Inorg. Chem. **1988**, *27*, 2571-2574 **2571**

Contribution from the Department of Chemistry and Biochemistry,
Texas Tech University, Lubbock, Texas 79409

Linkage Isomerism in Palladium(II)-Chloranilate Complexes. Synthesis and Mechanistic Studies of Bis(acetonitrile)(chloranilato)palladium(II) and Bis(triphenylphosphine)(chloranilato)palladium(II)

Woo-Yeong Jeong and Robert A. Holwerda*

Received February 3, 1988

Structural and mechanistic studies are reported of a linkage isomerization process in which the bidentate ligand 2,5-dioxo-3,6-dichloro-1,4-benzoquinone (chloranilate dianion, CA^{2-}) rearranges to a π-complexed diene (π-CA^{2-}) from an unusual bis(carbanion) resonance form (C-CA^{2-}) upon the substitution of acetonitrile by triphenylphosphine in the first coordination sphere of palladium(II). Yellow $[Pd(C\text{-}CA)(CH_3CN)_2]$ may be prepared in excellent yield from the reaction of $K_2Pd(C\text{-}CA)Cl_2$ with $AgNO_3$ in acetonitrile solution and combines readily with triphenylphosphine to give purple $[Pd(\pi\text{-}CA)(PPh_3)_2]$. Pd(II)-chloranilate complexes were structurally characterized through NMR (^{13}C and ^{31}P), UV-visible, and infrared spectra. Stopped-flow kinetic studies of the $[Pd(C\text{-}CA)(CH_3CN)_2]$ transformation to $[Pd(\pi\text{-}CA)(PPh_3)_2]$ in acetonitrile solution demonstrate that rate-limiting linkage isomerization (rate constant k_i) follows rapid, preequilibrium formation of $[Pd(C\text{-}CA)(PPh_3)_2]$ (stepwise formation constants K_1 and K_2). At 25.0 °C, $K_2 = 2.47 \times 10^2$ M^{-1} and $k_i = 8.44 \times 10^{-2}$ s^{-1}. Kinetic temperature dependence results gave the activation parameters that govern k_i ($\Delta H^* = 17.1$ kcal/mol; $\Delta S^* = -6$ eu) and standard enthalpy/entropy changes corresponding to K_2 ($\Delta H^\circ = -14.0$ kcal/mol; $\Delta S^\circ = -36$ eu). The exceptionally high enthalpic activation barrier to linkage isomerization reflects the considerable stability of the five-membered, bis(carbanion) chelate ring in $[Pd(C\text{-}CA)(CH_3CN)_2]$.

Introduction

Catalytic applications of palladium(II) compounds include such important organic transformations as the oxidation of ethylene to acetaldehyde[1] and the acetoxylation of olefins and dienes.[2] In virtually all well-characterized examples of olefin oxidations by Pd(II), insertion of an alkene coordinated through its π-bonding electron pair into a palladium(II)-ligand bond is an essential step in the catalytic cycle,[3] affording a Pd-C σ complex in which the hybridization of carbon has changed from sp^2 to sp^3. The exceptional stability of palladium(II) bonds to saturated carbon centers provides ample thermodynamic driving force for the conversion of olefin π complexes to σ-alkyl forms.[4-8] Although elegant kinetic studies of the Wacker process for ethylene oxidation have conclusively demonstrated that the rate-limiting step features a 1,2-addition reaction of the π-complexed olefin,[9] detailed understanding of the elementary processes leading to the Pd(II)-alkyl ($-CH_2CH_2OH$) intermediate is difficult in a catalytic cycle that encompasses several other organometallic reaction types. The development of new catalytic applications for Pd(II) organometallics depends upon the understanding of pathways followed in simpler reactions where palladium-carbon bonds are made or broken with an accompanying hybridization change at the ligated carbon atom.

Toward this end, we report here mechanistic and structural studies of a linkage isomerization reaction in which a hydroxyquinone ligand, bonded as a dicarbanion, rearranges to a π-complexed diene upon the substitution of acetonitrile by triphenylphosphine in the palladium first coordination sphere. The remarkable affinity of Pd(II) for sp^3-hybridized carbon is apparent from the X-ray crystal structure[10] of $K_2[Pd(CA)Cl_2]\cdot 4H_2O$ (CA^{2-} = 2,5-dioxo-3,6-dichloro-1,4-benzoquinone). Thus, instead of forming a conventional[11,12] adduct through olefinic π or phenolate oxygen electron pairs, chloranilate ligates palladium(II) as a bidentate, bis(carbanion) donor in which negative charges are localized on sp^3-hybridized carbon atoms bonded to both Pd and Cl substituents (Figure 1). The bend angle characteristic of this non-quinonoid, boat conformation of coordinated chloranilate is 46.0°, and the two Pd-C bond lengths are 2.02 and 2.07 Å.[10] Bis(carbanion), *p*-quinone, and *o*-quinone resonance forms of the chloranilate dianion (Figure 2) suggest at least three possibilities for linkage isomerism in Pd(II)-CA^{2-} complexes. We have undertaken the synthesis and characterization of an extensive family of $PdII(CA)L_2$ complexes in order to test the hypothesis that the electron-releasing, dicarbanion resonance form (C-CA^{2-}) will be preferred in the presence of π-accepting or weakly σ-donating ligands. Conversely, the π-accepting capability of chloranilate bonded through diene electron pairs in its *p*-quinone resonance form (π-CA^{2-}) should effectively complement good σ donors toward the soft Pd(II) center. In this paper, we report the synthesis of $[Pd(C\text{-}CA)(CH_3CN)_2]$ and a kinetic study of the linkage isomerization reaction (eq 1) induced by the substitution of acetonitrile ligands by triphenylphosphine.

$$[Pd(C\text{-}CA)(CH_3CN)_2] + 2PPh_3 \rightarrow [Pd(\pi\text{-}CA)(PPh_3)_2] + 2CH_3CN \quad (1)$$

Experimental Section

Potassium tetrachloropalladate was prepared quantitatively from the reaction of $PdCl_2$ (Aldrich) with a 10% excess of KCl in dilute aqueous HCl at 60 °C. Triphenylphosphine and its *p*-F, *p*-CH_3, and *m*-CH_3 derivatives were used as supplied by Strem. Reagent grade organic solvents were dried over molecular sieves before use in synthetic, spectroscopic, or kinetic work. Chloranilic acid was supplied by Sigma.

Synthesis of $K_2[Pd(C\text{-}CA)Cl_2]\cdot 0.5H_2O$ (1). The method was adapted from that of Krasochka et al.[10] K_2PdCl_4 (8.99 g, 27.5 mmol) was added to chloranilic acid (5.75 g, 27.5 mmol) in 300 mL of stirred, distilled water at room temperature. An immediate green precipitate slowly converted to a yellow, crystalline product over a period of 10 h. The solid was collected on a sintered-glass filter, and a second crop was obtained after evaporating the supernatant to 10 mL. The crude product was recrystallized from water, washed with cold water, methanol, and ether, and vacuum-dried. Yield: 12.1 g (95%). Anal. Calcd for $K_2[Pd(CA)Cl_2]\cdot 0.5H_2O$: C, 15.29; H, 0.21; Cl, 30.08; K, 16.59. Found: C, 15.12; H, 0.43; Cl, 29.94; K, 16.71. UV (H_2O): λ_{max} 236 nm (ϵ 2.2×10^4 M^{-1} cm^{-1}), 264 (1.8×10^4), 312 (1.5×10^4). IR (KBr pellet): 1690 s, 1655 s, 1625 s, 1270 w, 1210 m, 1175 m, 1160 m, 980 w, 860 s cm^{-1}. ^{13}C NMR (H_2O): δ 99.5, 169.4.

Synthesis of $[Pd(C\text{-}CA)(CH_3CN)_2]$ (2). $K_2[Pd(CA)Cl_2]\cdot 0.5H_2O$ (3.12 g, 6.7 mmol) was combined with $AgNO_3$ (2.28 g, 13.4 mmol) in 350 mL of stirred CH_3CN at room temperature. All of the palladium starting material dissolved within 20 min, yielding a yellow solution and precipitates of AgCl and KNO_3. After quantitative separation of the solids, yellow microcrystals were obtained upon evaporation of the supernatant to 10 mL. The product was recrystallized from acetonitrile,

---

(1) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; p 102.
(2) Pandley, R. N.; Henry, P. M. *Can. J. Chem.* **1975**, *53*, 2223.
(3) Majima, T.; Kurosawa, H. *J. Chem. Soc., Chem. Commun.* **1977**, 610.
(4) Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960**, 2008.
(5) Rosevear, D. T.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 164.
(6) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc. A* **1957**, 2496.
(7) Wipke, W. T.; Goeke, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 4244.
(8) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.
(9) Aguilo, A. *Adv.* Organomet. *Chem.* **1967**, *5*, 321.
(10) Krasochka, O. N.; Avilov, V. A.; Atovmyan, L. O. *Zh. Strukt. Khim.* **1974**, *15*, 1140.
(11) Dietropaolo, T.; Boschi, T.; Zanella, R.; Belluco, U. *J. Organomet. Chem.* **1973**, *49*, C88.
(12) Pierpont, C. G.; Francesconi, L. C.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 2367.

0020-1669/88/1327-2571$01.50/0

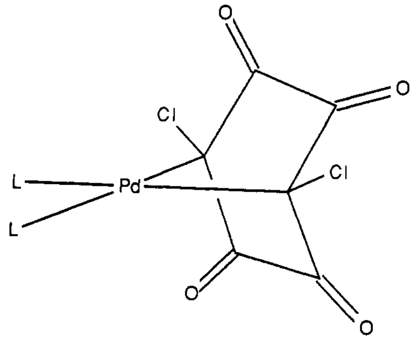

Figure 1. Boat conformation of carbon-bonded chloranilate in Pd(II) complexes with L = Cl^- (ref 10) and CH_3CN.

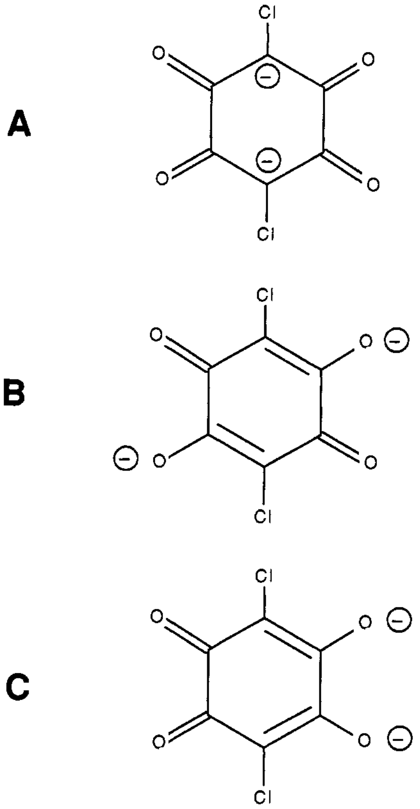

Figure 2. Resonance forms of the chloranilate dianion: (A) bis(carbanion); (B) *p*-quinone; (C) *o*-quinone.

washed with cold CH_3CN and ether, and vacuum-dried. Yield: 2.92 g (94%). The initial precipitate contained 99.8% and 97.5% of the theoretical yields of AgCl and KNO_3, respectively. Anal. Calcd for $[Pd(CA)(CH_3CN)_2]$: C, 30.37; H, 1.53; N, 7.08. Found: C, 30.02; H, 1.45; N, 7.07. UV (CH_3CN): λ_{max} 223 nm (ϵ 2.31 × 10^4 M^{-1} cm^{-1}), 264 (1.05 × 10^4), 306 (9.62 × 10^3). IR (KBr pellet): 2225 w, 1685 s, 1670 s, 1630 s, 1380 m, 1360 m, 1260 w, 1200 m, 1155 m, 1030 w, 970 w, 855 s cm^{-1}. ^{13}C NMR (CH_3CN): δ 102.4, 173.2 (CH_3CN resonances excluded).

Synthesis of $[Pd(\pi\text{-}CA)(PPh_3)_2]\cdot H_2O$ (3). $[Pd(CA)(CH_3CN)_2]$ (0.7910 g, 2.0 mmol) was dissolved in 50 mL of acetonitrile, and the solution was mixed with the stoichiometric amount of PPh_3 (1.0492 g, 4.0 mmol) at room temperature. An immediate color change from yellow to purple was noted, and precipitation of the product was complete within 30 min after mixing. After washing with CH_3CN and ether, the purple powder was recrystallized from dichloromethane, affording fragile plates. Yield: 1.57 g (94%). Anal. Calcd for $[Pd(CA)(PPh_3)_2]\cdot H_2O$: C, 58.93; H, 3.77. Found: C, 59.21; H, 3.39. UV-vis (CH_3CN): λ_{max} 231 nm (ϵ 3.68 × 10^4 M^{-1} cm^{-1}), 284 (1.88 × 10^4), 341 (3.44 × 10^4), 526 (1.13 × 10^3). IR (KBr pellet): 1635 m, 1520 s, 1475 w, 1430 m, 1350 s, 1295 m, 1225 w, 1180 w, 1155 w, 1090 m, 1020 w, 990 m, 830 m, 735 m, 700 w, 680 m cm^{-1}. ^{13}C NMR (CH_2Cl_2): δ 103.3, 127.0, 130.3, 132.6, 170.9, 174.7. ^{31}P NMR (CH_2Cl_2): δ 34.05. The presence of water in 3, evidently absorbed by the solvent during product workup, was confirmed by mass spectrometry (Hewlett-Packard 5995 B spectrometer).

Spectroscopic and Kinetic Measurements. Infrared and UV-visible measurements were acquired on Beckman Acculab 8 and Shimadzu UV-260 spectrophotometers, respectively. Broad-band decoupled carbon-13 (internal TMS reference) and phosphorus-31 (external 85% H_3PO_4 reference) NMR measurements were made on IBM 200- and 300-MHz Fourier transform spectrometers, respectively, at ambient temperature.

Kinetic studies of linkage isomerization induced by the reaction of PPh_3 with $[Pd(CA)(CH_3CN)_2]$ in acetonitrile were performed at 530 nm on a Durrum D-110 stopped-flow spectrophotometer, interfaced to an Apple II Plus computer.[13] Fresh solutions of $[Pd(CA)(CH_3CN)_2]$ in rigorously dry acetonitrile were prepared daily, since even small amounts of water transform the reactant into $[Pd(CA)(H_2O)_2]$ and related hydrolysis products. Pseudo-first-order conditions for the palladium reactant (0.20 mM) were employed, utilizing 8- to 200-fold excesses of triphenylphosphine. Reported pseudo-first-order rate constants (k_{obsd}), derived from the least-squares slopes of $\ln(A_\infty - A_t)$ vs time correlations, are the mean of at least three trials.

Results and Discussion

Preparations of $[Pd(C\text{-}CA)(CH_3CN)_2]$ and $[Pd(\pi\text{-}CA)(PPh_3)_2]\cdot H_2O$. Our preparation and spectroscopic characterization of yellow $K_2[Pd(CA)Cl_2]\cdot 0.5H_2O$ confirm that the chloranilate ligand has lost its quinonoid character. Thus, oxygen-bound CA^{2-} in a purple 1:1 complex with Cr(III) exhibits *p*-quinonoid, ligand-centered $\pi-\pi^*$ transitions at 330 ($^1B_{3u} \leftarrow {}^1A_g$) and 501 nm ($^1B_{1g} \leftarrow {}^1A_g$, overlapping $n-\pi^*$).[14] In contrast, the UV-visible spectrum of **1** is dominated by three intense features at 236, 264, and 312 nm and lacks significant absorption in the visible region. The infrared spectrum of chloranilate coordinated as a dicarbanion exhibits carbonyl stretching modes at 1690, 1655, and 1625 cm^{-1}, a C–Cl stretching band at 860 cm^{-1}, and a group of closely spaced vibrational transitions at 1210, 1175, and 1160 cm^{-1}, which are not observed in the spectra of chloranilic acid or its salts with other transition metals.[15] The presence of only two resonances in the ^{13}C NMR spectrum of **1**, at 99.5 (carbanion carbons) and 169.4 ppm (carbonyl carbons), is as expected from the published X-ray structure of $K_2[Pd(CA)Cl_2]\cdot 4H_2O$.[10]

$[Pd(C\text{-}CA)(CH_3CN)_2]$ was easily prepared in nearly quantitative yield by extracting chloride ion from **1** with $AgNO_3$ in acetonitrile solution. This complex is a useful precursor to **3** and numerous other coordination compounds of the form $Pd(CA)L_2$.[16] A comparison of the UV-visible, infrared, and NMR spectra of **1** and **2** clearly shows that the boat conformation of the chloranilate ligand is retained in the bis(acetonitrile) complex. Three charge-transfer transitions are observed at 223, 264, and 306 nm, but the visible feature near 500 nm responsible for the purple color of *p*-quinonoid chloranilate complexes is absent. Infrared spectra of **1** and **2** in the carbonyl and C–Cl regions are essentially identical, and distinctive new vibrations (probably Pd–C stretches) are observed once again in **2** at 1200 and 1155 cm^{-1}. Finally, the two chloranilate ^{13}C NMR resonances of **2** at 102.4 and 173.2 ppm, shifted slightly downfield from the analogous peaks of **1**, rule out the presence of either *p*- or *o*-quinone resonance forms of the chloranilate dianion, which should give rise to at least three ^{13}C NMR signals.

As anticipated, the displacement of CH_3CN from **2** by a more effective σ-donor ligand, triphenylphosphine, induces the rearrangement of $C\text{-}CA^{2-}$ to $\pi\text{-}CA^{2-}$ in purple $[Pd(CA)(PPh_3)_2]\cdot H_2O$. The positions and intensities of electronic absorption bands at 341 and 526 nm are comparable to those of the free HCA^- *p*-quinonoid anion.[14] Infrared peaks of **3** at 1635 (C=O), 1520 (C—O), 1350, and 830 (C—Cl) cm^{-1} are also characteristic of complexes containing 2,5-dioxo-3,6-dichloro-1,4-benzoquinone.[15,17] The sharp features in the 1150–1225-cm^{-1} region attributed to Pd–C stretches of **1** and **2** are absent in the IR spectrum of **3**, which exhibits much weaker PPh_3 modes in this interval. Chloranilate ^{13}C NMR resonances at 103.3, 170.9, and 174.7 ppm indicate three distinct types of carbon, consistent with the diene complex formulation of Figure 3. 1,4-Benzoquinone derivatives are known to form

---

(13) Johnston, R. J.; Holwerda, R. A. *Inorg. Chem.* **1985**, *24*, 3176.
(14) Johnston, R. J.; Holwerda, R. A. *Inorg. Chem.* **1985**, *24*, 157.
(15) Bottei, R. S.; Greene, D. L. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1469.
(16) Jeong, W.-Y.; Holwerda, R. A., unpublished results.
(17) Slifkin, M. A.; Smith, B. M.; Walmsley, R. H. *Spectrochim. Acta, Part A* **1969**, *25A*, 1479.

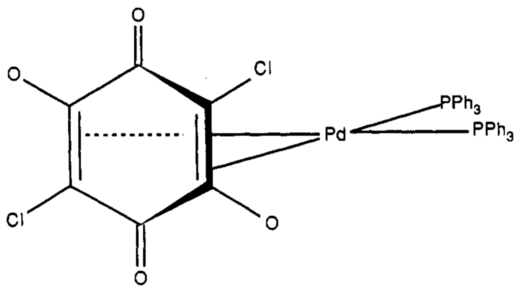

Figure 3. Proposed structure of [Pd(CA)(PPh$_3$)$_2$].

Table I. Pseudo-First-Order Rate Constants for the Reaction of [Pd(*C*-CA)(CH$_3$CN)$_2$] with Triphenylphosphine in Acetonitrile Solution[a]

[PPh$_3$], mM	10^2k_{obsd}, s^{-1}				
	25.0 °C	30.4 °C	34.7 °C	38.6 °C	45.4 °C
1.6	2.32	2.92	3.16	4.01	4.47
2.0	2.85	3.61	3.89	4.82	5.70
3.0	3.70	4.97	5.50	6.66	8.22
4.0	4.37	6.08	6.81	8.49	10.59
6.0	4.97	7.43	8.49	11.05	14.13
10	5.86	8.51	10.77	14.50	19.71
16	6.66	9.77	13.42	17.65	26.14
24		11.07	15.65	20.80	31.95
32		11.10	17.10	23.01	34.81
40	7.41	11.63	18.07	24.66	36.99

[a] [Pd(*C*-CA)(CH$_3$CN)$_2$]$_0$ = 0.20 mM. Uncertainty in rate constants estimated at ±2%.

analogous π-coordinated complexes with palladium(0) in the presence of tertiary phosphines.[11,18,19] Peaks at 127.0, 130.3, and 132.6 ppm may be assigned to PPh$_3$ phenyl carbon atoms. The similarity of ^{13}C chemical shift positions in **2** and **3** suggests that a comparatively small perturbation in overall electron density distribution accompanies the transformation of the chloranilate ligand from bis(carbanion) to *p*-quinone.

Magnetic equivalence of the two triphenylphosphine ligands in **3** is established by the appearance of a singlet at 34.05 ppm in the ^{31}P NMR spectrum. In order to confirm the cis geometrical orientation of the triphenylphosphine ligands, $^2J_{PP}$ coupling constants were evaluated for mixed complexes of the form [Pd(CA)(PPh$_3$)(P{PhX}$_3$)], where X = *p*-F, *m*-CH$_3$, and *p*-CH$_3$. Dichloromethane solutions of these complexes were generated in situ by mixing equimolar quantities of **2**, PPh$_3$, and P{PhX}$_3$. Singlets corresponding to **3** and [Pd(CA)(P{PhX}$_3$)$_2$][16] were resolved in addition to the doublet of doublets arising from the mixed phosphine complex. $^2J_{PP}$ coupling constants characteristic of X = *p*-F (25 Hz), *m*-CH$_3$ (21 Hz), and *p*-CH$_3$ (22 Hz) consistently fall within the range (20–40 Hz) expected for cis coupling and well below the much larger values (300–500 Hz) typical of *trans*-bis(phosphine)palladium(II) complexes.[20-22] Taken together, the ^{13}C and ^{31}P NMR results rule out the possibility that water occupies a square-planar coordination position in **3**, leaving CA^{2-} bonded as a monodentate ligand through a phenolate oxygen atom. Unfortunately, ^{31}P–^{13}C spin–spin coupling was not observed in the ^{13}C NMR spectrum of **3**, ruling out the use of potentially revealing multiplet splittings to distinguish among the structural alternatives.

Kinetic Studies of Linkage Isomerization. The kinetics of reaction 1 in acetonitrile solution was studied at five temperatures in the interval 25.0–45.4 °C. First-order analytical plots based on the appearance of [Pd(π-CA)(PPh$_3$)$_2$] (530 nm) in the presence of excess triphenylphosphine were consistently linear over greater than 4 half-lives of the reaction. Observed rate constants are presented in Table I. At all temperatures examined, k_{obsd} approaches a saturation limit with increasing triphenylphosphine concentration. The linearity of k_{obsd}^{-1} vs [PPh$_3$]$^{-1}$ plots (Figure 4) is consistent with an intermediate complex mechanism (eq 2) featuring rate-limiting linkage isomerization following rapid, preequilibrium formation of [Pd(*C*-CA)(PPh$_3$)$_2$].

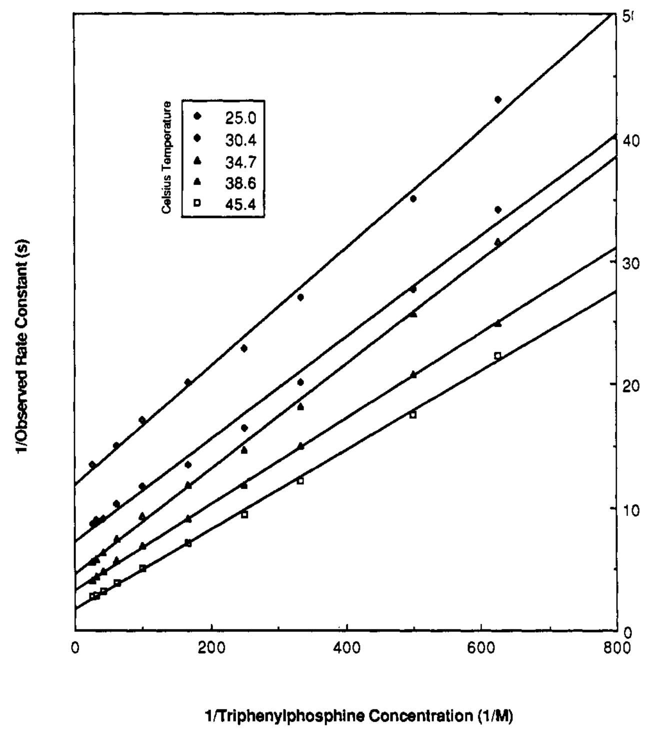

Figure 4. Plots of k_{obsd}^{-1} vs [PPh$_3$]$^{-1}$ supporting mechanism 2 for the reaction of [Pd(*C*-CA)(CH$_3$CN)$_2$] with triphenylphosphine in acetonitrile solution.

Table II. Rate Parameters for the Reaction of [Pd(*C*-CA)(CH$_3$CN)$_2$] with Triphenylphosphine in Acetonitrile Solution[a]

temp, °C	k_i, s^{-1}	K_2, M^{-1}
25.0	8.44 (0.02) × 10^{-2}	2.47 (0.08) × 10^2
30.4	1.39 (0.04) × 10^{-1}	1.74 (0.06) × 10^2
34.7	2.19 (0.01) × 10^{-1}	1.07 (0.02) × 10^2
38.6	3.01 (0.01) × 10^{-1}	9.6 (0.1) × 10
45.4	5.71 (0.02) × 10^{-1}	5.4 (0.1) × 10

[a] Rate parameters defined in eq 2 and calculated from double inverse plots based on eq 3, as described in the text. Standard deviations are shown in parentheses.

$$[Pd(C\text{-}CA)(CH_3CN)_2] + PPh_3 \xrightleftharpoons{K_1} [Pd(C\text{-}CA)(PPh_3)(CH_3CN)] + CH_3CN$$

$$[Pd(C\text{-}CA)(PPh_3)(CH_3CN)] + PPh_3 \xrightleftharpoons{K_2} [Pd(C\text{-}CA)(PPh_3)_2] + CH_3CN \quad (2)$$

$$[Pd(C\text{-}CA)(PPh_3)_2] \xrightarrow{k_i} [Pd(\pi\text{-}CA)(PPh_3)_2]$$

Assuming that $K_1 \gg K_2$ and that the PPh$_3$ association equilibria are established rapidly on the time scale of the k_i rate-determining step, eq 3 describes the predicted dependence of k_{obsd} on [PPh$_3$].

$$k_{obsd} = K_2k_i[PPh_3]/(1 + K_2[PPh_3]) \quad (3)$$

On this basis, the parameters K_2 and k_i (Table II) were calculated as least-squares (intercept/slope) and (intercept)$^{-1}$, respectively, from the double inverse lots shown in Figure 4. In order to rule out the possibility that K_1 rather than K_2 corresponds to the kinetically measured affinity constant, several kinetic experiments were carried out with PPh$_3$ as the limiting reagent. Although a purple palladium product still forms under these conditions, the

---

(18) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

(19) Minematsu, H.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1975**, *91*, 389.

(20) Goodfellow, R. J.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1676.

(21) Carty, A. J.; Jacobson, S. E. *J. Chem. Soc., Chem. Commun.* **1975**, 175.

(22) Brandon, J. B.; Dixon, K. R. *Can. J. Chem.* **1981**, *59*, 1188.

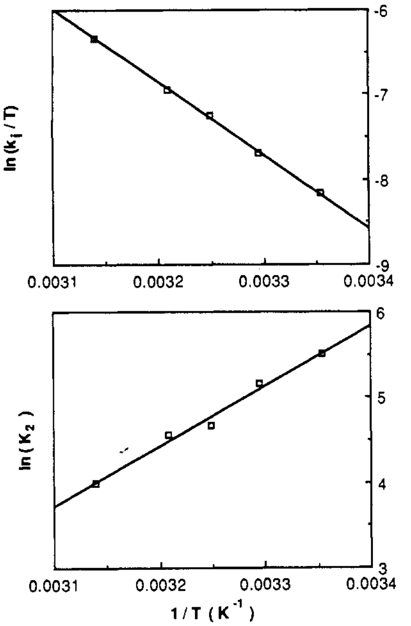

Figure 5. van't Hoff and Eyring plots illustrating the temperature dependences of K_2 and k_i (eq 2).

much slower isomerization rates observed ($t_{1/2} \gtrsim 1$ h) indicate that [Pd(*C*-CA)(PPh$_3$)$_2$] rather than [Pd(*C*-CA)(PPh$_3$)(CH$_3$CN)] must be the predominant precursor to [Pd(π-CA)(PPh$_3$)$_2$] in the presence of excess PPh$_3$. Eyring and van't Hoff plots of ln (k_i/T) and ln K_2 vs $1/T$, respectively (Figure 5), yield the activation parameters of the isomerization step ($\Delta H^{\ddagger} = 17.1 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = -6 \pm 2$ eu) and standard enthalpy/entropy changes corresponding to the uptake of a second PPh$_3$ ligand by [Pd(*C*-CA)(PPh$_3$)(CH$_3$CN)] ($\Delta H^{\circ} = -14.0 \pm 1.0$ kcal/mol; $\Delta S^{\circ} = -36 \pm 3$ eu).

The standard enthalpy and entropy changes related to K_2 are consistent with the bonding of a second PPh$_3$ ligand to Pd(II) at a sterically hindered coordination position cis to the first PPh$_3$ unit, which imposes a cone angle of 145°.[23] Indeed, an exceptionally negative $\Delta S^{\circ}(K_2)$ is primarily responsible for the unexpectedly small K_2 values that give rise to kinetic saturation behavior. In contrast, the activation barrier for linkage isomerization from [Pd(*C*-CA)(PPh$_3$)$_2$] to [Pd(π-CA)(PPh$_3$)$_2$] is predominantly enthalpic, as would be anticipated considering the stability of five-membered chelate rings containing one or more sp^3-hybridized carbon donor(s) to palladium(II).[24,25] Kinetic studies of tertiary phosphine substituent effects on the isomerization rate are currently being performed to elucidate the extent to which Lewis basicity of the P donor atoms trans to the carbanion leaving groups influences the activation barrier.[16] As measured by the product K_2k_i (2.1×10^1 M^{-1} s^{-1}, 25 °C; $\Delta H^{\ddagger} = 3.1$ kcal/mol, $\Delta S^{\ddagger} = -42$ eu), the overall substitutional reactivity of Pd(II) in reaction 1 is typical of that observed in related ligand-interchange processes.[26] Thus, these parameters closely resemble those for cyanide ligand exchange in Pd(CN)$_4^{2-}$ (k(24 °C) = 1.2×10^2 M^{-1} s^{-1}; $\Delta H^{\ddagger}$ = 4 kcal/mol, $\Delta S^{\ddagger} = -45$ eu).[27]

Linkage isomerization kinetic results reported here contrast strongly with mechanistic studies of β-elimination and reductive elimination reactions of coordinated alkyl groups in *cis*-PdL$_2$R$_2$ (L = tertiary phosphine) complexes.[28-30] Thus, reductive elimination of cis alkyl groups depends upon the prior *dissociation* of a phosphine ligand, such that the rate is strongly inhibited by excess phosphine in solution. However, treatment with 1,2-bis(diphenylphosphino)ethane induces the reduction of Pd(II) to Pd(0) in a palladacyclopentane complex, with concurrent evolution of *n*-butenes.[25]

Acknowledgment. Support of this research by the Robert A. Welch Foundation (Grant D-735) is gratefully acknowledged. We also wish to thank Dr. Jesse Yeh and Professor Jerry Mills for assistance in the acquisition of NMR spectra.

---

(23) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(24) Newkome, G. R.; Kiefer, G. E.; Frere, Y. A.; Onishi, M.; Gupta, V. K.; Fronczek, F. R. *Organometallics* **1986**, *5*, 348.

(25) Diversi, P.; Ingrosso, G.; Lucherini, A. *J. Chem. Soc., Chem. Commun.* **1978**, 735.

(26) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks-Cole: Monterey, CA, 1985.

(27) Pesek, J. J.; Mason, W. R. *Inorg. Chem.* **1983**, *22*, 2958.

(28) Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1319.

(29) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868.

(30) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4981.

Contribution from the Department of Chemistry,
University of Houston, University Park, Houston, Texas 77004

Facile Rearrangement and Electron Transfer of 19-Electron Radicals from the Reduction of the Bischelated Manganese Carbonyl Cation Mn(CO)$_2$[PPh$_2$(CH$_2$)$_2$PPh$_2$]$_2^+$

D. J. Kuchynka and J. K. Kochi*

Received December 17, 1987

The cathodic reduction of the bischelated manganese carbonyl cation *trans*-Mn(CO)$_2$(η^2-DPPE)$_2^+$ (I$^+$, where DPPE = PPh$_2$(CH$_2$)$_2$PPh$_2$) produces the metastable anion Mn(CO)$_2$(η^2-DPPE)(η^1-DPPE)$^-$ (II$^-$) via an overall 2e process at a Pt electrode in either tetrahydrofuran or acetonitrile solution. The unusual observation of a cathodic curve crossing and two isopotential points in the cyclic voltammogram of I$^+$ can be traced to an electron transfer with II$^-$ to afford a pair of neutral radicals, i.e., the 19e I$^\bullet$ and the 17e II$^\bullet$. The former (which is also generated during the initial step in the reduction of I$^+$) is a metastable species and spontaneously extrudes an end of one DPPE ligand to afford the second radical II$^\bullet$ with the rate constant $k_r \approx 4 \times 10^6$ s^{-1}. The structures of the anionic and radical intermediates II$^-$, II$^\bullet$, and I$^\bullet$ are discussed in the context of their transient electrochemical behavior as well as their ^{31}P NMR and ESR spectra. The rather slow rate of electron transfer between I$^+$ and II$^-$ is ascribed to steric effects in carbonylmanganese ions encumbered with a pair of DPPE ligands.

Introduction

Electrochemical methods can provide valuable mechanistic insight into the oxidation-reduction of various types of organometallic compounds, including metal carbonyls.[1,2] Among these, the reduction of diamagnetic carbonylmetal cations is especially intriguing since electron accession leads to electron-supersaturated 19e radicals that are highly labile and sensitive to ligand loss prior to dimerization.[2a,3] For example, the reduction of hexa-

---

(1) (a) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 18. (b) Carriedo, G. A.; Riera, V.; Connelly, N. G.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1769 and references therein.

(2) (a) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087. (b) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

0020-1669/88/1327-2574$01.50/0