Linkage Isomerization Equilibria in (Chloranilato)palladium(II) Complexes with Amine Ligands. Crystal Structure of (Chloranilato)bis(acetonitrile)palladium(II)

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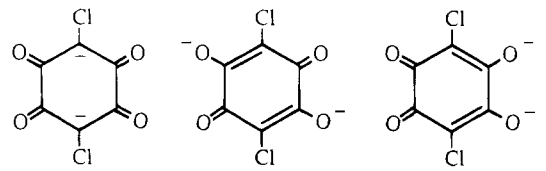
A series of (chloranilato)palladium(II) complexes of the type [Pd(CA)(amine)$_2$] have been prepared to probe inductive effects on linkage isomerization between dicarbanion (C-CA) and quinonoid (π-CA) forms of the bidentate chloranilate ligand. Electronic, infrared, and ^{1}H NMR spectra of [Pd(CA)(py-4-X)$_2$] species (X = H, C(CH$_3$)$_3$, COOH, C(O)NH$_2$, N(CH$_3$)$_2$, OH, CN, NH$_2$) show an unexpected mixture of C-CA and π-CA isomers whose distribution is insensitive to variations in the X substituent. Evidence is presented that Pd(CA) complexes with py-4-X ligands have variable structures which depend strongly on the solvent employed in their synthesis. The first high-resolution crystal structure of a C-bonded CA^{2-} complex is reported. [Pd(C-CA)(CH$_3$CN)$_2$] crystallizes in the triclinic $P\bar{1}$ space group with a = 8.681(2) Å, b = 11.371(2) Å, c = 13.997(3) Å, α = 91.32(1)°, β = 97.28(1)°, γ = 96.129(5)°, and V = 1361.5(7) Å^3; Z = 4. Chloranilate ligates Pd(II) through both C−Cl carbon atoms, with identical Pd−C and Pd−N bond lengths of 2.09 and 2.07 Å, respectively. Bond angles of the two carbon-donor atoms span the interval from 90.8 to 121.7°, with Pd−C−C and all other angles around the coordinated C atoms falling in the ranges 90.8−95.6 and 112.5−121.7°, respectively. The chloranilate ligand adopts a boat conformation (132.7° bend angle), and Pd(II) has a distorted square-planar coordination geometry characterized by average C−Pd−C, C−Pd−N, and N−Pd−N angles of 77.5, 95.1, and 92.4°, respectively.

Introduction

The bidentate 2,5-dioxo-3,6-dichloro-1,4-benzoquinone (CA^{2-}) ligand is capable of linkage isomerism among dicarbanion, carbon-bonded and quinonoid, oxygen-bonded forms in [Pd(CA)L$_2$] complexes.[1-6] Crystallographic evidence exists for resonance form **I** in K$_2$[Pd(CA)Cl$_2$],[1] while **III** is favored in



I II III

both [Pd(CA)(P{Ph-*m*-CH$_3$}$_3$)$_2$][2] and [Pd(CA)(P{*n*-C$_4$H$_9$}$_3$)$_2$].[3] Resonance form **II** contributes significantly in the solution phase for many (chloranilato)palladium(II) complexes, including those which favor **III** in the solid state.[4-6] The possibility of chloranilate diene ligation should be considered,[7-9] but has not been observed in a Pd(CA) system to date. In general, C-bonded chloranilate is favored in [Pd(CA)L$_2$] complexes for which L is a weak, hard σ donor. Complete conversion of chloranilate from structure **I** (C-CA) to a mixture of quinonoid forms **II** and **III** (π-CA) accompanies the reactions of yellow [Pd(CA)(CH$_3$CN)$_2$] with phosphines to give purple [Pd(CA)(PR$_3$)$_2$] products.[5,6] Although the stabilization of resonance form **I** by strong π-acceptor ligands has been proposed,[4] insufficient evidence is available to test this hypothesis.

Hammett linear free energy relationships successfully correlate phosphine substituent effects on ^{31}P coordination chemical shifts and the rates of [Pd(CA)(PR$_3$)$_2$] formation reactions.[6] To further explore inductive effects on chloranilate linkage isomerization, we have now prepared a series of (chloranilato)palladium(II) complexes with aliphatic and aromatic amine ligands. Of the three Pd(CA) complexes with nitrogen-donor ligands reported to date (L$_2$ = (CH$_3$CN)$_2$, tcnq, bpy),[4,5] only the CH$_3$CN complex favors C-CA ligation.[5] We report here the crystal structure of [Pd(CA)(CH$_3$CN)$_2$] and NMR studies of [Pd(CA)(py-4-X)$_2$] species which show an unexpected mixture of C-CA and π-CA structures in solution. In addition, evidence is presented that Pd(CA) complexes with pyridine ligands have variable structures which depend strongly on the solvent employed in their synthesis.

Experimental Section

Reagent grade chemicals (Aldrich) were used as received, and [Pd(CA)(CH$_3$CN)$_2$] (**1**) was prepared as previously described.[5] Glassware was acid-washed and rinsed with triply-distilled water before use. Elemental analyses of vacuum-dried samples were performed by Desert Analytics. Infrared spectra (KBr pellet) and electronic spectra of fresh solutions were measured on Perkin-Elmer Model 1600 FTIR and Shimadzu UV-260 spectrophotometers, respectively. It was noted that dilute solutions of chloranilic acid and many complexes reported here fade from purple to yellow over a 2−3 day period in DMF or DMSO, the only solvents in which solubility was sufficiently high to permit the acquisition of quantitative spectra. ^{1}H and broad-band decoupled ^{13}C NMR spectra of DMSO-d_6 or acetone-d_6 solutions were measured on an IBM AF-200 or AF-300 spectrometer; chemical shifts are reported relative to TMS.

A crystal of **1** grown by ether diffusion into an acetonitrile solution was sealed in a thin-walled glass capillary. The complex crystallized in space group $P\bar{1}$ with two molecules per asymmetric unit. Data were

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(1) Krasochka, O. N.; Avilov, V. A.; Atovmyan, L. O. *Zh. Strukt. Khim.* **1974**, *15*, 1140.
(2) Johnston, R. F.; Sen Gupta, P. K.; Jeong, W.-Y.; Holwerda, R. A. *Acta Crystallogr.* **1990**, *C46*, 1796.
(3) Johnston, R. F.; VanDerveer, D. G.; Holwerda, R. A. *J. Crystallogr. Spectrosc. Res.* **1992**, *22*, 755.
(4) Jeong, W.-Y.; Holwerda, R. A. *J. Organomet. Chem.* **1989**, *372*, 453.
(5) Jeong, W.-Y.; Holwerda, R. A. *Inorg. Chem.* **1988**, *27*, 2571.
(6) Jeong, W.-Y.; Holwerda, R. A. *Inorg. Chem.* **1989**, *28*, 2674.
(7) Pierpont, C. G.; Francesconi, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 2367.
(8) Wrobleski, J. T.; Brown, D. B. *Inorg. Chem.* **1979**, *18*, 498.
(9) Calvo, M. A.; Lanfredi, A. M. M.; Oro, L. A.; Pinillos, M. T.; Tejel, C.; Tiripicchio, A.; Ugozzoli, F. *Inorg. Chem.* **1993**, *32*, 1147.

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Table 1. Crystallographic Data for $[Pd(C_6O_4Cl_2)(CH_3CN)_2]$

chem formula	$C_{10}H_6Cl_2N_2O_4Pd$	V, Å^3	1361.5(7)
fw	395.5	Z	4
space group	triclinic, $P\bar{1}$ (No. 2)	temp, °C	23
a, Å	8.681(2)	λ, Å (Mo Kα)	0.710 73
b, Å	11.371(2)	ϱ(calc), g cm^{-3}	1.929
c, Å	13.997(3)	μ(Mo Kα), cm^{-1}	17.64
α, deg	91.32(1)	transm coeff	0.6844 −0.9892
β, deg	97.28(1)	R^a	0.0369
γ, deg	96.129(5)	$R_w{}^b$	0.0596

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F)$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Pd(C_6O_4Cl_2)(CH_3CN)_2]$

atom	x	y	z	U(eq)^a
Pd(1)	637(1)	3351(1)	1046(1)	40(1)
Cl(11)	3103(3)	2002(2)	−102(2)	105(1)
Cl(14)	−3158(2)	2641(2)	1175(3)	130(2)
O(12)	397(14)	2586(6)	−1479(4)	158(5)
O(13)	−2596(10)	2815(5)	−866(6)	147(4)
O(15)	−1464(6)	542(5)	1605(4)	75(2)
O(16)	1389(5)	246(4)	965(3)	60(2)
N(1)	2816(6)	4316(4)	1198(4)	49(2)
N(2)	−82(7)	4475(5)	2035(5)	63(2)
C(1)	3971(7)	4874(5)	1311(4)	42(2)
C(2)	5496(8)	5599(6)	1445(5)	58(2)
C(3)	−364(7)	5021(6)	2655(5)	53(2)
C(4)	−732(8)	5734(7)	3466(6)	68(3)
C(11)	1191(9)	2038(5)	130(5)	54(2)
C(12)	62(14)	2344(6)	−675(5)	86(4)
C(13)	−1555(12)	2494(6)	−345(6)	85(3)
C(14)	−1498(7)	2315(6)	694(6)	63(3)
C(15)	−927(7)	1208(5)	1052(4)	44(2)
C(16)	668(7)	1057(5)	701(4)	43(2)
Pd(2)	5716(1)	1620(1)	4677(1)	36(1)
Cl(21)	6839(2)	3071(1)	6805(1)	50(1)
Cl(24)	2943(2)	2117(2)	2886(1)	64(1)
O(22)	3420(5)	2459(4)	6539(3)	52(1)
O(23)	1596(5)	2092(4)	4735(3)	64(2)
O(25)	5312(6)	4236(4)	3355(3)	66(2)
O(26)	7000(5)	4733(4)	5167(3)	56(2)
N(3)	7583(6)	938(5)	5453(4)	49(2)
N(4)	5581(6)	438(5)	3512(4)	52(2)
C(5)	8656(8)	725(6)	5917(5)	50(2)
C(6)	10050(8)	459(7)	6537(6)	67(3)
C(7)	5378(7)	−27(5)	2787(5)	47(2)
C(8)	5032(9)	−622(6)	1824(5)	63(3)
C(21)	5630(6)	2965(5)	5705(4)	36(2)
C(22)	3956(6)	2646(4)	5792(4)	37(2)
C(23)	2983(7)	2440(5)	4816(4)	40(2)
C(24)	3934(7)	2549(5)	4025(4)	42(2)
C(25)	5048(7)	3651(5)	4042(4)	44(2)
C(26)	5999(6)	3900(5)	5025(4)	40(2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

collected on a Siemens Model P4 automated diffractometer using graphite-monochromated Mo Kα radiation. The unit cell parameters were determined and refined by a least-squares fit of 25 reflections. Data were corrected for Lorentz and polarization effects, and semiempirical absorption corrections based on Ψ-scans were applied. The space group determination was based upon a check of the Laue symmetry and confirmed by solution of the structure. The structure was determined using the Patterson technique followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using the SHELXTL-IRIS software package provided by Siemens Analytical X-Ray Instruments, Inc. The parameters refined included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The ORTEP drawing is shown with 50% probability ellipsoids. Crystallographic data and refinement details are given in Table 1. Table 2 presents the atomic coordinates and isotropic displacement parameters.

(Chloranilato)bis(amine)palladium(II) complexes were prepared by mixing stoichiometric amounts of the amine with **1** in methanol, acetone, or acetonitrile. Reaction mixtures were typically stirred for several days until no further color change was noted. In several cases, products collected in this way were shown to be identical with complexes isolated after reaction times of several weeks. Products were collected by filtration, washed with solvent and diethyl ether, and then air-dried. Since both the products isolated and the reaction intermediates observed in these systems are solvent-dependent, specific observations relating to each synthesis are given.

$[Pd(CA)(NH_2CH_2C_6H_5)_2]$ (2). **1** (0.0697 g, 0.176 mmol) was mixed with benzylamine (38.5 μL, 0.353 mmol) in 22 mL of CH_3CN. After 20 h, a pale green solid was collected. Yield: 56% (0.05 g). Anal. Calcd for $[Pd(CA)(NH_2CH_2C_6H_5)_2]$: C, 45.42; H, 3.44; N, 5.31. Found: C, 45.56; H, 3.24; N, 5.23. IR: ν(C−O) 1525m, 1655s, 1701m; ν(C−Cl) 861m; ν(C−C) 1166m cm^{-1}. UV−vis (DMF): λ_{max} (ϵ_{max}): 333 (1.3 × 10^4), 543 nm (3.8 × 10^2 M^{-1} cm^{-1}). ^{1}H NMR (DMSO-d_6): δ 3.22 (s, CH_2), 3.63 (t, CH_2), 4.15 (s, NH_2), 5.02 (t, NH_2), 7.22−7.47 (m, C_6H_5). ^{13}C NMR (acetone-d_6): δ 59.67 (CH_2), 128.64−130.48 (m, C_6H_5).

$[Pd(CA)(py\text{-}2\text{-}CH_2NH_2)]\cdot CH_3CN$ (3). 2-(Aminomethyl)pyridine (40 μL, 0.386 mmol) was mixed with **1** (0.1527 g, 0.386 mmol) in 20 mL of CH_3CN. The maroon precipitate which formed immediately slowly became lavender; the product was collected after 2 days. Yield: 61% (0.11 g). Anal. Calcd for $[Pd(CA)(py\text{-}2\text{-}CH_2NH_2)]\cdot CH_3CN$: C, 36.35; H, 2.40; N, 9.08. Found: C, 35.96; H, 2.26; N, 8.82. IR: ν(C−O) 1518s, 1662m, 1702m; ν(C−Cl) 826m, 861m; ν(C−C) 1166m cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 4.14 (t, CH_2), 4.41 (t, CH_2), 5.02 (t, NH_2), 6.21 (t, NH_2), 7.60−7.78, 8.04−8.31 (m, pyridyl H-3, H-4, H-5), 8.57 (d, pyridyl H-6) .

$[Pd(CA)(NH_2CH_2CH_2CH_3)_2]$ (4). **1** (0.1768 g, 0.447 mmol) was mixed with propylamine (73.4 μL, 0.894 mmol) in 18.5 mL of CH_3CN. The yellow solution turned colorless within 1 min and then became green through a maroon intermediate over a 2-day period; a dark green product was collected after 3 days. Yield: 57% (0.11 g). Anal. Calcd for $[Pd(CA)(NH_2CH_2CH_2CH_3)_2]$: C, 33.39; H, 4.20; N, 6.49. Found: C, 34.14; H, 4.50; N, 7.11. IR: ν(C−O) 1508s, 1525s, 1611m; ν(C−Cl) 832w, 852m cm^{-1}. UV−vis (DMF): λ_{max} (ϵ_{max}): 342 (1.9 × 10^4), 543 nm (8.9 × 10^2 M^{-1} cm^{-1}). ^{1}H NMR (DMSO-d_6): δ 0.91 (t, CH_3), 1.64 (sext, CH_2), 2.40−2.49 (m, CH_2), 4.58 (s, NH_2).

$[Pd(CA)(en)]\cdot H_2O$ (5). **1** (0.1997 g, 0.505 mmol) was combined with ethylenediamine (33.8 μL, 0.505 mmol) in 20 mL of CH_3CN. Subsequent to an immediate color change from yellow to lavender, a gray-green product was observed after 10 h. An olive product was collected after 6 days. Yield: 72% (0.14 g). Anal. Calcd for $[Pd(CA)(en)]\cdot H_2O$: C, 24.54; H, 2.57; N, 7.16. Found: C, 24.63; H, 2.06; N, 7.47. IR: ν(C−O) 1496s, 1645s, 1701m; ν(C−Cl) 843m, 862m; ν(C−C) 1163m cm^{-1}. UV−vis (DMSO): λ_{max} (ϵ_{max}): 312 (1.4 × 10^4), 527 nm (1.5 × 10^2 M^{-1} cm^{-1}). ^{1}H NMR (DMSO-d_6): δ 4.53 (s, NH_2), 4.66 (s, NH_2).

$[Pd(CA)(pip)_2]\cdot 2H_2O$ (6). **1** (0.2131 g, 0.539 mmol) was mixed with piperidine (106.5 μL, 1.08 mmol) in 10 mL of CH_3CN. An immediate yellow precipitate became blue over a 36 h period; the light-blue product was collected after 1 week. Yield: 71% (0.20 g). Anal. Calcd for $[Pd(CA)(pip)_2]\cdot 2H_2O$: C, 36.98; H, 5.04; N, 5.39. Found: C, 36.31; H, 4.22; N, 5.30. IR: ν(C−O) 1507s, 1618m; ν(C−Cl) 853m cm^{-1}.

$[Pd(CA)(py)_2]$ (7). **1** (0.1973 g, 0.50 mmol) was mixed with pyridine (80.7 μL, 1.0 mmol) in 18 mL of acetone. The initial yellow color faded to beige over a 6 h period. After several days, the mixture was olive green; a gray-green solid was collected after 1 week. Yield: 76% (0.18 g). Anal. Calcd for $[Pd(CA)(py)_2]$: C, 40.75; H, 2.14; N, 5.94. Found: C, 40.62; H, 1.96; N, 5.86. IR: ν(C−O) 1542m, 1664s, 1709s; ν(C−Cl) 856m; ν(C−C) 1146m cm^{-1}. UV−vis (DMF): λ_{max} (ϵ_{max}): 310 (1.1 × 10^4), 538 nm (2.5 × 10^2 M^{-1} cm^{-1}). ^{13}C NMR (acetone-d_6): δ 127.06 (py C-3,5), 140.48 (py C-4), 152.02 (py C-2,6).

$[Pd(CA)(py)_2]\cdot 0.5H_2O$ (8). **1** (0.2327 g, 0.588 mmol) was mixed with pyridine (95.2 μL, 1.18 mmol) in 15 mL of CH_3CN. The reaction mixture slowly darkened, depositing an olive green precipitate, which was collected after 1 week. Yield: 64% (0.18 g). Anal. Calcd for $[Pd(CA)(py)_2]\cdot 0.5H_2O$: C, 39.99; H, 2.31; N, 5.83. Found: C, 40.24; H, 2.07; N, 5.47. IR: ν(C−O) 1543s, 1637m; ν(C−Cl) 850m cm^{-1}. UV−vis (DMSO): λ_{max} (ϵ_{max}): 330 (2.1 × 10^4), 541 nm (1.0 × 10^3 M^{-1} cm^{-1}).

[Pd(CA)(py)$_2$]·0.5H$_2$O (9). **1** (0.1514 g, 0.38 mmol) was combined with pyridine (62 μL, 0.77 mmol) in 18.5 mL of CH$_3$OH. The yellow color faded immediately after mixing, becoming tan after 5 days; the product was collected on the sixth day. Yield: 78% (0.14 g). Anal. Calcd for [Pd(CA)(py)$_2$]·0.5H$_2$O: C, 39.99; H, 2.31; N, 5.83. Found: C, 40.02; H, 1.89; N, 5.67. IR: ν(C−O) 1543w, 1665s, 1709s; ν(C−Cl) 857m; ν(C−C) 1147m cm^{-1}. UV−vis (DMF): λ_{max} (ϵ_{max}): 308 (1.2 × 10^4), 535 nm (2.8 × 10^2 M^{-1} cm^{-1}).

[Pd(CA)(py-4-COOH)$_2$]·2H$_2$O (10). **1** (0.2452 g, 0.62 mmol) was mixed with isonicotinic acid (0.1530 g, 1.24 mmol) in 20 mL of CH$_3$CN. After 24 h, a yellow precipitate separated from the red-brown supernatant; this product was collected after 1 week. Yield: 75% (0.28 g). The synthesis was carried out in CH$_3$OH with a substantially higher yield (93%) but otherwise identical results. Anal. Calcd for [Pd(CA)(py-4-COOH)$_2$]·2H$_2$O: C, 36.30; H, 2.37; N, 4.70. Found: C, 36.23; H, 1.98; N, 4.52. IR: ν(C−O) 1654s, 1708s; ν(C−Cl) 863m; ν(C−C) 1172m cm^{-1}. UV−vis (DMF): λ_{max} (ϵ_{max}): 306 nm (1.3 × 10^4 M^{-1} cm^{-1}). ^{13}C NMR (DMSO-d_6): δ 98.18 (CA^{2-} C−Cl), 124.52 (py C-3,5), 140.18 (py C-4), 151.70 (py C-2,6), 165.18 (CO$_2$H), 171.80 (CA^{2-} C=O).

[Pd(CA)(py-4-CONH$_2$)$_2$]·H$_2$O (11). Isonicotinamide (0.1360 g, 1.1 mmol) was reacted with **1** (0.2202 g, 0.56 mmol) in 16 mL of CH$_3$CN. Within 4 min, the color changed from pale to bright yellow. After 17 h, a yellow precipitate separated from a colorless supernatant. This yellow intermediate persisted for 2 days, after which the color slowly turned to green; the product was collected after a further 5 days. Yield: 86% (0.28 g). Anal. Calcd for [Pd(CA)(py-4-CONH$_2$)$_2$]·H$_2$O: C, 37.56; H, 2.45; N, 9.73. Found: C, 37.41; H, 1.97; N, 10.02. IR: ν(C−O) 1560s, 1684m, 1719m; ν(C−Cl) 831w, 855m cm^{-1}.

The long-lived yellow intermediate (**12**) was isolated in 79% yield by the above procedure, except that the product was collected after 24 h. Anal. Calcd for [Pd(CA)(py-4-CONH$_2$)$_2$]·H$_2$O: C, 37.56; H, 2.45; N, 9.73. Found: C, 37.99; H, 2.21; N, 10.36. IR: ν(C−O) 1557m, 1649s, 1678s, 1701s; ν(C−Cl) 856m; ν(C−C) 1172m cm^{-1}. UV−vis (DMSO): λ_{max} (ϵ_{max}): 310 nm (1.5 × 10^4 M^{-1} cm^{-1}). ^{13}C NMR (DMSO-d_6): δ 98.37 (CA^{2-} C−Cl), 123.39 (py C-3,5), 143.64 (py C-4), 151.39 (py C-2,6), 165.22 (CONH$_2$), 171.85 (CA^{2-} C=O).

[Pd(CA)(py-4-CONH$_2$)$_2$]·H$_2$O (13). Isonicotinamide (0.1154 g, 0.94 mmol) was mixed with **1** (0.1870 g, 0.47 mmol) in CH$_3$OH. The reaction mixture faded to colorless immediately after mixing but became green over a period of several hours; the pale green product was collected after 2 days. Yield: 86% (0.23 g). Anal. Calcd for [Pd(CA)(py-4-CONH$_2$)$_2$]·H$_2$O: C, 37.56; H, 2.45; N, 9.73. Found: C, 37.71; H, 2.15; N, 9.77. IR: ν(C−O) 1525s, 1553s, 1648s, 1686s, 1713s; ν(C−Cl) 831w, 856m; ν(C−C) 1172w cm^{-1}. UV−vis (DMSO): λ_{max} (ϵ_{max}): 338 (1.6 × 10^4), 543 nm (5.5 × 10^2 M^{-1} cm^{-1}).

[Pd(CA)(py-4-N(CH$_3$)$_2$)$_2$]·2.5H$_2$O (14). **1** (0.2511 g, 0.635 mmol) was combined with 4-(dimethylamino)pyridine (0.1401 g, 1.27 mmol) in 20 mL of CH$_3$OH. The initial rust-brown solution quickly darkened; a purple product was collected after 3 days. Yield: 71% (0.27 g). Anal. Calcd for [Pd(CA)(py-4-N(CH$_3$)$_2$)$_2$]·2.5H$_2$O: C, 39.85; H, 4.18; N, 9.29. Found: C, 40.00; H, 3.40; N, 9.11. IR: ν(C−O) 1542s, 1684m, 1713w; ν(C−Cl) 839m, 860w; ν(C−C) 1138w cm^{-1}.

[Pd(CA)(py-4-OH)$_2$]·2H$_2$O (15). 4-Hydroxypyridine (0.1254 g, 1.3 mmol) was combined with **1** (0.2603 g, 0.658 mmol) in 20 mL of CH$_3$OH. The initial yellow color faded quickly, ultimately becoming dark blue-green within 33 h. The green product was collected after 4 days. Yield: 71% (0.25 g). Anal. Calcd for [Pd(CA)(py-4-OH)$_2$]·2H$_2$O: C, 35.61; H, 2.62; N, 5.19. Found: C, 35.51; H, 1.70; N, 5.08. IR: ν(C−O) 1508s, 1618m; ν(C−Cl) 844m cm^{-1}. UV−vis (DMF): λ_{max} (ϵ_{max}): 344 (2.1 × 10^4), 540 nm (1.3 × 10^3 M^{-1} cm^{-1}).

[Pd(CA)(py-4-CN)$_2$]·H$_2$O (16). 4-Cyanopyridine (0.0964 g, 0.926 mmol) was mixed with **1** (0.1838 g, 0.465 mmol) in 15 mL of CH$_3$CN. The pink precipitate which was present after 39 h became purple after 3 days. The solid was collected after a further 6 days, since no additional color change was noted. Yield: 39% (0.10 g). Anal. Calcd for [Pd(CA)(py-4-CN)$_2$]·H$_2$O: C, 40.06; H, 1.87; N, 10.38. Found: C, 40.17; H, 1.32; N, 10.67. IR: ν(C−O) 1507s, 1654s, 1699m; ν(C−Cl) 842m, 859w; ν(C−C) 1155w; ν(C≡N) 2239 cm^{-1}. UV−vis (DMF): λ_{max} (ϵ_{max}): 341 (1.2 × 10^4), 541 nm (5.1 × 10^2 M^{-1} cm^{-1}).

[Pd(CA)(py-4-NH$_2$)$_2$]·H$_2$O·CH$_3$CN (17). 4-Aminopyridine (0.0902 g, 0.958 mmol) was mixed with 25 mL of 0.019 M **1** in CH$_3$CN. The color of the reaction mixture quickly changed from yellow to pale orange. The pink solid which was present after 24 h slowly changed color to tan (isolated after 7 days). Yield: 75% (0.21 g). Anal. Calcd for [Pd(CA)(py-4-NH$_2$)$_2$]·H$_2$O·CH$_3$CN: C, 38.56; H, 3.06; N, 12.49. Found: C, 38.07; H, 2.47; N, 12.33. IR: ν(C−O) 1518s, 1630s, 1701m; ν(C−Cl) 834m, 861w; ν(C−C) 1166w cm^{-1}. UV−vis (DMF): λ_{max} (ϵ_{max}): 305 nm (1.1 × 10^4 M^{-1} cm^{-1}).

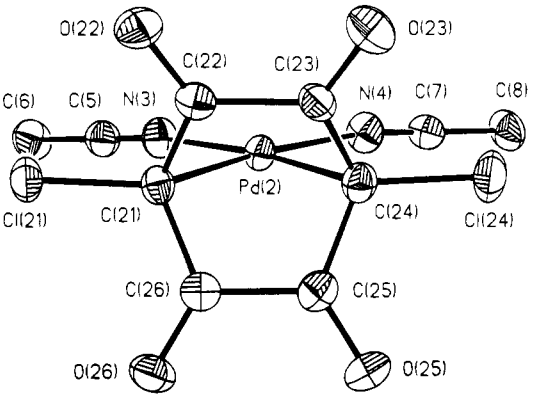

Figure 1. ORTEP diagram of molecule 2 from the X-ray crystal structure of [Pd(CA)(CH$_3$CN)$_2$].

[Pd(CA)(py-4-C(CH$_3$)$_3$)$_2$]·3H$_2$O (18). **1** (0.1883 g, 0.48 mmol) was combined with 4-*tert*-butylpyridine (140.8 μL, 0.95 mmol) in 18 mL of CH$_3$OH. The reaction mixture faded immediately from yellow to colorless. A dark purple precipitate formed within several days and was collected after 11 days. Yield: 60% (0.18 g). Anal. Calcd for [Pd(CA)(py-4-C(CH$_3$)$_3$)$_2$]·3H$_2$O: C, 45.19; H, 5.06; N, 4.39. Found: C, 44.85; H, 3.95; N, 4.31. IR: ν(C−O) 1509s, 1660m, 1710w; ν(C−Cl) 842m, 854w cm^{-1}. UV−vis (DMSO): λ_{max} (ϵ_{max}): 332 (2.2 × 10^4), 543 nm (6.2 × 10^2 M^{-1} cm^{-1}).

Results and Discussion

The crystal structure of **1** is illustrated in Figure 1, while bond lengths and angles are shown in Table 3. The structure clearly demonstrates that the chloranilate ligand ligates Pd(II) through C−Cl carbon atoms, with average Pd−C and Pd−N bond lengths of 2.09 and 2.07 Å, respectively, for both molecules in the asymmetric unit. The Pd−C bond lengths are identical, within experimental error, as are the Pd−N bond lengths. This is the first high-resolution structure reported for a CA^{2-} complex of this type, as structural parameters for K$_2$Pd(CA)Cl$_2$·4H$_2$O have high uncertainties.[1] Thus, the apparent difference of 0.05 Å between the Pd−C bond lengths in K$_2$Pd(CA)Cl$_2$·4H$_2$O (2.02 and 2.07 Å)[1] does not appear to be statistically significant.

Bond angles of the carbon donor atoms in **1** span the interval from 90.8 to 121.7°, with Pd−C−C and all other angles around the coordinated carbon atoms falling in the ranges 90.8−95.6 and 112.5−121.7°, respectively. The chloranilate ring adopts a boat conformation in **1**, as shown by the 132.7° angle between C(21)−C(22)−C(23)−C(24) and C(21)−C(24)−C(25)−C(26) planes. Pd(II) has a distorted square-planar coordination geometry characterized by average C−Pd−C, C−Pd−N, and N−Pd−N angles of 77.5, 95.1, and 92.4°, respectively. As compared with those of K$_2$Pd(CA)Cl$_2$·4H$_2$O,[1] the average C=O (1.21 Å) and C−Cl (1.74 Å) bond lengths of **1** are shorter by 0.06 Å and longer by 0.04 Å, respectively. Average bond lengths from C−Cl to C=O (1.47 Å) and from C=O to C=O (1.53 Å) carbon atoms are essentially identical in K$_2$Pd(CA)Cl$_2$·4H$_2$O and **1**.

One unusual aspect of the crystal structure is that there are two independent molecules in the asymmetric unit, and an examination of intermolecular close contacts revealed that the palladium atoms in the two molecules are in quite different environments with regard to long-range interactions (Figure 2). Pd(1) is 3.474 Å from one of the chlorine atoms (Cl(24)) of the chloranilate ligand attached to Pd(2), and Pd(2) is 3.925 Å

Table 3. Unique Bond Distances (Å) and Angles (deg) for $[Pd(C_6O_4Cl_2)(CH_3CN)_2]$

Molecule 1

Pd(1)–N(1)	2.067 (5)	Pd(1)–N(2)	2.060 (6)	O(16)–C(16)	1.208 (7)	N(1)–C(1)	1.119 (8)
Pd(1)–C(11)	2.080 (7)	Pd(1)–C(12)	2.610 (7)	N(2)–C(3)	1.123 (10)	C(1)–C(2)	1.471 (9)
Pd(1)–C(13)	2.635 (9)	Pd(1)–C(14)	2.083 (6)	C(3)–C(4)	1.468 (11)	C(11)–C(12)	1.471 (11)
Pd(1)–C(16)	2.645 (5)	Cl(11)–C(11)	1.736 (8)	C(11)–C(16)	1.453 (8)	C(12)–C(13)	1.557 (16)
Cl(14)–C(14)	1.736 (8)	O(12)–C(12)	1.227 (11)	C(13)–C(14)	1.469 (12)	C(14)–C(15)	1.477 (9)
O(13)–C(13)	1.182 (12)	O(15)–C(15)	1.197 (8)	C(15)–C(16)	1.552 (9)		

N(1)–Pd(1)–N(2)	90.3(2)	N(1)–Pd(1)–C(11)	95.6(2)	C(12)–C(11)–C(16)	116.2(6)	Pd(1)–C(12)–O(12)	136.0(6)
N(2)–Pd(1)–C(11)	172.4(2)	N(1)–Pd(1)–C(12)	109.1(3)	Pd(1)–C(12)–C(11)	52.7(3)	O(12)–C(12)–C(11)	124.3(11)
N(2)–Pd(1)–C(12)	146.6(3)	C(11)–Pd(1)–C(12)	34.2(3)	Pd(1)–C(12)–C(13)	73.6(4)	O(12)–C(12)–C(13)	123.7(9)
N(1)–Pd(1)–C(13)	138.7(3)	N(2)–Pd(1)–C(13)	114.9(3)	C(11)–C(12)–C(13)	111.6(7)	Pd(1)–C(13)–O(13)	139.4(5)
C(11)–Pd(1)–C(13)	62.9(3)	C(12)–Pd(1)–C(13)	34.5(3)	Pd(1)–C(13)–C(12)	71.9(4)	O(13)–C(13)–C(12)	122.5(9)
N(1)–Pd(1)–C(14)	171.8(3)	N(2)–Pd(1)–C(14)	96.9(3)	Pd(1)–C(13)–C(14)	52.1(3)	O(13)–C(13)–C(14)	127.0(10)
C(11)–Pd(1)–C(14)	77.5(3)	C(12)–Pd(1)–C(14)	62.7(3)	C(12)–C(13)–C(14)	110.2(7)	Pd(1)–C(14)–Cl(14)	121.4(4)
C(13)–Pd(1)–C(14)	33.8(3)	N(1)–Pd(1)–C(16)	114.3(2)	Pd(1)–C(14)–C(13)	94.2(5)	Cl(14)–C(14)–C(13)	114.4(6)
N(2)–Pd(1)–C(16)	139.5(2)	C(11)–Pd(1)–C(16)	33.2(2)	Pd(1)–C(14)–C(15)	95.2(4)	Cl(14)–C(14)–C(15)	112.8(5)
C(12)–Pd(1)–C(16)	56.4(2)	C(13)–Pd(1)–C(16)	67.5(2)	C(13)–C(14)–C(15)	116.8(6)	O(15)–C(15)–C(14)	128.5(6)
C(14)–Pd(1)–C(16)	61.9(2)	Pd(1)–N(1)–C(1)	176.7(5)	O(15)–C(15)–C(16)	121.2(5)	C(14)–C(15)–C(16)	110.0(5)
Pd(1)–N(2)–C(3)	171.6(6)	N(1)–C(1)–C(2)	179.1(6)	Pd(1)–C(16)–O(16)	140.6(4)	Pd(1)–C(16)–C(11)	51.5(3)
N(2)–C(3)–C(4)	180.0(10)	Pd(1)–C(11)–Cl(11)	120.3(3)	O(16)–C(16)–C(11)	126.9(6)	Pd(1)–C(16)–C(15)	73.5(3)
Pd(1)–C(11)–C(12)	93.0(5)	Cl(11)–C(11)–C(12)	116.5(6)	O(16)–C(16)–C(15)	120.7(5)	C(11)–C(16)–C(15)	112.2(5)
Pd(1)–C(11)–C(16)	95.3(4)	Cl(11)–C(11)–C(16)	112.5(5)				

Molecule 2

Pd(2)–N(3)	2.066 (5)	Pd(2)–N(4)	2.073 (5)	N(3)–C(5)	1.119 (8)	N(4)–C(7)	1.118 (8)
Pd(2)–C(21)	2.089 (5)	Pd(2)–C(24)	2.093 (6)	C(5)–C(6)	1.461 (10)	C(7)–C(8)	1.475 (9)
Pd(2)–C(25)	2.590 (6)	Pd(2)–C(26)	2.606 (6)	C(21)–C(22)	1.481 (8)	C(21)–C(26)	1.480 (8)
Cl(21)–C(21)	1.744 (5)	Cl(24)–C(24)	1.745 (5)	C(22)–C(23)	1.512 (8)	C(23)–C(24)	1.462 (8)
O(22)–C(22)	1.211 (7)	O(23)–C(23)	1.217 (7)	C(24)–C(25)	1.496 (8)	C(25)–C(26)	1.516 (8)
O(25)–C(25)	1.215 (7)	O(26)–C(26)	1.210 (7)				

N(3)–Pd(2)–N(4)	94.5(2)	N(3)–Pd(2)–C(21)	94.2(2)	O(22)–C(22)–C(23)	122.6(5)	C(21)–C(22)–C(23)	111.7(5)
N(4)–Pd(2)–C(21)	171.0(2)	N(3)–Pd(2)–C(24)	171.1(2)	O(23)–C(23)–C(22)	121.6(5)	O(23)–C(23)–C(24)	125.5(5)
N(4)–Pd(2)–C(24)	93.7(2)	C(21)–Pd(2)–C(24)	77.5(2)	C(22)–C(23)–C(24)	112.4(5)	Pd(2)–C(24)–Cl(24)	121.3(3)
N(3)–Pd(2)–C(25)	137.7(2)	N(4)–Pd(2)–C(25)	108.6(2)	Pd(2)–C(24)–C(23)	95.6(4)	Cl(24)–C(24)–C(23)	115.2(4)
C(21)–Pd(2)–C(25)	63.0(2)	C(24)–Pd(2)–C(25)	35.3(2)	Pd(2)–C(24)–C(25)	90.8(3)	Cl(24)–C(24)–C(25)	114.3(4)
N(3)–Pd(2)–C(26)	108.4(2)	N(4)–Pd(2)–C(26)	138.9(2)	C(23)–C(24)–C(25)	116.2(5)	Pd(2)–C(25)–O(25)	136.0(5)
C(21)–Pd(2)–C(26)	34.6(2)	C(24)–Pd(2)–C(26)	63.0(2)	Pd(2)–C(25)–C(24)	53.9(3)	O(25)–C(25)–C(24)	126.3(5)
C(25)–Pd(2)–C(26)	33.9(2)	Pd(2)–N(3)–C(5)	170.4(5)	Pd(2)–C(25)–C(26)	73.6(3)	O(25)–C(25)–C(26)	121.6(5)
Pd(2)–N(4)–C(7)	166.3(5)	N(3)–C(5)–C(6)	179.0(8)	C(24)–C(25)–C(26)	111.6(5)	Pd(2)–C(26)–O(26)	140.1(4)
N(4)–C(7)–C(8)	177.1(7)	Pd(2)–C(21)–Cl(21)	121.7(3)	Pd(2)–C(26)–C(21)	53.2(3)	O(26)–C(26)–C(21)	127.0(5)
Pd(2)–C(21)–C(22)	94.4(3)	Cl(21)–C(21)–C(22)	113.8(4)	Pd(2)–C(26)–C(25)	72.5(3)	O(26)–C(26)–C(25)	121.1(5)
Pd(2)–C(21)–C(26)	92.2(3)	Cl(21)–C(21)–C(26)	115.1(4)	C(21)–C(26)–C(25)	111.7(4)		
C(22)–C(21)–C(26)	116.6(5)	O(22)–C(22)–C(21)	125.4(5)				

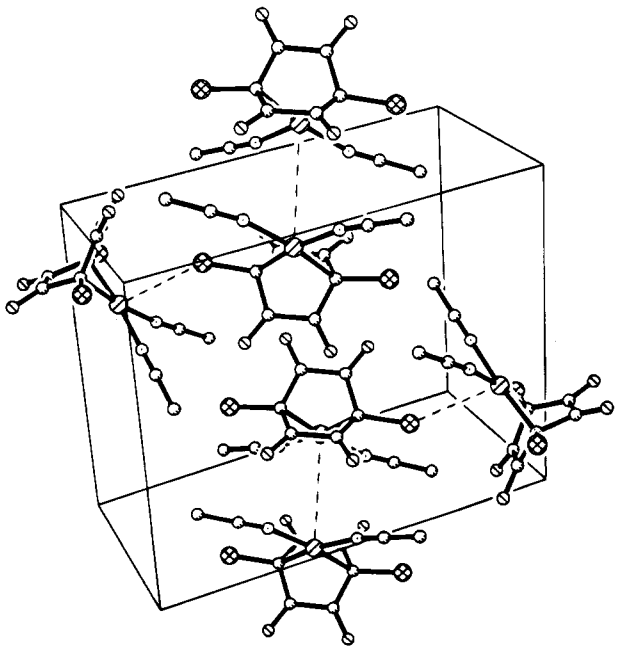

Figure 2. Unit cell packing diagram for $[Pd(CA)(CH_3CN)_2]$ showing intermolecular close contacts.

from a symmetry-related Pd(2) in another molecule. Both distances are slightly greater than the sum of van der Waals radii of the two atoms (r_{vdW} for Pd and Cl are 1.60 and 1.70–1.90 Å, respectively),[10] and there do not appear to be any chemically significant interactions in either case.

Structural findings on $[Pd(CA)(P\{Ph\text{-}m\text{-}CH_3\}_3)_2]$[2] and $[Pd(CA)(P\{n\text{-}Bu\}_3)_2]$[3] contrast strongly with those for **1**. Thus, chloranilate ligates Pd(II) through the phenolate oxygen atoms of *o*-quinone resonance form **III** in the former compound, as indicated by three distinct chloranilate carbon–carbon bond lengths of 1.35, 1.43, and 1.52 Å, coupled with two C–O bond lengths of 1.23 and 1.29 Å.[2] Palladium–oxygen bond lengths in both phosphine complexes are 2.05 Å. In an effort to compare chloranilate bonding parameters for two complexes with PdC_2N_2 donor atom sets, an X-ray data set was acquired for a yellow crystal of the pyridine complex **9** after repeated attempts to grow diffraction-quality crystals. Unfortunately, the poor quality of the data did not permit the extraction of quantitatively-meaningful bond lengths or angles, although it is clear that **9** contains carbon-bonded CA^{2-} and a pair of N-bonded pyridine ligands.

The reactions of $[Pd(CA)(CH_3CN)_2]$ with phosphines are rapid, proceeding to completion within minutes or hours to give dark purple products in which the chloranilate ligand is bonded to palladium exclusively as a quinone.[6] In contrast, **1** reacts with aromatic and aliphatic amines in several phases, typified by immediate loss of yellow color followed by slow formation

(10) Bondi, A. J. *J. Phys. Chem.* **1964**, *68*, 441.

Table 4. ^{1}H NMR Data for [Pd(CA)(4-py-X)$_2$] Complexes[a]

			complex			free ligand		
no.	X	% π-CA[b]	δ_{ortho}	δ_{meta}	other	δ_{ortho}	δ_{meta}	other
7	−H	<10	m, 8.62−8.65	m, 7.50−7.57	m, 7.90−7.99 (p-H)	m, 8.61−8.64	m, 7.36−7.44	m, 7.75−7.85 (p-H)
9	−H	<10	m, 8.78−8.81	m, 7.56−7.64	m, 7.99−8.06 (p-H)			
10	−CO_2H	<10	d, 8.81 (6.4)	d, 7.92 (6.4)	s, 3.4 (OH)	d, 8.76 (6.0)	d, 7.80 (6.0)	s, 3.4 (OH)
12	−$CONH_2$	<10	d, 8.77 (6.3)	d, 7.86 (6.3)	s, 8.31 ($CONH_2$)	d, 8.74 (6.1)	d, 7.80 (6.1)	s, 8.30 ($CONH_2$)
13	−$CONH_2$	20	d, 8.76 (6.3) d, 8.90 (6.0)	d, 7.83 (6.3) m, 7.95−8.08	s, 8.29 s, 8.45 ($CONH_2$)			
15	−OH	70	d, 8.25 (7.0) d, 8.54 (6.7) s, 8.48	m, 6.92−6.99	s, 7.96, 6.59, 3.37, 2.89, 2.73, 1.76	d, 7.73 (7.3)	d, 6.20 (7.3)	OH not resolved
16	−CN	50	d, 8.90 (6.2) d, 9.01 (6.3) d, 9.16 (6.2)	d, 7.98 (6.2) d, 8.19 (6.3) d, 8.27 (6.2)		d, 8.86 (6.0)	d, 7.88 (6.0)	
17	−NH_2	<10	d, 7.91[c]	d, 6.91	m, 6.43−6.50 (NH)	d, 7.97 (6.3)	d, 6.45 (6.3)	s, 5.99 (NH)
18	−$C(CH_3)_3$	45	d, 8.54 (6.5) d, 8.63 (6.7)	d, 7.54 (6.5) d, 7.71 (6.7)	s, 1.24 s, 1.28 (CH_3)	d, 8.50 (6.2)	d, 7.39 (6.2)	s, 1.27 (CH_3)

[a] In DMSO-d_6 with the exception of **9** (acetone-d_6); coupling constants (Hz) shown in parentheses. [b] Percentage of [Pd(CA)(4-py-X)$_2$] species in solution which contains the π-CA linkage isomer, calculated from the relative integrations of of upfield (C-CA) and downfield (π-CA) doublets for ortho and meta protons; for **15**, the downfield resonances correspond to the C-CA linkage isomer. [c] Doublet falls within broad, unassigned resonance, 7.74−8.03 ppm.

of purple, blue, green or yellow products at equilibrium over a period of several days. It is apparent that the incoming amine ligands rapidly displace CH_3CN with retention of C-CA^{2-} bonding, but also trigger chloranilate linkage isomerization reactions to extents that depend strongly on both amine substituents and the reaction solvent. Thus, gray-green (**7**), olive green (**8**), and tan (**9**) complexes are generated from the reactions of **1** with 2 equiv of pyridine in acetone, acetonitrile and methanol, respectively. An isolable, long-lived yellow intermediate (**12**) was observed for the reaction of isonicotinamide with **1** in CH_3CN, but only the ultimate green product was seen when this reaction was carried out in methanol. Prior to this study, the only precedent for a solvent dependence of the Pd(CA) product distribution was the isolation of [Pd(C-CA)(cod)]·THF and [Pd(π-CA)(cod)]·H_2O from the reactions of 1,5-cyclooctadiene with **1** in THF and CH_2Cl_2, respectively.[4]

Analytically-pure complexes of the type [Pd(CA)(py-4-X)$_2$] were obtained from the reactions of **1** with stoichiometric amounts of pyridine derivatives (X = H, COOH, C(O)NH_2, $N(CH_3)_2$, OH, CN, NH_2 and $C(CH_3)_3$). In addition, Pd(CA) adducts with benzylamine, 2-(aminomethyl)pyridine, propylamine, ethylenediamine, and piperidine were readily prepared by the same method. Considering that most of these solid complexes are actually mixtures of linkage isomers (vide infra), the criterion of purity used in this research is a fixed ratio of Pd:CA:amine ligand rather than homogeneity at the molecular level.

Pd(C-CA) complexes have several strong C=O vibrations in the 1620−1720 cm^{-1} region, medium-intensity C−C stretching bands between 1150 and 1220 cm^{-1} and a C−Cl stretching frequency larger than 855 cm^{-1} in most cases. Electronic spectra of these yellow complexes are dominated by a strong C−Pd(II) LMCT transition near 310 nm.[4] In contrast, Pd(π-CA) species generally have a very strong C−O stretch between 1500 and 1535 cm^{-1} coupled with a single C=O band above 1600 cm^{-1} and a C−Cl mode below 855 cm^{-1}.[4-6] Purple [Pd(π-CA)(PR$_3$)$_2$] complexes exhibit allowed $^1B_{3u} \leftarrow {}^1A_{1g}$ (ϵ (2.5−4.5) × 10^4 M^{-1} cm^{-1}) and symmetry-forbidden $^1B_{1g} \leftarrow {}^1A_{1g}$ (ϵ (0.9−1.4) × 10^3 M^{-1} cm^{-1}) $\pi-\pi$ * transitions near 340 and 530 nm, respectively.[6]

Both infrared and electronic spectral evidence suggests that a majority of Pd(CA) adducts with amine ligands are found in both solid and solution phases as mixtures of C-CA and π-CA linkage isomers. Thus, **2**, **3**, **5**, **7**, **13**, **14**, **16**, and **17** exhibit both the distinctive C−C stretch characteristic of C-CA and the strong C−O stretch below 1600 cm^{-1} typical of the π-CA isomer. Furthermore, all of these species except **2** and **7** have two C−Cl stretching bands, above and below 850 cm^{-1}. On the basis of solid-state infrared evidence alone, **9**, **10**, and **12** appear to contain C-CA only, while **4** and **6** are entirely composed of the π-CA linkage isomer; assignments for products **8** and **11** and for **15** and **18** cannot be made on the basis of infrared data alone. ^{13}C NMR spectra of **10** and **12** show two rather than three chloranilate carbon resonances, confirming that CA^{2-} ligates Pd(II) exclusively as dicarbanion resonance form **I** in these complexes.

Carbon-bonded Pd(CA) complexes lack significant absorption above 500 nm, consistent with electronic spectral findings for **10** and **12**. Extinction coefficients for the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition of 16 [Pd(π-CA)(PR$_3$)$_2$] complexes vary only slightly from the average value of 1.2 × 10^3 M^{-1} cm^{-1}.[6] On this basis, we estimate the percentage of π-CA present in solutions of Pd(CA) bis(amine) complexes from the relationship %(π-CA) ≈ [ϵ(observed)/1.2 × 10^3] × 100%, assuming that [Pd(π-CA)(amine)$_2$] species also have essentially ligand-independent $^1B_{1g} \leftarrow {}^1A_{1g}$ band intensities: **2** (30%, DMF), **4** (75%, DMF), **5** (10%, DMSO), **7** (20%, DMF), **8** (85%, DMSO), **9** (25%, DMF), **13** (45%, DMSO), **15** (100%, DMF), **16** (40%, DMF), and **18** (50%, DMSO). Thus, we attribute the high degree of variation in visible extinction coefficients for Pd[(CA)(amine)$_2$] complexes (1.5 × 10^2 (**5**) to 1.3 × 10^3 M^{-1} cm^{-1} (**15**)) to fluctuations in the relative concentrations of C-CA and π-CA linkage isomers from one product to the next. It should be stressed that the quoted percentages are rough estimates at best and cannot be compared on an equal basis since two solvents (DMF and DMSO) were used of necessity to achieve solubilities large enough to acquire quantitative spectra. Consistent with our previous finding for [Pd(π-CA)(PR$_3$)$_2$] complexes,[6] the $^1B_{1g} \leftarrow {}^1A_{1g}$ transitions of [Pd(π-CA)(amine)$_2$] species are strongly red-shifted relative to that of the free chloranilate ion (481 nm in DMSO).

To further probe the equilibria between C-CA and π-CA linkage isomers, ^{1}H NMR spectra of [Pd(CA)(py-4-X)$_2$] complexes in DMSO solutions were acquired and compared with those of the free pyridines (Table 4). ^{1}H NMR spectra of py-4-X compounds show a pair of equal-intensity doublets (J = 6.0−7.5 Hz) in the range 6.0−9.0 ppm, separated by about 1 ppm. Spin−spin coupling between protons ortho and meta to the N atom gives rise to this doublet pattern, with small unresolved, additional splittings of doublet components being

attributed to second-order coupling across the pyridine ring. Homonuclear decoupling of the [Pd(CA)(py)$_2$] (**7**) 4-protons reduced a complex spectrum to a pair of doublets (δ 8.64 (H-2,6) and 7.53 (H-3,5)) with J = 5.8 Hz. Spectra of [Pd(CA)(py-4-X)$_2$] complexes typically exhibit two pairs of equal-intensity doublets, assigned to *m*-H and *o*-H protons of slowly-interconverting [Pd(C-CA)(py-4-X)$_2$] (upfield doublet) and [Pd(π-CA)(py-4-X)$_2$] species. Thus, dicarbanion-ligated chloranilate is expected to be the better σ-donor toward Pd(II), giving rise to more effective shielding of trans pyridine ligands than is possible with O-bonded CA^{2-} in a π-CA complex. Inductive effects on the ^{1}H NMR spectra of coordinated pyridine derivatives are well-documented.[11-17] Unequal integrated intensities of upfield and downfield doublet pairs, whose ratio varies with the substituent X, were used to calculate percentages of C-CA and π-CA linkage isomers in solution (Table 4). Values calculated in this way correspond reasonably well with those estimated from $\pi-\pi^*$ band extinction coefficients, supporting our assignment of downfield doublet pairs to the [Pd(π-CA)(py-4-X)$_2$] linkage isomer; agreement in the cases of **13** and **15** is only fair.

The characteristic four-doublet ^{1}H NMR spectra of [Pd(CA)(py-X)$_2$] complexes cannot be accounted for in terms of spin–spin coupling within a single species. Decoupling experiments showed that the ortho and meta protons of each doublet set couple only with each other. The 4-cyanopyridine complex (**16**) has a third pair of doublets, suggesting the presence of a third isomer. When the decoupler frequency was centered on the most upfield meta proton resonance of **16** (7.98 ppm), the analogous ortho resonance collapsed from a doublet to a singlet (8.90 ppm), leaving the other four pyridyl resonances unaffected. Similarly, decoupling of the other two ortho resonances collapsed only one associated meta doublet. Although the possibility of nitrile rather than pyridyl nitrogen coordination should be considered for 4-cyanopyridine complexes,[18,19] we have no direct evidence to support the existence of the former in any of the three observed [Pd(CA)(py-4-CN)$_2$] isomers; ν(CN) for **16** is essentially identical to that of py-4-CN (2243 cm^{-1}). In the case of py-4-OH complex **15**, distinct doublet pairs corresponding to ortho protons were seen, but meta resonances of the two linkage isomers were not separately resolved (m, 6.88–6.97 ppm). Decoupling of this meta multiplet reduced both of the downfield doublets to singlets (8.25 and 8.55 ppm). In agreement with this observation, the combined integrated intensities of the two ortho doublets equaled that of the upfield multiplet. Consistency of % π-CA calculations by extinction coefficient and integrated NMR peak methods may be achieved for **15** only if it is assumed that the *downfield* doublet pairs correspond to the C-CA isomer for this complex.

Several Pd(CA) complexes with aliphatic nitrogen-donor atoms (**2**, **3**, and **5**) also have ^{1}H NMR spectra which indicate the presence of both C-CA and π-CA linkage isomers. Assignments of aliphatic amine proton resonances were confirmed by the observation of broadening upon the addition of D_2O. For py-2-CH_2NH_2 complex **3**, pairs of amine and methylene peaks attributed to C-CA and π-CA (downfield) linkage isomers were identified by the COSY NMR method; both CH_2 and NH_2 integrated peak intensities indicate a 70% C-CA, 30% π-CA distribution. Relative CH_2 intensities for benzylamine complex **2** (30% π-CA) were in excellent agreement with the spectrophotometric prediction.

Table 5. ^{1}H NMR Coordination and Linkage Shifts for [Pd(CA)(4-py-X)$_2$] Complexes

compd	substituent	Hammett σ_p	$\Delta\delta_{ortho}$[a]	$\Delta\delta_{meta}$[b]	linkage Δ, ortho[c]	linkage Δ, meta[d]
17	-NH_2	−0.66	−0.06	0.46		
15	-OH	−0.37	0.81		0.29	
			0.52			
18	-$C(CH_3)_3$	−0.20	0.13	0.32	0.09	0.17
			0.04	0.15		
7	-H	0.00	0.02	0.14		
12	-$CONH_2$	+0.36	0.03	0.06		
13	-$CONH_2$	+0.36	0.16		0.14	
			0.02			
10	-COOH	+0.43	0.05	0.12		
16	-CN	+0.66	0.30	0.39	0.26	0.29
			0.15	0.31	0.11	0.21
			0.04	0.10		

[a] Calculated as $\delta_{complex} - \delta_{free\ ligand}$ for protons ortho to the N atom. [b] Calculated as $\delta_{complex} - \delta_{free\ ligand}$ for protons meta to the N atom. [c] Calculated as $\delta_{\pi\text{-CA}} - \delta_{\text{C-CA}}$ for protons ortho to the N atom. [d] Calculated as $\delta_{\pi\text{-CA}} - \delta_{\text{C-CA}}$ for protons meta to the N atom.

Table 5 records coordination chemical shifts for ortho and meta protons of [Pd(CA)(py-4-X)$_2$] complexes, including data for both C-CA and π-CA linkage isomers where possible. As a measure of the difference between electronic polarizations of a given pyridine ligand in these isomers, we define the "linkage Δ" parameter as $\delta_{\pi\text{-CA}}-\delta_{\text{C-CA}}$. Although ^{31}P coordination chemical shifts for [Pd(π-CA)(P{Ph-*p*-X}$_3$)$_2$] complexes correlate linearly with Hammett para substituent constants,[6] no such relationship pertains in the case of py-4-X complexes. Indeed, only the 4-hydroxypyridine complex exhibits a large $\Delta\delta$ value. Furthermore, there is no clear correlation between the linkage Δ parameter and pyridine substituent inductive effects. On this basis, we conclude that the polarization of nitrogen electron density toward the palladium(II) center is sufficiently small in [Pd(CA)(py-4-X)$_2$] systems such that electronic characteristics of amine substituents have little impact on Pd–chloranilate bonding in both C-CA and π-CA linkage isomers. This conclusion is underscored by our surprising finding that mixtures of C-CA and π-CA linkage isomers may be found in solution for pyridine complexes with both electron-withdrawing (CN) and -donating ($C(CH_3)_3$, OH) functional groups in the para position. Although the distribution of linkage isomers for py-4-X complexes is not readily understood, the clear advantage of π-CA in the case of complexes with propylamine and piperidine ligands is in accord with the prediction that enhancements in the σ-donor strength of L should destabilize carbon-bonded chloranilate.

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Supplementary Material Available: Tables of crystallographic data and anisotropic displacement factors for [Pd(CA)(CH$_3$CN)$_2$] (3 pages). Ordering information is given on any current masthead page.

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(11) Selbin, J.; Gutierrez, M. A. *J. Organomet. Chem.* **1983**, *246*, 95
(12) Gopinathan, S.; Unny, I. R.; Deshpande, S. S.; Gopinathan, C. *Indian J. Chem.* **1986**, *25A*, 1015.
(13) Gopinathan, S.; Unny, I. R.; Gopinathan, C. *Polyhedron* **1986**, *5*, 1921.
(14) Baghlaf, A. O.; Ishaq, M.; Rashad, A. K. A. *Polyhedron* **1987**, *6*, 837.
(15) Miki, S.; Ohno, T.; Iwasaki, H.; Maeda, Y.; Yoshida, Z. I. *Tetrahedron* **1988**, *44*, 55.
(16) Ganis, P.; Saporito, A.; Vitagliano, A.; Valle, G. *Inorg. Chim. Acta* **1988**, *142*, 75.
(17) Sliwa, *Transition Met. Chem. (London)* **1989**, *14*, 321.
(18) Walton, R. A. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2229.
(19) Clark, R. J. H.; Williams, C. S. *Inorg. Chem.* **1965**, *4*, 350.