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Notes

Spectroscopic Identification and Electrochemical Behavior of the Dihydride Tetrapalladium Cluster $[Pd_4(dppm)_4(H)_2]X_2$ (X = Cl, Br)

**Isabelle Gauthron,[1a] Jonathan Gagnon,[1b]
Tianle Zhang,[1b] Dominic Rivard,[1b] Dominique Lucas,[1a]
Yves Mugnier,*,[1a] and Pierre D. Harvey*,[1b]**

Laboratoire de Synthèse et d'Électrosynthèse
Organométalliques, CNRS UMR 5632, Faculté des Sciences
Gabriel, 6 boulevard Gabriel, 2100 Dijon, France, and
Département de chimie, Université de Sherbrooke,
Sherbrooke, Québec, Canada, J1K 2R1

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Introduction

The number of reliably characterized soluble complexes of palladium is much smaller than the number of platinum analogues, due to their relative instability.[2] However, these species are crucial for a number of catalytical processes and stoichiometric organic reactions such as hydrogenation, oxidation, reduction, isomerization, carboxylation, and others.[2,3] Although a number of mono- and binuclear palladium hydrides have been successfully identified structurally and spectroscopically,[4] very rare are the hydrido polynuclear Pd complexes that have been convincingly characterized. To our knowledge there is no X-ray structure of $Pd_3(H)_x$ or Pd_n ($n \geq 4$) complexes in the literature. Recently Puddephatt et al.[5a,b] prepared the unstable compound $[Pd_3(dppm)_3(\mu^3\text{-}S)(H)]PF_6$ which was characterized by NMR and IR by comparison with the X-ray crystallographically characterized Pt analogue. Furthermore, attempts to prepare $[Pd_3(dppm)_3(\mu^3\text{-}H)]^+$ were unsuccessful,[5c] while the Pt congener was prepared and characterized by X-ray crystallography.[5c,d] Eight years ago Kirss and Eisenberg studied the reaction between $Pd_2(dppm)_2Cl_2$ and $NaBH_4$ which produced "$Pd_2(dppm)_2(H)_x$".[6] The reported chemical analysis did not add up to 100%, while it was known that the same reaction with $Pt_2(dppm)_2Cl_2$ formed $[Pt_2(dppm)_2(H)_3]Cl$.[7] We have reinvestigated the reaction between $Pd_2(dppm)_2X_2$, where X = Cl, Br, or I, and $NaBH_4$ under the same experimental conditions. While no reaction is observed for the I derivative, we have obtained the same diamagnetic product according to color, spectra, and chemical behavior, except that both compounds (X = Cl, **I**; X = Br, **II**) contain halides. We now wish to report the characterization of the first tetrapalladium hydride cluster formulated as $[Pd_4(dppm)_4(H)_2]X_2$ (X = Cl, **I**; X = Br, **II**), along with some of its electrochemical properties in relation to electrocatalysis.

Experimental Section

Materials. $Pd_4(dppm)_4(H)_2Cl_2$. This compound was prepared in the same way as that reported by Kirss and Eisenberg.[6a] The compound exhibited a limited stability, and the C elemental analysis has always been poor but identical to that reported in ref 6. Anal. Calcd: C 58.98, H 4.45, P 12.17, N 0.00, Cl 3.48, Pd 20.90. Found: C 57.3, H 4.41, P 12.55, N 0.00, Cl 3.91. ^1H NMR (CD_2Cl_2): δ 6.3−7.8 (complex, 80H, $^3J(H,H) = 7.6$ Hz, C_6H_5), 4.96 (nonet, rel int = 1:8:28:56:70:56:28:8:1, $^2J(H,P) = 13.7$ Hz, PdH), 3.97 (s, broad, fwhm = 7.4 Hz, 8H, PCH_2P). ^{31}P NMR: ($CDCl_3$) −8.15 ppm (s), ($(CD_3)_2CO$) −2.94 ppm (s). UV−vis (CH_2Cl_2): 626, 572 sh, 422 sh, 378 sh, 324 sh, 286 nm. FAB mass spectra (nitrobenzyl alcohol): calcd for $Pd_4(dppm)_4Cl_2$ 2034.2, found 2034.

$Pd_4(dppm)_4(H)_2Br_2$. $Pd_2(dppm)_2Br_2$[8] (0.1025 g, 0.0898 mmol) and $NaBH_4$ (0.0891 g, 2.355 mmol) were mixed in the solid state and stirred under nitrogen for 1 h. Degassed methanol (5 mL) was injected into the flask at room temperature, and a color change from orange to blue followed as well as a temperature rise (i.e., reaction between $NaBH_4$ and methanol). After 1 h, the crude product was collected by filtration and washed with diethyl ether (0.0500 g, 0.0235 mmol). The crude product was purified from triple recrystallization using dichloromethane and diethyl ether to yield a dark-blue solid. Yield: 52.4%. Anal. Calcd: C 56.52, H 4.27. Found: C 56.27, H 4.30. ^1H NMR (CH_2Cl_2): δ 6.3−7.7 (complex, 80H, $^3J(H,H) = 7.7$ Hz, C_6H_5), 5.00 (nonet, rel int = 1:8:28:56:70:56:28:8:1, $^2J(H,P) = 13.7$ Hz, PdH), 4.98 (s, broad, fwhm = 6.7 Hz, 8H, PCH_2P). UV−vis (CH_2Cl_2): 622, 564 sh, 422 sh, 370 sh, 326 sh, 286 nm. FAB mass spectra (nitrobenzyl alcohol): calcd for $Pd_4(dppm)_4Br_2$ 2123.1, found 2121.

Mass FAB Spectra. The mass FAB data were obtained on a Kratos MS-50 TCTA spectrometer at the Université de Montréal using an Iontech saddle field source (model FAB 11 NF) operating at 70 kV with a 2-mA current. Both thiolglycerol and nitrobenzyl alcohol matrixes were used and gave the same results. The data analysis is provided in the Supporting Information. The comparison of the bandwidths in the low-resolution spectra and the isotopic distribution in the high-resolution spectra between the simulated and experimental data for these fragments also confirmed the assignments for Pd_4 and Pd_3 species observed in the spectra. Even under large-slit conditions, a careful examination of the spectra indicated no weak peak at higher masses.

Instruments. NMR spectra were measured on a Bruker WM 300 spectrometer. UV−visible spectra were obtained on a Hewlett-Packard

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* To whom correspondence should be addressed. (a) Laboratoire de Synthèse et d'Électrosynthèse. Tel and Fax: 3 80 39 60 91. E-mail: ymugnier@satie.u-bourgogne.fr. (b) Université de Sherbrooke. Tel: (819) 821-7092 or (819) 821-8000 ext 2005. Fax: (819) 821-8017. E-mail: pharvey@structure.chimie.usherb.ca or pierre.harvey@courrier.usherb.ca.

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

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(3) (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer: Heidelberg, Germany, 1980. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

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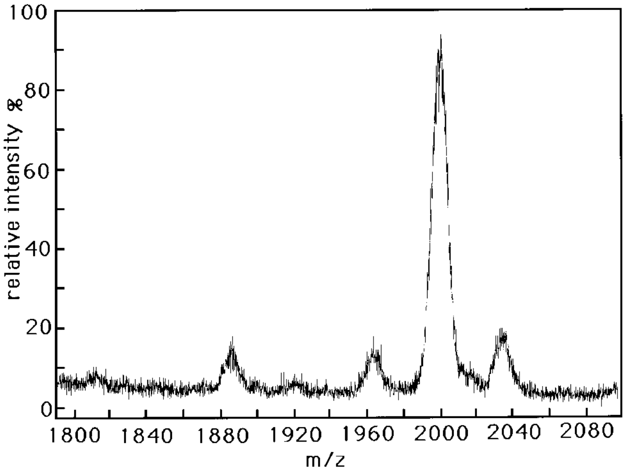

Figure 1. Mass FAB spectra of **I** in nitrobenzyl alcohol under low-resolution conditions (continuum). Only the high molecular fragment regions are shown.

(HP 8452A) diode array spectrophotometer. The elemental analysis was performed at the Université de Montréal (C/H/N), and in our department using a Kevex-700 X-ray emission spectrometer operating at 60 kV (Pd/Cl). The FT-Raman spectra were obtained on a Bruker IFS 66/CS FT-IR spectrometer coupled with an FRA 106 FT-Raman module using a Nd:YAG laser (1064-nm excitation) and a notch filter (cutoff ~60 cm^{-1}). The spectra were acquired using 5000 scans and a 2.60-cm^{-1} resolution.

Electrochemistry. All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free nitrogen or argon gases. Tetrahydrofuran was distilled under argon from sodium and benzophenone. Acetonitrile (ACN) was purified by simply passing the solvent through a column packed with alumina previously dried at 120 °C; it was deoxygenated by argon bubbling immediately before use. The supporting electrolyte was 0.2 M Bu_4NPF_6 which was dried and degassed before use. In cyclic voltammetry experiments, the concentration of **I** was nearly 10^{-3} M. Voltammetry analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire. For all voltammetric measurements, the working electrode was a vitreous carbon electrode. The controlled potential electrolysis was performed with an Amel 552 potentiostat coupled to an Amel 552 potentiostat coupled to an Amel 721 electronic integrator. High-scale electrolysis was performed in a cell with three compartments being separated with fritted glasses of medium porosity. A carbon gauze was used as the cathode, a platinum plate was used as the anode, and a saturated calomel electrode was used as the reference electrode. For thin-layer cyclic voltammetry, the vitreous carbon electrode was lowered until it made contact with the flat floor of the electrolytic scale cell so that only a thin layer of solution existed between them.

Results and Discussion

The $Pd_2(dppm)_2X_2$ complexes (X = Cl, Br) react with $NaBH_4$ to produce purple compounds exhibiting quasi-identical spectroscopic features. On the basis of chemical analysis we have first improved the previously proposed formulation for **I**, "$Pd_2(dppm)_2(H)_x$" for $Pd_2(dppm)_2(H)_xCl$, particularly for the presence of chloride. Polarography measurements also indicated the presence of chloride in the solutions of **I**. The comparison of the polarograms of Cl^--containing solutions of known concentration readily confirmed a 2:1 Pd:Cl ratio. The tetranuclear nature for **I** and **II** is clearly demonstrated by mass FAB spectrometry where the $Pd_4(dppm)_4X_n$ fragments (X = Cl, Br; $n = 0, 1, 2$) were readily detected (Figure 1). The number of hydrides is established from the comparison of the integration of the PdH and CH_2-dppm signal in the ^1H NMR spectra. Although our ^1H NMR spectra in CD_2Cl_2 are identical to that reported in the literature,[6] the relative integration 1:3 has never been reproduced. In fact, we obtained much less. The data are available in the Supporting Information. In $(CD_3)_2CO$, the ratio 1:4 is obtained reproducibly as shown in Figure 2. These findings lead to the reformulation of $Pd_4(dppm)_4(H)_2X_2$. We suspect a slow reactivity for **I** and **II** in CD_2Cl_2, explaining the different ratios. The fact that the ^1H NMR, UV−vis, and FT-Raman (Supporting Information) spectra for **I** and **II** are essentially identical indicates no evidence for covalent Pd−X bondings. The most appropriate formulation becomes $[Pd_4(dppm)_4(H)_2]X_2$.

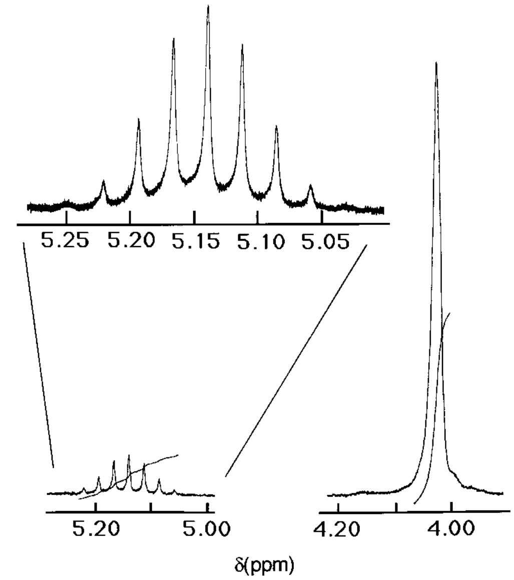

Figure 2. ^1H NMR spectrum of **I** in $(CD_3)_2CO$ for the hydrides at 4.98 ppm showing the nonet and the methylene protons. Note that the integration of the nonet corresponds to 1:8:28:56:70:56:28:8:1. $T_1 = 1.2 \pm 0.1$ s (300 MHz).

Braunstein et al.[9,10] reported the preparation of a closely related 60-electron cluster $[Pd_4(dppm)_4(\mu\text{-}Cl)_2](BF_4)_2$ from the reaction between $Pd_2(dppm)_2Cl_2$ and $[Cu(NCCH_3)_4]BF_4$ where the CuCl precipitation drives the reaction. The situation here is somewhat similar where NaCl is produced. The difference is, of course, that the counteranion (H^-) is not innocent toward the metal. While $[Pd_4(dppm)_4(Cl)_2]^{2+}$ is not fluxional at room temperature, Kirss and Eisenberg claimed that **I** is. Much can be learned from the ^1H NMR analysis. First the hydride signal is a nonet for both **I** and **II** in both $(CD_3)_2CO$ (Figure 2 for **I**) and CD_2Cl_2 (Supporting Information) with $^2J(P,H) = 13.6$ Hz, not a septet.[6] The relative intensity of the individual peaks of the nonet is 1:8:28:56:70:56:28:8:1, which is consistent with a P−H coupling model for 8 chemically equivalent P atoms. Upon cooling the samples, the CH_2-dppm signals for **I** and **II** in CD_2Cl_2 slightly shift to ~3.8 ppm but remain broad (fwhm = 19 Hz at 183 K). The PdH signals shift to ~5.6 ppm but still remain a nonet. Finally the complex phenyl region shifts slightly to the low-field region (~0.2 ppm) and remains unchanged. However, when the samples are irradiated for the ^{31}P (^{31}P-decoupled), the nonet becomes a singlet (fwhm = 1.7 Hz), and the broad signal located at ~4 ppm (CH_2 signal) becomes much narrower (i.e., fwhm = 2.5 Hz). Clearly the $J(PH)$ coupling was responsible for the broad CH_2 NMR signal,

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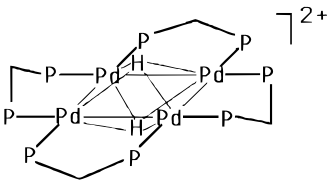
Scheme 1



not a fluxionality process. In addition a single line is observed in the ^{31}P NMR spectra (for **I** in $(CD_3)_2CO$ and $CDCl_3$, $\delta = -2.94$ and -8.15, respectively). The structure for the cluster is now best described by Scheme 1. On the basis of these observations, one would now expect ionic species of the type $[Pd_4(dppm)_4(\mu^4\text{-}H)_2]^{2+}{:}2X^-$. However conductivity measurements for $Pd_2(dppm)_2Cl_2$ (nonionic), $[Pd_3(dppm)_3(CF_3CO_2)](CF_3CO_2)$ (1:1 salt), and **I** using nitromethane as solvent provided the data $\Lambda = 23.9$, 84.5, and 30.2 Ω^{-1} M^{-1} cm^{-1}, respectively. In DMF, **I** has a conductivity of 34.6 Ω^{-1} M^{-1} cm^{-1}, and surprisingly the overall data suggest that **I** is weakly ionic. In addition, anion exchanges proved very difficult using common anions such as PF_6^- and BF_4^-, as the exchanges were never complete, with products exhibiting more X^- in them than the entering anion.

The answer to this is found in the well-known behavior that substrates such as Cl^-, Br^-, I^-, and $CF_3CO_2^-$ have with the related $Pd_3(dppm)_3CO^{2+}$ cluster.[11] Interactions between halides and the unsaturated $Pd_3(dppm)_3CO^{2+}$ are strong enough that the $[Pd_3(dppm)_3(CF_3CO_2)]^-$ (CF_3CO_2), for instance, behaves as a 1:1 salt. We anticipate that a similar behavior is occurring here, involving both halides. Clearly, an X-ray structure is required here to see exactly where the halide counteranions position themselves around the dicationic cluster. Our numerous attempts to obtain a crystal of suitable quality for X-ray crystallography failed.

No reaction between $Pd_2(dppm)_2I_2$ and $NaBH_4$ is observed. In addition, the reaction between $Pd_2(dppm)_2Br_2$ and $NaBH_4$ is slower than that of the Cl congener. To explain this we suspect that, during the dimerization process of the $Pd^I{-}Pd^I$ species, the rate-determining step of the reaction is the labilization of the leaving group X. For X = I, the halide seems not to be labile enough to be displaced by H^-.

The following section deals with the electrochemical properties of **I**. The cyclic voltammogram of **I** in DMF (+0.2 M Bu_4NPF_6) exhibits a two-electron reduction system (C/C′) at −1.36 V vs SCE (see Figure 3A) and an irreversible two-electron wave (E′) at $E_{1/2} = \pm 0.07$ vs SCE (see Supporting Information). By coulometry the reduction wave corresponds to $n_{exp} = 2.1$ F mol^{-1}. Assignment for the number of electrons was also examined using the comparison of the cyclic voltammetric peak currents with those of $Pd_3(dppm)_3CO^{2+}$ which undergo a two-electron transfer.[12] A plot of the peak current versus the square root of the scan rate is linear between 0.05 and 1.0 V s^{-1}, confirming diffusion control over this range of scan rates. For both **I** (2+/0) couples, the potential separation between the peaks (ΔE_p) is greater than expected for a reversible two-electron step (28.5 mV at 25 °C),[13a] suggesting the involvement of closely spaced stepwise electron transfers, slow electrode kinetics, and/or coupled homogeneous reactions.[13b] The assignment for the number of electrons for the oxidation process was based upon the comparison of the wave heights with that of the reduction wave. Bulk electrolysis of **I** in DMF at −1.5 V consumes 2 F mol^{-1} ($n_{exp} = 2.19$) accompanied by a color change to brown. The generated species **III** exhibits an oxidation wave at −1.32 V vs SCE (C′; $E_{1/2} = -1.36$ V) and E′ from rotating disk electrode voltammetry (Supporting Information). This reduction process is totally chemically reversible and indicates the following reactions:

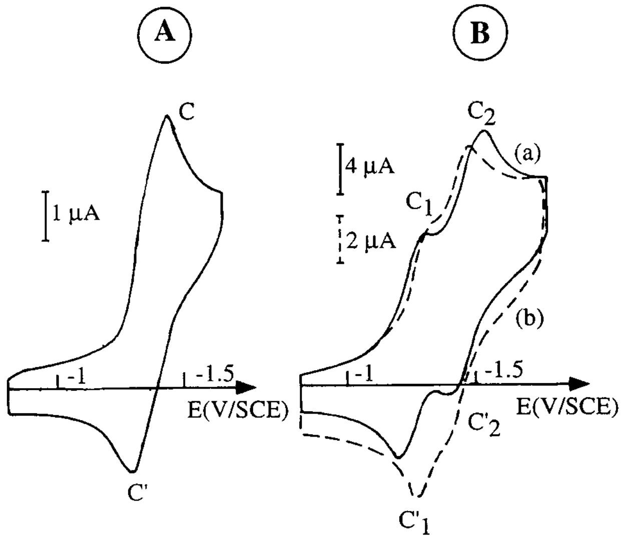


Figure 3. (A) Cyclic voltammogram of **I** in DMF containing 0.2 M Bu_4NPF_6 as supporting electrolyte recorded at a vitreous carbon electrode at $\upsilon = 0.045$ V s^{-1}. (B) Cyclic voltammogram of **I** in THF (full line) containing 0.2 M Bu_4NPF_6 as supporting electrolyte ($\upsilon = 0.2$ V s^{-1}). Dotted line: same except DMF was added to the solutions. Note that the peak potential separation decreased.

$$Pd_4(dppm)_4(H)_2Cl_2 + 2e^- \rightleftarrows \text{“}Pd_4(dppm)_4(H)_2\text{”} + 2Cl^- \tag{1}$$

or

$$Pd_4(dppm)_4(H)_2^{\;2+} + 2e^- \rightleftarrows \underset{\textbf{III}}{\text{“}Pd_4(dppm)_4(H)_2\text{”}} \tag{2}$$

III is relatively stable on the time scale of the electrolysis, but a very slow evolution occurs giving the initial cluster **I** on the basis of comparison with ^{31}P NMR data. Attempts to separate cluster **III** for analysis failed, and **I** was always recovered quantitatively.

The cyclic voltammogram of **I** in THF (+0.2 M Bu_4NPF_6) exhibits two reversible closely spaced one-electron processes at −1.25 V (C_1/C_1') and −1.50 V vs SCE (C_2/C_2') (see Figure 3B). When the anodic scan is reversed after peak C_1, only peak C_1' is seen on the return scan. These results indicate that two one-electron reduction reactions are taking place at slightly different potentials. Additions of DMF to the THF solutions (+0.2 M Bu_4NPF_6) gradually decrease the potential difference between C_1/C_1' and C_2/C_2' (Figure 3B). Electrochemical data were obtained using various experimental conditions and are summerized in Table 1.

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Table 1. Cyclic Voltammetric Data Obtained at Vitreous Carbon Electrode for **I**[a]

solvent	electrolyte salt (0.2 M)	oxidation potential[b] E'	reduction potential[b]		
			C_1	C_2	C
THF[c]	NBu_4PF_6	+0.16	−1.25	−1.5	
DMF[d]	NBu_4PF_6	+0.05			−1.42
THF[c]	$NaBPh_4$	+0.1	−1.5	−1.69	
DMF[d]	$NaBPh_4$	+0.08			−1.47

[a] Sweep rate = 0.2 V s^{-1}. [b] V vs SCE, at room temperature. [c] [complex] = 0.75 mM at room temperature. [d] [complex] = 1.5 mM at room temperature.

I can also be chemically prepared from a direct reaction of $Pd_2(dppm)_2Cl_2$ with HCO_2Na or electrochemically generated under reduction of $Pd_2(dppm)_2Cl_2$ in the presence of CO_2 and H_2O or in the presence of HCO_2H. In these cases, a tetranuclear formato complex is identified to be an intermediate in the reactions. Further, **I** is a good homogeneous catalyst of electrochemical hydrogen evolution. These studies will be reported in due course.

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Supporting Information Available: **Available:** ^1H NMR spectra of **I**, FAB mass data analysis for **I** and **II**, cyclic voltammogram of **I** on rotary disk electrode before and after electrolysis, and low-frequency FT-Raman spectra of solid **I** and **II** (8 pages). Ordering information is given on any current masthead page.

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