Chemical Properties of the $Pd_4(dppm)_4(H)_2^{2+}$ Cluster and the Homogeneous Electrocatalytical Behavior of Hydrogen Evolution and Formate Decomposition

Daniel Meilleur,[1a] Dominique Rivard,[1a] Pierre D. Harvey,*[,1a] Isabelle Gauthron,[1b] Dominique Lucas,[1b] and Yves Mugnier*[,1b]

Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1, and
Laboratoire de Synthèse et d'Électrosynthèse Organométalliques, CNRS UMR5632,
Faculté des Sciences Gabriel, 6 Boulevard Gabriel, 21000 Dijon, France

Received December 6, 1999

Two new reductive electrochemical ($CO_2 + H_2O + 2e^-$; $HCO_2H + 2e^-$) and two new chemical methods ($Al(CH_3)_3$ + proton donor; NaO_2CH) to prepare the title compound from $Pd_2(dppm)_2Cl_2$ are reported. For the latter method, an intermediate species formulated as $Pd_2(dppm)_4(O_2CH)_2^{2+}$ is identified spectroscopically (^1H NMR, ^{31}P NMR, IR, and FAB-MS). Limited stability of the title compound in the presence of Cl^- and Br^- as counteranions is noticed and is due to sensitivity of the cluster toward nucleophilic attack of the halide ions. This result is corroborated by the rapid decomposition of these clusters in the presence of CN^- to form the binuclear species $Pd_2(dppm)_2(CN)_4$ and by the preparation of the stable salts $[Pd_4(dppm)_4(H)_2](X)_2(X^- = BF_4^-, PF_6^-, BPh_4^-)$. Upon a two-electron electrochemical reduction of this cluster to the neutral species ($E_{1/2} = -1.42$ V vs SCE in DMF) in the presence of 1 equiv of HCO_2H, a highly reactive species formulated as $[Pd_4(dppm)_4(H)_3]^+$ is generated and characterized by ^1H NMR, ^{31}P NMR, and cyclic voltammetry. Subsequent addition of H^+ (via RCO_2H; R = H, CH_3, CF_3, C_6H_5) under the same reducing conditions, induces the homogeneous catalysis of H_2 evolution. The turnover number is found to be 134 in 2 h, with no evidence for catalyst decomposition. This same species also exhibits a one-electron oxidation process ($E_{1/2} = -0.61$ V vs SCE in DMF) that induces the catalytical decomposition of formate ($HCO_2^- \rightarrow CO_2 + {}^1/_2H_2 + 1e^-$). This double catalysis from the same cluster intermediate is unprecedented.

Introduction

The reduction of protons to dihydrogen is one of the most fundamental chemical redox reactions,[2] and a search for molecular catalysts or electrocatalysts for this reaction, along with the understanding of the reaction mechanisms, is important for resolving problems, particularly in relevance with hydrogenases.[3] The design of efficient molecular catalysts for proton reduction has recently become a subject of increasing interest.[4−7] However, the number of examples of catalysis of electrochemical and chemical hydrogen evolution from acidic solutions by molecules dispersed in solutions, or imbedded in a supporting matrix coating the electrode surface, is quite limited.[8,9] Proposed mechanisms have been described[8,9] and involve the formation of hydride species followed by the addition of protons, subsequently leading to dihydrogen evolution. It is interesting to note that a large number of these few examples include mono- and dinuclear complexes of porphyrin systems.

Recently, we reported the identification and electrochemical characterization of a tetrapalladium dihydride cluster $[Pd_4(dppm)_4(H)_2](X)_2$ ($X^- = Cl^-$ (**Ia**), Br^- (**Ib**)).[10] Because this cluster exhibits hydrides and an electrochemically reversible (two-electron) reduction system,[10] one can hope for hydrogen evolution electrocatalysis. This work reports the first homogeneous electrocatalytic hydrogen evolution reaction induced by a cluster compound. Experimental results indicate that the intermediate is another polyhydride species, $Pd_4(dppm)_4(H)_3^+$ (**II**), that is relatively stable. This study also reports the electrocatalytic decomposition of the formate ion ($HCO_2^- \rightarrow CO_2 + {}^1/_2H_2 + 1e^-$) by this same intermediate. Finally, we report some chemical properties of the title cluster (**I**), which can be prepared chemically and electrochemically by various methods using the starting $Pd_2(dppm)_2Cl_2$ material. **I** is sensitive to nucleophiles such as Cl^-, Br^-, and CN^-, but the $[Pd_4(dppm)_4(H)_2](X)_2$ salts ($X^- = BF_4^-$ (**Ic**), PF_6^- (**Id**), BPh_4^- (**Ie**)) proved to be particularly stable, even for weeks in solution.

Experimental Section

Materials. $Pd_2(dppm)_2Cl_2$ was prepared according to literature procedures.[11] HCO_2H (Aldrich), CF_3CO_2H (Aldrich), $C_6H_5CO_2H$ (Aldrich), CH_3CO_2H (Fisher), NaO_2CH (Aldrich), $Na(BF_4)$ (Aldrich), and CO_2 (99.99% Praxair) were used as received. NaO_2CCF_3 was generated in situ electrochemically from the reduction of CF_3CO_2H. Tetrabutylammonium formate (TBAF) was prepared from a simple methathesis between NaO_2CH and TBAHFP (Aldrich) (tetrabutylammonium hexafluorophosphate) in acetone. The purity was checked by ^1H NMR using the H integration of the HCO_2^- vs Bu_4N^+ signals. $[Pd_4(dppm)_4(H)_2]$-

---

* To whom correspondence should be addressed.

(1) (a) Université de Sherbrooke. (b) Université de Bourgogne.

(2) Recent review: Koelle, U. *New J. Chem.* **1992**, *16*, 157.

(3) Schlegel, H. G.; Schneider, K. *Hydrogenases: Their Catalytic Activity, Structure and Function*; Schlegel, H. G., Schneider, K., Eds.; Verlag: Erich Goltze K_XG_X: Göttinger, Germany, 1978; pp 15−44.

(4) Bhughun, I.; Lexa, D.; Savéant, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 3982.

(5) Collman, J. P.; Ha, Y.; Wagenknecht, P. S.; Lopez, M.-A.; Guilard, R. *J. Am. Chem. Soc.* **1993**, *115*, 9080.

(6) Collman, J. P.; Ha, Y.; Wagenknecht, P. S.; Lewis, N. S. *J. Am. Chem. Soc.* **1992**, *114*, 5665.

(7) Grass, V.; Lexa, D.; Savéant, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 7526.

(8) See refs 4 and 5 and references therein.

(9) Mairanovskii, S. G. *Catalytic and Kinetic Waves in Polarography*; Plenum Press: New York, 1968; pp 245−261.

(10) Gauthron, I.; Gagnon, J.; Zhang, T.; Rivard, D.; Lucas, D.; Mugnier, Y.; Harvey, P. D. *Inorg. Chem.* **1998**, *37*, 1112.

(11) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099.

10.1021/ic9913987 CCC: \$19.00 © 2000 American Chemical Society
Published on Web 06/06/2000

(Cl)$_2$ (**Ia**) was prepared according to a method outlined in ref 10 and was used for comparison purposes.

Preparation of Ia from NaO$_2$CH. Under a N_2 atmosphere, 50.6 mg (0.048 mmol) of $Pd_2(dppm)_2Cl_2$ was dissolved in 6 mL of DMF containing 4.2 mg of NaO_2CH and 1 mL of methanol. The solution was stirred for 10 h, and the dark-blue product was obtained from evaporation to dryness using a diffusion pump for 24 h. Then the crude product was purified from rapid recrystallization using dichloromethane and diethyl ether. Yield: >80%. A comparison of the spectroscopic data (^{1}H NMR) with an authentic sample[10] clearly identified the product.

Preparation of Ia from Al(CH$_3$)$_3$. Under a N_2 atmosphere, a 2.5 mL CH_2Cl_2 solution containing 40 mg (0.04 mmol) of $Pd_2(dppm)_2Cl_2$ was added to a 50 mL CH_2Cl_2 solution containing 0.08 mmol of Al(CH$_3$)$_3$ at −78 °C After the solution was warmed to room temperature, the solution was carefully neutralized via two methods. Method 1: to the solution was added 25 mL of a saturated water solution containing NH_4Cl. Then the solution was extracted twice with CH_2Cl_2 and dried over $MgSO_4$ prior to being filtered and evaporated to ∼5 mL of solution. Then the product was precipitated and washed several times with diethyl ether. The purple product was dried under vacuum. Yield: 40%. Method 2: to the solution was added 25 mL of CH_3OH. Then the solution was evaporated to ∼5 mL, and the product was precipitated and washed with ether and dried under vacuum. Yield: ∼40%. The ^{1}H NMR data were identical to that reported for **I** in ref 10 except that in method 2, some impureties were present.

Preparation of Ic. A quantity of 330 mg (0.31 mmol) of $Pd_2(dppm)_2Cl_2$ and 690 mg (6.2 mmol) of $NaBF_4$ are dissolved in 25 mL of dry DMF and stirred for 10 min under N_2 atmosphere. To this solution 105 mg (1.55 mmol) of NaO_2CH in 3 mL of DMF was added by cannular under a N_2 atmosphere. The solution was stirred for 1 h, and the orange solution turned brown-green and then dark-blue. Then 300 mL of diethyl ether was added in order to precipitate the purple-blue solid, which was subsequently filtered and washed twice with 30 mL of water and three times with 30 mL of diethyl ether. The violet solid was dried under vaccuum overnight. Yield: 90−95%. Anal. Calcd for $C_{100}H_{88}B_2F_8P_8Pd_4$: C, 56.15; H, 4.24. Found: C, 56.15; H, 4.59. ^{1}H NMR (acetone-d_6): δ 7.79(d), 7.39(t), 7.14(t), 6.90(t), 6.62(t), 6.42(d) (^3J(H,H) = 7.7 Hz, 80H, Ph), 5.12 (nonet, rel intens = 1:8:28:56:70:56:28:1, ^2J(H,P) = 13.5 Hz, 2H, Pd−H), 4.11 (br, fwhm = 14.6 Hz, 8H, PCH_2P). ^{31}P NMR (acetone-d_6): δ 0.44. IR(solid): 1053 cm^{-1} (ν(BF)). UV−vis (ACN) $\lambda_{max}(\epsilon)$: 618(43200), 312(36300), 286 nm (13000 M^{-1} cm^{-1}). FAB-MS: 2050, $Pd_4(dppm)_4(BF_4)$ (calcd, 2052.2).

Preparation of Id. **Id** was prepared in the same way as **Ic** except that the method was adapted for $NaPF_6$ instead of $NaBF_4$. Yield: 90−95% Anal. Calcd for $C_{100}H_{90}F_{12}P_{10}Pd_4$: C, 56.25; H, 4.02. Found C 55.40, H 4.08. ^{1}H NMR (acetone-d_6) 7.79(d), 7.39(t), 7.14(t), 6.90(t), 6.62(t), 6.42(d) (^3J(H,H) = 7.5 Hz, 80H, Ph), 5.10 (nonet, rel int. = 1:8:28:56:70:56:28:1, ^2J(H,P) = 13.4 Hz, 2H, Pd−H), 4.10 ppm (br, fwhm = 14.6 Hz, 8H, PCH_2P). IR (solid): 840 cm^{-1} (ν(PF)). UV−vis (ACN) λ_{max}: 618, 312, 286 nm.

Preparation of Ie. **Ie** was prepared in the same way as **Ic** except that the method was adapted for $NaBPh_4$ instead of $NaBF_4$. Yield: 90−95%. Anal. Calcd for $C_{148}H_{130}B_2P_8Pd_4$: C, 68.29; H, 4.96; N, 0.00. Found: C, 68.15; H, 4.67. ^{1}H NMR (acetone-d_6): δ 7.79(d), 7.39(t), 7.14(t), 6.90(t), 6.62(t), 6.42(d) (^3J(H,H) = 7.5 Hz, 80H, Ph−P), 7.32-(m, 16H), 6.92(m, 16H), 6.76(tt, 8H) (Ph−B), 5.09 (nonet, rel intens = 1:8:28:56:70:56:28:1, ^2J(H,P) = 13.5 Hz, 2H, Pd−H), 4.11 (br, fwhm = 14.7 Hz, 8H, PCH_2P). UV−vis (ACN) λ_{max}: 618, 312, 286 nm. A weakly diffracting thin plate (thickness ≤ 1 mm) obtained with CH_2Cl_2/pentane gave a monoclinic system; a = 11.914 Å, b = 22.446 Å, c = 22.835 Å, α = 109.26°.

Attempts To Prepare Pd$_4$(dppm)$_4$H$_3^+$ (II). An amount of 25.0 mg (0.0117 mmol) of $[Pd_4(dppm)_4(H)_2](BF_4)_2$ (**Ic**) was dissolved in 10 mL of dry DMF or THF under N_2. An amount of 30 equiv of tetrabutylammonium formate (TBAF; 0.35 mmol; 0.10 g) was then added, and the solution was stirred for 16 h at room temperature. The reaction was monitored by ^{1}H NMR, ^{31}P NMR, and cyclic voltammetry (CV). The same signals as that of **II** generated electrochemically (see text) were observed. ^{1}H NMR (acetone-d_6): δ 7.33(t), 7.17(t), 6.88(t), 6.78-(t), 6.65(d) (^3J(H,H) = 7.7 Hz, Ph). ^{31}P NMR (DMF/C_6D_6, 1:1): δ +12.4. Cyclic voltammetry (DMF/C_6D_6 (1:1)/0.25 M TBAHPF): $E_{1/2}$(oxi) = −0.61V vs SCE. Unfortunately, the NMR spectra that evolved with time (under N_2) contained a decomposition product that was always present as a minor component during the early stage of the reaction and as a major component later (δ = +24.2).

Attempts To Prepare [Pd$_4$(dppm)$_4$(O$_2$CH)$_2$](Cl)$_2$ (III). An amount of 50.6 mg (0.048 mmol) of $Pd_2(dppm)_2Cl_2$ was dissolved in 6 mL of DMF, which was kept under N_2 at all times. After the solution was cooled to −80 °C, 4.2 mg of NaO_2CH in 1 mL of methanol was added to the DMF solution. The solution was then stirred and removed from the −80 °C bath until it reached about −10 °C (∼263 K). When the solution was turned green, it was recooled at −80 °C to stop the reaction and evaporated to dryness using a diffusion pump for 20 h at this same temperature. Since the product evolves rapidly in solution at room temperature to form **I**, the analysis was performed in the solid state only. From the FAB-MS analysis (see Supporting Information) and ^{31}P NMR spectra at low temperatures there is no evidence of **I** in the solid, in comparison with an authentic sample. The spectroscopic features are provided and discussed in the text.

Electrochemistry (CV). All manipulations were performed using standard Schlenck techniques in an atmosphere of dry and oxygen-free argon. Dimethylformamide (DMF) was freshly purified and dried from distillation over CaH_2 (under vacuum). This solvent was deoxygenated by argon-bubbling immediately before use. The supporting electrolytes were TBAHFP or LiCl dried and degassed before use. Typically the concentration was 0.2 M. In cyclic voltammetry experiments the concentration of analyte was nearly 10^{-3} M. Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode (SCE) separated from the analyzed solution by a sintered glass disk. The auxiliary electrode was a platinum wire. For all voltammetric measurements the working electrode was a carbon disk electrode initially polished with alumina. The number of electrons involved in each electrochemical process was determined by coulometry. The controlled potential electrolysis was performed with an Amel 552 potentiostat coupled to an Amel 771 integrator. A carbon gauze was used as the working electrode either as a cathode or as an anode for a reduction or oxidation, respectively. A platinum plate was the anode and a saturated calomel electrode was the reference electrode, each electrode being separated from the others by sintered glass disks.

Results and Discussion

Preparation and Stability. **I** can be prepared quantitatively using $Pd_2(dppm)_2Cl_2$ in DMF in the presence of TBAHPF according to two electrochemical methods. The two consist of a complete electrolysis of the dinuclear complex at −1.2 V vs SCE in the presence of HCO_2H (method 1) or $H_2O + CO_2$ (method 2), both being performed with a consumption of 2 equiv of electricity ($n_{exp} = 2.2 \pm 0.1$ F mol^{-1}). As a typical example, monitoring of the electrosynthesis of **I** is presented in Figure 1, showing the evolution of the cyclic voltammetry traces of the dinuclear species in the absence and presence of H_2O and CO_2. After complete electrolysis, **I** is formed as the sole Pd-containing product, as identified from a comparison of the ^{31}P NMR spectra and cyclic voltammogram with an authentic sample.[10] The global reactions can be written as

$$2Pd_2(dppm)_2Cl_2 + 2HCO_2H + 4e^- \rightarrow Pd_4(dppm)_4(H)_2^{\,2+} + 4Cl^- + 2HCO_2^- \quad (1)$$

$$2Pd_2(dppm)_2Cl_2 + 2\text{ “}H^+\text{” (from } H_2O) + 4e^- \xrightarrow{CO_2} Pd_4(dppm)_4(H)_2^{\,2+} + 4Cl^- \quad (2)$$

No mechanistic detail is provided at this time, but electrolysis in the presence of a very small amount of H_2O (with no added CO_2) generates **I** and $Pd_2(dppm)_3$, also identified by ^{31}P NMR and CV of an authentic sample.[12] The presence of **I** illustrates that H_2O acts as a source of protons, whereas $Pd_2(dppm)_3$ is an

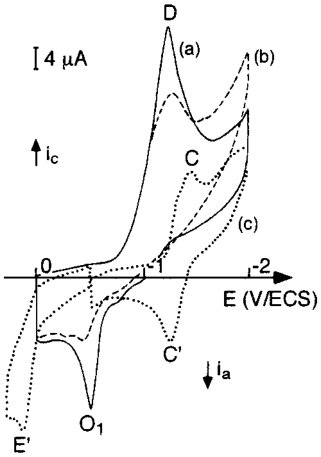


Figure 1. Cyclic voltammograms for $Pd_2(dppm)_2Cl_2$ in DMF/0.2 M $TBAHFP_6$: (a) −, alone; (b) - - -, in the presence of H_2O and CO_2 ($DMF/H_2O = 10/0.75$ v:v) at the early stage of electrolysis; (c) ···, after a bielectronic reduction at −1.2 V vs SCE. Initial potentials are 0.0, 0.0, and −0.5 V for curves a, b, and c, respectively. The sweep rate is 200 mV/s. The C/C′ wave corresponds to the redox process for **I**/**IV**, while the ill-defined wave E′ is the oxidation process for **I**.

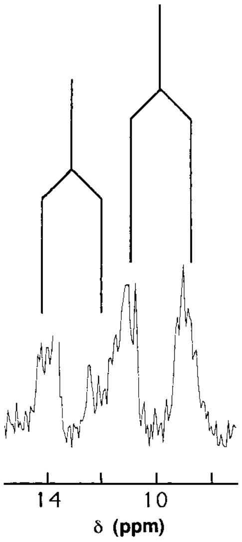


Figure 2. ^{31}P NMR spectrum at 253 K of the intermediates formed during the reaction of $Pd_2(dppm)_2Cl_2$ with NaO_2CH in a 1:1 DMF-d_7/methanol-d_4 mixture. The signals at about 11 and 9 ppm are due to cluster **III**.

electroreduction product generally obtained in aprotic media.[13] When the relative amount of H_2O is decreased, the concentration of **I** decreases. When the concentration of CO_2 is increased, the relative amount of **I** increases as well. We suggest that the formation of **I** according to method 2 is in fact promoted via the well-known formation of carbonic acid ($CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^-$).

I can also be chemically prepared in good yield from the same d^9-d^9 dimer using NaO_2CH. The direct reaction between the two leads to a color change from orange to red to purple within a minute at room temperature. Again, from CV and ^1H NMR and ^{31}P NMR spectroscopy, **I** is identified as the sole product. The overall reaction can be written as

$$2Pd_2(dppm)_2Cl_2 + 2HCO_2^- \rightarrow Pd_4(dppm)_4(H)_2^{2+} + 4Cl^- + 2CO_2 \quad (3)$$

In this case, attempts to isolate one of the intermediates (**III**) is made. The variable temperature ^{31}P NMR spectra for a DMF-d_7/methanol-d_4 mixture containing $Pd_2(dppm)_2Cl_2/NaO_2CH$ indicate that only the starting dinuclear species is present in solution between 193 and 233 K. The NMR peak experiences only a small shift from 3.23 (193 K) to 3.07 ppm (233 K), keeping a full-width-at-half-maximum (fwhm) of ∼0.2 ppm. At 243 K, two new signals grow in at ∼12.0 and 14.0 ppm (fwhm, ∼1 ppm) (Figure 2). When the sample is subsequently warmed to 263 K, the peak associated with the starting material disappears and the peaks at ∼8.7 and 11.2 ppm (intermediate **III**) are now dominant in the spectra. The relative intensity ratio is ∼8:1 for the peaks at ∼8.7 and 11.2 ppm versus those at ∼12.0 and 14.0 ppm. Finally, when the temperature reaches 273 K, the signal associated with cluster **I** appears at −4.4 ppm and the others disappear completely. When reaction 3 is performed at about 263 K, the subsequent evaporation of DMF affords a green solid that exhibits about same 263 K spectrum described above. This compound proves to be readily unstable in solution at room temperature, so its isolation in the pure state is not possible. The spectral analysis for low-temperature solutions, or for solid samples at room temperature, provides the following information. There is no evidence for **I** in the samples according to ^1H and ^{31}P NMR spectroscopy and FAB mass spectrometry.[14] The FAB mass spectra indicates the presence of Pd_4 fragments at masses greater than 1700 and the presence of HCO_2 groups (Supporting Information). For instance, a higher mass peak at 1993 can only be explained by the fragment "$Pd_4(dppm)_4(OCH)$" (calcd mass = 1992.2). The ^1H NMR spectra do not show any evidence of hydrides (generally encountered between 0 and −10 ppm, or at about +5 ppm for **I**). The solid-state IR spectra exhibit $\nu(C{=}O)$ and $\nu(C{-}O)$ at 1672 and 1385 cm^{-1}, respectively. In this case $\Delta = 287\ cm^{-1}$ and indicates that the formate ligand is M-bounded only via the $-O^-$ moiety.[15] The presence of two ^{31}P NMR signals of similar intensity demonstrates a C_s plane of symmetry. On the basis of these findings, the structure of intermediate **III** can be proposed as a rectangular $Pd_4(dppm)_4$ cluster where two $-O_2CH$ ligands bridge two Pd metals in a C_{2h} symmetry (Chart 2), somewhat similar to that found crystallographically for $Pd_4(dppm)_4(Cl)_2^{2+}$ (Chart 3).[16,17] The bridging of two M atoms via the $-O^-$ moiety of a carboxylate ligand is not unprecedented,[18] and the instability of this formato complex is not surprising.[19]

I can also be prepared somewhat unexpectedly from the reaction between $Pd_2(dppm)_2Cl_2$ and $Al(CH_3)_3$ and subsequently

---

(12) (a) ^{31}P NMR data in a 1:1 $DMF/CDCl_3$ mixture: for **I**, −8.8 ppm; for $Pd_2(dppm)_2Cl_2$, −4.86 ppm; for PF_6^- as supporting electrolyte, −145.5 ppm; for $Pd_2(dppm)_3$, 15.9 ppm. In the last case, this $d^{10}-d^{10}$ dimer reacts with $CHCl_3$ to form the d^8-d^8 A-frame $Pd_2(dppm)_2(\mu\text{-}CH_2)Cl_2$ complex.[12b] So the signal at 15.9 ppm is due to its oxidized form. (b) Caspar, J. V. *J. Am. Chem. Soc.* **1988**, *110*, 2145.

(13) Gauthron, I.; Mugnier, Y.; Hierso, K.; Harvey, P. D. *New J. Chem.* **1998**, 237.

(14) **I** provides good signal-to-noise ratios in the FAB mass spectra where the detector sensitivity can be low. The relatively unstable product **III** exhibits a worse signal-to-noise ratio, so the detector sensitivity must be increased for the measurements. Little contamination of **I** inside sample **III** would be readily noticed. This was not the case.

(15) The Δ value is a function of the coordination mode. For instance, for a small Δ value (<100 cm^{-1}), the formate acts as a bridging ligand. Nakamoto K. Z. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; p 232.

(16) Braunstein, P.; Luke, M. A.; Tiripicchio, A.; Camellini, M. T. *Angew. Chem.* **1987**, *26*, 768.

(17) Braunstein, P.; Luke, M. A.; Tiripicchio, A.; Camellini, M. T. *New. J. Chem.* **1988**, *12*, 429.

(18) Fortin, D.; Drouin, M.; Harvey, P. D.; Herring, F. G.; Summers, D. A.; Thompson, R. C. *Inorg. Chem.* **1999**, *38*, 1253.

(19) Darensbourg, D. J.; Wiegreffe, P.; Riordam, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 5759.

Chart 1

$Pd_4(dppm)_4(H)_2^{2+}$			I
$Pd_4(dppm)_4(H)_2(X)_2$	X=	Cl^-	Ia
		Br^-	Ib
		BF_4^-	Ic
		PF_6^-	Id
		BPh_4^-	Ie
$Pd_4(dppm)_4(H)_3^+$			II
$Pd_4(dppm)_4(O_2CH)_2^{2+}$			III
$Pd_4(dppm)_4(H)_2^0$			IV

Chart 2

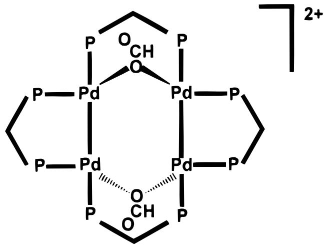
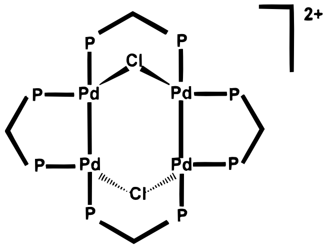


Chart 3



with either NH_4^+/H_2O (method 1) or CH_3OH (method 2). The procedure employed is the same as that reported by Stille et al.[21] where an unstable intermediate, $Pd_2(dppm)_2(Cl)(CH_3)$, evolves at room temperature to form the crystallographically characterized $Pd_2(dppm)_2(Cl)_2(CH_3)_2$ and the very reactive $[Pd_2(dppm)_2]$ species (observed spectroscopically). It is strongly suspected that this very reactive $d^{10}-d^{10}$ dimer oxidatively adds H^+ (from NH_4^+/H_2O, method 1; CH_3OH, method 2) to form **I**. The yields (<50% relative to Pd) are consistent with this conclusion. Although this method is not convenient for the preparation of **I**, it provides an important clue to what happens in the electrochemical preparation of **I** described above. Hence, the same highly reactive intermediate is also generated electrochemically from the two-electron reduction of $Pd_2(dppm)_2Cl_2$.[13] To our knowledge, only one $Pd^0_2(diphos)_2$ species (diphos $= (Cy_2PCH_2)_2$) has been clearly isolated and crystallographically characterized.[22]

I is also known to be relatively reactive toward halogenated solvents, HCl and I_2, to form, among other products, the mononuclear $Pd(dppm)X_2$, binuclear $Pd_2(dppm)_2X_2$, or both species (X = halogen), and on some occasions, a third uncharacterized Pd-containing species.[23] Our previous study indicated that in fact **Ia** and **Ib** are similarly reactive.[10] but limited stability has been observed in some solvents. During the decomposition process, ^1H NMR spectroscopy and FAB mass spectrometry reveal the presence of $Pd(dppm)X_2$ (^1H NMR[24−26]), $Pd_2(dppm)_2X_2$ (^1H NMR,[24−26] FAB), and an unidentified species with fragment masses larger than **I** (i.e., >2034; FAB) as inorganic products. Upon addition of halides (Cl^- or Br^-), this decomposition process is readily accelerated, and even the catalytic processes described below are inhibited. To shed some light on what might initiate this instability/reactivity, addition of CN^- and the preparation of **Ic**, **Id**, and **Ie** are made. The reaction of CN^- with **I** also accelerates the decomposition and generates $Pd_2(dppm)_2(CN)_4$ as the Pd-containing product.[27] **Ic**, **Id**, and **Ie**, which are prepared from a counteranion metathesis with **Ia** and $NaBF_4$, $NaPF_6$, and $NaBPh_4$, respectively, are readily stable for weeks in solution. The nucleophile nature of the counteranion (CN^-, Cl^-, Br^-) appears to be a key factor in the relative stability. No attempt was made to identify the organic product, if any.

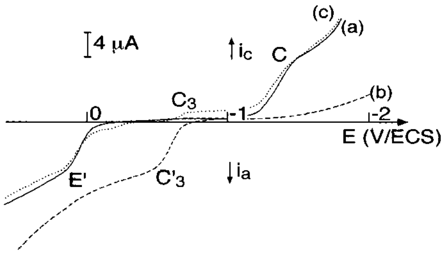


Figure 3. RDE voltammogram of **I** in DMF/0.2 M $TBAHFP_6$: (a) in the presence of 3 equiv of HCO_2H; (b) after a five-electron reduction at −1.5 V vs SCE; (c) after a subsequent four-electron oxidation at −0.45 V vs SCE.

Homogeneous H_2-Evolution Catalysis. **I** is reduced to the highly reactive neutral species $Pd_4(dppm)_4(H)_2^0$ (**V**) at −1.42 V vs SCE in DMF/0.2 M TBAHFP via two one-electron processes.[10] The ^{31}P NMR spectra for **IV** exhibits a singlet at $\delta = +13.9$ ppm using a DMF/C_6D_6 (1:1) mixture. The rotating disk electrode (RDE) voltammogram (Figure 3a) exhibits an oxidation wave E′ ($E_{1/2} = +0.07$ V vs SCE) and a reduction wave C ($E_{1/2} = 1.35$ V vs SCE), which correspond to $\mathbf{I} + 2\,e^- \rightleftarrows \mathbf{IV}$ (C/C′) and $\mathbf{I} \rightarrow Pd_4(dppm)_4(H)_2^{4+} + 2e^-$ (E′/E), respectively.[28] Electrolysis of **I** in the presence of 2 and 20 equiv of HCO_2H under the same conditions consumes 4 and 22 equiv of electrons, respectively ($n_{exp} = 3.90$ and 22.5 F mol^{-1}). These results indicate the presence of an electrocatalytical reduction of HCO_2H within the electrochemical time scale. The presence of H_2 as an electroproduct is readily demonstrated using the $PdCl_2$ method ($PdCl_2 + H_2(g) \rightarrow Pd(0) + 2HCl$),[29] and the amount of H_2 produced is quantitative with respect to the amount

---

(20) Grushin, V. V.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3259.

(21) Young, S. J.; Kellenberger, B.; Reibenspies, J. M.; Himmel, S. E.; Manning, M.; Anderson, O. P.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 5744.

(22) Pan, Y.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 3842.

(23) Kirss, R. U.; Eisenberg, R. *Inorg. Chem.* **1989**, *28*, 3372.

(24) Hunt, D. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2267.

(25) Balch, A. L.; Hunt, C. T.; Lee, C.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

(26) Balch, A. L.; Bonner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996.

(27) (a) The compound was spectroscopically identified from a comparison with an authentic sample.[27b,c] (b) Yip, H.-K.; Lai, T.-F.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1991**, 1639. (c) Hassan, F. S.; Markham, D. P.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1985**, 279.

(28) The cyclic voltammograms exhibit an electrochemically irreversible oxidation wave for $\mathbf{Ia} \rightarrow Pd_4(dppm)_4(H)_2^{4+} + 2e^-$.[10] The FAB mass spectra of the bulk electrolysis mixture clearly indicate the presence of fragment peaks such as $Pd_4(dppm)_4(Cl)_3(PF_6)$ (2214.6), $Pd_4(dppm)_4(Cl)_3$ (2069.7), $Pd_4(dppm)_4(Cl)$ (1998.7), etc., illustrating that the Pd_4 core remains intact upon the two-electron oxidation. However, the presence of Pd hydrides is not formally established in this case.

(29) Conneley, P.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 2684.

of current used.[30] The turnover number has been found to be 134 for a period of 2 h with no evidence of catalyst decomposition. So the global reaction can be written as

$$2HCO_2H + 2e^- \xrightarrow{\textbf{IV}} H_2 + 2HCO_2^- \qquad (4)$$

A better understanding of the mechanism can be provided by the evolution of the RDE voltammogram along the electrolysis. In the presence of 3 equiv of sample, the electrolysis consumes nearly 4 equiv of electrons ($n_{exp} = 4.31$ F mol^{-1}) and the RDE voltammogram exhibits the oxidation wave C′3 (Figure 3b), indicating that an intermediate of the type $Pd_4(dppm)_4(H_3)^+$, **II**, is formed according to

$$\underset{\textbf{IV}}{Pd_4(dppm)_4(H)_2^{\,0}} + HCO_2H \rightarrow \underset{\textbf{II}}{Pd_4(dppm)_4(H)_3^{\,+}} + HCO_2^- \qquad (5)$$

II is stable enough for ^{31}P NMR analysis ($\delta = 12.4$ ppm in DMF/C_6D_6 1:1, ^{1}H coupled and decoupled) but could not be isolated because of the supporting electrolyte nor could it be prepared chemically in a pure state.[31] One of the reasons for this is that for subsequent addition of HCO_2H, intermediate **II** is decomposed to form **I** and H_2:

$$\underset{\textbf{II}}{Pd_4(dppm)_4(H)_3^{\,+}} + HCO_2H \rightarrow \underset{\textbf{I}}{Pd_4(dppm)_4(H)_2^{\,2+}} + HCO_2^- + H_2 \qquad (6)$$

Hence, additions of H$^+$ lead to two consecutive reactions with **II** as an intermediate, which can be observed confidently. This intermediate is best observed when the solutions are stirred vigorously, along with slow addition of acid. Depending on the experimental conditions, **II** is stable for periods varying from a few hours to a few days.

To confirm the acid−base chemistry described in eqs 5 and 6, subsequent additions of the more soluble TBAF salt (1−10 equiv) are made. In these cases, the H_2 production and the catalytical current expectedly decrease with an increase of HCO_2^- concentration. This excess in conjugated base reduces the amount of H$^+$ available but not enough to preclude the appearance of **II**. With larger amounts of TBAF (≥30 equiv), H_2 production is stopped and **II** is generated quantitatively. These experiments also indicate that **IV** must be strongly basic.

The catalytical cycle is completed when **I** is again reduced to **IV** at constant potential. The catalytical cycle is shown in Figure 4, and the replacement of HCO_2H by CF_3CO_2H gives the same results for catalysis. Addition of large amounts of LiCl (1 or more equiv) completely inhibits the catalysis as the Cl$^-$ ions decompose **I**, as previously noted.

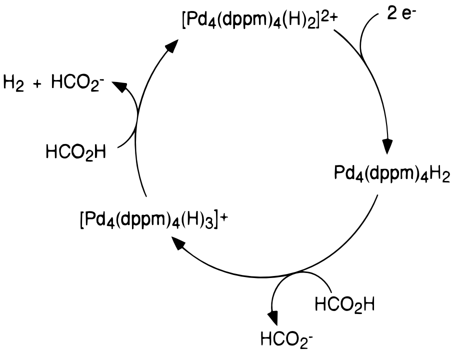


Figure 4. Catalytic cycle for the electroreduction of HCO_2H by **I**.

Kinetic Analysis. The rate (r) of decomposition of **II**, as described by reaction 6, has been kinetically measured at −22 °C, a temperature allowing for a reaction time scale of several minutes. The [**II**] has been monitored vs time by cyclic voltammetry using the height of peak C′$_3$. Here, r can be expressed as

$$r = -\frac{d[\textbf{II}]}{dt} = k[\textbf{II}][RCO_2H] \qquad (7)$$

It can easily be demonstrated that

$$kt = -\frac{1}{[A]_0 - [B]_0}\left\{\ln \frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}\right\} \qquad (8)$$

where $[A]_0 = [\textbf{II}]$ at $t = 0$, $[B]_0 = [HCO_2H]$ at $t = 0$, and $x =$ [**II**] that has been consumed at a given t. For [HCO_2H] and [HCO_2^-] = 10 and 20 equiv, respectively, a slope of 1.27 (±0.02) × 10^{-3} s^{-1} M^{-1} is reproducibly obtained.

By assuming a mechanism in which a very unstable intermediate "$Pd_4(dppm)_4(H)_4^{2+}$" participates, it can be easily shown that r involving reactions

$$\underset{\textbf{II}}{Pd_4(dppm)_4(H)_3^{\,+}} + HCO_2H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\textbf{V}}{\text{“}Pd_4(dppm)_4(H)_4^{\,2+}\text{”}} + HCO_2^- \qquad (9)$$

and

$$\underset{\textbf{V}}{\text{“}Pd_4(dppm)_4(H)_4^{\,2+}\text{”}} \xrightarrow[\text{very fast}]{k_2} \underset{\textbf{I}}{Pd_4(dppm)(H)_2^{\,2+}} + H_2 \qquad (10)$$

is given by

$$r = -\frac{d[\textbf{II}]}{dt} = \frac{k_1k_2[\textbf{II}][HCO_2H]}{k_2 + k_{-1}[HCO_2^-]} \qquad (11)$$

assuming the stationnary state (i.e., d[**V**]/dt = 0). If $k_{-1}[HCO_2^-] \gg k_2$, then the r is given by

$$r = \frac{k_1k_2}{k_{-1}[HCO_2^-]}[\textbf{II}][HCO_2H] \qquad (12)$$

If $k_2 \gg k_{-1}[HCO_2^-]$, then the equation can be rewritten as

$$r = -\frac{d[\textbf{II}]}{dt} = \{k_1\}[\textbf{II}][HCO_2H] \qquad (13)$$

Experimentally, when [HCO_2^-] increases, r decreases, indicating

---

(30) A comparison between the number of moles of H_2 theoretically produced ($n = Q/F$, F = Faraday constant, Q = charge determined by integration of the electrolysis current) and the number effectively produced (experimentally obtained from the expansion of volume caused by the electrolysis in the hermetically closed electrochemical cell connected to a water-containing U-shaped tube; $n = (DV)P)/(RT)$, DV = expansion of volume, P = pressure, R = gas constant, T = temperature) at regular stages of the electrolysis (10, 20, 30, 40, and 50 C) gives a yield that is practically constant at 100%. $HClO_4$ was used as a standard to test this methodology.

(31) Additions of $LiAlH_4$, $LiAlEt_3H$, or LiAl(O−t-Bu)$_3$H to **Ia**, or treatment of **I** with Na/Hg and then with H$^+$ under an inert atmosphere, led to decomposition, forming Pd(dppm)Cl_2 as one of the products. Addition of $NaBH_4$ did not lead to any reaction. However, additions of a large amount of TBAF slowly led to the formation of **II** as stated in the Experimental Section. **II** proves to be slightly unstable with time and could never be prepared pure.

that eq 12 applies. For an excess of HCO_2^- in solution, $[HCO_2^-]$ is about constant and the rate of reaction becomes pseudo-second-order (Supporting Information). For comparative purposes, under the same experimental conditions of temperature and concentration, reaction 6 occurs very rapidly (i.e., within a few seconds). No kinetic data could in fact be obtained for the first protonation. This observation is consistent with the fact that an electron-richer, unsaturated complex should be more readily protonated than an electron-poorer one. Here, the formal oxidation states for the Pd metals are 0.5 and 1.0 for **IV** and **II**, respectively.

Catalysis of H_2 evolution using other carboxylic acids are also observed. For instance, **I** is reduced in the presence of 5 equiv of CH_3CO_2H to form **II** and consumes the expected 7 equiv of electrons ($n_{exp} = 7.2$ F mol^{-1}). However, the rates of reaction are clearly pK_a-dependent. Qualitatively, the rates of H_2 evolution follow $CF_3CO_2H > HCO_2H > C_6H_5CO_2H > CH_3CO_2H$.[32] In addition, cluster **II** could only be observed quantitatively for CF_3CO_2H and HCO_2H and *not quantitatively* for the two other acids. This behavior is not understood at this point, and consequently, irreproducible kinetic data have been acquired, despite rigorous identical concentrations and material purity. When large amounts of HCO_2^- are added to the solutions prior to electrolysis (typically 20 equiv) and when the second acid RCO_2H ($R = C_6H_5$, or CH_3) is subsequently added, cluster **II** is again observed quantitatively during electrolysis.

Homogeneous Formate Decomposition Catalysis. The chemically reversible C3/C3′ process occurs at −0.61V vs SCE as stated above, but coulometry indicates that the number of equivalents of electrons necessary to bring this system to zero current is a function of the number of equivalents of HCO_2^- ions in solution. The presence of HCO_2^- is due to reduction of HCO_2H necessary to generate **II** (reaction 5) and due to the added NaO_2CH. Hence, the total number of electrons necessary to perform the oxidation of **II** at the C_3' wave is reproducibly measured according to the following equation:

$$n(\text{oxidation}) = n(HCO_2^-) + 1 \tag{14}$$

where n(oxidation) represents the total number of equivalents of electrons necessary to perform the oxidation of **II** and HCO_2^-, $n(HCO_2^-)$ is the total number of equivalents of HCO_2^- present in solution, and 1 is the residual number of equivalents of electrons necessary to oxidize **II** alone. As an example, the oxidation of **II** at −0.61 V vs SCE in the presence of 10 equiv of HCO_2^- consumes 11 equiv of electrons ($n_{exp} = 11.5$ F mol^{-1}). These results demonstrate that this process is also catalytic. No such behavior is observed for $CF_3CO_2^-$ and $CH_3CO_2^-$. The presence of H_2 as an electroproduct readily detected according to the $PdCl_2$ method[28] and quantified as described earlier[30] allows us to write the following catalytical decomposition equation:

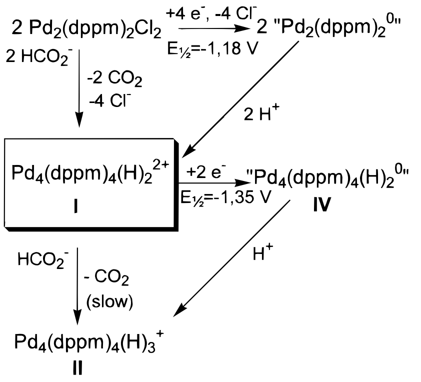
$$HCO_2^- \rightarrow {}^1/{}_2H_2 + CO_2 + 1e^- \qquad E_0 = -0.61 \text{ V vs SCE} \tag{15}$$

Equation 15 is in agreement with the known reducing ability of the HCO_2^- ion.[33] As expected, additions of HCO_2^- (from TBAF) induce an increase in the catalytical oxidation current and H_2 production.

Concluding Remarks

I can be prepared via two general ways (Scheme 1): (1) addition of "H^+" to a chemically or electrochemically generated $Pd_2(dppm)_2$ species ($d^{10}-d^{10}$); (2) addition of "H^-" to $Pd_2(dppm)_2Cl_2$ (d^9-d^9). **I** is relatively stable but is sensitive to the nucleophility of its counteranion environment. Similarly, **II** can also be generated chemically from **I** and HCO_2^- ("H^-" donnor) or electrochemically (**I** + $2e^-$ + H^+; Scheme 1). Indeed, a two-electron reduction of **I** generates the electron-rich species **IV**, which is a strong base readily capable of adding H^+ to form the relatively stable cluster **II**. This cluster can act as an acceptor of a second proton, clearly more slowly than the first one, and as an oxidizing agent when electrochemically oxidized. Both catalytical H_2 evolution from carboxylic acids (RCO_2H) and decomposition/oxidation of HCO_2^- are observed. This dual electrocatalytical property is, to our knowledge, unprecedented.[34] Other electrocatalysis are also likely to occur with **I**. In addition, Kirss and Eisenberg[23] reported thermal hydrogenation catalysis of phenylacetylene into styrene under NMR conditions. Preliminary results show that under high pressures of H_2 at 50 °C, catalytical production of ethylbenzene as a major product is observed. It is anticipated that some intermediate species similar to that investigated in this work are also present in this catalytical hydrogenation.

Scheme 1



Acknowledgment. Y.M. acknowledges financial support from EDF/Novelect Bourgogne and Club d'Électrochimie Organique and from the Conseil Regional de Bourgogne. P.D.H thanks NSERC (Natural Sciences and Engineering Research Council) and FCAR (Fonds Concerté pour l'Avancement de la Recherche) for funding.

Supporting Information Available: Tables listing FAB-MS data for **Ic** and **III** and graph of $([A]_0 - [B]_0)^{-1} \ln\{[A]_0([B]_0 - x)\}/\{[B]_0([A]_0 - x)\}$ as a function of time. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9913987

---

[32] pK_a values for CF_3CO_2H, HCO_2H, $C_6H_5CO_2H$, and CH_3CO_2H in water are 2.30, 3.75, 4.20, and 4.76, respectively, and in DMF are unknown, 11.6, 12.3, and 14.2, respectively. *Handbook of Chemistry and Physics*, 60th ed., p D-165. Demange-Guerin, G. *Talanta* **1970**, *17*, 1099. For CF_3CO_2H, $k = 2.53\ (\pm 0.04) \times 10^{-4}$ s^{-1} M^{-1} at −22 °C with $[B]_0 = [CF_3CO_2H] = 2$ equiv and $[CF_3CO_2^-] = 20$ equiv. The smaller relative concentration in $[CF_3CO_2H]$ is used to ensure a slower protonation. Otherwise, the reaction is too fast (several seconds to less than a minute) to accurately measure the rate constant. For instance, when $[CF_3CO_2H] = 4$ or 5 equiv, then the protonation reaction is completed in less than 1 min.

[33] Koelle, U. *New J. Chem.* **1992**, *16*, 157.

[34] The catalytical decomposition of HCO_2H in H_2 and CO_2 has recently been reported. Gao, Y.; Kuncheria, J.; Yap, G. P. A.; Puddephatt, R. J. *Chem. Commun.* **1998**, 2365.