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Searching for Precursors to Metal–Metal Bonded Dipalladium Species: A Study of Pd_2^{4+} Complexes

John F. Berry, F. Albert Cotton,* Sergey A. Ibragimov, Carlos A. Murillo,* and Xiaoping Wang

Department of Chemistry and Laboratory for Molecular Structure and Bonding, P.O. Box 30012,
Texas A & M University, College Station, Texas 77842-3012

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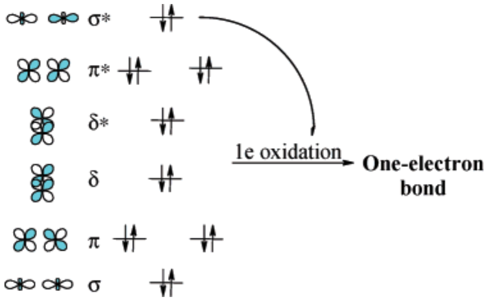
Reactions of $Pd_3(OAc)_6$ with lithium salts of mononegative bidentate N,N-ligands, L, of various types, such as formamidinates, benzamidinates, triazinates, and guanidinates, were investigated in a search for ways to obtain Pd_2^{4+} compounds that could serve as precursors to paddlewheel complexes with a metal–metal bond and a Pd_2^{5+} core. It was found that the reactions are complex and that either square planar mononuclear or dinuclear species may be formed depending on the reaction conditions or the method of isolation. For Pd_2L_4 compounds, α and β isomers were sometimes obtainable. In the α isomer, all N,N-ligands serve as bridges, whereas in the β isomer, two ligands bridge the Pd_2^{4+} unit and each of the other two chelate to a metal atom. Electrochemistry shows that the paddlewheel compounds $Pd_2(TolNC(H)NTol)_4$, $Pd_2(PhNC(Ph)NPh)_4$, and $Pd_2(PhNC(Ph)NPh)_3(OAc)$ and the orthometalated complex *cis*-$Pd_2[\eta^2\text{-}C_6H_4NC(Ph)N(H)Ph]_2(\mu\text{-}OAc)_2$ have reversible oxidation waves between 0.70 and 0.92 V vs Ag/AgCl, which makes them good candidates for chemical oxidation.

Introduction

Palladium and its complexes are widely used in catalysis,[1] medicine,[2] and many other fields of research such as H_2 storage[3] and thin film deposition.[4] The divalent state is the most common, and the electron configuration produces almost invariably square planar complexes.[5]

Scheme 1



This research group has been interested in transition-metal compounds containing metal−metal bonds. Although an enormous variety of dimetal compounds with metal−metal bonds has been described in the literature,[6] dipalladium compounds are very scarce. A generalized molecular orbital diagram for D_{4h} compounds containing bonded pairs of metal atoms is shown on the left of Scheme 1, where it can be seen that, for elements with d^8 configurations of the M_2^{n+} core, both bonding and antibonding orbitals are filled, leading to an M−M bond order of zero. Therefore, it is necessary

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* To whom correspondence should be addressed. E-mail: cotton@tamu.edu (F.A.C.); murillo@tamu.edu (C.A.M.).

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Table 1. Interpalladium Separations in Some Pd_2L_4 Paddlewheel Compounds

compound	distance (Å)	ref
$Pd_2(DTolF)_4$	2.622(3)	8
$Pd_2(DPhBz)_4$	2.576(1)	9
$Pd_2(hpp)_4$	2.555(1)	7
$Pd_2(dtpa)_4$ (dtpa = $C_6H_5CH_2CS_2^-$)	2.715(3)	13
$Pd_2(dta)_4$ (dta = $CH_3CS_2^-$)	2.738(1)	14
cis-$Pd_2(mhp)_4$ [mhp = (6-methyl-2-oxypyridine)]	2.559(3)	15
trans-$Pd_2(mhp)_4$	2.547(6)	15
$Pd_2(chp)_4$ [chp = (6-chloro-2-oxypyridine)]	2.563(1)	15
$Pd_2(DPhTA)_4$ (DPhTA = 1,3-diphenyltriazene)	2.5626(7)	16
$Pd_2(bttz)_4$ [bttz = tetrakis(μ-1,3-benzothiazole-2-thiolato-*N*,*S*)]	2.745(1)	17

to look to higher oxidation states to find metal−metal bonds in paddlewheel complexes.

Up to now, there has been only one dipalladium paddlewheel compound known with an unequivocal metal−metal single bond.[7] This $Pd_2(hpp)_4Cl_2$ compound (where hpp is the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2*a*]pyrimidine) was prepared almost a decade ago. Four hpp ligands are embracing the singly bonded Pd_2^{6+} unit, and the molecule possesses 4-fold symmetry. The two chlorine atoms are located in axial positions on the 4-fold axis. This molecule was obtained by oxidation of $Pd_2(hpp)_4$ with several oxidizing agents. Two other binuclear dipalladium compounds with presumed bond orders of $^1/_2$ between the palladium atoms have also been described; they have Pd_2^{5+} cores.[8,9] Oxidation of $Pd_2(DTolF)_4$ (DTolF = *N*,*N*′-di-*p*-tolylformamidinate) with 1.6 equiv of $AgPF_6$[8] gave $Pd_2(DTolF)_4PF_6$. The metal−metal distance in the oxidized compound did not differ significantly from that in the Pd_2^{4+} precursor, which does not have a Pd−Pd bond. Because oxidation is expected to give rise to a bond within the Pd_2^{5+} unit, shortening of the metal−metal distance might have been expected. However, there is also an increase in electrostatic repulsion between the two positively charged metal atoms which may explain the invariance in bond distance, as has been observed before in some dirhenium[10] and ditechnetium[11] compounds. Calculations done for the oxidized species suggest that the unpaired electron resides mainly in a metal-based orbital, but an EPR spectrum of the $Pd_2(DTolF)_4^+$ species showed only one isotropic peak, suggesting that perhaps the unpaired electron is ligand-based rather than metal-based.

Bear and co-workers[9] synthesized and structurally characterized two Pd_2^{4+} isomers containing four DPhBz ligands (DPhBz = the anion of *N*,*N*′-diphenylbenzamidine). One was shown to be the α isomer where all four ligands bridge the dimetal unit to form a paddlewheel. In the β isomer, there are two bridging and two chelating ligands. Electrochemical oxidation of the α isomer, followed by an EPR spectrum of the singly oxidized species, revealed anisotropy of the *g*-value and hyperfine splitting of the signal consistent with the nuclear spin of $^5/_2$ of the ^{105}Pd isotope, which suggest that the unpaired electron is in the dimetal unit. It is important to note, however, that no direct structural evidence for the presence of an α-$Pd_2(DPhBz)_4^+$ species was provided.

As the above summary shows, information about compounds containing palladium−palladium bonds is fragmentary and somewhat contradictory. It is a goal of our research group to explore bond formation (if any) between two palladium atoms in compounds with the general formula $Pd_2L_4^+$ (where L is a bidentate-bridging, singly charged anionic ligand). The strategy that we shall employ, which is similar to that used in previous work,[7−9] is schematically shown in Scheme 1. Starting with Pd_2L_4 paddlewheel compounds, one electron will be removed from an antibonding molecular orbital by chemical oxidation. This should lead (if oxidation occurs from a mainly metal-based molecular orbital) to the formation of a net one-electron metal−metal bond.[12]

A first stage in the present work is to identify new precursors to metal−metal bonded dipalladium species, thereby expanding the limited pool for which structures are available (see Table 1).[7−9,13−17] In this report, we describe optimized syntheses for seven Pd_2^{4+} compounds and one mononuclear compound. We have focused our attention on the ligands shown in Scheme 2, where the abbreviations used for the ligands are also defined. We note also that Bear and co-workers[9] have mentioned some species that they made but were not able to characterize unambiguously while preparing $Pd_2(DPhBz)_4$ and $Pd_2(\mu\text{-DPhBz})_2(\eta^2\text{-DPhBz})_2$. Therefore, we also re-examined more thoroughly the Pd^{2+}/$DPhBz^-$ system. Numerically, the compounds described here

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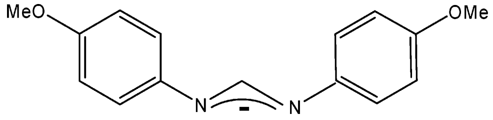
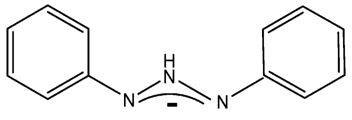
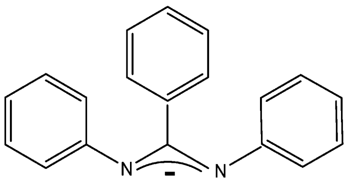
Scheme 2



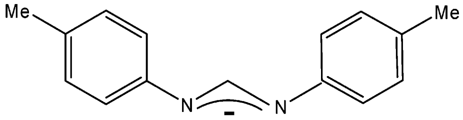
N,*N*′-di-*p*-anisylformamidinate (DAniF)



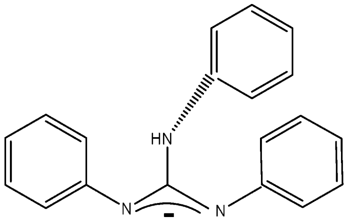
N,*N*′-diphenyltriazene (DPhTA)



N,*N*′-diphenylbenzamidinate (DPhBz)



N,*N*′-di-*p*-tolylformamidinate (DTolF)



N,*N*′,*N*″-triphenylguanidinate (TPG)

are α-$Pd_2(DAniF)_4$ (**1**), *β*-$Pd_2(TPG)_2(\eta^2\text{-}TPG)_2$ (**2**), α-$Pd_2(DPhTA)_4$ (**3**), $Pd(DPhBz)_2$ (**4**), *β*-$Pd_2(DPhBz)_2(\eta^2\text{-}DPhBz)_2$ (**5**), $Pd_2(DPhBz)_3(OAc)$ (**6**), α-$Pd_2(DPhBz)_4$ (**7**), and *cis*-$Pd_2[\eta^2\text{-}C_6H_4NC(PH)N(H)Ph]_2(\mu\text{-}OAc)_2$ (**8**). The structures of **3**,[16] **5**,[9] and **7**[9] have been described earlier, and the rest are given here along with electrochemical data for all compounds to help in the evaluation of the best candidates for chemical oxidation, which will be carried out in a separate study.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of dry nitrogen gas using standard Schlenk techniques, unless otherwise specified. Solvents were either distilled over appropriate drying agents in a nitrogen atmosphere or purified using a Glass Contour solvent system. The organic amines *N*,*N*′,*N*″-triphenylguanidine (HTPG) and *N*,*N*′-diphenyltriazine (HDPhTA) were purchased from TCI and Acros, respectively, and used as received. The formamidine[18] *N*,*N*′-di-*p*-anisylformamidine (HDAniF) and the benzamidine *N*,*N*-diphenylbenzamidine[19] (HDPhBz) were synthesized according to published procedures. Palladium acetate was either purchased from Aldrich or was synthesized from $PdCl_2$.[20] A new procedure used for the synthesis of $Pd_2(DPhTA)_4$ is given below.[21]

Physical Measurements. The IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets. Cyclic voltammograms were measured on a CH Instruments electrochemical analyzer using dichloromethane solutions with 1 M NBu_4PF_6 and 0.1 mM analyte; the electrodes were Pt disk (working), Pt wire (auxiliary), and Ag/AgCl (reference). The redox couple for ferrocene/ferrocenium consistently appeared at +450 mV under these conditions. Elemental analyses were carried out by Canadian Microanalytical Services in British Columbia, Canada. Samples were vacuum-dried prior to elemental analyses to remove the interstitial solvent molecules of the crystals. ^1H and ^{13}C NMR spectra were obtained on VXR-300 and VXR-500 NMR spectrometers. Mass spectrometry data (electrospray ionization) were recorded in the Laboratory for Biological Mass Spectrometry at Texas A & M University, College Station, Texas, using an MDS Series Qstar Pulsar with a spray voltage of 5 keV. Visible spectra were obtained on either a Shimadzu UV-2501 PC spectrophotometer or a Cary 17D spectrophotometer.

Synthesis of α-$Pd_2(DAniF)_4$, 1. To a solution of $Pd_3(OAc)_6$ (300 mg, 0.446 mmol, 1.34 mmol of Pd^{2+}) in 20 mL of THF was added LiDAniF dissolved in 20 mL of THF. The latter was prepared in situ by deprotonation of HDAniF (686 mg, 2.68 mmol) with a 1.6 M solution of Bu^nLi in *n*-hexane (1.68 mL, 2.7 mmol). The solution was stirred overnight at room temperature. The solvent was then removed under vacuum. The resulting orange solid was washed several times with water and dried under vacuum with a yield of 0.759 g (92%). X-ray quality crystals were grown by dissolving $Pd_2(DAniF)_4$ in 10 mL of CH_2Cl_2 and layering with 45 mL of hexane. Anal. Calcd for $C_{60}H_{60}N_8O_8Pd_2$: C, 58.44; H, 4.87; N, 9.09. Found: C, 58.35; H, 4.85; N, 9.11. ^1H NMR ($CDCl_3$, 300 MHz; δ, ppm): 3.767 (s, OCH_3, 6H), 6.674−6.865 (m, aromatic, 8H), 7.035 (s, CH, 1H). IR (KBr, cm^{-1}): 2948 (w), 2832 (w), 1618 (s), 1695 (m), 1499 (vs), 1459 (w), 1438 (w), 1345 (w), 1295 (w), 1243 (s), 1222 (s), 1179 (w), 1108 (w), 1035 (m), 968 (w), 828 (m), 766 (w). ESI+ mass spectrum (*m*/*z*, amu): 1232, M^+. UV−vis (CH_2Cl_2 solution; λ, nm; ϵ, $M^{-1}cm^{-1}$): 494, 2×10^3.

Synthesis of *β*-$Pd_2(TPG)_2(\eta^2\text{-}TPG)_2$, 2. To a solution of $Pd_3(OAc)_6$ (300 mg, 0.446 mmol, 1.34 mmol of Pd^{2+}) in 20 mL of THF was added LiTPG dissolved in 20 mL of THF. The latter was prepared in situ by deprotonation of HTPG (769 mg, 2.68 mmol) with a 1.6 M solution of Bu^nLi in *n*-hexane (1.68 mL, 2.7 mmol). After the reaction mixture was stirred overnight at room temperature, the solvent was removed under vacuum. The resulting orange solid was washed several times with water and dried under vacuum with a yield of 0.799 g (88%). X-ray quality crystals were grown by dissolving $Pd_2(\mu\text{-}TPG)_2(\eta^2\text{-}TPG)_2$ in 8 mL of CH_2Cl_2 and layering with 47 mL of hexane. Anal. Calcd for $C_{76}H_{66}N_{12}OPd_2$: C, 66.33; H, 4.83; N, 12.21. Found: C, 66.34; H, 4.87; N, 12.06. ^1H NMR (C_6D_6, 300 MHz; δ, ppm): 5.461 (s, NH, 1H), 5.638 (d, aromatic, 2H), 5.887 (s, NH, 1H), 6.4−7.1 (m, aromatic, 28H). IR (KBr, cm^{-1}): 3393 (w), 3054 (w), 1602 (m), 1592 (m), 1540 (vs), 1472 (s), 1443 (m), 1423 (s), 1396 (m), 1380 (s), 1307 (m), 1278 (w), 1263 (m), 1247 (w), 1206 (w), 1173 (w), 1074 (w), 1027 (w), 922 (w), 774 (w), 754 (m), 747 (m), 733 (w), 691 (m),

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518 (vw), 483 (vw). UV−vis ($CHCl_3$ solution; λ, nm; ϵ, $M^{-1}cm^{-1}$): 485, 2×10^3; 392, 3×10^3.

Synthesis of α-$Pd_2(DPhTA)_4$, 3. To a solution of $Pd_3(OAc)_6$ (300 mg, 0.446 mmol, 1.34 mmol of Pd^{2+}) in 20 mL of THF was added LiDPhTA dissolved in 20 mL of THF. The latter was prepared in situ by deprotonation of HDPhTA (528 mg, 2.68 mmol) with a 1.6 M solution of Bu^nLi in *n*-hexane (1.68 mL, 2.7 mmol). The solution was stirred overnight at room temperature, and the solvent was then removed under vacuum. The reddish-brown residue was washed several times with methanol and had a yield of 0.460 g (69%). ^1H NMR ($CDCl_3$, 300 MHz; δ, ppm): 7.051 (t, 1H), 7.154 (t, 2H), 7.572 (d, 2H). IR (KBr, cm^{-1}): 1593 (m), 1483 (m), 1456 (w), 1400 (vs), 1330 (vw), 1292 (vw), 1267 (vw), 1226 (vw), 1211 (m), 1167 (w), 1076 (vw), 1024 (vw), 953 (vw), 902 (vw), 826 (vw), 759 (s), 697 (s), 662 (m), 522 (w), 502 (w). UV−vis ($CHCl_3$ solution; λ, nm; ϵ, $M^{-1}cm^{-1}$): 574, 5×10^3.

Synthesis of $Pd(DPhBz)_2$, 4. To a solution of HDPhBz (729 mg, 2.67 mmol) in 20 mL of toluene was added a 1.6 M solution of Bu^nLi in *n*-hexane (1.68 mL, 2.7 mmol). The mixture was stirred at room temperature for 10 min, and then, it was added to a solution of $Pd_3(OAc)_6$ (300 mg, 0.446 mmol, 1.34 mmol of Pd^{2+}) in 20 mL of toluene. The mixture was stirred overnight at room temperature, resulting in a dark red solution and a dark red precipitate. After removal of the solvent under vacuum, the residue was washed first with 2 × 25 mL of water and then with 2 × 10 mL of ether, leaving a bright red product that was analytically pure as shown by NMR in a yield of 0.648 g (74%). ^1H NMR ($CDCl_3$, 300 MHz; δ, ppm): 6.401 (m, 4H), 6.856 (m, 6H), 6.993 (d, 2H), 7.113 (t, 2H), 7.226 (t, 1H). ^{13}C NMR ($CDCl_3$; δ, ppm): 123.0, 125.1, 128.4, 128.4, 129.3, 129.9, 131.5, 144.4 (all aromatic). IR (KBr, cm^{-1}): 3057 (vw), 1592 (m), 1581 (m), 1494 (vs), 1477 (s), 1433 (s), 1298 (w), 1274 (w), 1211 (w), 1170 (w), 1072 (w), 1025 (w), 958 (w), 794 (w), 777 (w), 706 (m), 693 (m), 499 (w). ESI+ mass spectrum (*m*/*z*): 699 (M^+). UV−vis (λ, nm; ϵ, $M^{-1}cm^{-1}$): 378 nm, 2×10^5; 496 nm, 2×10^3.

Synthesis of β-$Pd_2(DPhBz)_2(\eta^2\text{-}DPhBz)_2$, 5. A solution containing 100 mg of $Pd(DPhBz)_2$ in 50 mL of methanol was heated to reflux for 30 min. The color of the solution darkened, and a small amount of palladium metal was observed. Prolonged heating was avoided to prevent further decomposition. The solvent was removed, and the residue was extracted with 15 mL of CH_2Cl_2. To this extract was added 15 mL of hexanes, and the mixture was separated on a silica gel column using a 1:1 mixture of CH_2Cl_2 and hexanes. The first bright orange band corresponded to β-$Pd_2(DPhBz)_2(\eta^2\text{-}DPhBz)_2$. Removal of the solvent gave a bright orange powder in a yield of 0.020 g (40%). ^1H NMR (22 °C; $CDCl_3$, 300 MHz; δ, ppm): 5.915 (d), 6.138 (d), 6.338 (d), 6.558 (d), 6.629−7.036 (m), 6.729−7.036 (m), 7.141 (t). ^1H NMR (−45 °C; $CDCl_3$, 300 MHz; δ, ppm): 5.712 (d), 5.951 (d), 6.048 (d), 6.195 (t), 6.355 (d), 6.474 (t), 6.614−6.949 (t), 7.024 (t), 7.166 (t), 7.522 (t), 7.695 (d), 8.081 (d). ^{13}C NMR ($CDCl_3$; δ, ppm): 122.1, 122.5, 122.6, 123.0, 125.3, 125.9, 126.9, 127.1, 127.3, 128.1, 128.2, 128.4, 129.3, 130.6, 131.2, 131.4, 132.2, 136.027, 146.1, 146.5, 150.1, 152.1, 152.7, 170.0, 174.6. IR (KBr, cm^{-1}): 1655 (vs), 1638 (s), 1561 (s), 1542 (vs), 1508 (m), 1492 (m), 1432 (w), 1263 (w), 1210 (w), 1027 (w), 793 (w), 695 (m). ESI+ mass spectrum (*m*/*z*): 1298 (M+). UV−vis (λ, nm; ϵ, $M^{-1}cm^{-1}$): 486, 8×10^3.

Synthesis of $Pd_2(DPhBz)_3(OAc)$, 6. To a solution of HDPhBz (729 mg, 2.68 mmol) in 25 mL of CH_2Cl_2 was added a 1.6 M solution of Bu^nLi in *n*-hexane (1.67 mL, 2.68 mmol) at 0 °C, and then the mixture was allowed to reach room temperature. This was added to a solution of $Pd_3(OAc)_6$ (300 mg, 0.450 mmol) in 25 mL of CH_2Cl_2. The mixture was stirred overnight at room temperature, resulting in a dark red solution. The solvent was removed under vacuum, and the dark red residue was washed with 40 mL of MeOH and dried under vacuum with a yield of 0.752 g (75%). ^1H NMR ($CDCl_3$, 300 MHz; δ, ppm): 1.946 (s, OCH_3, 3H), 6.486-7.270 (m, aromatic, 45H). ^{13}C NMR ($CDCl_3$, 300 MHz; δ, ppm): 25.0, 122.8, 123.1, 127.4, 127.7, 127.589, 128.0, 128.4, 131.2, 131.9, 135.6, 135.7, 151.9, 171.8, 172.1, 184.5. IR (KBr, cm^{-1}): 1655 (w), 1580 (vs), 1543 (vw), 1500 (s), 1483 (w), 1440 (m), 1408 (w), 1265 (m), 1215 (m), 1074 (vw), 1026 (vw), 792 (m), 695 (s), 513 (vw). ESI+ mass spectrum (*m*/*z*): 1086 (M+). UV−vis (λ, nm; ϵ, $M^{-1}cm^{-1}$): 550 (very broad).

Synthesis of α-$Pd_2(DPhBz)_4$, 7. A round-bottomed flask was charged with $Pd_3(OAc)_6$ (100 mg, 0.45 mmol), HDPhBz (607 mg, 2.23 mmol), Et_3N (1 mL), and 40 mL of THF. The mixture was refluxed in air for 3.5 h. After the removal of THF under vacuum, the residue was dissolved in CH_2Cl_2. The mixture was separated by chromatography on a TLC plate. The first bright orange band was collected, and a yield of 0.035 g (30%) was obtained. ^1H NMR (22 °C; $CDCl_3$, 500 MHz; δ, ppm): 6.239 (br, 8H), 6.381 (br, 8H), 6.649−6.752 (m, 20H), 6.786 (br, 16H), 7.046 (br, 8H). ^1H NMR (−45 °C; $CDCl_3$, 300 MHz; δ, ppm): 6.215 (br, 8H), 6.456 (br, 8H), 6.685−6.837 (m, 20H), 6.894 (br, 16H), 7.147 (br, 8H). ^1H NMR (+45 °C; $CDCl_3$, 300 MHz; δ, ppm): 6.402 (br, 16H), 6.742−6.830 (m, 20H), 6.900 (br, 16H), 7.100 (br, 8H). ESI+ mass spectrum (*m*/*z*): 1086 (M+). UV−vis (λ, nm; ϵ, $M^{-1}cm^{-1}$): 500, 398, 350.

Synthesis of *cis*-$Pd_2[\eta^2\text{-}C_6H_4NC(Ph)N(H)Ph]_2(\mu\text{-}OAc)_2$, 8. To a solution of HDPhBz (729 mg, 2.68 mmol) in 25 mL of CH_2Cl_2 was added a 1.6 M solution of Bu^nLi in *n*-hexane (1.67 mL, 2.68 mmol), and the mixture was allowed to reach room temperature. This was added to a solution of $Pd_3(OAc)_6$ (300 mg, 0.450 mmol) in 25 mL of CH_2Cl_2. The mixture was stirred overnight at room temperature, resulting in a dark red solution. The solvent was removed under vacuum, and the residue was extracted with one 40 mL portion of MeOH. The MeOH solution was transferred into a Petri dish and allowed to evaporate in air. A mixture of pale yellow and dark red crystals formed. The yellow crystals of **8** were separated manually from the red ones of **6**, with a yield of 0.058 g (10%) of yellow crystals. ^1H NMR ($CDCl_3$, 300 MHz; δ, ppm): 1.463 (s), 6.442 (d), 6.600 (d), 6.739−7.223 (m), 7.858 (d). ^{13}C NMR ($CDCl_3$, 300 MHz; δ, ppm): 23.5, 114.3, 120.9, 122.4, 124.8, 124.9, 127.1, 127.3, 127.6, 128.1, 128.2, 129.4, 134.1, 134.8, 136.8, 147.4, 153.9, 179.9. IR (KBr, cm^{-1}): 2363 (w), 2344 (w), 1655 (m), 1625 (s), 1583 (vs), 1535 (s), 1509 (m), 1490 (m), 1462 (w), 1414 (w), 1346 (m), 1283 (s), 1265 (w), 1135 (w), 1028 (w), 833 (w), 803 (w), 754 (m), 698 (m), 512 (vw). UV−vis (λ, nm; ϵ, $M^{-1}cm^{-1}$): 305, 6×10^3.

X-ray Crystallography. Single crystals of each of the compounds **1**, **2**·$5C_6H_6$, **4**, **6**·$^2/_3$ acetone, and **8**·$2CH_3OH$ were mounted and centered on the goniometer of a Bruker SMART 1000 CCD area detector diffractometer and cooled to −60 °C. Geometric and intensity data were collected using SMART software.[22] The data were processed using SAINT software,[23] and corrections for absorption were applied using the program SADABS.[24]

All structures were solved using the Patterson method available in the SHELX-97 software package.[25] Crystal data are shown in Table 2, and Table 3 lists pertinent bond distances and angles.

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(22) *SMART V 5.618 Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(23) *SAINTPLUS V 6.45A Software for the CCD Detector System*; Bruker Analytical X-ray System, Inc.: Madison, WI, 1998.

Table 2. Crystal Data for **1**, **2**·5C_6H_6, **4**, **6**·$^2/_3CH_3C(O)CH_3$, and **8**·2CH_3OH

compound	**1**	**2**·5C_6H_6	**4**	**6**·$^2/_3$ acetone	**8**·2 methanol
formula	$C_{60}H_{60}N_8O_8Pd_2$	$C_{106}H_{94}N_{12}Pd_2$	$C_{38}H_{30}N_4Pd$	$C_{61}H_{52}N_6O_{2.67}Pd_2$	$C_{88}H_{88}N_8O_{12}Pd_4$
fw	1233.96	1748.73	649.06	1130.55	1875.26
cryst syst	triclinic	triclinic	triclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	*Pnn*2
a (Å)	10.306(3)	11.676(2)	11.584(6)	11.527(4)	11.027(1)
b (Å)	10.337(3)	17.172(3)	11.651(6)	22.807(7)	18.183(2)
c (Å)	13.774(5)	22.102(3)	13.222(7)	58.40(2)	10.062(1)
α (deg)	81.103(5)	93.980(3)	105.079(9)	90	90
β (deg)	76.778(5)	100.526(3)	112.883(8)	90	90
γ (deg)	81.146(6)	95.357(3)	96.779(9)	90	90
V (Å^3)	1400.7(8)	4320.7(1)	1538.5(1)	15353(8)	2017.4(4)
Z	1	2	2	12	2
d (calcd) (g cm^{-3})	1.463	1.344	1.401	1.467	1.544
R1,[a] wR2[b] ($I > 2\sigma I$)	0.0337, 0.0890	0.0762, 0.1586	0.0509, 0.1353	0.0494, 0.1141	0.0207, 0.0473
R1,[a] wR2[b] (all data)	0.0353, 0.0910	0.1389, 0.1875	0.0590, 0.1445	0.0608, 0.1210	0.0276, 0.0512

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**, **2**·5C_6H_6, **4**, **6**·$^2/_3$ Acetone, and **8**·2 Methanol[a]

	1	**2**·5C_6H_6	**4**	**6**·$^2/_3$ acetone	**8**·2 methanol
Pd···Pd	2.6486(8)	2.8971(9)		2.5634[9]	2.9435(4)
Pd−N	2.042[2]		2.045[4]	2.021[5]	2.013(2)
Pd−O				2.070[5]	2.114[2]
Pd−N_{bridge}		2.043[6]			
Pd−$N_{chel.}$		2.054[6]			
Pd−C					1.960(3)
Pd···Pd−N	85.90[6]			85.7[2]	
Pd···Pd−O				86.1[1]	79.02[6]
trans-N−Pd−N	171.75[8]		116.3[1]	171.2[2]	
cis-N−Pd−N	89.71[9]		63.8[1]	90.3[2]	
N−Pd···Pd−N torsion angle	0			14.4	
O−Pd···Pd−O torsion angle				13.5	
Pd···Pd−N_{bridge}		78.5[2]			
Pd···Pd−$N_{chel.}$		107.5[2]			
C−Pd−N					90.7(1)

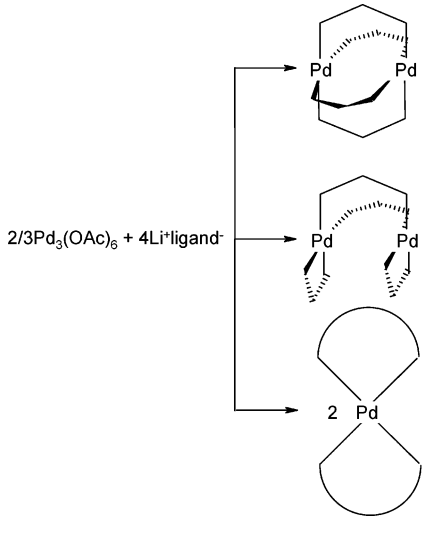
[a] Values in square brackets are averages.

Results and Discussion

Reactions of trinuclear palladium(II) acetate with a variety of mononegative N,N-ligands, which include the formamidinate DAniF, the guanidine-type ligand TPG, the triazine DPhTA, and the benzamidine DPhBz, may be complex. Such reactions afford mononuclear or dinuclear species depending on the reaction conditions or the method of isolation. Additionally, the dinuclear species $Pd_2(N,N)_4$ may produce isomeric compounds. In the α isomer, there are four bridging N,N-ligands forming a paddlewheel, and in the *β* isomer, there are two bridging and two chelating groups. In all cases, however, the palladium atoms are in an essentially square planar environment as shown in Scheme 3.

Whether there were mononuclear and/or dinuclear species in the reaction mixture was easily distinguished by using mass spectrometry, whereas ^1H and/or ^{13}C NMR were useful techniques in distinguishing between the α and the *β* isomers or their mixtures. Our studies show that with DAniF the only product observed under the experimental conditions reported above is the α form. The presence of a single signal in the methine region of the ^1H NMR spectrum at *δ* of 7.035 ppm, recorded on noncrystalline samples obtained from the reaction mixture, is diagnostic of a single configuration having D_{4h} symmetry because two signals in a 1:1 ratio would be expected for the *β* isomer. The M^+ peak at 1232 amu in the mass spectrum is consistent with the presence of a dinuclear species, as is the crystal structure which is shown in Figure

Scheme 3



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(24) SADABS program for absorption correction using SMART CCD data based on the method of Blessing: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(25) Sheldrick, G. M. *SHELXTL97*; University of Göttingen: Göttingen, Germany, 1997.

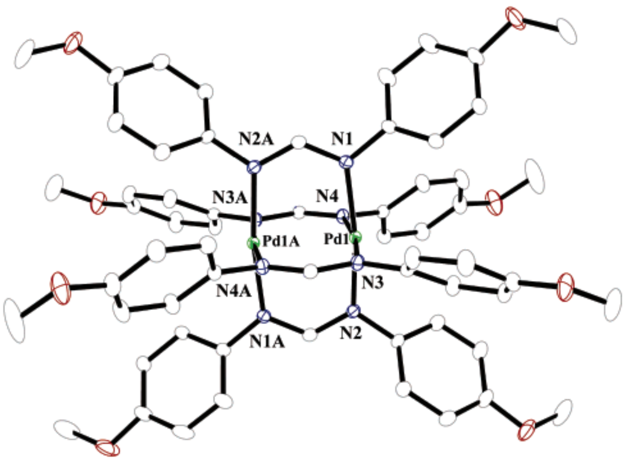

Figure 1. Paddlewheel **1** having a fully eclipsed configuration. Displacement ellipsoids are drawn at the 30% probability level, and hydrogen atoms have been omitted. Selected bond distances: Pd1−N2 = 2.033(2), Pd1−N3 = 2.040(2), Pd1−N1 = 2.045(2), Pd1−N4 = 2.050(2), Pd1···Pd1A = 2.6486(8) Å.

1. The structure is that of a typical tetragonal paddlewheel similar to those of $Pd_2(DTolF)_4$[8] and $Pd_2(DPhBz)_4$.[9] One important feature is that the $DAniF^-$ ligands wrap around the dimetal unit so that a fully eclipsed structure is formed with a dihedral angle N−Pd···Pd−N of 0°. This contrasts with $Pd_2(DTolF)_4$ where the torsion angle is 15.1(6)°[8] and **6** (vide infra) where the N−Pd···Pd−N and O−Pd···Pd−O torsion angles are 15.4 and 14.5°, respectively. In the α isomer of $Pd_2(DPhBz)_4$, there is also a considerable torsion angle of 14°.[9]

Similarly, results from the reaction of $Pd_3(OAc)_6$ with LiDPhTA show that the only observed product corresponds to the dinuclear α form. A synthesis[21] and structure[16] of $Pd_2(DPhTA)_4$ have been described. The compound was made in unspecified yield in a two-step reaction. First, an unstable diphenyltriazine−palladium species was reported to be obtained by mixing sodium tetrachloropalladate, sodium acetate, and HDPhTA, which then yielded a brown precipitate after standing in a solution of acetone at 50 °C. Our method of preparation using $Pd_3(OAc)_6$ and LiDPhTA gives the pure product straightforwardly in one step and in 69% yield.

In contrast to **1** and **3**, reaction with the guanidine-type ligand[26] TPG yields exclusively the β isomer **2**. The ^1H NMR spectrum is characteristically complex because of the appearance of signals from both the chelating and bridging groups, which when resolved are in a ratio of 1:1. For example, there are two singlets of equal intensities at 5.461 and 5.887 which have been assigned to signals of the −NH hydrogen for the chelating and bridging ligands. The mass spectrum shows the presence of the peak for the dinuclear species, which is also consistent with the solid-state structure shown in Figure 2.

It should be pointed out that the presence of both α and β isomers was reported earlier in the Pd/DPhBz system[9] and also in $Pt_2(DArF)_4$ compounds, where DArF is a diarylformamidinate in which Ar is either phenyl or tolyl.[27] These reports indicate that the α isomer can sometimes be obtained by heating the β isomer in nucleophilic solvents for a short time. However, care must be exercised as prolonged periods in boiling solvents may lead to metal deposition, as we have observed in unpublished results using $Pd_2(hpp)_4$. Another example was found when the guanidine-type compound **2** was heated in MeOH for 1 h; this led to complete decomposition and formation of Pd metal. Also, when heating was attempted using the reaction mixture of $Pd_3(OAc)_6$ and LiTPG, orthometalation of one TPG ligand was observed with formation of $Pd_2(\mu\text{-TPG})(\eta^2\text{-TPG})[\eta^2\text{-}C_6H_4N(CNHPh)N(H)Ph](\mu\text{-OAc})$, as determined by X-ray crystallography.[28]

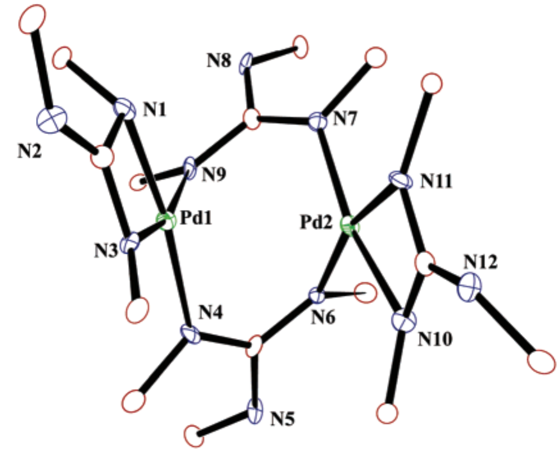

Figure 2. Core structure of $Pd_2(TPG)_2(\eta^2\text{-TPG})_2$ with displacement ellipsoids drawn at the 30% probability level. For simplicity, only the attached carbon atom (shown in red) for each of the three phenyl groups of each TPG ligand is shown. The remaining carbon atoms and all hydrogen atoms have been omitted. Selected bond distances: Pd1−N9 = 2.024(6), Pd1−N4 = 2.051(7), Pd1−N3 = 2.059(6), Pd1−N1 = 2.069(7), Pd1···Pd2 = 2.8971(9), Pd2−N6 = 2.037(6), Pd2−N10 = 2.039(6), Pd2−N11 = 2.049(6), Pd2−N7 = 2.058(6) Å.

Palladium/Diphenylbenzamidinate System. The reaction of $Pd_3(OAc)_6$ and Li(DPhBz) was first studied in the Bear group that reported the crystal structures of both the α and β isomers of $Pd_2(DPhBz)_4$ and also the possible existence of a species containing the cation $Pd_2(DPhBz)_4^+$.[9] Because the latter was of special interest to us, we tried to make the precursor α-$Pd_2(DPhBz)_4$. It was quickly found that this system is far more complex than originally recognized. Furthermore, some of the reported spectroscopic data deviated significantly from what we were finding. A decision was made to reinvestigate this system very carefully to resolve the inconsistencies.

To put the problem in perspective, we begin with a summary of the published report that is relevant to the understanding of our results. The reaction of $Pd_3(OAc)_6$ and Li(DPhBz) was carried out in CH_2Cl_2 at room temperature

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(26) For a review on guanidine-type ligands see: Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91.

(27) Cotton, F. A.; Matonic, J. H.; Murillo, C. A. *Inorg. Chem.* **1996**, *35*, 498.

(28) Crystallographic data for $Pd_2(\mu\text{-TPG})(\eta^2\text{-TPG})[\eta^2\text{-}C_6H_4N(CNHPh)N(H)Ph](\mu\text{-OAc})\cdot 2CD_3CN$: triclinic; $P\bar{1}$; $a = 11.209(1)$ Å, $b = 12.0459(1)$ Å, $c = 23.011(3)$ Å; $\alpha = 74.877(2)°$, $\beta = 89.529(2)°$, $\gamma = 71.256(2)°$; $V = 2830.3(5)$ Å^3; R (all data) = 0.0410; Pd···Pd = 2.9202(4) Å, average Pd−N = 2.037[2] Å, Pd−C = 2.483(3) Å, Pd−O = 2.105[2] Å.

for 14 h.[9] The solvent was then removed, and the solid was dissolved in a minimum amount of CH_2Cl_2. Methanol was then added. After the mixture had been stirred overnight, an orange precipitate was isolated. Following "extensive purification" of the solid, it was assigned the formula of the β form, $Pd_2(\mu\text{-DPhBz})_2(\eta^2\text{-DPhBz})_2$, on the basis of a crystal structure; a 14% yield was reported. The β isomer was said to give a UV−vis spectrum with two absorption peaks, at 378 and 496 nm, on the edge of a strong band rising into the UV region. The CV (cyclic voltammetry) in CH_2Cl_2 showed two irreversible waves at 1.02 and 1.26 V vs SCE (1.06 and 1.30 V vs Ag/AgCl).

It was further reported that, when a methanol solution of this compound was refluxed for 2 h, a small amount of Pd metal formed and it was removed. Elimination of the solvent from the remaining solution, followed by chromatography, produced another product in a reported yield of 40%. An X-ray study of a crystal showed that it was the isomer $\alpha\text{-}Pd_2(\text{DPhBz})_4$, in which all benzamidinate ligands bridge the Pd_2^{4+} unit. This complex was reported to give a broad absorbance in the visible region centered at 500 nm and a reversible electrochemical wave at 0.695 V from CV or 0.745 V vs Ag/AgCl, as obtained from bulk controlled-potential electrolysis. No additional characterization for any of these compounds, such as elemental analyses[29] or NMR data, was provided. Also, it was stated that other products were observed during chromatography, but they were not identified.

When trying to reproduce the synthesis of $Pd_2(\mu\text{-DPhBz})_2(\eta^2\text{-DPhBz})_2$, we noticed that addition of methanol to the reaction mixture, as reported, consistently gave an oily substance instead of the reported solid. This oil prevented the isolation of any crystalline material even when chromatographic separation was attempted. We then decided to modify the synthetic procedure with the hope of overcoming the synthetic difficulties.

A similar reaction of $Pd_3(OAc)_6$ and Li(DPhBz) was carried out in dichloromethane but without methanol. Methanol was used only later to wash the solid obtained after elimination of CH_2Cl_2 from the reaction mixture, and this procedure led to an analytically pure product in high yield that was shown by NMR to contain a ratio of benzamidate to acetate of 3:1. The ratio suggested that the formula is $Pd_2(\text{DPhBz})_3(\text{OAc})$, and this was confirmed by the structure, shown in Figure 3, where all ligands bridge the dipalladium unit. The CV showed a reversible oxidation at 0.776 V vs Ag/AgCl, a value that is similar to that reported for the α isomer.[9]

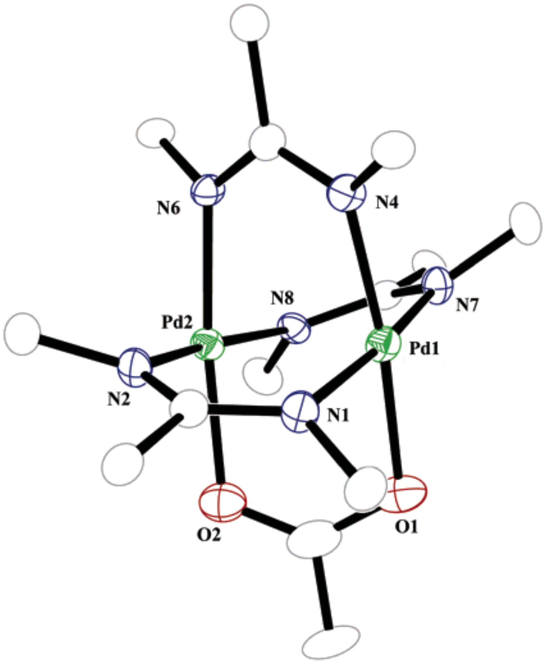

Figure 3. Core structure of the unsymmetrical compound $Pd_2(\text{DPhBz})_3(\text{OAc})$. Only one of the phenyl carbon atoms for each of the bridging DPhBz ligands is shown. Displacement ellipsoids are drawn at the 30% probability level, and hydrogen atoms have been omitted. Selected bond distances: Pd1−N4 = 2.002(5), Pd1−N1 = 2.027(5), Pd1−N7 = 2.032(5), Pd1−O1 = 2.079(5), Pd1···Pd2 = 2.5678(9), Pd2−N6 = 2.012(5), Pd2−N8 = 2.027(5), Pd2−N2 = 2.036(5), Pd2−O2 = 2.092(5) Å.

By changing the reaction solvent from CH_2Cl_2 to toluene, another product was formed, as shown by NMR and mass spectrometry. The ^1H NMR spectrum is complex; however, it indicates that benzamidinate ligands are present, and there is no acetate. Furthermore, it is consistent with the presence of two types of phenyl rings in a 2:1 ratio. This is consistent with the presence of a highly symmetrical species and only one kind of benzamidinate group. The ^{13}C NMR spectrum, which shows eight sharp peaks in the region between 123 and 145 ppm, is simple and also consistent with equivalent benzamidinate groups. Four of the eight peaks correspond to the unique carbon atoms in the phenyl rings bonded to the nitrogen atoms, and the other four are from the phenyl ring bonded to the bridgehead carbon atom. There are only four unique carbon atoms in each ring because each ring is free to rotate. The signal for the carbon bridgehead was not observed, but this is not unusual as it is bound to two nitrogen atoms, each with a large quadrupole moment. The mass spectrum showed only a $[M^+]$ peak consistent with that of a mononuclear molecule of formula $Pd(\text{DPhBz})_2$. This molecular formula is also supported by the crystal structure, shown in Figure 4, which shows two chelating benzamidinate groups around a single Pd atom in a distorted square planar environment. The CV showed two irreversible oxidation processes at 1.005 and 1.465 V (vs Ag/AgCl). Interestingly, the UV−vis spectrum of $Pd(\eta^2\text{-DPhBz})_2$ with two bands at 376 and 496 nm is very similar to that reported for the β isomer.[9]

Boiling of mononuclear $Pd(\eta^2\text{-DPhBz})_2$ in MeOH followed by chromatographic separation produces an orange product. Its ^1H NMR spectrum is consistent with the existence of only one type of DPhBz group, but it is significantly more complex than that of its precursor. The ^{13}C NMR spectrum is also very complex. Upon slow evaporation of the NMR solvent, all of the solute was recovered as orange crystals.

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(29) It should be mentioned that we have had serious difficulties obtaining elemental analyses for all compounds having benzamidinate ligands. In all cases, the experimental percentage of C was well below the calculated value. It is our belief that this is due to the formation of carbides that could form upon heating of the samples because orthometalation to form Pd−C bonds occurs, for example, in compound **8**.

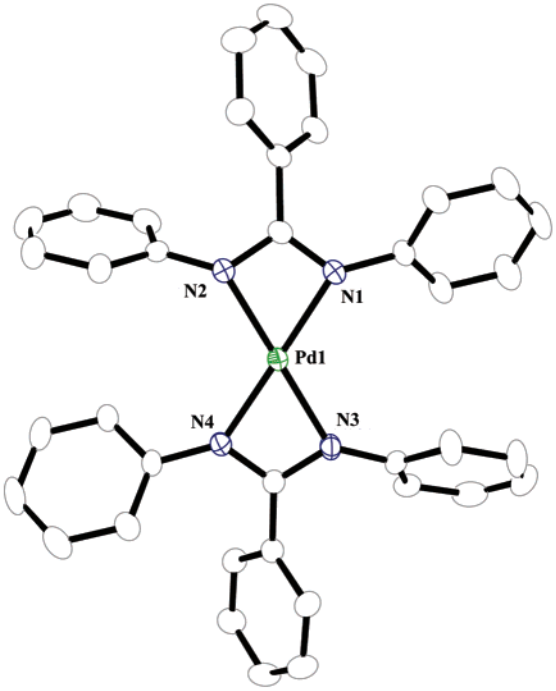

Figure 4. Structure of the mononuclear compound Pd(η^2-DPhBz)$_2$ showing the distorted square planar arrangement. Displacement ellipsoids are drawn at the 30% probability level, and hydrogen atoms have been omitted. Selected bond distances: Pd1−N1 = 2.037(3), Pd1−N4 = 2.041(3), Pd1−N3 = 2.048(4), Pd1−N2 = 2.053(4) Å.

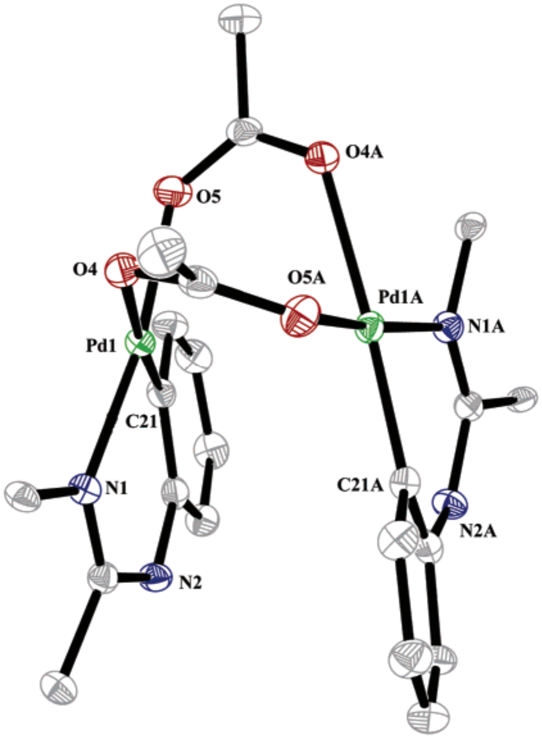

Figure 5. Core structure of the chiral orthometalated compound *cis*-Pd$_2$(η^2-C$_6$H$_4$NC(Ph)NPh)$_2$(μ-OAc)$_2$, **8**. Only one carbon atom of each of the non-orthometalated phenyl groups is shown. Displacement ellipsoids are drawn at the 30% probability level, and all hydrogen atoms have been omitted. Selected bond distances: Pd1−C21 = 1.960(3), Pd1−N1 = 2.013(2), Pd1−O5 = 2.057(2), Pd1−O4 = 2.170(2), Pd1−Pd1 = 2.9435(4) Å.

The structure was determined by single-crystal X-ray diffraction, and it is the same as that described earlier for the β isomer, Pd$_2$(μ-DPhBz)$_2$(η^2-DPhBz)$_2$.[9] The complexity of the ^{1}H and ^{13}C NMR spectra may be attributed to restricted rotation of the phenyl groups in each of the benzamidinate ligands, as shown by the changes in the spectra when the temperature is modified. The yield of 40% is significantly higher than that reported earlier (14%). However, there are again some discrepancies in the spectroscopic data. The CV taken by dissolving crystalline samples shows two irreversible processes at 0.927 and 1.291 V (vs Ag/AgCl). These values are somewhat different from those reported earlier (1.065 and 1.305 V vs Ag/AgCl). Also, the electronic spectrum, with only one band at 486 nm, is different from that reported earlier.[9]

All attempts to prepare the α-Pd$_2$(DPhBz)$_4$ from the β isomer by boiling in MeOH were unsuccessful. Once again, a different synthetic approach was sought, and the one used resembled that for the preparation of Ru$_2$(DMBz)$_4$Cl$_2$ (DMBz = *N*,*N*′-dimethylbenzamidinate),[30] in which Ru$_2$(OAc)$_4$Cl was refluxed with 5 equiv of HDMBz in THF in the presence of an excess of LiCl and Et$_3$N. By analogy, refluxing of a THF mixture of Pd$_3$(OAc)$_6$ with 5 equiv of HDMBz in the presence of Et$_3$N followed by chromatography yielded a dark purple mixture. After separation of a bright orange band by TLC, an ^{1}H NMR spectrum showed peaks only in the aromatic region, as expected for a compound with only benzamidinate ligands. The spectrum changed as the temperature was varied, giving a pattern that was significantly simpler at 45 °C than at −45 °C. This is consistent with greater rotational freedom of the phenyl rings at high temperatures. The pattern and integration of these signals are consistent with the presence of a highly symmetrical species in solution. The NMR spectrum, supported by the mass spectrum ([M$^+$] of 1086 amu), is consistent with a molecule with close to D_{4h} symmetry. Indeed, crystallization of this compound produced crystals in ca. 30% yield, and they have the same structure as that reported earlier for the α isomer.[31] In this case, the electrochemistry and UV−vis data were the same as those reported.[9]

We were also interested in the byproducts formed during the synthesis of Pd$_2$(DPhBz)$_3$(OAc). Washing the red powder formed after reaction of Pd$_3$(OAc)$_6$ with Li$^+$DPhBz$^-$ in CH$_2$Cl$_2$ yielded a dark solution. After slow and complete evaporation of MeOH, a mixture of yellow and red crystals was obtained. The dark red crystals were identified as Pd$_2$(DPhBz)$_3$(OAc), **6**, and the yellow crystals were identified as *cis*-Pd$_2$[η^2-C$_6$H$_4$NC(Ph)N(H)Ph]$_2$(μ-OAc)$_2$, **8**. In this compound, the two metal atoms are bridged by two cis acetate linkers and there are two chelating orthometalated DPhBz$^-$ ligands which envelop the palladium centers, as shown in Figure 5. Six-membered rings that consist of three carbon atoms, two nitrogen atoms, and a palladium atom are formed. In these rings, the nitrogen atom not bound to a palladium atom has a hydrogen atom. Its presence is strongly supported by a distance of 2.876 Å between that nitrogen atom and the oxygen atom of an interstitial methanol

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(30) Xu, G.; Campana, C.; Ren, T. *Inorg. Chem.* **2002**, *41*, 3521.

(31) Another way to synthesize the α isomer in low yield is by reaction in THF of Pd$_2$(DPhBz)$_3$(OAc) and one equivalent of a DPhBz anion.

Table 4. $E_{1/2}$ (V vs Ag/AgCl) Values for Compounds **1**−**8**

compound	$E_{1/2}{}^1$	$E_{1/2}{}^2$	$E_{1/2}{}^3$	$E_{1/2}{}^4$
1	0.70	0.97	1.12	1.27
2	0.729 irr[a]	1.031 irr[a]		
3	1.3 irr[a]			
4	1.005 irr[a]	1.465 irr[a]		
5	0.927 irr[a]	1.291 irr[a]		
6	0.776			
7	0.698			
8	0.920			

[a] Irreversible.

molecule, a separation that is only consistent with the presence of a hydrogen bond. Thus, the orthometalated groups are mononegative and the dimetal unit has a Pd_2^{4+} core. For this compound, the ^1H NMR and ^{13}C NMR are very complex. The CV and differential pulse voltammogram show one reversible oxidation wave at 0.930 V (vs Ag/AgCl).

A Look Ahead. Because compounds **1**, **6**, **7**, and **8** have reversible oxidation potentials, as shown in Table 4, these compounds appear to be good candidates for chemical oxidation and, thus, good candidates to serve as precursors to metal−metal bonded dipalladium species. This will be done as a second part of this study. It should be noted that the $E_{1/2}$ values in these compounds are dependent on the electron-donating ability of the bridging ligand with the very basic DAniF$^-$ ligand exhibiting the lowest oxidation potential. Interestingly, $Pd_2(DAniF)_4$ can be oxidized reversibly four times, and this will be discussed more thoroughly in a later report where we will explore the electronic structure using DFT calculations.

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Supporting Information Available: Crystallographic data in CIF format for **1**, **2**·$5C_6H_6$, **4**, **6**·$^2/_3$ acetone, and **8**·2 methanol, as well as for $Pd_2(\mu\text{-TPG})(\eta^2\text{-TPG})[\eta^2\text{-}C_6H_4N(CNHPh)N(H)Ph](\mu\text{-OAc})$. Displacement ellipsoid plots of the entire molecules in **2**, **6**, **8**, $Pd_2(\mu\text{-TPG})(\eta^2\text{-TPG})[\eta^2\text{-}C_6H_4N(CNHPh)N(H)Ph](\mu\text{-OAc})$, and $Pd_2(\mu\text{-TPG})(\eta^2\text{-TPG})[\eta^2\text{-}C_6H_4N(CNHPh)N(H)Ph](\mu\text{-OAc})\cdot 2CD_3CN$ in pdf format. This material is available free of charge via the Internet at http://pubs.acs.org.

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