Electrochemically Induced C−Br and C−I Bond Activation by the $Pd_3(dppm)_3CO^{2+}$ Cluster, and Characterization of the Reactive $Pd_3(dppm)_3CO^+$ Intermediate: The First Confidently Identified Paramagnetic Pd Cluster

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Received July 5, 2000
Revised Manuscript Received December 26, 2000

Simple ligand substitution processes represent the very basis of many important organometallic reactivities and catalyses. However, these processes can be very slow or impossible for a given metal at a given oxidation state. Upon a one-electron reduction or oxidation, the substitution may become very fast. These well-known catalytic processes are called "zero electron" processes[2,3] and have recently been described for organometallic systems by Amatore et al.[4]

We now wish to report an unprecedented electron-transfer chain catalyzed ligand substitution reactivity for a Pd cluster, specifically applied for C−Br and C−I bond activation. The reductive cleavage of the C−X bonds (X = halogen) represents a very important topic of research, particularly for polyhalogenated compounds.[5] During the course of this work, the formal identification of the reactive key intermediate, $Pd_3(dppm)_3CO^+$, is made. This complex is the first confidently characterized paramagnetic Pd cluster.

The relatively fast reactions between $[Pd_3(dppm)_3CO](CF_3CO_2)_2$[6] and various RX substrates have been monitored by cyclic voltammetry, coulometry, and ^{31}P NMR spectroscopy in THF containing 0.2 M NBu_4PF_6 as supporting electrolyte. The electrochemically induced reactions proceed according to eq 1,

$$Pd_3(dppm)_3(CO)(L)^+ + RX \rightleftharpoons Pd_3(dppm)_3(CO)(X)^+ + \text{“}R^+\text{”} + L^- \quad (1)$$

where $L^- = CF_3CO_2^-$ and $X^- = Br^-, I^-$. This reaction also applies for $L^- = Cl^-$ and Br^-.

Table 1. Consumed *Q* for RX Activation[a]

RX	molar ratio $RX/Pd_3(dppm)_3(CO)(CF_3CO_2)^+$	Q^b mol of electron/mol of $Pd_3(dppm)_3(CO)^{2+}$
n-BuBr	1.1	no reactivity
Me_2CHBr	1.1	no reactivity
Me_3CBr	1.5	0.86
$PhCH_2Br$	1.1	0.80
MeI	1.1	0.39
	10	0.18
EtI	1.1	0.72
$PhCH_2CH_2I$	1.2	0.70
n-BuI	1.1	0.81
CH_2I_2	1.1	0.45
Me_3CI	1.1	0.16

[a] Only the data for the starting material $Pd_3(dppm)_3(CO)(CF_3CO_2)^+$ are summarized. For $L^- = Cl^-$ or Br^-, reactivity with R−X is also observed, but not quantified. [b] *Q* is determined for systems at completion by using the same electrochemical cell and electrodes. Note that the common R−Cl molecules are not activated.

The cluster products are readily identified by the comparison of the cyclic voltammograms and ^{31}P NMR spectra of authentic samples,[7a] while evidence for "R^+" has been provided by GCMS.[7b] Coulometric measurements indicate that less than one electron/mole of cluster (*Q*) is necessary to complete the electrolysis (Table 1). When the quantity of RX substrates is increased, *Q* reproducibly decreases, consistent with the increased rate of reactivity. By injecting a small amount of electricity (0.04 equiv/cluster for 1.1 equiv of substrate MeI for instance), and stopping the electrolysis before the current reaches zero, the substitution reactions go to completion after 1 h. Doing so, the turnover number for this specific example becomes 24 ((1 − 0.04)/0.04) vs 1.5 ((1 − 0.39)/0.39) for the exhaustive electrolysis (Table 1, entry no. 5).

This electron-transfer chain catalyzed process occurs via the generation of the 45-electron $Pd_3(dppm)_3(CO)(L)$ species, which is found to be stable at the electrochemical time scale, and provides an interpretable EPR spectrum (see below). For $L^- = CF_3CO_2^-$, a complete adduct dissociation ($Pd_3(dppm)_3(CO)(CF_3CO_2) \rightarrow Pd_3(dppm)_3(CO)^+ + CF_3CO_2^-$) is readily expected.[6] These intermediates are reactive toward R−X species (X = Br, I) to form the $Pd_3(dppm)_3(CO)(X)$ complex, and are also stable on the electrochemical time scale. In the presence of $Pd_3(dppm)_3(CO)(L)^+$ as starting material, the electron transfer between Pd_3-

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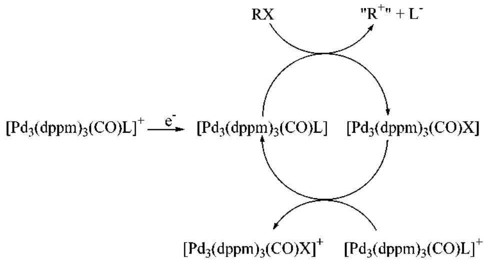
(6) (a) X-ray crystallographic data and host−guest binding measurements indicate that one of the $CF_3CO_2^-$ anions is located inside the cavity described by the dppm-phenyl groups above the unsaturated Pd_3-face.[6b,c] The binding constants are weak and the cluster is best formulated as $Pd_3(dppm)_3(CO)^{2+}\cdots(CF_3CO_2)^-$. For the analogue $[Pd_3(dppm)_3(CO)](PF_6)_2$, the larger counteranion PF_6^- is not found in the cavity.[6b] The corresponding halide adducts (X = Cl, Br, I) exhibit much stronger binding constants,[6c] and are appropriately referred to as $Pd_3(dppm)_3(CO)(X)^+$. An exhaustive study shows that $Pd_3(dppm)_3(CO)^{2+}$ in the presence of PF_6^-, $CF_3CO_2^-$, or X^- exhibits either a single two-electron, or two one-electron reduction waves. The occurrence of one or the other depends on temperature, solvent, and anion concentration.[6d,e] While the reactive intermediate is issued from a one-electron reduction of $Pd_3(dppm)_3(CO)(CF_3CO_2)^+$, the bulk two-electron electrolysis experiments show no reactivity toward these halocarbons. Selected electrochemical data for the PF_6^- and $CF_3CO_2^-$ salts are the following: $Pd_3(dppm)_3(CO)^{2+}$ (as PF_6^- salt), $E_{1/2}{}^{2+/+} = -0.29V$, $E_{1/2}{}^{+/0} = -0.66V$ vs SCE; $Pd_3(dppm)_3(CO)(CF_3CO_2)^+$ (as $CF_3CO_2^-$ salt), $E_{1/2}{}^{2+/0} = -0.48V$ vs SCE, both in THF solutions containing 0.2 M *n*-Bu_4NPF_6. (b) Provencher, R.; Aye, K. T.; Drouin, M.: Gagnon, J.; Boudreault, N.; Harvey, P. D. *Inorg. Chem.* **1994**, *33*, 368. (c) Harvey, P. D.; Hierso, K.; Braunstein, P.; Morise, X. *Inorg. Chim. Acta* **1996**, *250*, 337. (d) Gauthron, I.; Mugnier, Y.; Hierso, K.; Harvey, P. D. *Can. J. Chem.* **1997**, *75*, 1182. (e) Lemaître, F.; Brevet, D.; Vallat, A.; Lucas, D.; Mugnier, Y. In preparation.

(7) (a) The complexes have been prepared according to literature methods[7c] and the ^{31}P NMR and electrochemical data are as follow: δ(acetone-d_6) = −1.26 (PF_6^-), −7.03 ($CF_3CO_2^-$), −6.53 (Cl^-), −6.14 (Br^-), and −6.40 ppm (I^-), and $E_{1/2}{}^{2+/0} = -0.77V$ (Cl^-), −0.68V (Br^-), and −0.77V (I^-), in THF solutions containing 0.2 M *n*-Bu_4NPF_6. (b) The presence of the generated R^+ fragment has been demonstrated by performing the electrocatalysis of Me_3CI (see Table 1, entry 11) in the presence of phenol (in the same molar quantity of Me_3CI). At the end of the reaction, the solvent has been evaporated and the residue was extracted in Et_2O. The Ph−O−CMe_3 ether coupling product is readily detected by GCMS, which results from an electrophilic attack of the carbocation onto the phenol substrate. The low yield of 25% is due to inefficient trapping for this 1:1 stoichiometric reaction. No R−R coupling or R−H products were observed, indicating that radical-type reaction does not occur. In the absence of cluster, the blank tests show no reactivity. (c) Manojlovic-Muir, L.; Muir, K. W.; Lloyd, B. R.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 536.

10.1021/ja002417a CCC: $20.00

Scheme 1. Reaction Mechanism for the Electrochemically Induced X^-/L^- Exchange ($L^- = CF_3CO_2^-$, Cl^-, Br^-; $X^- = Br^-$, I^-)



$(dppm)_3(CO)(X)$ and $Pd_3(dppm)_3(CO)(L)^+$ is thermodynamically favorable (potentials provided in refs 6a and 7a), hence driving the catalytic cycle (Scheme 1). To demonstrate this, the ligand exchange between $Pd_3(dppm)_3(CO)(Br)^+$ and BuI was attempted, and Q was found to be also <1 equiv/mol. The reverse reaction, however, does not occur. We find no reactivity for common chlorocarbons and the data included in Table 1 indicate that the rate of reactivity varies as I (smaller Q values) > Br (larger Q values) > Cl (no reactivity), illustrating the expected trend in C−X bond strength. Stabilized carbocations such as Me_3C^+ provide lower Q, reducing the probability of back reactions ($R^+ + X^- \rightarrow RX$). Interestingly no reactivity is observed for *i*-PrBr and *n*-BuBr, further illustrating the importance of the carbocation stability. This stability appears to be fine-tuned between *i*-PrBr and *t*-BuBr, where no and slower reactivities are observed, respectively. Finally, Q for MeI is unexpectedly significantly smaller than Q for RCH_2CH_2I (R = H, Et, Ph), the latter values being similar. Speculatively, the smaller MeI substrate may interact more efficiently with the Pd_3^+ center inside its phenyl-dppm cavity than that of the longer RCH_2CH_2I substrates.[6b]

Attempts to chemically prepare the related and important 43-electron cluster intermediate $Pd_3(dppm)_3CO^+$ were made. Indeed this cluster is cleanly prepared with $[Pd_3(dppm)_3(CO)](PF_6)_2$ as starting material and BPh_4^- (as reducing agent).[8,9] The IR spectrum exhibits an IR ν(CO) absorption at 1785 cm^{-1}, which is expectedly red-shifted in comparison with the more oxidized $Pd_3(dppm)_3(CO)^{2+}$ species due to back-bonding (ν(CO) = 1835 cm^{-1} [6b]). The isotropic EPR spectrum of this cluster in THF at 293 K (Figure 1) exhibits a well-defined septet with a relative intensity approaching 1:6:15:20:15:6:1, along with weaker hyperfine structures.[10] Curve fitting analysis allowed interpretation of the spectrum and the results indicate the presence of a single electron delocalized over the three equivalent Pd atoms: $g = 2.065$, $A(^{31}P) = 75.8 \times 10^{-4}$ cm^{-1}, $A(^{105}Pd) = 7.6 \times 10^{-4}$ cm^{-1} (^{105}Pd, $S = {}^5/_2$, 22.2% natural abundance). Evidence for coupling with both the Pd and P atoms is completely consistent with the atomic contributions of the SOMO (a_2). Previous EHMO calculations on the dication indicated that this MO is composed of in-plane metal d orbitals (d_{xy}, $d_{x^2-y^2}$ with minor p_x and p_y contributions) and some phosphorus components (p_y, p_x), forming M−M and M−P antibonding MO's.[11] The $g_{||}$, $g_{\perp}$, $A_{||}(^{31}P)$, and $A_{\perp}(^{31}P)$ values extracted from EPR spectra of frozen solutions (100 K) are 2.059, 2.078, 88.8 × 10^{-4} cm^{-1}, and 85.0 × 10^{-4} cm^{-1}, respectively. The larger EPR signals precluded spectral resolution for Pd coupling in this case. The relative magnitude of the A constants ($A(^{31}P) \gg A(^{105}Pd)$) is also consistent with literature data for other polynuclear compounds.[12]

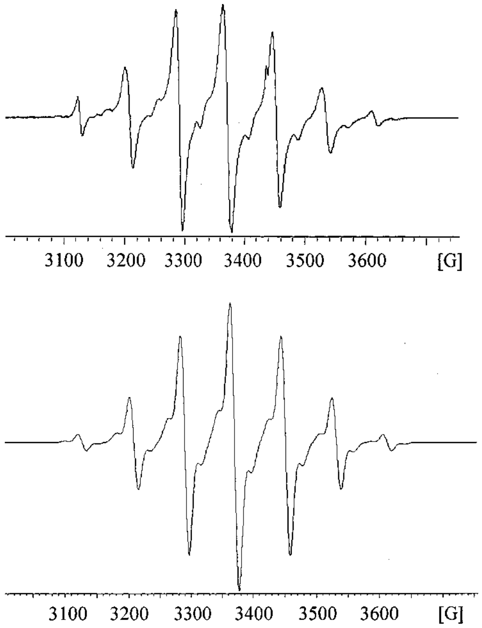


Figure 1. Top: Experimental EPR spectrum of $Pd_3(dppm)_3(CO)^+$ in THF at 293 K Bottom: Calculated EPR spectrum.

Attempts to chemically prepare the corresponding X-adducts, $Pd_3(dppm)_3(CO)X$ (X = Cl, Br, I), uniformly failed, including using BPh_4^-.[13] Voltammetric studies on the electrochemical behavior of $Pd_3(dppm)_3(CO)I^+$ show that the intermediate $Pd_3(dppm)_3(CO)I$ is observed upon high sweep rates, or in the presence of an excess of iodide salt.[6e]

Paramagnetic compounds of palladium are scarce and this series is limited primarily to mononuclear Pd(III) species with some rare examples of mononuclear Pd(I) and binuclear Pd(II)−Pd(III) complexes.[14−16] To our knowledge, the $Pd_3(dppm)_3(CO)^+$ is the first example of a confidently identified paramagnetic Pd cluster.

Acknowledgment. P.D.H. thanks NSERC (Natural Sciences and Engineering Research Council) and FCAR (Fonds Concertés pour l'Avancement de la Recherche) for funding. Y.M. is grateful to CNRS (Centre National de la Recherche Scientifique) for funds.

Supporting Information Available: Experimental EPR spectrum of $Pd_3(dppm)_3(CO)^+$ in a frozen solution and Experimental Section for the electrochemistry (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927. (b) The biphenyl product is readily identified by GCMS from the borate anion oxidation for the reactions between $Pd_3(dppm)_3(CO)^{2+}$ and BPh_4^-.

[9] (a) A two-step procedure to generate this same paramagnetic species is also possible from the two-electron reduction of $Pd_3(dppm)_3(CO)^{2+}$ (i.e. at −0.62V vs SCE), followed by a one-electron oxidation with Tl^+ ($E_{1/2}{}^{0/+}$(Tl) = −0.582V vs SCE).[9b] (b) *CRC Handbook of Chemistry and Physics*, 64th ed.; CRC Press Inc.: Boca Raton, FL, 1983; p D-159.

[10] The EPR spectra were acquired on a Bruker ESP 300 instrument and spectral analyses were performed with the commercially available software WinEPR of SimFonia (Version1.25; Bruker Analytisch Messteknic).

[11] Harvey, P. D.; Provencher, R. *Inorg. Chem.* **1993**, *32*, 61.

[12] Data for the $Rh_2(O_2CEt)_4(PPh_3)_2^+$ dimer as an example: $A_{||}(^{31}P) = 205 \times 10^{-4}$ cm^{-1}; $A_{\perp}(^{31}P) = 152 \times 10^{-4}$ cm^{-1}; $A_{||}(^{103}Rh) = 13 \times 10^{-4}$ cm^{-1}; $A_{\perp}(^{103}Rh)$ = not resolved. Kawamura, T.; Fukamachi, K.; Sowa, T.; Hayashida, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 364.

[13] These paramagnetic species exhibit limited stability after several hours even at −30 °C. Cyclic voltammetry, EPR, ^{31}P NMR, and IR spectroscopy indicate evolution towards decomposition where a strong IR absorption at 1669 cm^{-1} and ^{31}P NMR peak at 30.1 ppm (acetone − d_6) are clearly observed for these uncharacterized products. Further studies on these species will be published in due course.[6e]

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