

collection. A systematic search revealed a monoclinic lattice with systematic extinctions corresponding to space groups  $Cc$  or  $C2/c$ . The structure was solved in the non-centric space group  $Cc$  but transformed to the centric  $C2/c$  after examination of the resulting structure. All atoms, including hydrogens, were located and refined.

A final difference Fourier was featureless, the largest peak being  $0.21 \text{ e}/\text{\AA}^3$ .

**Hf(OAr-2,6-*t*-Bu<sub>2</sub>)<sub>2</sub>( $\eta^2$ -PhNCCH<sub>3</sub>)<sub>2</sub> (IIg).** Details of the data collection and structure refinement has been given previously<sup>32</sup> and are summarized in Table XIII. The crystals were examined under deoxygenated Nujol and mounted in an appropriate sized glass capillary surrounded by epoxy resin. The hydrogen atom positions were calculated after several cycles of anisotropic refinement assuming idealized geometries and a carbon-hydrogen bond distance of  $0.95 \text{ \AA}$ . For methyl groups, one hydrogen position was located in the difference Fourier map, this position idealized and the other two hydrogen positions calculated. The hydrogens were not refined.

**Zr(OAr-2,6-*t*-Bu<sub>2</sub>)<sub>2</sub>( $\eta^2$ -*t*-BuNCCH<sub>2</sub>Ph)<sub>3</sub> (VIa).** A suitable sample was selected and transferred to the goniostat with use of standard inert atmosphere handling techniques and cooled to  $-155 \text{ }^\circ\text{C}$  for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed a set of reflections which exhibited no symmetry or systematic extinctions. The data were indexed as triclinic with the space group  $P\bar{1}$ .

The crystal structure was solved by locating the Zr atom by means of direct methods (Mulan), and the remaining non-hydrogen atoms were located in a difference Fourier phased by the Zr atom. The hydrogen atoms were introduced in calculated positions ( $B = B + 1$ ,  $C-H = 0.95 \text{ \AA}$ ). The structure was refined by full-matrix least squares, using anisotropic thermal parameters on all non-hydrogen atoms. The hydrogen atoms were fixed.

A final difference Fourier was essentially featureless, the largest peak being  $0.35 \text{ e}/\text{\AA}$ .

**Ta(OAr-2,6-Me<sub>2</sub>)<sub>2</sub>( $\eta^2$ -xyNCCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>) (VIa).** A suitable sample was cleaved from a larger crystal with use of standard inert atmosphere handling techniques and transferred to the goniostat where it was cooled to  $-160 \text{ }^\circ\text{C}$  for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima with no apparent symmetry or systematic absences and indicating the probable space group  $P\bar{1}$ . Subsequent solution and refinement confirmed the choice.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were located and refined.

A final difference Fourier was featureless, the largest peak being  $0.91 \text{ e}/\text{\AA}^3$ , located at the metal site.

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**Supplementary Material Available:** Tables of fractional coordinates of hydrogen atoms, anisotropic thermal parameters, and complete bond distances and angles (54 pages); listing of observed and calculated structure factors (94 pages). Ordering information is given on any current masthead page.

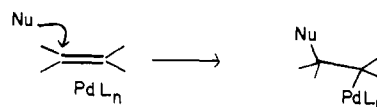
## Palladium(I) $\pi$ Radicals. Electrochemical Preparation and Study of Their Reaction Pathways

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**Abstract:** The reduction of a series of Pd(II) complexes has been studied by electrochemistry and spectroscopy. Neutral Pd(I) radicals may be obtained from the reduction of ( $\eta^5$ -C<sub>5</sub>Ph<sub>5</sub>)Pd( $\eta^4$ -diolefin) cations, where diolefin = 1,5-cyclooctadiene, norbornadiene, or dibenzocyclooctatetraene. The one-electron processes are diffusion-controlled and highly reversible, yielding the first stable Pd(I)  $\pi$  radicals. The dibenzocyclooctatetraene derivative is isolable. These complexes undergo radical reaction with water, chlorinated hydrocarbons, and peroxides to give  $\pi, \sigma$ -Pd(II) complexes identical with those obtained by direct attack of nucleophiles on the starting Pd(II) cationic complexes. Reversible oxidation of ( $\eta^5$ -C<sub>5</sub>Ph<sub>5</sub>)Pd( $\eta^4$ -diolefin) cations demonstrates the existence of formal Pd(III) complexes in these systems. The pentaphenylcyclopentadienyl ligand gives kinetic stabilization to both Pd(I) and Pd(III), compared to the unsubstituted cyclopentadienyl analogues.

The catalytic oxidation of olefins by Pd(II) is an important reaction, being the basis of the well-known Wacker industrial process, in which ethylene is oxidized to acetaldehyde.<sup>1-3</sup> Although a Pd  $\pi$  complex has not been isolated from the Wacker reaction mixture, it is generally agreed that the key step in the process is attack on a Pd-ethylene complex by a nucleophile, probably water, with accompanying  $\pi$ - $\sigma$  rearrangement of the coordinated olefin.<sup>4-7</sup> Eventually, the organic moiety is released,



with formation of Pd metal, which is reoxidized to Pd(II) by excess Cu(II). Extensive studies of this and related reactions have failed to uncover any evidence that the intermediate oxidation state Pd(I) is involved in the reaction or, indeed, that any radical routes are important.<sup>8</sup>

(1) For leading references concerning the Wacker process, see: (a) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; Dept. 5. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (c) Henry, P. *Adv. Organomet. Chem.* **1975**, *13*, 363. (d) Davies, S. G. *Organotransition Metal Chemistry: Application to Organic Synthesis*; Pergamon: Oxford, 1982; pp 304-308.

(2) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

(3) Stille, J. K.; Hines, L. F.; Fries, R. W.; Wong, P. K.; James, D. E.; Lau, K. *Adv. Chem. Ser.* **1974**, *132*, 90.

(4) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981; pp 190-193.

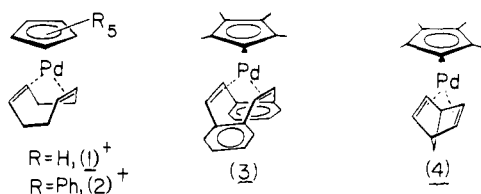
(5) Backvall, J. E.; Akermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.

(6) Stille, J. K.; Divakaruni, R. *J. Organomet. Chem.* **1979**, *169*, 239.

(7) Stille, J. K.; Divakaruni, R. *J. Am. Chem. Soc.* **1978**, *100*, 1303.

(8) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; p 113.

Although Pd(I) appears to be exceedingly rare, it has been detected during the oxidative addition of alkyl halides to Pd(PPh<sub>3</sub>)<sub>3</sub> (by CIDNP NMR)<sup>9a</sup> and in other stoichiometric or catalytic Pd(II)/Pd(0) reactions.<sup>9b,10</sup> Since virtually all of the isolated Pd(I) complexes are diamagnetic dimers,<sup>11</sup> very little is known about the reaction pathways of Pd(I) radicals. Thus, we set about to generate some Pd(I)  $\pi$  radicals and to study their reactions. Access to the desired complexes was by electrochemical reduction of the Pd(II) pentaphenylcyclopentadienyl complexes [( $\eta^5$ -C<sub>5</sub>Ph<sub>5</sub>)PdL<sub>2</sub>]<sup>+</sup> by one electron, as reported earlier.<sup>12</sup> We now show that the Pd(I) radicals <sup>\*</sup>CpPd( $\eta^4$ -diene), <sup>\*</sup>Cp = ( $\eta^5$ -C<sub>5</sub>Ph<sub>5</sub>), react with radical sources to give  $\pi,\sigma$  complexes identical with those produced by nucleophilic attack on the analogous Pd(II) complex. The results suggest that radical mechanisms should not be ignored when considering the pathways of reductive elimination or oxidative addition of Pd(II) or Pd(0) complexes, respectively. During this work we were able to prepare what appears to be the first isolable mononuclear Pd(I) species, <sup>\*</sup>CpPd(dbcot), <sup>\*</sup>CpPd( $\eta^4$ -dibenzocyclooctatetraene)<sup>13</sup> (3). The Pd(II)/Pd(I) reduction of  $\pi$  complexes of 1,5-cyclooctadiene(cod) (Cp complex 1<sup>+</sup> and <sup>\*</sup>Cp complex 2<sup>+</sup>) and norbornadiene (<sup>\*</sup>Cp complex 4<sup>+</sup>) are also discussed.



### Experimental Section

The compounds [<sup>\*</sup>CpPdL<sub>2</sub>][PF<sub>6</sub>], L<sub>2</sub> = cod, nbd, and dbcot,<sup>13</sup> were prepared from the dinuclear complex <sup>\*</sup>Cp<sub>2</sub>Pd<sub>2</sub>(Ph<sub>2</sub>C<sub>2</sub>)<sup>14</sup> by methods reported previously.<sup>15</sup> The complexes with L<sub>2</sub> = nbd-OH (7), dbcot-OH (6), and dbcot-OCOPh (5) were prepared by electrochemical methods, and details of their preparation and characterization are given below. All syntheses were done under a nitrogen or argon atmosphere either in standard Schlenk apparatus or in a drybox. Burdick and Jackson CH<sub>2</sub>Cl<sub>2</sub> was distilled from calcium hydride before use. Hydrocarbon solvents were treated successively with sulfuric acid and aqueous sodium hydroxide and then distilled from sodium.

<sup>\*</sup>CpPd(nbd-OH) (7) was obtained from bulk reduction of [<sup>\*</sup>CpPd(nbd)][PF<sub>6</sub>] (200 mg) in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. Bulk electrolysis negative of the first reduction wave produced <sup>\*</sup>CpPd(nbd) which slowly reacted to give <sup>\*</sup>CpPd(nbd-OH). Fifty milliliters of benzene was added, and the CH<sub>2</sub>Cl<sub>2</sub> was removed under vacuum. Bu<sub>4</sub>NPF<sub>6</sub> precipitated and was filtered from solution. The volume of the orange benzene solution was reduced to ca. 15 mL, and 30–50 mL of CH<sub>3</sub>NO<sub>2</sub> was added. The orange complex precipitated from solution. Recrystallization from

(9) (a) Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7832. (b) Moiseev, I. I.; Grigorev, A. A. *Bull. Akad. Nauk. SSSR* **1968**, *178*, 132. (10) Detection of Pt(I) radical intermediates is more common: (a) Hall, T. L.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc. Dalton Trans.* **1980**, 1448. (b) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345. (c) Stille, J. K.; Lau, K. *Acc. Chem. Res.* **1977**, *10*, 434. (d) Otsuka, S.; Ataka, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1118. (e) Labinger, J. A.; Osborn, J. A. *Inorg. Chem.* **1980**, *19*, 3230. (f) Lal, D.; Grilley, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355.

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(13) Abbreviations used in this paper are as follows: cod = cyclo-1,5-octadiene; Cp = cyclopentadienyl; dbcot = dibenzocyclooctatetraene; CV = cyclic voltammetry; E<sub>pc</sub> (or E<sub>pa</sub>) = cathodic (or anodic) peak potential;  $\Delta E_p$  = |E<sub>pc</sub> - E<sub>pa</sub>|; i<sub>c</sub>/or i<sub>a</sub>, cathodic (or anodic) current; RPE = rotating platinum electrode; SCE = saturated calomel electrode; v = CV scan rate.

(14) Jack, T. R.; Mey, C. J.; Powell, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 4707.

(15) Broadley, K.; Connelly, N. G.; Lane, G. A.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1986**, 373.

Table I. Redox Potentials of Palladium  $\pi$  Complexes<sup>a</sup>

| complex         | Pd oxidation state change |            |            |
|-----------------|---------------------------|------------|------------|
|                 | III/II                    | II/I       | I/0        |
| 1 <sup>b</sup>  | +1.85 (IR) <sup>c</sup>   | -0.76 (IR) |            |
| 2 <sup>b</sup>  | +1.65                     | -0.47      | -1.30 (IR) |
| 3 <sup>b</sup>  | +1.71                     | -0.22      | -1.00 (IR) |
| 4 <sup>b</sup>  | +1.68                     | -0.47      | -1.19 (IR) |
| 5 <sup>d</sup>  | +0.98                     |            |            |
| 6 <sup>d</sup>  | +0.87 (IR)                |            |            |
| 7 <sup>d</sup>  | +0.78 (IR)                |            |            |
| 8 <sup>d</sup>  | +0.89                     |            |            |
| 10 <sup>d</sup> | +0.72                     |            |            |

<sup>a</sup> E° values vs. SCE in CH<sub>2</sub>Cl<sub>2</sub>/Bu<sub>4</sub>NPF<sub>6</sub> electrolyte, measured by cyclic voltammetry. <sup>b</sup> Complexes 1–4 contain formal Pd(II) as monoanions. Thus, the Pd(II)/Pd(I) couple is assigned to 1<sup>+</sup>/1<sup>0</sup>, etc. <sup>c</sup> Irreversible wave. Peak potential given for scan rate 0.1 V/s. <sup>d</sup> Complexes 5–8 and 10 contain formal Pd(II) as neutral compounds. Thus, the Pd(III)/Pd(II) couple is assigned to 5<sup>+</sup>/5, etc.

benzene/CH<sub>3</sub>NO<sub>2</sub> or column chromatography on neutral alumina may be used to purify the material. For chromatography a column of neutral alumina in benzene is prepared and the complex eluted with a 5% THF/benzene solution. Characterization was by <sup>1</sup>H and <sup>13</sup>C NMR and chemical analysis (see Table II).

<sup>\*</sup>CpPd(dbcot-OCOPh) (5) was prepared by addition of 0.03 g of benzoyl peroxide to a 50-mL CH<sub>2</sub>Cl<sub>2</sub> electrolysis solution containing <sup>\*</sup>CpPd(dbcot) produced by bulk reduction of [<sup>\*</sup>CpPd(dbcot)][PF<sub>6</sub>] (225 mg, 5 mM solution). The solution was held at 243 K during the bulk electrolysis and subsequent addition of benzoyl peroxide. Fifty milliliters of benzene was added and the CH<sub>2</sub>Cl<sub>2</sub> removed under vacuum. Bu<sub>4</sub>NPF<sub>6</sub> precipitated, giving an orange solution containing the complex. After concentration of this solution hexane was added, causing precipitation of the complex. Successive recrystallizations from benzene/hexane gave the complex as an orange powder. Characterization was by NMR (Table II) and IR. An absorption due to the C=O stretching vibration was observed at 1712 cm<sup>-1</sup>.

<sup>\*</sup>CpPd(dbcot-OH) (6) was produced in a manner similar to 5 except that the benzene solution of the complex was chromatographed on a column of alumina with use of a benzene/5% THF eluant. Addition of octane and removal of the benzene precipitated the complex. Characterization was by NMR (Table II) and FD (field desorption) mass spectrometry. A molecular ion cluster is observed at m/e 772 representing the formula C<sub>31</sub>H<sub>38</sub>OPd for <sup>106</sup>Pd. A computer-simulated spectrum based on isotope distributions matched the observed intensities of the molecular ion cluster.

**Electrochemical Techniques and Procedures.** Electrochemical techniques and apparatus were as previously described.<sup>16</sup> The supporting electrolyte used was 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, and potentials are reported vs. the aqueous saturated calomel electrode (SCE). Solvents used for electrochemistry were from Burdick and Jackson (spectrograde) and were either used as received (transferred under nitrogen) or distilled from suitable drying agents. Vacuum electrochemistry was performed in a cell somewhat modified from that described by Smith and Bard.<sup>17</sup>

**Other Analytical Methods.** <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectra were obtained with a 250-MHz Bruker WM-250 spectrometer, using solvent resonances as a secondary reference to Me<sub>4</sub>Si. Infrared data were acquired with a Nicolet Series 6000 Fourier transform spectrometer. FD mass spectra were obtained from the NSF regional facility at Massachusetts Institute of Technology, Cambridge, MA. ESR measurements were performed on a modified Varian E-3 spectrometer with an external DPPH standard.

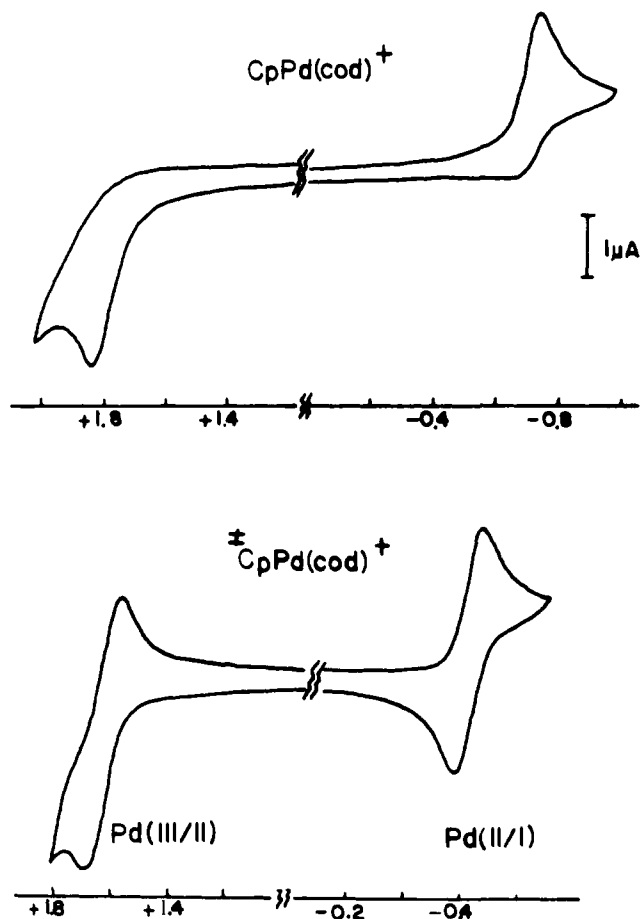
### Results

**I. Comparison of Cp- and <sup>\*</sup>CpPd(cod)<sup>+</sup> (1<sup>+</sup> and 2<sup>+</sup>).** Since CpNi(cod)<sup>+</sup> had proven to be a suitable precursor to the Ni(I) complex CpNi(cod),<sup>18</sup> reduction of CpPd(cod)<sup>+</sup> was first investigated. The reduction of (1)<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> was reversible (E° = -0.76 V, Table I) only at CV sweep rates above several volts per second at ambient temperature. An irreversible oxidation was also observed (Table I, Figure 1). At a temperature of 263 K and sweep rate of v = 0.5 V/s, the ratio of anodic to cathodic currents for the reduction was 0.8. A room temperature half-life

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(17) Smith, W. H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 5203.

(18) CpNi(cod) disproportionates into Cp<sub>2</sub>Ni<sup>+</sup> and (cod)<sub>2</sub>Ni: Lane, G. A.; Geiger, W. E. *Organometallics* **1982**, *1*, 401.



**Figure 1.** CV scans of  $5 \times 10^{-4}$  M (top)  $\text{CpPd(cod)}^+$  ( $1^+$ ) and (bottom)  $\text{CpPd(cod)}^+$  ( $2^+$ ) in  $\text{CH}_2\text{Cl}_2/0.1$  M  $\text{Bu}_4\text{NPF}_6$ . Scan rate 200 mV/s, Pt bead electrode; potentials referenced to SCE.

of ca. 0.1 s was indicated for **1**.

Although at high sweep rates the reduction wave was an apparent one-electron process (approximately the same peak current as that of the oxidation of ferrocene), bulk coulometry gave  $n$  values of ca. 2 and black insoluble powders. These observations are consistent with disproportionation of **1** and overall formation of palladium metal or insoluble zerovalent complexes. Since this route to Pd(I) was unpromising, we turned to complexes of the perphenylated cyclopentadienyl ligand, reasoning that the ring substitution would strengthen the weak Cp-Pd bond.<sup>19</sup> It was expected that perphenylation of the Cp ring would also enhance the thermodynamic stability of the Pd(I) complex, because of the electron-withdrawing effect of the phenyl substituents.

These expectations were realized quite dramatically (Figure 1, bottom). At ambient temperatures and slow sweep rates, both the Pd(II)/Pd(I) and Pd(III)/Pd(II) couples of  $2^+$  were chemically reversible. The  $E^\circ$  of the Pd(III)/Pd(II) couple was +1.65 V. Although the oxidation wave suggests the generation of rare Pd(III) complexes, we have not yet studied these processes in detail.<sup>20</sup> The reduction wave ( $E^\circ = -0.47$  V) was diffusion controlled and chemically reversible on either Pt or Hg. CV peak separations were ca. 80 mV at  $v = 0.03$  V/s, comparable to those of  $\text{Cp}_2\text{Fe}^{0/+}$  in the same medium.

Choice of solvent influenced the stability of the Pd(I) radical. Chemical reversibility of the Pd(II)/Pd(I) couple was lower in

(19) Maitlis, P. *Chem. Soc. Rev.* **1981**, *10*, 1.

(20)  $\Delta E_p$  values of 100–110 mV were observed at slow sweep rates, with  $i_c/i_a$  values being close to unity. Uncertainty in the latter is introduced by the close proximity of the electrolyte breakdown. Peak currents for the oxidation roughly corresponded to those of the one-electron reduction of this molecule. Diminished chemical reversibility was noted in more coordinating and nucleophilic solvents like  $\text{CH}_3\text{CN}$ . The oxidation processes are currently under study (Orsini, J., work in progress).

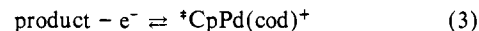
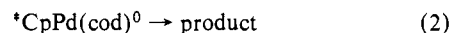
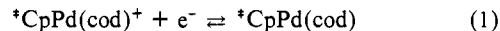


**Figure 2.** Fluid solution ESR spectrum of  $\text{CpPd(cod)}^{\cdot}$  ( $2^0$ ) in  $\text{CH}_2\text{Cl}_2$ ,  $T = 233$  K. Four of the six expected Pd satellite lines are visible. The small vertical line marks the position of dpph resonance ( $g = 2.0036$ ).

$\text{CH}_3\text{CN}$  ( $i_a/i_c = 0.8$  when  $v = 0.23$  V/s), and virtually all electrolyses were conducted in  $\text{CH}_2\text{Cl}_2$ , in which the radical displayed greater stability.

**II. Coulometric Reduction of  $2^+$ .** In a typical bulk electrolysis, a green 0.5 mM solution of  $2^+$  in  $\text{CH}_2\text{Cl}_2$  was reduced at a platinum basket with an applied potential of  $-0.6$  V. A deep red-orange solution was produced,  $n = 1.0e^-$ , which exhibited the electron spin resonance (ESR) spectrum of Figure 2 in fluid media. A  $g$  value of 2.0706 was observed for  $2^0$ , with the central line being flanked by satellites from  $^{105}\text{Pd}$  ( $I = 5/2$ , 22.2% natural abundance),<sup>21</sup>  $\langle a \rangle_{\text{Pd}} = 25$  G.

Solutions of  $2^0$  were stable at 233 K, but at higher temperatures the Pd(I) radical reacted to form another complex, as demonstrated by voltammetric studies after electrolysis. After 30 min at 263 K, half of the Pd(I) radical had converted to a new species having an irreversible oxidation wave at +0.62 V ( $i_p$ ). After 2 h at 263 K, the solution contained little of either  $2^+$  or  $2^0$ . Rather, almost quantitative conversion<sup>22</sup> to the new product oxidizing at +0.6 V was evident. Figure 3, top, shows a RPE<sup>13</sup> scan after electrolysis and decay of  $2^0$ . The CV scan (Figure 3, bottom) of that solution to more positive potentials revealed the important information that after scanning through the oxidation wave at +0.6 V, the Pd(III)/Pd(II) and Pd(II)/Pd(I) waves of original  $2^+$  were observed. Bulk coulometry established the re-formation of the starting material as quantitative, the overall processes being described by eq 1–3. The product listed in this scheme defied



isolation as a pure species but is probably a hydroxy adduct resulting from reaction with trace water (vide infra, section IV). Work on products from the reactions of the analogues  $3^0$  and  $4^0$  showed that radical addition reactions to the diene ligand are occurring.

**III. CpPd(dbcot)<sup>+</sup> Reductions. A. Electrochemistry.**  $3^+$  reduces at a higher potential ( $E^\circ = -0.22$  V) than does  $2^+$ , reflecting the electron-accepting effect of the phenyl substituents. Detailed CV studies were made on this system to confirm its model electrodic behavior. With use of optimum conditions for minimization of ohmic loss (concentrations of  $2 \times 10^{-4}$  M, luggin reference electrode probe, positive feedback  $iR$  compensation),  $\Delta E_p$  values of  $60 \pm 2$  mV were observed over a decade change

(21) Detailed ESR studies are being conducted: Rieger, P. H.; Geiger, W. E., unpublished results.

(22) Assignment of yields necessarily required assumption of the  $n$ -value of the oxidation at +0.6 V. We assumed  $n = 1$ , a value later shown to be correct for the product isolated from the reactions of (3)<sup>0</sup>.

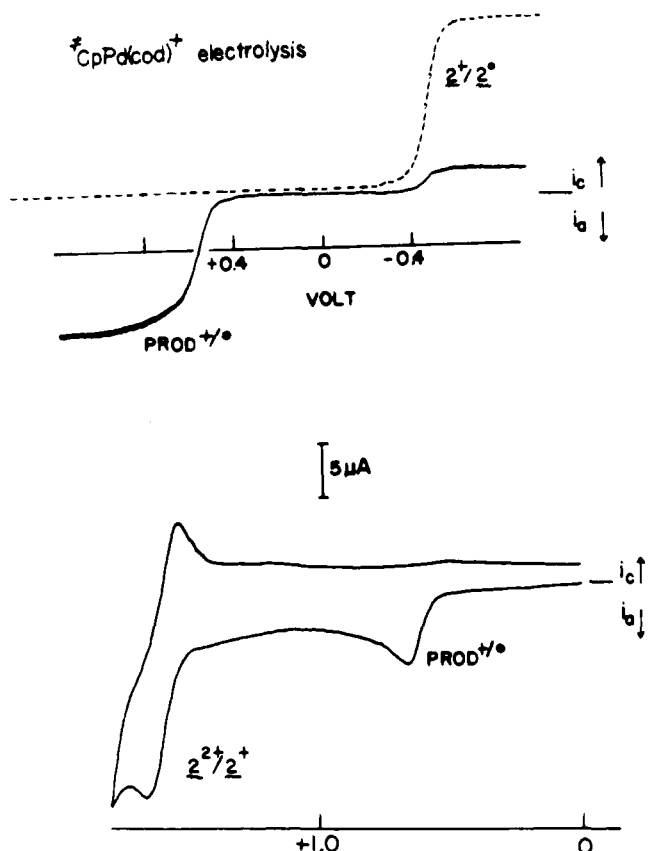
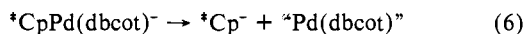
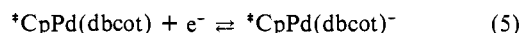
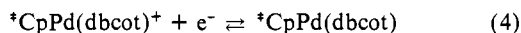


Figure 3. (Top) RPE scans of  $5 \times 10^{-4}$  M  $^*\text{CpPd}(\text{cod})^+$  ( $2^+$ ) before electrolysis (---) and 2 h after 90% electrolysis (—) at  $-0.8$  V in  $\text{CH}_2\text{Cl}_2/0.1$  M  $\text{Bu}_4\text{NPF}_6$  at 280 K. The new oxidation wave at ca.  $+0.6$  V is the "product" in eq 2 and eq 3, most likely a hydroxyl adduct of  $2$ . (Bottom) CV scan of electrolyzed solution, showing irreversible oxidation of product at  $+0.6$  V which results in production of  $2^+$  at the electrode surface (reversible wave at  $+1.65$  V); Pt electrode,  $v = 200$  mV/s.

in scan rates, indicating a rapid and reversible electron-transfer step.

Each of the Pd(II) complexes studied had a second, irreversible, reduction at more negative potentials. This wave (Figure 4) was examined in detail for  $3^+$ , and a cathodic peak potential of  $-1.0$  V at  $v = 0.20$  V/s was measured. All three Pd(II) complexes  $2^+ - 4^+$  have a reversible product wave at  $E^0 = -0.28$  V appearing after scanning through the second cathodic wave, apparently arising from  $(\text{C}_5\text{Ph}_5)^{0/-}$ . For  $3$ , this wave is hidden under that of  $3^{+/0}$ . Thus, we may write eq 4-6.



The second electron transfer is highly irreversible (no reverse current up to  $v = 15$  V/s). Its peak potential shifts negative by 58 mV with each tenfold increase in scan rate,<sup>23,24</sup> and its peak current was 0.78 times that of the Pd(II)/Pd(I) couple. These values are diagnostic of a completely irreversible charge transfer with  $n = 1$  and  $\alpha = 0.5$  and/or an extremely rapid follow-up reaction. Apparently, the Pd(0) species  $^*\text{CpPd}(\text{dbcot})^-$  is very short lived. Bulk reduction of  $3^+$  negative of the second wave consumed 1.9 faradays and gave a solution with the yellow color and reversible wave ( $E^0 = -0.28$ ) of free  $\text{C}_5\text{Ph}_5^{0/-}$ . Oxidation

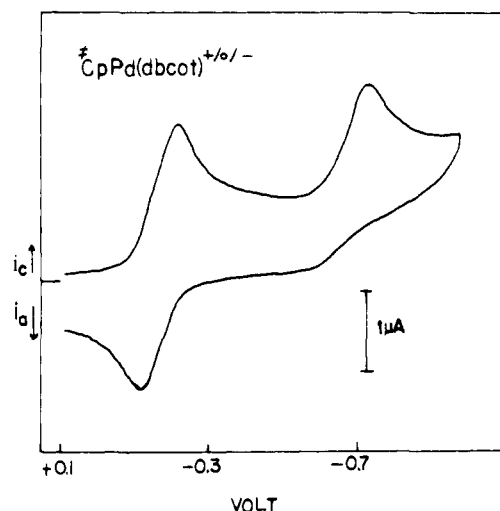


Figure 4. CV scan of  $5 \times 10^{-4}$  M  $^*\text{CpPd}(\text{dbcot})^+ / 0^-$  ( $3^+$ ) in  $\text{CH}_2\text{Cl}_2$  at the Pt electrode,  $v = 75$  mV/s.

of this solution positive of  $-0.28$  V gave the characteristic purple of the  $\text{C}_5\text{Ph}_5$  radical and a narrow, intense ESR signal at  $g = 2.00$ .

The Pd(III)/Pd(II) wave,  $E^0 = +1.71$  V, was quite reversible for  $3^+$ , having  $\Delta E_p = 76$  mV and  $i_c/i_a = 1$  at  $v = 0.05$  V/s in  $\text{CH}_2\text{Cl}_2$ .

**B. Isolation of Neutral 3.** Electrolytic preparations of  $3^0$  from  $3^+$  showed that the Pd(I) radical was stable for several hours at 300 K without decomposition. Addition of hexane to the electrolysis solution precipitated most of the supporting electrolyte. Subsequent removal of solvent gave neutral  $3$ , as confirmed by RPE voltammetry of solutions of the red-brown powder. However, the radical was always contaminated with some  $\text{Bu}_4\text{NPF}_6$  and eluded acceptable elemental analysis. Attempts at further purification resulted in a mixture of  $3$  and products having oxidation waves in the range  $+0.5$  to  $+1.0$  V. However, this crude  $3$  was useful in characterizing the reactions of  $^*\text{CpPd}(\text{dbcot})$  with radical sources, particularly peroxides, the products of which were finally isolated in pure form.

**C. Radical Addition Reactions of 3.** The Pd(I) radical reacted with substrates known to be susceptible to homolytic cleavage. These reactions could be followed electrochemically by following the CV peak heights of  $3^0$  and its addition products after adding the substrate to the electrochemically generated Pd(I) radical.

Neutral  $3$  reacted with H-atom donors such as isopropylbenzene and  $\text{CHCl}_3$  to give transient products.  $\text{CCl}_4$  with  $3^0$  gave new waves between  $+0.5$  and  $+1.0$  V, but stable products could not be isolated. However, reactions with peroxides gave tractable products with both  $3^0$  and  $4^0$ .

When 1 equiv of benzoyl peroxide was added to neutral  $3$  at 243 K in  $\text{CH}_2\text{Cl}_2$  a single product was obtained in quantitative yield, later identified as the  $\pi, \sigma$ -complex  $5$  in which the  $\text{C}_5$  ring has undergone addition of the  $\text{OCOPh}$  group. The benzoyl complex has a reversible oxidation wave at  $+0.98$  V.

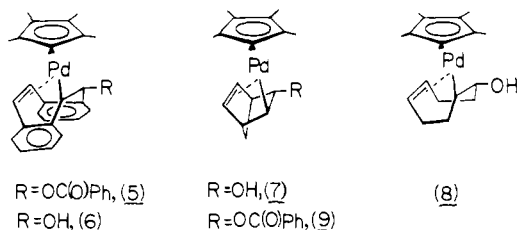


Figure 5 shows how this reaction was followed in an electrochemical experiment. CV curves are distorted because of ohmic effects enhanced by the high concentrations of the electrolysis solution. However, conclusions are easily reached. The dotted line was recorded after reduction of 5 mM  $3^+$  to  $3^0$  and has the characteristic reversible couple at  $-0.4$  V ( $E^0 = -0.22$  V when converted to SCE reference). After addition of equimolar benzoyl

(23) This value is corrected for ohmic loss by comparison to the Pd(II)/Pd(I) wave, which underwent no shift of  $E_{pc}$  vs.  $v$  compared to an internal  $\text{Cp}_2\text{Fe}$  standard giving equal peak currents.

(24) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1963**, *36*, 706.

(25) In subambient temperature electrolytes a silver wire was used as a quasireference electrode.

Table II. Chemical Analysis and NMR Data for New Compounds

| complex                          | C-H analysis<br>found (calcd)               | <sup>1</sup> H NMR  | <sup>13</sup> C NMR   |
|----------------------------------|---|---|---|
| [*CpPd(nbd)][PF <sub>6</sub> ]   | C 63.84 (63.93)<br>H 4.26 (4.20)            | 1.83, t ( <i>J</i> = 1.5 Hz), 2 H<br>4.20, s, 2 H<br>5.41, t ( <i>J</i> = 2.5 Hz), 4 H<br>6.89, 7.22, 7.32, m, 25 H   | 132.4, 130.5, 126.6, 129.1, 120<br>120 (olefin)<br>65.5 (bridgehead)<br>49.5 (-CH <sub>2</sub> -)                                       |
| *CpPd(nbd-OH) <sup>b</sup>       | C 75.66 (76.30)<br>H 5.06 (5.18)            | 6.95, m, 25 H <sup>d</sup><br>5.04, s, 1 H<br>4.84, t ( <i>J</i> = 4 Hz), 1 H<br>2.82, s br, 1 H<br>2.22, s br, 1 H<br>2.08, s, 1 H<br>2.02, q ( <i>J</i> = 2 Hz), 1 H<br>0.4, s, 1 H | 135.5, 132.4, 127.6, 125.8, 114<br>102.3 (olefin)<br>63.5, 61.1 (-CMH-, -CHOH-)<br>48.9, 43.3 (bridgehead)<br>29.7 (-CH <sub>2</sub> -) |
| [*CpPd(dbcot)][PF <sub>6</sub> ] | C 65.7 (65.6) <sup>c</sup><br>H 4.20 (4.10) | 6.05, s, 4 H<br>6.93, 7.18, 7.38, m, 33 H   |   |
| *CpPd(dbcot-OCOPh) <sup>b</sup>  |   | 6.90, m, 33 H <sup>d</sup><br>5.53, m, 2 H<br>4.02, d ( <i>J</i> = 4 Hz), 1 H<br>2.65, m, 1 H   |   |
| *CpPd(dbcot-OH) <sup>b</sup>     |   | 6.90, m, 33 H <sup>d</sup><br>5.5, m, 2 H<br>5.30, d of d ( <i>J</i> = 4.7 Hz), 1 H<br>3.80, D ( <i>J</i> = 4 Hz), 1 H<br>1.63, d ( <i>J</i> = 7 Hz), 1 H                             |   |

<sup>a</sup>σ referenced to Me<sub>4</sub>Si, CH<sub>2</sub>Cl<sub>2</sub> solvent unless otherwise noted, NMR designations: s = singlet, d = doublet, t = triplet, m = multiplet. <sup>b</sup><sup>1</sup>H NMR in benzene-*d*<sub>6</sub>. <sup>c</sup>Calculated for 0.25 CH<sub>2</sub>Cl<sub>2</sub> of crystallization (see ref 15). <sup>d</sup>Solvent obscures \*Cp resonances.

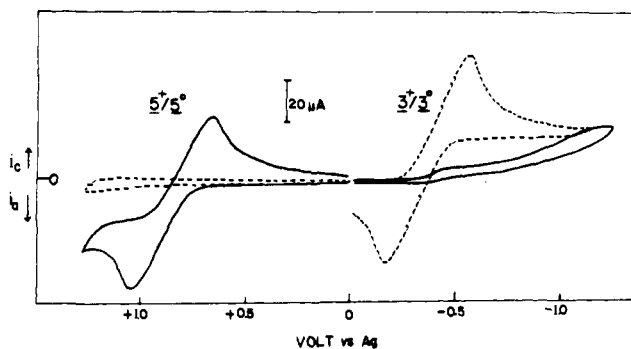
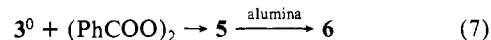


Figure 5. CV scans ( $v = 200$  mV/s) showing formation of **5** from **3**<sup>0</sup> plus benzoyl peroxide. Dashed lines: scans after formation of neutral **3** by bulk reduction of **3**<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> at 243 K. Solid lines: scans after addition of benzoyl peroxide to electrolyzed solution, showing disappearance of the wave for **3**<sup>+</sup>/**3**<sup>0</sup> and appearance of the wave for **5**<sup>+</sup>/**5**<sup>0</sup>. Waves are distorted due to high ohmic loss in these rather concentrated ( $5 \times 10^{-3}$  M) solutions. Potentials are referenced to a Ag wire quasi-reference electrode, which had a potential of ca. +150 mV vs. SCE in this experiment. Thus, the  $E^\circ$  of **3**<sup>+</sup>/**3** was measured as -0.37 V vs. Ag wire in this experiment, compared to -0.22 V vs. SCE (Table I).

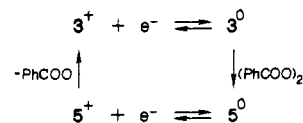
peroxide, the wave for neutral **3** essentially disappeared and the new couple at +0.8 V (+0.98 V vs. SCE) diagnostic of **5**<sup>0/+</sup> was produced essentially quantitatively (solid line). The solution went from deep red in color to light orange. Addition of benzene, followed by removal of CH<sub>2</sub>Cl<sub>2</sub> under vacuum and filtration of supporting electrolyte, gave a solution from which orange **5** could be isolated by addition of hexane. NMR (see Table II for assignments of the spectrum of the OH analogue) and infrared spectroscopy [ $\nu_{\text{CO}}(\text{KBr}) = 1712$  cm<sup>-1</sup>] allowed the structural assignment of **5**, in which addition of the OCOPh group has taken place to the C<sub>8</sub> ring of **3**, and the substituted dbcot ligand is now bonded in a  $\pi, \sigma$  fashion to the metal.

**5** was purified by successive recrystallizations from benzene/hexane. If, instead, it was eluted from a column of neutral alumina with benzene/THF, a new orange compound was obtained, first diagnosed by its CV curve which was different than that of **5**,  $E_{\text{pa}} = +0.87$  V (irrev). This compound was identified as the hydroxy-adduct **6** by its field desorption mass spectrum (molecular formula C<sub>51</sub>H<sub>38</sub>OPd) and <sup>1</sup>H NMR spectrum (Table II). Addition

of D<sub>2</sub>O to solutions of this complex caused disappearance of the OH resonance. Apparently, hydrolytic cleavage of the benzoyl group occurs on the alumina column:



The reversible CV wave for the oxidation of **5**<sup>0</sup> to **5**<sup>+</sup> demonstrates the existence of a Pd(III) ( $\pi, \sigma$ ) complex. However, bulk oxidation of **5** (CH<sub>2</sub>Cl<sub>2</sub>, 258 K,  $n = 1.0e^-$ ) gave back, quantitatively, a green solution of **3**<sup>+</sup> identified by its reversible wave at -0.22 V. Thus, the benzoyl group is cleaved back off the  $\pi, \sigma$  complex in what is analogous to an oxidatively induced reductive elimination, completing an overall redox/radical reaction cycle:



#### IV. Reactions of Pd(I) Radicals **2**<sup>0</sup> and **4**<sup>0</sup> with Trace Water.

The norbornadiene complex **4**<sup>+</sup> behaves very similarly to the cod complex **2**<sup>+</sup>, both in its electrochemical behavior (see  $E^\circ$  potentials in Table I) and its reactivity after one-electron reduction. Bulk reduction of **4**<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> negative of the Pd(II)/Pd(I) couple initially gave the characteristic red-brown of the radical, followed by change to an orange color, demise of the Pd(II)/Pd(I) waves, and appearance of a single product oxidation wave at  $E_{\text{pa}} = 0.78$  V (irreversible). Cycling through this wave or bulk oxidation at +0.9 V regenerated the original cationic complex **4**<sup>+</sup>.

Isolation of the orange product was accomplished by the procedure described above (section IIIC), using alumina to help remove supporting electrolyte. This material was sparingly soluble in polar solvents (acetone, THF, CH<sub>3</sub>CN) but very soluble in benzene or toluene. CV measurements confirmed that the isolated product had the same electrochemistry as that immediately seen after electrolysis ( $E_{\text{pa}} = +0.78$  V), suggesting that no change in structure arose because of the isolation procedure.

Elemental analysis and NMR spectroscopy identify the orange product as the hydroxy adduct **7**, similar to **6** (Table II). In dry benzene the OH signal appeared at  $\delta$  0.4. Saturation of this solution with D<sub>2</sub>O resulted in elimination of this signal but did not affect the other proton resonances, allowing the assignment of this peak. The analogous cod complex **2** also appears to yield

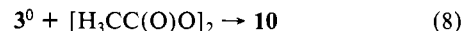
a hydroxyl adduct under these conditions. In this case, structural assignment of the OH adduct **8** is aided by a close match between its NMR spectrum and that of the Cp analogue CpPd-(C<sub>8</sub>H<sub>12</sub>OH).<sup>26</sup> Oxidation of either **7** or **8** by Ag<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> gave the original cations **4**<sup>+</sup> and **2**<sup>+</sup>, respectively. The Pd(II) cations were isolated in quantitative yield by addition of benzene to the oxidized solutions and were identified by their electrochemical curves and NMR spectra.

Since these hydroxyl adducts arise from reduction of the Pd(II) complexes in CH<sub>2</sub>Cl<sub>2</sub>/Bu<sub>4</sub>NPF<sub>6</sub>, the source of the OH radical is not obvious. Of course, although the solvent is distilled under vacuum from CaH<sub>2</sub>, it certainly contains trace amounts of water, as does the electrolysis glassware and atmosphere inside the drybox. The norbornadiene complex was therefore investigated by vacuum electrolysis, before which the cell and electrolyte were heated under vacuum to eliminate adsorbed water. Under these drier conditions, the radical **4**<sup>0</sup> was stable for over 2 h at room temperature without any evidence of formation of **7** or other decomposition products. Upon opening of the electrolysis cell to laboratory atmosphere, however, **7**, is formed as indicated by the characteristic irreversible voltammetry wave at +0.78 V. Although this experiment does not strictly prove that **4** and **2** react with water to give **7** and **8** it certainly lends considerable support to that hypothesis.

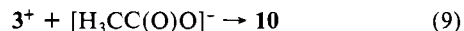
**V. Comparison of Rates of Radical and Nonradical Reactions of Pd.** The radical reactions which lead to the  $\pi,\sigma$ -complexes **5**–**8** represent a new route to a well-known class of compounds. These complexes are normally prepared by nucleophilic addition to 18-electron complexes, these reactions being well-studied because of their relevance to the Wacker reaction. We wanted to compare the relative rates of the Pd(I)/radical reactions with their Pd(II)/nucleophilic analogues. Thus the rates of two reactions were measured: (a) Pd(I), **3**<sup>0</sup> with acetyl peroxide; (b) Pd(II), **3**<sup>+</sup> with acetate ion. Acetyl, rather than benzoyl, adducts were chosen to avoid the complication of electron transfer between **3**<sup>0</sup> and benzoyl peroxide.<sup>27</sup>

Pseudo-first-order rate conditions were not employed because of electrochemical measurement difficulties which would have occurred with very large concentrations of the peroxide or acetate. Rather, a 1:1 ratio (each 0.5 mM) of **3**<sup>0</sup> and [H<sub>3</sub>CC(O)O]<sub>2</sub> (for reaction 8) or **3**<sup>+</sup> and [Bu<sub>4</sub>N][OAc] (for reaction 9) were compared to derive a relative empirical rate difference. The con-

centrations of **3**<sup>0</sup> (or **3**<sup>+</sup>) and the adduct (\*CpPd[ $\pi,\sigma$ -dbcot-OC-(O)CH<sub>3</sub>])<sup>10</sup> ( $E^\circ = +0.72$  V) were monitored in an electrochemical cell by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> at 258 K. The measured half-life of the radical **3**<sup>0</sup> in reaction 8 was 2.8 min.



In contrast, the Pd(II) complex **3**<sup>+</sup> had a half-life of 560 min in reaction 9.



Since the Pd(I) reaction is 200 times faster, it allows us to conclude that it does not proceed through a two-step mechanism (eq 10 and 11) involving electron-transfer and subsequent nucleophilic attack, i.e.,



since that mechanism would require that the overall rate of the Pd(I)/peroxide reaction be at least as slow as the Pd(II)/RO<sup>-</sup> reaction. Thus we favor a mechanism involving homolytic cleavage (eq 12) of the peroxide by **3**<sup>0</sup>:



### Conclusions

1. ( $\eta^5\text{-C}_5\text{R}_5$ )Pd<sup>II</sup>( $\eta^4$ -diene) (R = H, Ph) cations may be reduced by one electron to the corresponding neutral complexes at relatively mild potentials. The redox process involves the Pd(II)/Pd(I) couple.

2. Complexes of the pentaphenylcyclopentadienyl ligand (R = Ph) are considerably more stable than their cyclopentadienyl (R = H) analogues, and allow actual isolation of the Pd(I) radical when diene = dibenzocyclooctatetraene. These complexes appear to be the first reported stable Pd(I)  $\pi$  radicals.

3. The Pd(I) complexes undergo radical addition reactions to yield  $\pi,\sigma$ -Pd(II) complexes in a formal oxidation addition reaction. These  $\pi,\sigma$  complexes may be reoxidized by one electron to Pd(III) complexes which undergo reductive elimination of a radical fragment to yield the original Pd(II) cationic  $\pi$  complex.

4. Reaction of Pd(I)  $\pi,\pi$  radicals with peroxyacids gives the same  $\pi,\sigma$  Pd(II) complexes as found from the reaction of Pd(II) complexes with carboxylates. The results suggest that radical mechanisms should be more often considered for reactions involving the formal Pd(II)/Pd(0) couple.

**Acknowledgment.** This work was generously supported by grants from the National Science Foundation (CHE83-08974) and from N.A.T.O. We also thank the Johnson Matthey Corp. for a generous loan of palladium acetate.

(26) White, D. A. *J. Chem. Soc. A* **1971**, 145.

(27) Acetyl peroxide has a reduction wave at ca. -1 V under the voltammetric conditions used to obtain  $E^\circ = -0.22$  V for (**3**)<sup>+/0</sup>. Unless the reduction of acetyl peroxide is governed by a huge overpotential, the >700-mV difference in reduction potentials effectively eliminates the need to consider the reactions Pd<sup>I</sup> + ROOR → Pd<sup>II</sup> + ROOR<sup>-</sup> and ROOR<sup>-</sup> → RO<sup>•</sup> + RO<sup>-</sup> as a source of attacking reagent. Benzoyl peroxide reduces within 200 mV of (**3**)<sup>+</sup>.