Journal of Organometallic Chemistry, 372 (1989) 453–463
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20036

Factors influencing linkage isomer preference in palladium(II)-chloranilate complexes

Woo-Yeong Jeong and Robert A. Holwerda *

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409 (U.S.A.)

(Received February 10th, 1989)

Abstract

The factors influencing linkage isomer preference in the bonding between palladium(II) and the chloranilate dianion (CA^{2-}) are addressed through the synthesis and spectroscopic characterization of 16 $[Pd(CA)L_2]$ compounds, where $L_2 = 2Cl^-$, $2CH_3CN$, $2H_2O$, ox^{2-}, $acac^-$, 2dmso, $2SCN^-$, $2F^-$, $2Br^-$, bpy, tcnq, $2CN^-$, CA^{2-}, and cod. The (C–CA) linkage isomer containing chloranilate ligated as a dicarbanion through C–Cl carbon atoms is favored in the presence of weak σ-donor ligands towards the soft Pd^{II} center (all L_2 groups except dmso, bpy and CN^-), while strong σ-donors invariably give (π-CA) products in which the conventional *p*-quinonoid form of CA^{2-} is present. $[Pd(C\text{–}CA)L_2]$ compounds are characterized by three infrared characteristics: (1) several strong C=O vibrations in the 1620–1720 cm^{-1} interval but no 1500–1550 cm^{-1} C–O mode; (2) 1–4 medium-intensity C–C stretching bands between 1150 and 1220 but no C=C feature near 1350 cm^{-1}; and (3) a relatively high-energy C–Cl vibration, i.e. > 855 cm^{-1}. Distinct C-to-Pd^{II} LMCT transitions in the vicinity of 310 and 230–260 nm indicate that the non-equivalence of Pd–C bonds first demonstrated by the X-ray crystal structure of $K_2[Pd(C\text{–}CA)Cl_2] \cdot 4H_2O$ is a general feature of the (C–CA) series. $[Pd(C\text{–}CA)L_2]$ complexes are surprisingly susceptible to hydrolysis, affording $[Pd(C\text{–}CA)(H_2O)_2]$ within several minutes in weakly acidic solution (pH 3.7). A kinetic *trans* effect linked to the strengthening of Pd-chloranilate C bonds by the departure of competing σ donor ligands is suggested.

Introduction

The remarkable affinity of palladium(II) for saturated carbon centers is exemplified by the unusual structure of $K_2[Pd(CA)Cl_2] \cdot 4H_2O$ (CA^{2-} = 2,5-dioxo-3,6-

---

* To whom correspondence should be addressed.

(π-CA)

(C-CA)

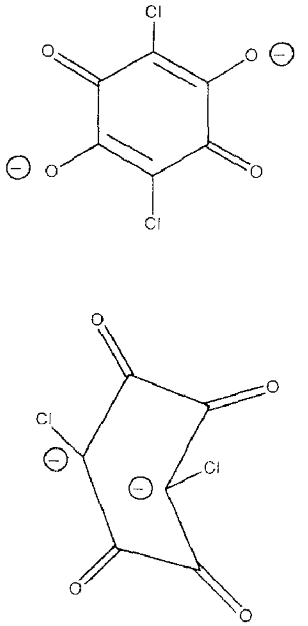

Fig. 1. Chloranilate C–CA^{2-} and π-CA^{2-} ligands.

dichloro-1,4-benzoquinone; chloranilate dianion), in which the chloranilate *p*-quinonoid resonance energy is sacrificed in favor of dicarbanion ligation through the C–Cl carbon atoms [1]. As part of our effort to better understand the thermodynamic and kinetic factors which influence the interconversion of sp^3 and sp^2 hybridization states of carbon in the first coordination sphere of Pd^{II}, we have undertaken synthetic and mechanistic studies of [Pd(CA)L$_2$] complexes, where L$_2$ represents a pair of complementary monodentate donors or a bidentate chelating ligand [2–4]. Recently reported studies of [Pd(CA)(CH$_3$CN)$_2$] and [Pd(CA)(PPh$_3$)$_2$] demonstrated that dicarbanion chloranilate ligation (C–CA) is retained in the former complex, while the replacement of weak σ-donor acetonitrile ligands by triphenylphosphine induces linkage isomerization to CA^{2-} coordination as a *p*-quinone (π-CA) in the latter compound [2] (Fig. 1). As a working hypothesis, we propose that the electron-releasing, (C–CA) linkage isomer will be favored when L$_2$ is a strong π-acceptor or a weak σ donor. Conversely, (π-CA) ligation could maximize back-bonding to chloranilate in the presence of potent σ donors towards the soft Pd^{II} center.

Enhancements in linkage isomerization rate constants with increasing electron-donating power of X in the conversion of [Pd(C–CA)(P{Ph-*p*-X}$_3$)$_2$] to [Pd(π-CA)(P{Ph-*p*-X}$_3$)$_2$] suggest that the polarization of phosphine electron density towards Pd^{II} destabilizes the *trans* Pd–carbanion C bonds, forcing chloranilate to function as a weaker σ donor in the (π-CA) linkage isomer [4]. Similarly, the chloride incoming group plays a significant role in the rate-determining step for acid hydrolysis of [Pd(C–CA)Cl$_2$]$^{2-}$ to PdCl$_4^{2-}$ and H$_2$CA [3]. We report here the synthesis and characterization of 14 [Pd(CA)L$_2$] species, with the primary purpose of isolating the largest possibly family of Pd(C–CA) compounds. The factors influencing linkage isomer preference are discussed with consideration of the possible trans-labilizing influence exerted by chloranilate bonded in the (C–CA) mode.

Experimental

Reagent grade chemicals were used without further purification. Palladium chloride, 2,4-pentanedione (Hacac), 1,5-cyclooctadiene (cod), 2,2′-bipyridine (bpy) and 7,7,8,8-tetracyanoquinodimethane (tcnq) were supplied by Aldrich. Triply-distilled water was used throughout. The preparations of $K_2[Pd(CA)Cl_2] \cdot 0.5H_2O$ (**1**) and $[Pd(CA)(CH_3CN)_2]$ (**2**) have already been described [2]. Elemental analyses of vacuum-dried (25 °C) products were performed by Desert Analytics (Tucson, Arizona). Infrared and UV-visible spectra were acquired by using the slowest scan speeds available on Beckman Acculab 8 and Shimadzu UV-260 spectrophotometers, respectively.

Preparations

$[Pd(CA)(H_2O)_2] \cdot H_2O$ (3). $K_2[Pd(CA)Cl_2] \cdot 0.5H_2O$ (2.37 g, 5.0 mmol) was dissolved in 150 ml of water and the pH was adjusted to 2.0 with HNO_3. $AgNO_3$ (1.70 g, 10.0 mmol) was then added slowly with stirring over the period of 1 h, at which point AgCl was collected by filtration in 99% yield. Yellow-orange needles of the product were obtained by evaporation of the supernatant to 30 ml, followed by filtration and washes with cold water and ether. Yield: 1.10 g, 60%. Chloranilatodiaaquapalladium(II) is reasonably stable towards loss of CA^{2-} in acidic solution (pH 1–4), but decomposes rapidly to give elemental palladium in neutral or basic media.

$K_2[Pd(CA)(ox)] \cdot H_2O$ (4). Potassium oxalate (0.18 g, 1.0 mmol) was mixed with a slight excess of **3** (0.40 g, 1.1 mmol) in 50 ml of methanol. The product was isolated as a yellow-green powder after continuous stirring for 2 days. Excess starting material was removed by washes with methanol and ether. Yield: 0.45 g, 95%.

$K[Pd(CA)(acac)]$ (5). KOH (1 mmol, 1.4 ml of 0.713 *M* KOH) was slowly added to a stirred mixture of acetylacetone (0.50 g, 5.0 mmol) and **3** (0.37 g, 1.0 mmol) in 30 ml of water. The bright yellow product which precipitated within 30 minutes was washed with cold water and ether. Yield: 0.24 g, 53%.

$[Pd(CA)(dmso)_2]$ (6). The stoichiometric amounts of **3** (0.37 g, 1.0 mmol) and dmso (0.16 g, 2.0 mmol) were combined in 30 ml of tetrahydrofuran with stirring. Precipitation of the brown-green product was complete after 1 day, at which time **6** was collected and washed with cold THF and ether. Yield: 0.45 g, 96%.

$K_2[Pd_2(CA)_2(SCN)_2]$ (7). Several attempts to prepare $K_2[Pd(CA)(SCN)_2]$ were unsuccessful, owing to the displacement of CA^{2-} by thiocyanate ion in the presence of a 2/1 SCN^- to Pd^{II} ratio. A binuclear, thiocyanate bridged complex could be isolated, however, when this ratio was reduced to 1/1. KSCN (0.10 g, 1.0 mmol) was allowed to react with 0.40 g (1.0 mmol) of **2** in 50 ml of stirred ethanol. The color of the solution slowly changed from yellow to brown, followed by the deposition of a yellow-green gelatinous precipitate. The filtered product was washed with cold THF and ether. Upon vacuum drying, the solid changed color from yellow-green to brown. Yield: 0.38 g, 93%.

$K_2[Pd(CA)F_2] \cdot H_2O$ (8). **2** (0.20 g, 0.5 mmol) was dissolved in 20 ml of methanol saturated with KF. The red-yellow precipitate which formed over a

30-minute interval was collected by filtration and washed with cold methanol and ether. Yield: 0.15 g, 65%.

$K_2[Pd(CA)Br_2]\cdot H_2O$ (9). A large excess of KBr (1.19 g, 10 mmol) was added to **2** (0.20 g, 0.5 mmol) in 20 ml of water. The yellow-orange product formed rapidly, reaching completion within 15 minutes. After filtration, **9** was washed with cold water and ether. Yield: 0.20 g, 70%.

$K_2[Pd_2(CA)_2Br_2]\cdot 4H_2O$ (10). Attempts to recrystallize **9** from water containing equimolar KBr produced yellow-green plates of a binuclear, bis(μ-bromo) analog. The product was washed with cold water and ether.

[Pd(CA)(bpy)] (11). 2,2′-Bipyridine (0.08 g, 0.5 mmol) and 0.20 g of **2** (0.5 mmol) were combined in 25 ml of stirred acetone. An immediate color change from yellow to gray-brown was observed, followed by precipitation of the highly-insoluble product. The filtered solid was washed with cold acetone and ether. Yield: 0.18 g, 77%.

$[Pd(CA)(tcnq)]\cdot H_2O$ (12). 7,7,8,8-Tetracyanoquinodimethane (0.10 g, 0.5 mmol) was allowed to react with **2** (0.20 g, 0.5 mmol) for one week in 30 ml of stirred THF. The brown-green product was washed with THF and ether. Yield: 0.15 g, 56%.

$K_2[Pd(CA)(CN)_2]\cdot H_2O$ (13). A cyanide adduct with Pd(CA) could only be isolated under conditions where CN^- was the limiting reagent and the product was highly insoluble in the reaction medium. Otherwise, facile displacement of CA^{2-} by CN^- was invariably observed. KCN (0.13 g, 2.0 mmol) was mixed with 0.30 g of **3** (1.0 mmol) in 30 ml of stirred methanol. Color changes from yellow to green to gray and finally to red-brown were observed within a few minutes. A red-brown precipitate of **13** was then collected and washed with cold methanol and ether. Yield: 0.40 g, 87%.

$K_2[Pd(CA)_2]\cdot 2H_2O$ (14). Equimolar 3 (0.37 g, 1.0 mmol) and K_2CA were combined in 30 ml of water with stirring. A color change from yellow to blue-purple occurred within several minutes. Purple-brown needles of **14** formed upon evaporation of the solvent and were washed with cold water, methanol and ether. Yield: 0.29 g, 46%.

$[Pd(CA)(cod)]\cdot THF$ (15) and $[Pd(CA)(cod)]\cdot H_2O$ (16). Different complexes, yellow $[Pd(CA)(cod)]\cdot THF$ and dark purple $[Pd(CA)(cod)]\cdot H_2O$, were obtained from the reactions of **2** with 1,5-cyclooctadiene in THF and CH_2Cl_2, respectively. **2** (0.60 g, 1.5 mmol) was combined with cod (0.18 g, 1.7 mmol) in 50 ml of stirred THF. The precursor complex is very slightly soluble in THF, but slowly converted to yellow-green **15** over a 2-day period. The filtered product was washed with THF and ether. Yield: 0.60 g, 56%. When cod (0.11 g, 1.0 mmol) was allowed to react with **2** (0.40 g, 1.0 mmol) in dichloromethane for one week, **16** precipitated as a purple powder and then was washed with dichloromethane and ether. Yield: 0.43 g, 98%.

Unsuccessful synthesis. Although the fluoride, chloride and bromide adducts with Pd(CA) are quite stable, immediate displacement of chloranilate followed by precipitation of black PdI_2 was observed upon mixing two equivalents of KI with **2** in methanol. **Caution**: When NaN_3 (0.07 g, 1.0 mmol) was combined with 0.20 g of **2** (0.5 mmol) in 25 ml of stirred acetone, a gradual color change from yellow to bright red occurred and a red-brown product presumed to be $K_2[Pd(CA)(N_3)_2]$ precipitated. The azide complex exploded when subjected to mild mechanical friction in the filtration step. No further attempt was made to isolate this product.

Numerous attempts were made to prepare Pd(CA)-olefin and diolefin complexes from the reactions of **2** or **3** with 2,5-dihydroxy-1,4-benzoquinone, tetrahydroxy-1,4-benzoquinone, 5-hydroxy-1,4-naphthoquinone, 5,8-dihydroxy-1,4-naphthoquinone, duroquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (ddq), 1,2-dihydroxy-3,4,5,6-tetraoxo-1-cyclohexene (disodium salt) and tetracyanoethylene (tcne). Immediate color changes from yellow to purple accompanied the reactions of hydroxyquinones with chloranilatopalladium(II) precursor complexes, but facile ligand oxidations afforded palladium metal as the only isolable product. Tetracyanoethylene displaces CA^{2-} from the Pd^{II} coordination sphere, giving a white product which was not characterized further. Duroquinone failed to react with 2 in both polar and non-polar solvents.

Results and discussion

An extensive family of chloranilatopalladium(II) compounds was prepared with excellent yields from the precursors $[Pd(CA)(CH_3CN)_2]$ and $[Pd(CA)(H_2O)_2]$. Although **2** proved to be the best starting material in most cases, owing to the ease of CH_3CN displacement, **3** was a superior choice in several preparations which feature hydrophilic incoming groups that are not appreciably soluble in non-aqueous solvents. The analytical data presented in Table 1 confirm the purity of new compounds **3–16**. Although the majority of L_2 functions considered readily formed stable adducts with Pd(CA), olefinic and quinonoid ligands generally are unreactive or cause the displacement of CA^{2-}. The failures of strong π-acids (ddq and tcne) to enter the Pd first coordination sphere without concurrent cleavage of the $Pd–CA^{2-}$ bond implies that the chloranilate negative charge is not sufficiently polarized towards Pd^{II} to enhance back-bonding to other olefinic ligands.

Several of the chloranilatopalladium(II) compounds described here are not sufficiently soluble or stable in solution to permit the measurement of electronic or NMR spectra. Fortunately, solid-state infrared spectroscopy offers an unambiguous means by which (C–CA) compounds may be distinguished from (π-CA) and other linkage isomers [2]. Table 2 exhibits the principal features of KBr pellet infrared spectra, electronic spectra (where possible) and our proposed assignment of linkage isomer type for each $[Pd(CA)L_2]$ species. Three infrared characteristics: (1) several strong C=O vibrations in the 1620–1720 cm^{-1} interval but no 1500–1550 cm^{-1} C–O mode; (2) 1–4 medium-intensity C–C stretching bands between 1150 and 1220 but no C=C feature near 1350 cm^{-1}; and (3) a relatively high-energy C–Cl vibration, i.e. > 855 cm^{-1} are distinctive of the yellow $[Pd(C\text{–}CA)L_2]$ compounds [2]. In contrast, $[Pd(\pi\text{-}CA)(PPh_3)_2]$ exhibits a single medium-intensity C=O band at 1640 cm^{-1}, a very strong C–O mode at 1530 cm^{-1}, only weak PPh_3 features in the 1150–1250 cm^{-1} interval and a C–Cl stretch below 855 (846) cm^{-1} [2]. On this basis, the infrared data indicate that the (C–CA) linkage isomer is present in 12 of the 16 compound treated in this paper, with exceptions in the cases of $L_2 = 2dmso$ (**6**), bpy (**11**), $2CN^-$ (**13**), and cod (**16**). It should be noted that the distinction between (π-CA) diene carbon-bonded and oxygen-bonded chelation alternatives is not possible on the basis of spectroscopic evidence presented here.

The (C–CA) isomer medium-intensity IR peaks near 1200 cm^{-1} are most reasonably assigned to C–C vibrations, perhaps mixed with some Pd–C stretching character, similar to those observed in the structurally-analogous norbornane mole-

Table 1

Analytical data for chloranilatopalladium(II) complexes

Formula	(Found (calcd.) (%))		
	C	H	N
$K_2[Pd(CA)Cl_2]\cdot 0.5H_2O$ [a]			
(1)			
$[Pd(CA)(CH_3CN)_2]$ [a]			
(2)			
$[Pd(CA)(H_2O)_2]\cdot H_2O$	19.65	1.51	
(3)	(19.61)	(1.64)	
$K_2[(CA)(ox)]\cdot H_2O$	19.30	0.63	
(4)	(19.31)	(0.40)	
$K[Pd(CA)(acac)]$	29.30	1.49	
(5)	(29.26)	(1.56)	
$[Pd(CA)(dmso)_2]$	25.69	2.44	
(6)	(25.58)	(2.58)	
$K_2[Pd_2(CA)_2(SCN)_2]$	20.50	0.06	3.15
(7)	(20.48)	(0.00)	(3.41)
$K_2[Pd(CA)F_2]\cdot H_2O$	16.02	0.79	
(8)	(16.10)	(0.45)	
$K_2[Pd(CA)Br_2]\cdot H_2O$	12.78	0.29	
(9)	(12.66)	(0.35)	
$K_2[Pd_2(CA)_2Br_2]\cdot 4H_2O$	15.37	0.36	
(10)	(15.39)	(0.86)	
$[Pd(CA)(bpy)]$	40.71	1.67	6.00
(11)	(40.93)	(1.72)	(5.97)
$[Pd(CA)(tcnq)\cdot H_2O$	40.82	2.28	10.24
(12)	(40.37)	(1.13)	(10.46)
$K_2[Pd(CA)(CN)_2]\cdot H_2O$	20.69	0.37	6.29
(13)	(20.82)	(0.43)	(6.07)
$K_2[Pd(CA)_2]\cdot 2H_2O$	22.51	0.28	
(14)	(22.71)	(0.63)	
$[Pd(CA)(cod)\cdot THF$	43.18	3.99	
(15)	(43.80)	(4.08)	
$[Pd(CA)(cod)]\cdot H_2O$	38.29	2.61	
(16)	(38.25)	(3.21)	

[a] Previously reported in ref. 2.

cule. Thus, 2-chlorobicyclo[2,2,1]heptane (1260, 1318 cm^{-1}), 7-chloro-2-bromobicyclo[2,2,1]heptane (1240, 1260, 1300, 1315 cm^{-1}) and 2,7-dichlorobicyclo[2,2,1]-heptane (1270, 1310, 1325 cm^{-1}) [5] manifest well-defined C–C stretches at slightly higher energy than the distinctive features of the $[Pd(C\text{-}CA)L_2]$ compounds. There does not appear to be a simple relationship between the number and positions of $[Pd(C\text{-}CA)L_2]$ complex C–C vibrations and the nature of the L substituent. These skeletal vibrations are expected to be sensitive to the chloranilate ring bend angle and to the hybridization state of carbon, making them potentially revealing with regard to the $Pd\text{-}CA^{2-}$ bonding interaction. Within neutral (C–CA) complexes, a red-shift in the highest energy C–C mode is found with increasing softness of L, i.e. 1213 (H_2O) > 1208 (CH_3CN) > 1183 (tcnq) > 1120 cm^{-1} (cod). Such a trend could reflect increasing *p*-character in the carbanion donor orbitals with decreasing

Table 2. Spectroscopy of chloranilatopalladium(II) complexes [a]

	ν(CO) (cm^{-1})	ν(C–Cl) (cm^{-1})	ν(C–C) (cm^{-1})	λ_{max} (ϵ, M^{-1} cm^{-1}) (nm)	Isomer
1	1695	865	1214	236 (2.2×10^{4})	C–CA
	1661		1180	264 (1.8×10^{4})	
			1161	312 (1.5×10^{4})	
2	1695	866	1208	223 (2.3×10^{4})	C–CA
	1680		1161	264 (1.1×10^{4})	
	1635			306 (9.6×10^{3})	
3	1690	868	1213	224 (1.6×10^{4})	C–CA
	1635		1190	256 (9.7×10^{3})	
			1175	315 (1.1×10^{4})	
			1165		
4	1650	866	1177	243 (2.3×10^{4})	C–CA
				310 (8.4×10^{3})	
5	1695	867	1195	232 (1.8×10^{4})	C–CA
	1679		1175	311 (1.5×10^{4})	
	1640				
6	1660	837			π-CA
	1645				
	1633				
	1625				
	1525				
7	1690	868	1190	219 (1.8×10^{4})	C–CA
	1652		1163	258, sh (1.1×10^{4})	
				319 (1.7×10^{4})	
8	1659	862	1170	214 (1.5×10^{4})	C–CA
	1636			256, sh (7.6×10^{3})	
				310, sh (6.4×10^{3})	
9	1687	857	1215	242 (1.5×10^{4})	C–CA
	1656		1176	286 (2.4×10^{4})	
				310, sh (1.9×10^{4})	
10	1710	861	1214		C–CA
	1685		1176		
	1664		1152		
11	1700	850			π–CA
	1688				
	1665				
	1639				
	1510				
12	1657	863	1183		C–CA
	1638				
13	1660	833		213 (2.5×10^{4})	π-CA
	1520			332 (2.1×10^{4})	
				340, sh (2.0×10^{4})	
				528 (1.6×10^{3})	
14	1710	865	1215	217 (3.1×10^{4})	πCA and C–CA
	1690	837	1168	258, sh (1.3×10^{4})	
	1658			321 (2.5×10^{4})	
	1640			537 (3.5×10^{2})	
	1525				
15	1720	860	1120		C–CA
	1680				
16	1644	848			π-CA
	1546				

[a] Infrared spectra are of KBr pellets. Electronic spectra were measured in aqueous solution (pH 3.7, $HClO_4$) with 100-fold excesses of L_2 present to suppress the dissociation of [Pd(C–CA)L_2] complexes to [Pd(C–CA)(H_2O)$_2$], except in the case of 7 (see text).

complementary group σ-donating capability, maximizing Pd–(C–CA) bond covalency.

Infrared results are also helpful in understanding the bonding modes of acac$^-$ (**5**), dmso (**6**), NCS$^-$ (**7**) and tcnq (**12**) in their respective chloranilatopalladium(II) complexes. The acetylacetonate ligand is known to form both bidentate, O-bonded and monodentate, γ-carbon-bonded linkage isomers in Pd^{II} complexes [6,7]. Strong oxygen-bonded acac$^-$ CO (1569 cm^{-1}) and CC (1524 cm^{-1}) bands in $Pd(acac)_2$ [8,9] are virtually identical in both energy and intensity to those of K[Pd(C–CA)(O–acac)] at 1578, 1570 (shoulder) and 1513 cm^{-1}, respectively, while carbon-bonded acac$^-$ exhibits a very strong C=O absorption at higher energy (ca. 1650 cm^{-1}) that is lacking in the Pd(CA) complex. In contrast, the dmso ligands of $[Pd(C{-}CA)(dmso)_2]$ evidently are sulfur-bonded, in view of SO stretches at 1032, 1095 and 1103 cm^{-1}, blue-shifted relative to ν(SO) bands below 1000 cm^{-1} that are typical when coordination occurs through oxygen [10].

The empirical formula of thiocyanate complex 7, KPd(CA)(SCN), suggests a bridged, dimeric configuration that would permit each Pd^{II} center to interact with four ligands in the most favorable square planar coordination geometry. Thiocyanate ν(CN) absorption occurs above 2100 cm^{-1} when bonding is through sulfur, as in $(Et_4N)_2[Pd(SCN)_4]$ (2109, 2112 cm^{-1}), while N-bonded SCN$^-$ exhibits a CN stretch shifted to lower energy (< 2100 cm^{-1}) [11]. For example, ν(CN) values characteristic of the S- and N-bonded linkage isomers of *trans*-$[Pd(AsPh_3)_2(SCN)_2]$ are 2119 and 2089 cm^{-1}, respectively [12]. The exceptionally high, single CN stretching frequency of $K_2[Pd_2(CA)_2(SCN)_2]$ (2160 cm^{-1}) not only points to S-bonding, but indicates the presence of bridging (Pd–SCN–Pd) [13] thiocyanate ligands in a dimer, $[(C{-}CA)Pd(SCN)_2Pd(C{-}CA)]^{2-}$. Thus, CN stretching frequency ranges of 2100–2120 and 2150–2182 cm^{-1} pertain for terminal, S-bonded SCN$^-$ and bridging thiocyanate ligands in Pt^{II} compounds, respectively [14].

The Pd[C–CA)(tcnq)] · H_2O complex shows two IR peaks in the CN stretching region with approximately equal intensity (medium; 2160, 2230 cm^{-1}), whereas $K_2[Pd(\pi\text{-}CA)(CN)_2] \cdot H_2O$ and $[Pd(C{-}CA)(CH_3CN)_2]$ exhibit single bands at 2220 and 2225 cm^{-1}, respectively. Considering that free 7,7,8,8-tetracyanoquinodimethane also has a single CN absorption at 2210 cm^{-1}, we conclude that tcnq is bound to Pd^{II} as a bidentate ligand through 7,7-$(CN)_2$ nitrogen atoms rather than C=C bonds. This hypothesis reconciles the successful synthesis of **12** with failures to isolate similar Pd(CA) adducts with most olefinic ligands. It is very much unclear, however, why the CN functions of tcne and ddq do not promote the formation of stable adducts with Pd(CA) analogous to the tcnq complex.

Although the insolubilities of $[Pd(CA)(dmso)_2]$, [Pd(CA)(bpy)], and [Pd(CA)-(cod)] · H_2O limit their structural characterization to the solid state, electronic spectra of the other complexes assigned to the (π-CA) class clearly confirm the presence of *p*-quinonoid CA^{2-}. The 332 and 528 nm bands of $K_2[Pd(\pi\text{-}CA)(CN)_2] \cdot H_2O$ are readily assigned to allowed ($^1B_{3u} \leftarrow {}^1A_g$) and symmetry-forbidden ($^1B_{1g} \leftarrow {}^1A_g$) quinonoid π–π^* transitions by comparison with the spectra K_2CA and an extensive family of $[Pd(\pi\text{-}CA)(PR_3)_2]$ complexes [2,4]. Similarly, $K_2[Pd(CA)_2] \cdot 2H_2O$ exhibits π–π^* bands at 321 and 537 nm and therefore most likely contains the complex anion $[Pd(C{-}CA)(\pi\text{-}CA)]^{2-}$ in view of infrared evidence for the presence of both (C–CA) and (π-CA) linkage types; i.e. distinct C–Cl vibrations at 865 and 837 cm^{-1}, strong C–O (1525 cm^{-1}) and C=O stretches (1640–1710

cm^{-1}), and the medium-intensity C–C bands (1168, 1215 cm^{-1}) that only appear in the IR spectra of (C–CA) compounds. The possibility exists, however, that **14** is better formulated as a complex salt, $[Pd(C\text{–}CA)(H_2O)_2] \cdot K_2CA$, in which one CA^{2-} unit interacts weakly or not at all with the Pd^{II} center. The unusually low extinction coefficient of the 537 nm $^1B_{1g} \leftarrow {}^1A_g$ transition (3.5×10^2 M^{-1} cm^{-1}) as compared with the majority of (π-CA) complexes (9×10^2 to 1.3×10^3 M^{-1} cm^{-1}) [4] suggests that the quinonoid CA^{2-} of **14** is not unsymmetrically ligated in solution, consistent with the presence of free ionic chloranilate. This structural ambiguity can only be resolved by X-ray crystallographic studies of the compound.

In the course of measuring the electronic spectra of (C–CA) compounds in weakly acidic ($HClO_4$) aqueous solution (pH 3.7), it was discovered that the fluoride, chloride, bromide, acetylacetonate and oxalate complexes rapidly hydrolyze to $[Pd(C\text{–}CA)(H_2O)_2]$ in the absence of excess ligand to suppress the dissociation of $[Pd(C\text{–}CA)L_2]$. Ultraviolet spectra of all (C–CA) complexes except the thiocyanate-bridged dimer indicated that quantitative conversions to the diaqua species were complete within three minutes. This reaction appears to be acid-catalyzed, since displacement of chloride from $[Pd(C\text{–}CA)Cl_2]^{2-}$ was negligible within 15 minutes in neutral solution. Such a hydrolysis reaction is contrary to expectations from hard-soft acid-base theory, since the hard water molecule ranks among the poorest donors towards the soft Pd^{II} center. These unexpected hydrolyses may be driven thermodynamically be a strengthening of the Pd–chloranilate C bonds engendered by the departure of competing sigma donor ligands. A kinetic *trans* effect of the (C–CA) functional unit may be linked, therefore, to factors other than σ-donating ability of the dicarbanion in its ground state configuration. Further spectroscopic and kinetic studies of this interesting behavior are in progress to better understand the surprising stability of $[Pd(C\text{–}CA)(H_2O)_2]$ and the trans influence/effect contributions to its formation from other $[Pd(C\text{–}CA)L_2]$ complexes.

The ultraviolet spectra of most $[Pd(C\text{–}CA)L_2]$ compounds, evaluated in the presence of 100-fold excesses of free ligand (Table 2), exhibit a strong band near 220 nm which may be assigned to the π–π^* transition of the localized chloranilate carbonyl groups. In addition, two broad bands with extinction coefficients on the order of 10^4 M^{-1} cm^{-1} are consistently found in the vicinity of 310 and 230–260 nm. It was established that these strong bands are not ligand-centered or L–to–Pd^{II} charge transfer absorptions, leaving chloranilate carbon-to-palladium(II) charge transfer as the most reasonable spectroscopic assignment for both transitions. Unfortunately, an extensive literature review failed to produce a precedent for C-to-Pd^{II} LMCT transitions, but analogous bands originating from the σ-bonding electrons of halide and sulfur-donor ligands are well-known in the ultraviolet region [15]. Indeed, the 264 and 286 nm features of **1** and **9**, respectively, may be attributed to halide-to-Pd^{II} charge transfer. The C-to-Pd^{II} LMCT assignment is supported by the fact that the X-ray crystal structure of $K_2[Pd(C\text{–}CA)Cl_2] \cdot 4H_2O$ shows the Pd–C bonds to be non-equivalent, with a substantial bond length difference of 0.05 Å (2.02 and 2.07 Å) [1]. Assuming that the interconversion of the two Pd–C bonds is slow on the spectroscopic time scale, two distinguishable C-to-Pd^{II} LMCT bands with different energies could in principle be observed. These carbon atoms evidently interchange rapidly on the much longer ^{13}C NMR time scale, however, since only two resonances attributable to carbonyl and carbanion carbon atoms were found for both **1** and **2** [2].

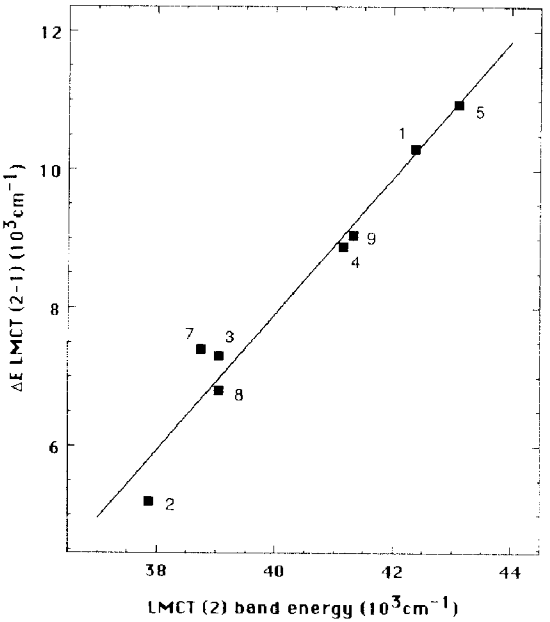

Fig. 2. Correlation between the energy of the shortest wavelength C-to-Pd^{II} charge transfer band (LMCT (2)) and the energy difference between the two C-to-Pd^{II} bands (ΔE LMCT (2-1)) for [Pd(C–CA)L_2] complexes. Compounds are numbered as in Table 1 and all band positions are shown in Table 2.

Figure 2 illustrates an intriguing linear relationship of the transition energy difference between the two proposed C-to-Pd^{II} charge transfer bands to the energy of the feature at shorter wavelength. The quality of this correlation suggests the presence of a single variable structural feature in the (C–CA) class which strongly influences the relative energies of the carbon orbitals implicated in the LMCT transitions. This variable most reasonably is the difference in length between the two Pd–C bonds, which imparts an asymmetric aspect to the chelating dicarbanion unit. The spectroscopic results show that the higher frequency LMCT band varies in energy considerably more than the other transition, which deviates only slightly from 310 nm with changes in the L group. On this basis, we propose that one chloranilate C–Cl carbon atom retains full sp^3, carbanion character in all [Pd(C–CA)L_2] complexes, while the other carbon donor, bonded at the shorter Pd–C length [16,17], is capable of assuming partial allylic character (sp^2 hybridization). Although this model cannot be fully defended on the basis of results presented in this paper, it does offer a useful hypothesis to be tested in continuing studies of the (C–CA) complexes.

Finally, the factors influencing linkage isomer preference in [Pd(CA)L_2] complexes should be addressed. The prediction that weak σ donors would promote (C–CA) chloranilate coordination is verified by the finding of this isomer for $L_2 = 2F^-$, $2Cl^-$, $2Br^-$, acac$^-$, ox^{2-}, $2CH_3CN$ and $2H_2O$, but not in the cases of softer L_2 groups such as S-bonded dmso and CN^-. Pd–SCN–Pd bridging in 7 evidently provides the weaker, harder average σ-donation to Pd^{II} that is required to stabilize the (C–CA) bonding mode. Also consistent with expectations is the destabilization of the (C–CA) mode by soft, strong σ donors such as phosphines, which invariably give complexes of the form [Pd(π-CA)$(PR_3)_2$] [4]. Enhanced π

acceptance by chloranilate is not a major contributor to the driving force of phosphine-induced linkage isomerization, however, as the interactions of electron-rich phosphorus donors with Pd^{II} appear to be optimized by the weakening of chloranilate σ bonding through (C–CA) to (π-CA) isomerization [4]. Considering the failure of most olefinic ligands examined to form isolable Pd(CA) adducts, it is difficult to judge whether strong π-acceptors also stabilize the (C–CA) bonding mode. The preference of (π-CA) ligation in cyanide and 2,2′-bipyridine complexes implies that the availability of low-lying π^* orbitals is not sufficient to prevent the destabilization of the (C–CA) mode by σ donation from the CN^- and bpy ligands.

The surprising syntheses of both Pd(C–CA) and Pd(π-CA) complexes with cod in THF and CH_2Cl_2 media, respectively, indicates that the preference for (C–CA) or (π-CA) isomers is not a function of the complementary donor only, but also depends on the solvation of the product. Indeed, the presence of THF and H_2O molecules of crystallization in complexes **15** and **16**, respectively, strongly suggests that solvents which are capable of weakly interacting with Pd^{II} through an axial coordination position or of hydrogen-bonding with chloranilate oxygen atoms contribute significantly to the ultimate preference of linkage isomer type. It should also be noted that some of the species reported here may be kinetic rather than thermodynamic products, particularly when synthetic constraints required the use of solvents in which neither the palladium starting material nor the product was appreciably soluble.

Acknowledgment

We thank the Robert A. Welch Foundation for generous financial support of this research (Grant D-735) and Professor Robert Walkup for helpful discussions of palladium organometallic chemistry. A reviewer is thanked for pointing out the consistency of Pd–SCN–Pd bridging with (C–CA) linkage isomer preference in compound 7.

References

1 O.N. Krasochka, V.A. Avilov, and L.O. Otovmyan, Zh. Struckt. Khim., 15 (1974) 1140.
2 W.-Y. Jeong and R.A. Holwerda, Inorg. Chem., 27 (1988) 2571.
3 W.-Y. Jeong and R.A. Holwerda, Inorg. Chem., 27 (1988) 4316.
4 W.-Y. Jeong and R.A. Holwerda, Inorg. Chem., in press.
5 Sadtler Standard Infrared Prism Spectra, Sadtler Research Laboratories, Inc., 1972.
6 S. Baba, T. Ogura, and S. Kawaguchi, Bull. Chem. Soc. Jpn., 47 (1974) 665.
7 M. Horike, Y. Kai, N. Yasuoka, and N. Kasai, Inorg. Chem., 17 (1978) 910.
8 S. Pinchas, B.L. Silver and I. Laulicht, J. Chem. Phys., 46 (1967) 1506.
9 M. Mikami, I. Nakagawa, and T. Shimanouchi, Spectrochim. Acta, 23A (1967) 1037.
10 F.A. Cotton, R. Francis, and W.D. Horrocks, J. Phys. Chem., 64 (1960) 1534.
11 A. Sabatini and I. Bertini, Inorg. Chem., 4 (1965) 959.
12 F. Basolo, J.L. Burmeister and A.J. Poe, J. Am. Chem. Soc., 85 (1963) 1700.
13 A.M. Golub, H. Kohler, and V.V. Skopenko (Eds.), Chemistry of Pseudohalides, Elsevier, Amsterdam, 1986, p. 239.
14 J. Chatt and L.A. Duncanson, Nature, 178 (1956) 997.
15 A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd edit., Elsevier, Amsterdam, 1984.
16 S. Suzuki, K. Itoh, Y. Ishii, K. Simon, and J.A. Ibers, J. Am. Chem. Soc., 98 (1976) 8494.
17 Y. Zenitani, H. Tokunan, Y. Kai, N. Yasuoka, and N. Kasai, Bull. Chem. Soc. Jpn., 51 (1978) 1730.