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carbon atoms of **4** exhibited a labeling pattern consistent with partial degradation of pyruvate to acetate. The specific incorporation of C-2 and C-3 of pyruvate into **4** was confirmed by administration of (2,3-<sup>13</sup>C<sub>2</sub>)pyruvate and analysis of the labeled **4** by a COSYX experiment (experiment 11). The COSYX revealed connectivity between C-3 and C-3a as well as the connectivities expected from degradation of the precursor to doubly labeled acetate. Coronafacic acid therefore appears to be biosynthesized from a branched polyketide with pyruvate serving as the starter unit for one of the polyketide chains (Scheme I). The mechanism for formation of the C-C single bonds between C-3 of pyruvate and C-2 of two acetate units is presently obscure.

Preliminary investigations of coronamic acid (**3**) biosynthesis have also been carried out. The resemblance between **3** and isoleucine suggested a possible biosynthetic relationship. Mitchell has recently reported<sup>7</sup> that administration of [U-<sup>14</sup>C]-L-isoleucine to *Ps. syringae* pv. *atropurpurea* yielded radioactive coronatine that carried most of the radioactivity in the coronamic acid moiety. We have obtained more rigorous evidence for the role of isoleucine as a precursor by administration of a mixture of (1-<sup>13</sup>C)-DL-isoleucine and (1-<sup>13</sup>C)-DL-alloisoleucine<sup>8</sup> to *Ps. syringae*. The <sup>13</sup>C NMR spectrum of the coronatine methyl ester (**5**) obtained from this experiment displayed a high level of enrichment at C-1' (171.4 ppm) (experiment 12). Elucidation of the mechanism of the novel cyclization of isoleucine to **3** will require further study.

**Acknowledgment.** We are pleased to thank the National Institutes of Health (GM 26569) and the Robert A. Welch Foundation (C-729) for financial support, Dr. R. E. Mitchell for samples of coronatine and coronafacic acid, the Arco foundation for funds to purchase the IBM AF300 spectrometer, and Dr. Alan Kook for the COSYX spectra.

(7) Mitchell, R. E. *Phytochemistry* **1985**, *24*, 247.

(8) The labeled amino acids were prepared from 2-methylbutanal and (<sup>13</sup>C)cyanide by the Strecker synthesis.

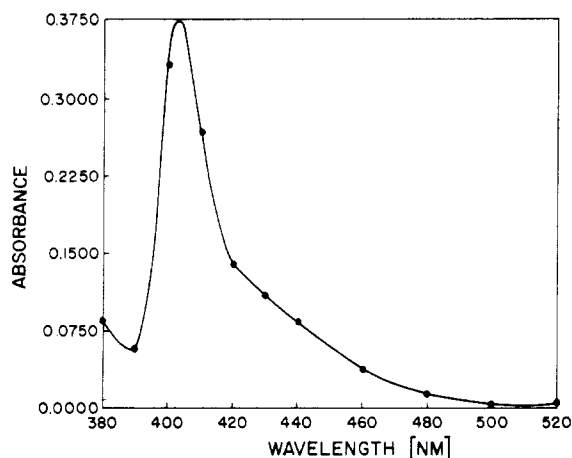
## Photochemistry of Pd-Pd σ-Bonds: Electron-Transfer Reactions of Photogenerated Pd(CNMe)<sub>3</sub><sup>•+</sup> Radicals

Patricia A. Metcalf and Clifford P. Kubiak\*

Department of Chemistry, Purdue University  
West Lafayette, Indiana 47907

Received March 10, 1986

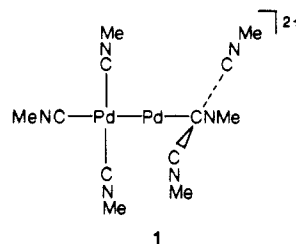
We report the first direct observation of electron transfer from a photogenerated organometallic radical of the platinum group. The photochemistry of metal-metal σ-bonds has been an area of intense interest.<sup>1</sup> Photochemical metal-metal bond homolysis,<sup>3,4,6,9</sup> disproportionation,<sup>7</sup> metal-ligand bond dissociation,<sup>3-5</sup> and atom-transfer<sup>3,8,9</sup> reactions are now all familiar. It has been recognized that photogenerated \*ML<sub>n</sub> radicals are both potentially stronger oxidants and reductants than their parent ground-state, metal-metal bonded L<sub>n</sub>M-ML<sub>n</sub> complexes.<sup>2</sup> Curiously, however, there have been few reports of electron-transfer reactivity of



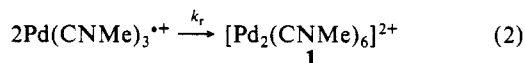
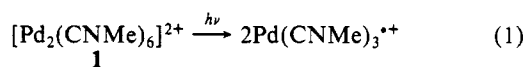
**Figure 1.** Transient absorbance spectrum of photogenerated Pd(CNMe)<sub>3</sub><sup>•+</sup> radicals obtained by measuring Δ*A* as a function of λ<sub>monitor</sub>. Each data point represents Δ*A* for a single flash on a fresh solution sample.<sup>10b</sup>

photogenerated organometallic radicals.<sup>1,2</sup>

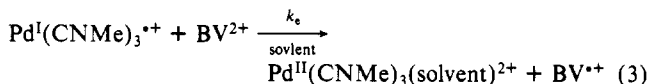
The Pd-Pd σ-bonded complex [Pd<sub>2</sub>(CNMe)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub> (**1**) pre-



viously was shown to exhibit photochemistry characteristic of Pd-Pd bond homolysis.<sup>9</sup> We therefore sought to identify the properties and chemical reactivity of the transients formed upon σ-σ\* excitation of **1**. Flash photolysis of acetonitrile solutions of **1** was found to give rise to an intense transient absorbance with λ<sub>max</sub> ~ 405 nm.<sup>10</sup> In contrast, 10<sup>-4</sup> M acetonitrile solutions of **1** exhibit no significant absorbance in the 380-520-nm region.<sup>9</sup> The transient absorbance spectrum is shown in Figure 1.<sup>10b</sup> The observed transient decayed by a second-order process, assigned to recombination of photogenerated Pd(CNMe)<sub>3</sub><sup>•+</sup> radicals, eq 1, 2. The rate expression for second order recombination, 2*k<sub>r</sub>*/ε<sub>405</sub>,



is 4 × 10<sup>4</sup> cm<sup>-1</sup> by flash photolysis. We have determined the extinction coefficient, ε<sub>405</sub>, and with it the rate of recombination, *k<sub>r</sub>*, of photogenerated Pd(CNMe)<sub>3</sub><sup>•+</sup> radicals by examining their quantitative reduction of benzylviologen (BV<sup>2+</sup>) to BV<sup>•+</sup>, eq 3 (vide infra). The extinction coefficient, ε<sub>603</sub>, of BV<sup>•+</sup> has been de-

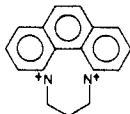
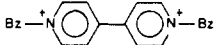
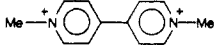
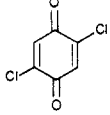


ε<sub>405</sub>(Pd<sup>•+</sup>) = 50 000 M<sup>-1</sup> cm<sup>-1</sup>    ε<sub>603</sub>(BV<sup>•+</sup>) = 14 000 M<sup>-1</sup> cm<sup>-1</sup>  
 terminated by several workers to be 14 000 M<sup>-1</sup> cm<sup>-1</sup> in acetonitrile.<sup>11</sup> The disappearing Pd(CNMe)<sub>3</sub><sup>•+</sup> radical therefore is characterized

- (1) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.
- (2) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258.
- (3) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249.
- (4) Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 4550.
- (5) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5935.
- (6) Hughey, J. L.; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440.
- (7) Stiegman, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 527 and references therein.
- (8) Mechstroth, W. M.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 1842.
- (9) Reinking, M. K.; Kullberg, M. L.; Cutler, A. R.; Kubiak, C. P. *J. Am. Chem. Soc.* **1985**, *107*, 3517.

- (10) (a) The laser flash photolysis system employed has been described previously: Guarr, T.; McGuire, M.; McLendon, G. *J. Am. Chem. Soc.* **1985**, *107*, 5104. Pulse duration, 8 ns; pulse energy, 60 mJ; λ<sub>excitation</sub>, 355 nm; path length, 1 cm. (b) The conventional flash photolysis system employed has been described previously: Ferraudi, G. *Inorg. Chem.* **1981**, *20*, 2306. Flash duration, 30 μs; flash energy, 40-250 J; λ<sub>excitation</sub>, 350 nm; path length, 20 cm.
- (11) Tsukahara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2632 and references therein.

**Table I.** Electron-Transfer Rate Constants for Reduction of Electron Acceptors, A, by Photogenerated  $\text{Pd}(\text{CNMe})_3^{++}$  Radicals

A	$E^\circ(\text{A}/\text{A}^{++})$ vs. SCE, V	$k_e, \text{M}^{-1} \text{s}^{-1}$
 (PPQ <sup>2+</sup> )	−0.13	$2 \times 10^8$
 (BV <sup>2+</sup> )	−0.36	$1 \times 10^8$
 (MV <sup>2+</sup> )	−0.45	$3 \times 10^7$
 (DCBQ)	−0.18	$3 \times 10^7$

by  $\epsilon_{405} = 50\,000 \text{ M}^{-1} \text{ cm}^{-1}$ , and recombination of  $\text{Pd}(\text{CNMe})_3^{++}$  to give **1** occurs with a rate constant,  $k_r = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The rate of  $\text{Pd}(\text{CNMe})_3^{++}$  recombination thus approaches, within an order of magnitude, the diffusion-controlled limit in acetonitrile solution.<sup>12</sup> The rate of  $\text{Pd}(\text{CNMe})_3^{++}$  recombination is essentially unaffected by solvent and shows similar rates in MeCN and  $\text{CH}_2\text{Cl}_2$  solutions.

A significant finding of this study is that the absorbance of the  $d^9$   $\text{Pd}(\text{CNMe})_3^+$  radical is both more intense and significantly red-shifted compared to either the  $\sigma\text{--}\sigma^*$  excitation of **1** or to the MLCT band of  $d^8$   $\text{M}(\text{CNMe})_3(\text{acetonitrile})^{2+}$  photoproduct.<sup>9,13</sup> We assign the unusually intense transient absorbance of the  $\text{Pd}(\text{CNMe})_3^+$  radical to an allowed  $d \rightarrow p$  electronic transition. A rather similar conclusion was recently reached in the case of related  $d^{10}$   $\text{Pd}(0)$  phosphine complexes.<sup>14</sup>

In the presence of electron acceptors, A (A = methylviologen (MV<sup>2+</sup>), benzylviologen (BV<sup>2+</sup>), *N,N'*-propylenepheneanthrolinium (PPQ<sup>2+</sup>), dichlorobenzoquinone (DCBQ)), photogenerated  $\text{Pd}(\text{CNMe})_3^+$  radicals engage in rapid electron-transfer reactions. Flash photolysis of a  $1.0 \times 10^{-4} \text{ M}$  acetonitrile solution of **1** in the presence of benzylviologen (BV<sup>2+</sup>) leads to the synchronous first-order disappearance of  $\text{Pd}(\text{CNMe})_3^{++}$  and appearance of BV<sup>•+</sup>. The kinetically coupled disappearance of  $\text{Pd}(\text{CNMe})_3^{++}$  and appearance of BV<sup>•+</sup> clearly imply that  $\text{Pd}(\text{CNMe})_3^{++}$  radicals participate in the electron-transfer process. The rates for electron transfers from  $\text{Pd}(\text{CNMe})_3^+$  radicals are quite rapid. The electron transfer rate,  $k_e$ , to BV<sup>2+</sup> has been determined to be  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The metal-containing product in these reactions is the solvated,  $d^8$  mononuclear complex  $[\text{Pd}(\text{CNMe})_3(\text{NCMe})]^{2+}$ . Table I summarizes the rate constants for reduction of several electron acceptors, PPQ<sup>2+</sup>, BV<sup>2+</sup>, MV<sup>2+</sup>, and DCBQ, by photogenerated  $\text{Pd}(\text{CNMe})_3^+$  radicals. All electron-transfer rate constants,  $k_e$ , were determined by pseudo-first-order kinetics at several concentrations of the electron acceptor, A. For the three substituted viologens, rate constants show an expected decrease from  $2 \times 10^8$  (PPQ<sup>2+</sup>) to  $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (MV<sup>2+</sup>) as the driving force for electron transfer decreases from  $E^\circ(\text{PPQ}^{2+}/^{++}) = -0.13 \text{ V}$  to  $E^\circ(\text{MV}^{2+}/^{++}) = -0.45 \text{ V}$  vs. SCE. Whether the acetonitrile solvent associates with the  $\text{Pd}(\text{CNMe})_3^{++}$  fragment prior or subsequent to the electron-transfer event will be investigated in future studies.

(12) The diffusion-limited rates for  $\text{Pd}(\text{CNMe})_3^+$  recombination are calculated to be  $k_D = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{CH}_3\text{CN}$ , 25 °C) and  $k_D = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ , 25 °C). These values are obtained from the Smoluchowski and Stokes–Einstein equations, corrected for interionic repulsion,

$$k_D = \frac{8RT}{3\eta} \left( \frac{\delta}{e^{\delta} - 1} \right)$$

where  $\delta = Z_A Z_B e^2 / 4\pi\epsilon k T d_{AB}$ . See, for example: Wilkinson, F. *Chem. Kinetics and Reaction Mechanisms*; Van Nostrand Reinhold: New York, 1980.

(13) UV–vis ( $\lambda_{\text{max}}$ , nm ( $\epsilon$ )) ( $\text{CH}_3\text{CN}$ ):  $[\text{Pd}(\text{CH}_3\text{NC})_4][\text{PF}_6]_2$ , 224 (2200), 275 (200) sh;  $[\text{Pd}(\text{CH}_3\text{NC})_3(\text{CH}_3\text{CN})][2\text{PF}_6]$ , 226 (1100), 308 (750) sh.

(14) Caspar, J. V. *J. Am. Chem. Soc.* **1985**, 107, 6718.

The rather potent reducing ability and rapid electron-transfer kinetics of the photogenerated  $\text{Pd}(\text{CNMe})_3^+$  radicals make them attractive candidates for other mediated photoreductions. Recently, photogenerated organometallic radicals have found application in the highly quantum efficient photodeposition of metal films for “laser writing” onto insulating and semiconducting supports.<sup>15</sup>

**Acknowledgment.** We thank NASA (NAG-3-586) and NSF (CHE84-11836) for support. We are particularly indebted to Dr. Guillermo Ferraudi of the Radiation Laboratory, University of Notre Dame, and Professor George McLendon of the University of Rochester for assistance, advice, and patience in collecting flash photolysis data.

(15) Montgomery, K. R.; Mantei, T. D. *Appl. Phys. Lett.* **1986**, 48, 493.

### Stereocontrolled [*m* + *n*] Annulation Reactions. A [3 + 2] Cycloaddition of 3-Iodo-2-[(trimethylsilyl)methyl]propene onto 1,2-Diones

Gary A. Molander\* and David C. Shubert<sup>†</sup>

Department of Chemistry and Biochemistry  
University of Colorado, Boulder, Colorado 80309-0215

Received March 27, 1986

The Diels–Alder reaction represents the most efficient means yet devised for the construction of six-membered carbocyclic rings.<sup>2</sup> The unprecedented stereochemical control achievable at multiple stereocenters, combined with predictable regiochemical control and a high degree of chemoselectivity, has made this process one of unparalleled utility in organic synthesis. The obvious need to extend equally efficient cycloaddition strategies to the construction of five-membered carbocyclic ring systems has led to many elegant studies of [3 + 2] annulation processes.<sup>3</sup> Perhaps the most widely utilized strategy in this regard is one in which dipolar synthons are utilized in conjunction with electron-deficient olefins to achieve net [3 + 2] annulation.<sup>3,4</sup>

Although some notable exceptions do exist,<sup>3,5</sup> these and other approaches often do not address the important problem of stereoselectivity in generation of functionalized cyclopentanoids via [3 + 2] annulation strategies. In an effort to develop general [*m* + *n*] approaches to carbocyclic ring systems that lead to stereocontrolled syntheses of five-, six-, and seven-membered rings, we considered the advantages of utilizing dianionic synthons<sup>6</sup> along with various dielectrophilic partners. Utilizing this conceptually novel approach to annulations, one is not necessarily constrained to generation of a single ring size. Furthermore, we perceived that significant stereochemical control could be achieved through intramolecular chelation control<sup>7</sup> by appropriate choice of a latent

(1) National Science Foundation Predoctoral Fellow, 1984–1987.

(2) (a) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, 61, 537. (b) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, 5, 211. (c) Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1967**, 6, 16.

(3) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 1 and references therein.

(4) (a) Ito, Y.; Nakayama, K.; Yonezawa, K.; Saegusa, T. *J. Org. Chem.* **1974**, 39, 3273. (b) Marino, J. P.; Landick, R. C. *Tetrahedron Lett.* **1975**, 4531. (c) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, 98, 3495. (d) Altenbach, H.-J. *Angew. Chem., Int. Ed. Engl.* **1979**, 18, 940. (e) Noyori, R. *Accs. Chem. Res.* **1979**, 12, 61. (f) Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B. *J. Chem. Soc., Perkin Trans. 1* **1982**, 285. (g) Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 295. (h) Abram, T. S.; Baker, R.; Exon, C. M.; Rao, V. B.; Turner, R. W. *J. Chem. Soc., Perkin Trans. 1* **1982**, 301. (i) Marino, J. P.; Laborde, E. *J. Am. Chem. Soc.* **1985**, 107, 734.

(5) (a) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, 39, 935. (b) Trost, B. M.; Lynch, J.; Renaut, P. *Tetrahedron Lett.* **1985**, 26, 6313.

(6) Molander, G. A.; Shubert, D. C. *Tetrahedron Lett.* **1986**, 27, 787.