Diastereospecific Dimerization in Bridging Amido Complexes of Dipalladium

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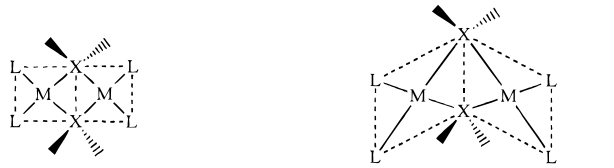
Summary: Chirality is conserved in the deprotonation of the complex $PdCl_2(\mathbf{L_a})$ *(*$\mathbf{L_a}$ *= 2-[(N-p-tolylamino)-methyl]pyridine;* ***1a****) leading to the folded diastereomer of* $[PdCl(\mu\text{-}L_a\text{-}H)]_2$ *(****2a****), where the p-tolyl groups are syn exo and the same enantiomer of* ***1a*** *shapes both halves of the amido-bridged dimer. The dimerization of different enantiomers of* ***1a*** *(R with S), which should lead to the achiral unfolded diastereomer of* ***2a*** *where p-tolyl groups would arrange anti, is not observed.*

The synthesis of alkylamido and arylamido complexes of the electron-rich late transition metals has recently attracted considerable attention, in part due to the nucleophilic nature of the metal−amido bond, able to promote addition reactions across unsaturated organic functional groups leading to C−N bond formation through catalytic or stoichiometric pathways.[1] In addition, single−electron oxidative reactions of arylamido complexes can lead to C−C couplings in the *para* position of the NPh rings as recently reported.[2] These findings and the apparent renaissance of interest about "nitrogen donors"[3] have prompted us to continue the search for new arylamido complexes.

In order to facilitate the synthesis of such compounds we have explored the bidentate, potentially chelating ligands 2-[[*N*-(aryl)amino]methyl]pyridine (aryl = *p*-tolyl, $\mathbf{L_a}$; *p*-MeOPh, $\mathbf{L_b}$). Coordination to the palladium through the pyridine nitrogen in the first step, followed by further treatment with a deprotonating agent, should lead to the expected Pd−N amido bond. However, one of the features of such a bond, when the metal is electron-rich, is the big tendency to form bridged dimeric amido compounds by using the nitrogen lone pairs which are not involved in π-donation.[1f,4] In the case that we present here, dimerization occurs with total isomeric diastereoselectivity, and the palladium−palladium distance observed, 2.875 Å, is to our knowledge the shortest length reported to date for a dimeric palladium complex with bridging amido ligands.

Chart 1



Planar dimers: Two isomers, *syn* and *anti*

Non-planar dimers: Three isomers, *syn endo, syn exo* and *anti*

Binuclear complexes of the platinum group metals with bridging ligands X (X = halide, RO^-, RS^-, R_2N^-, R_2P^-) can display both planar and nonplanar geometries as depicted in Chart 1, holding the square-planar coordination around each metal in both cases. Three geometric isomers (*syn endo*, *syn exo*, and *anti*)[5] can be anticipated for nonplanar complexes with the general formula $[L_2M(\mu\text{-}X)_2ML_2]$ where L is a monodentate (neutral or anionic) ligand, X has two different substituents or one lone pair and one substituent, and M is a d^8 transition metal. For the planar geometry only two isomers (*syn* and *anti*) can be expected.

The presence of isomers in such palladium dimers has been reported in solution although in every case only one of them has been characterized by X-ray diffraction.[1f,4c,6] Isomeric mixtures have also been reported as solids but without X-ray structural characterization.[4e]

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(4) (a) Kolel-Veetil, M. K.; Rahim, M.; Edwards, A. J.; Rheingold, A. L.; Ahmed, K. J. *Inorg. Chem.* **1992**, *31*, 3877. (b) Kolel-Veetil, M. K.; Rheingold, A. L.; Ahmed, K. J. *Organometallics* **1993**, *12*, 3439. (c) Ruiz, J.; Martínez, M. T.; Vicente, C.; García, G.; López, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1993**, *12*, 4321. (d) Kolel-Veetil, M. K.; Curley, J. F.; Yadav, P. R.; Ahmed, K. J. *Polyhedron* **1994**, *13*, 919. (e) Okeya, S.; Yoshimatsu, H.; Nakamura, Y.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 483.

(5) The terminology *syn*, *anti* indicates the relative position of the same substituents attached to the bridging X atoms. Considering the folded geometry as a roof with the summit defined by the bridging X atoms, *endo* indicates the same substituents attached to X pointing out downward from the roof and *exo* indicates pointing out upward of the roof.

(6) Usón, R.; Forniés, J.; Usón, M. A.; Tomás, M.; Ibáñez, M. A. *J. Chem. Soc., Dalton Trans.* **1994**, 401.

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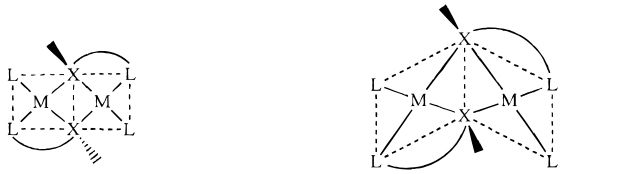
Chart 2



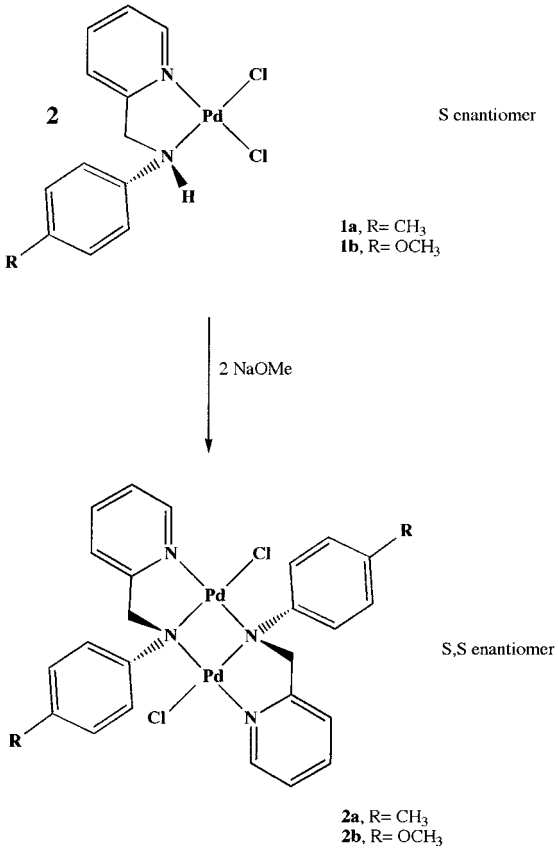
Planar dimers: One isomer, *anti* Non-planar dimers: One isomer, *syn exo*

Nevertheless, dimeric nonplanar arylamido complexes of iridium(I) give rise to pure samples both in solution and as solids.[4b] To date, only three X-ray structural characterizations have been reported of bis(μ-arylamido)palladium(II) complexes. In two cases planar isomers were obtained,[1f] and the third one is a nonplanar example[4c] with the palladium−palladium distances ranging between 3.05 and 3.19 Å. However, not one of these three structures involves the bridging amido atom in a chelate ligand.

As depicted in Chart 2, the number of possible isomers is drastically reduced when the bridge donor atom X is attached to one of the terminal ligands L, thus leading to only two structural possibilities, one folded and one planar. Furthermore, the planar centrosymmetric diastereomer (*meso*) has to be *anti* and the nonplanar chiral diastereomer (racemic) has to be *syn exo*. The syntheses of secondary amines $\mathbf{L_a}$ and $\mathbf{L_b}$ were carried out by simple condensation of 2-pyridinecarbaldehyde with the appropriate arylamine and further treatment of the resulting imine with Na[BH_4]. Treatment of these ligands with methanolic solutions of $Li_2[PdCl_4]$ at room temperature afforded compounds of general formula [$PdCl_2$(L)] (**1**) with L acting as chelate ligands. The ligands and complexes gave satisfactory elemental analysis.

Mononuclear complexes **1** are chiral and have always been obtained as racemates (R + S). Treatment of solutions of **1** in dimethyl sulfoxide with NaOMe in methanol at room temperature afforded the chiral nonplanar (*syn exo*) *rac* diastereomer amido complex **2** indicated in Scheme 1, where only the reaction for dimerization of the *S* enantiomer has been represented. Obviously, the enantiomer *R* dimerizes in the same way, leading to the (*R*,*R*) dimer, which is not represented in Scheme 1. The complete absence of the *meso* diastereomer (*R*,*S*) indicated that the dimerization reaction between different enantiomers had been precluded in some way, accounting for the observed diastereospecificity. The origin of this isomeric preference is not obvious from molecular models, which apparently show the same probability toward formation of both diastereomers. On the other hand, MO calculations such as those recently reported for edge-sharing planar dimers of square-planar complexes,[7] have not been reported for nonplanar isomers and, thus, energetics cannot currently be invoked to explain the preference for the hinged structure. The folding could also arise from steric hindrance imposed by the chelate ring, but since a nonplanar dimer containing only monodentate ligands has been reported,[4c] other subtle factors can be driving the folding as indicated for structurally related μ-dithiolato dimers of nickel.[8] In order to obtain a proper answer to the questions arising from this result, more structurally related data need to be accumulated.

Scheme 1



Whereas the formation of only one diastereomer in the dimerization reaction had been clearly revealed by ^{1}H NMR, an X-ray structural characterization[9] had to be carried out in order to establish whether the *rac* or the *meso* isomer had been formed. A thermal ellipsoid plot of **2a** is found in Figure 1. The crystal structure confirms the stereochemistry of **2a** and consists of disymmetric dimers with 2-fold rotational symmetry with the axis of rotation perpendicular to the Pd−Pd line. Both enantiomers (*R*,*R*) and (*S*,*S*) are packed together in the triclinic unit cell, related by the center of symmetry. The Pd−Pd′ distance is 2.875(1) Å, shorter than those observed in the three cases reported of μ-arylamido bridged dipalladium dimers and ranging between 3.05 and 3.190 Å.[1f,4c] The *p*-tolyl groups are in the *syn exo* configuration. The geometry about each metal center is significantly deviated from planarity. The average folding angle between the "pseudo square planes" defined by palladium atoms is 135.25(6)°. Other bond lengths and angles fall within expected ranges.

Experimental Section

$\mathbf{L_a}$ and $\mathbf{L_b}$. These secondary aromatic amines were prepared by initial condensation of 2-pyridinecarbaldehyde with

(7) Aullón, G.; Alemany, P.; Alvarez, S. *J. Organomet. Chem.* **1994**, 75.

(8) Colpas, G. J.; Kumar, M.; Day, R. O.; Maroney, M. J. *Inorg. Chem.* **1990**, 4779.

(9) Crystal data for **2a**: $C_{26}H_{26}Cl_2N_4Pd_2$, M = 678.22, triclinic, space group P, a = 9.142(1) Å, b = 9.259(3) Å, c = 15.442(4) Å, α = 94.80(2)°, β = 98.86(1)°, γ = 103.97(2)°, V = 1243.3(5) Å^3, Z = 2. A total of 308 parameters refined to R = 0.023 (R_w = 0.026) for 3810 reflections with $I \geq 3\sigma(I)$.

(10) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, E., Ed.; Clarendon Press: Oxford, England, 1982; p 528.

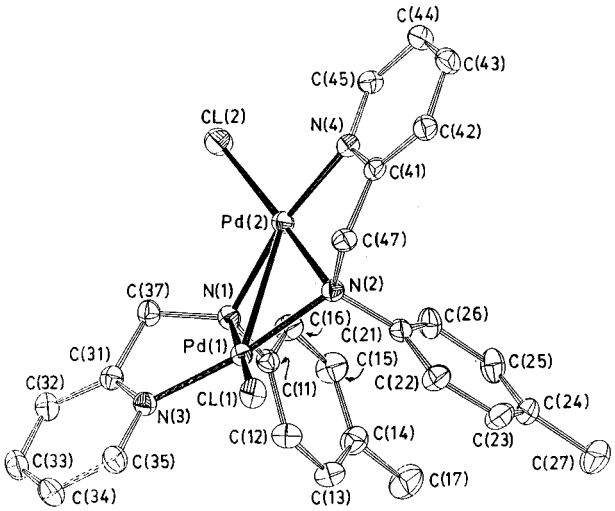


Figure 1. Perspective view (EUCLID Package)[10] of one of the enantiomers (*S*,*S*) of compound **2a**.

the appropriate amine to yield the related imine and further hydrogenation of the imine with Na[BH_4] following cognate experimental procedures.[11] $\mathbf{L_b}$: ^{1}H NMR (80 MHz, $CDCl_3$, 25 °C, TMS) δ 2.23 (s, 3H, CH_3), 4.45 (s, 2H, CH_2), 6.79 (m, 4H, *p*-C_6H_4), 7.47 (m, 3H, C_5H_4N), 8.58 (m, 1H, C_5H_4N); IR (KBr) $\tilde{\nu} = 3302$ cm^{-1} (N−H). Anal. Calcd (found): C, 78.75 (78.88); H, 7.12 (7.10); N, 14.13 (14.02). $\mathbf{L_b}$: ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 3H, OCH_3), 4.43 (s, 2H, CH_2), 6.71 (m, 4H, *p*-C_6H_4), 7.43 (m, 3H, C_5H_4N), 8.58 (m, 1H, C_5H_4N); IR (KBr $\tilde{\nu} = 3279$ cm^{-1} (N−H). Anal. Calcd (found): C, 72.87 (72.49); H, 6.59 (6.62); N, 13.07 (12.92).

1a and 1b. The same procedure was used for the synthesis of both complexes, and that for **1a** is described below.

(11) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Longman S&T: New York, 1989; p 905.

To a cooled and filtered solution of $Li_2[PdCl_4]$, obtained by treatment of $PdCl_2$ (0.4 g, 2.26 mmol) with LiCl (0.48 g, 4.52 mmol) in hot methanol, was slowly added $\mathbf{L_a}$ (0.48 g, 2.26 mmol). A microcrystalline orange compound was formed: yield, 0.72 g (82%); ^{1}H NMR (DMSO-d_6) δ 2.23 (s, 3H, CH_3), 4.62 (m, 2H, CH_2), 7.63 (m, 4H, *p*-C_6H_4), 7.94 (m, 3H, C_5H_4N), 8.75 (m, 2H, C_5H_4N and NH); IR (KBr, cm^{-1}) $\tilde{\nu} = 3197$ (N−H), 351 and 332 (Pd−Cl). Anal. Calcd (found): C, 41.58 (41.65); H, 3.76 (3.76); N, 7.46 (7.34). **1b**: ^{1}H NMR (DMSO-d_6) δ 3.71 (s, 3H, CH_3), 4.65 (m, 2H, CH_2), 6.97 (m, 4H, *p*-C_6H_4), 7.90 (m, 3H, C_5H_4N), 8.72 (m, 2H, C_5H_4N and NH); IR (KBr, cm^{-1}); $\tilde{\nu} = 3195$ (N−H), 338 and 330 (Pd−Cl). Anal. Calcd (found): C, 39.88 (39.37); H, 3.60 (3.60); N, 7.15 (7.01).

2a and 2b. The procedure for the synthesis of **2a** is described below. **2b** was prepared in the same way.

To a solution of **1a** (0.2 g, 0.533 mmol) in dimethyl sulfoxide (1 mL) was added sodium methoxide (0.95 mL of a 0.562 M solution in methanol). Methanol (20 mL) was added, and an orange microcrystalline solid was obtained. The product was washed with methanol (50 mL) and diethyl ether (50 mL): yield 0.135 g (75%); ^{1}H NMR (DMSO-d_6) δ 2.13 (s, 3H, CH_3), 4.47 (m, 2H, CH_2), 7.26 (m, 4H, *p*-C_6H_4), 7.39 (m, 3H, C_5H_4N), 8.63 (m, 1H, C_5H_4N); IR (KBr, cm^{-1}) $\tilde{\nu} = 332$ (Pd−Cl). Anal. Calcd (found): C, 46.05 (46.19); H, 3.86 (3.92); N, 8.26 (8.11). **2b**: ^{1}H NMR (DMSO-d_6) δ 3.67 (s, 3H, CH_3), 4.75 (m, 2H, CH_2), 7.17 (m, 4H, *p*-C_6H_4), 7.41 (m, 3H, C_5H_4N), 8.64 (m, 1H, C_5H_4N); IR (KBr, cm^{-1}) $\tilde{\nu} = 339$ (Pd−Cl). Anal. Calcd (found): C, 43.97 (43.26); H, 3.69 (3.79); N, 7.89 (7.40).

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Supporting Information Available: Tables of crystallographic data for **2a** (13 pages). Ordering information is given on any current masthead page.

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