl)-2,3-dihydro-1H-imidazol-2-ylidene](diethylamino)diiodopalladium(II) (**5**): Yield: 131 mg (92%). – $[\alpha]_D^{25} = -122$ (0.15, $CHCl_3$). – M.p. 170°C. – IR ($CHCl_3$): $\tilde{\nu} = 3240\ cm^{-1}$, 3160, 3140, 3060 (w), 2980 (s), 2920, 2880 (m), 1600, 1500 (m), 1450, 1420, 1380, 760, 700, 690 (s). – ^1H NMR (300 MHz): δ = 1.52 (br. t, $^3J = 7.05$ Hz, 6H, CH_2CH_3), 1.98 (d, $^3J = 7.05$ Hz, 6H, $CHCH_3$), 2.86 (m, 2H, CH_2CH_3), 2.96 (m, 1H, NH), 3.29 (m, 2H, CH_2CH_3), 6.52 (q, $^3J = 7.48$ Hz, 2H, $CHCH_3$), 6.56 (s, 2H, *CHCH*), 7.29–7.41 (m, 6H, C_6H_5), 7.65 (m, 4H, C_6H_5). – ^{13}C NMR: δ = 15.4 (CH_2CH_3), 19.9 ($CHCH_3$), 48.5, 48.6 (CH_2CH_3), 58.6 ($CHCH_3$), 119.7 (*CHCH*), 128.1, 128.2, 128.6 (C_5H_5CR), 139.4 (C_5H_5CR), 147.5 (NCPd). – FAB-MS (70 eV); *m/z* (%). 709 (0.7) [M^+], 582 (12.8) [$M^+ - I$], 509 (5.3) [$M^+ - I - HNEt_2$], 381 (18.6), 277 (100.0), 171 (30.5). – $C_{23}H_{31}I_2N_3Pd$ (709.75): calcd. C 38.92, H 4.40, N 5.92; found C 38.92, H 4.47, N 5.69.

trans-(S,S)-Diiodo[2-(methoxymethyl)pyrrolidine][1-phenyl-4-(1-phenylethyl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene]palladium(II) (**6**): Yield: 133 mg (92%). – $[\alpha]_D^{25} = -78$ (0.10, $CHCl_3$). – M.p. 52–54°C. – IR (KBr): $\tilde{\nu} = 3210\ cm^{-1}$, 3120, 3060, 2980 (w), 2920, 2880, 1600, 1540 (m), 1500, 1460, 1420, 1380, 1110, 760, 700 (s). – ^1H NMR (300 MHz): δ = 1.62–1.86 (m, 4H, $NCH_2CH_2CH_2$), 2.13 (d, $^3J = 7.10$ Hz, 3H, $CHCH_3$), 3.11 (m, 1H, NCH_2), 3.22 (m, 1H, NCH_2), 3.36 (s, 3H, OCH_3), 3.52 (d/d, $^2J = 9.73$ Hz/$^3J = 2.01$ Hz, 1H, CH_2OCH_3, m, 1H, $NCHCH_2$), 3.75 (d/d, $^2J = 9.73$ Hz/$^3J = 2.01$ Hz, 1H, CH_2OCH_3), 3.80 (m, 1H, NH), 6.59 (q, $^3J = 7.05$ Hz, 1H, $CHCH_3$), 7.44 (m, 4H, C_6H_5), 7.53 (m, 2H, C_6H_5), 7.72 (m, 2H, C_6H_5), 7.84 (s, 1H, NCHN), 8.26 (m, 2H, C_6H_5). – ^{13}C NMR: δ = 20.2 ($CHCH_3$), 25.1 ($NCH_2CH_2CH_2$), 26.3 ($NCH_2CH_2CH_2$), 50.9 (NCH_2), 58.3, 59.1 ($NCHCH_2$, $CHCH_3$), 63.7 (OCH_3), 70.0 (CH_2OCH_3), 125.2, 128.0, 128.6, 128.9, 129.0, 129.1 (C_5H_5CR), 138.0, 139.8 (C_5H_5CR), 141.5 (NCHN), 157.3 (NCPd). – FAB-MS (70 eV); *m/z* (%): 725 (2.7) [M^+], 597 (57.3) [$M^+ - I$], 354 (18.8) [$M^+ - I$ – SMP], 250 (49.6), 116 (100.0), 114 (90.9). – $C_{22}H_{28}I_2N_4OPd$ (724.72): calcd. C 36.46, H 3.89, N 7.73; found C 36.18, H 3.89, N 7.46.

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