

New Insights into the Stoichiometric and Catalytic Reactivity of Unsaturated $\text{Pd}_3(\text{dppm})_3\text{CO}^{n+}$ Clusters ($n = 0, 1$) Towards Halocarbons – First Evidence for Inorganic By-Products

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The title clusters, $\text{Pd}_3(\text{dppm})_3(\text{CO})^+$ and $\text{Pd}_3(\text{dppm})_3(\text{CO})^0$ can be electrochemically generated from the 1- and 2-electron reductions, respectively, of the $\text{Pd}_3(\text{dppm})_3(\text{CO})^{2+}$ cluster [dppm = bis(diphenylphosphanyl)methane; Pd_3^{2+}]. Pd_3^+ reacts in a stoichiometric ratio with methyl iodide, MeI, and benzyl bromide, BzBr, in THF to provide the corresponding $\text{Pd}_3(\text{X})^+$ adducts ($\text{X} = \text{I}, \text{Br}$ respectively) as inorganic products. Other products are Bz_2 and PhMe for BzBr but, for MeI, no organic product was observed (since they are too volatile). In the presence of the same substrates, Pd_3^0 also reacts in a stoichiometric ratio to form the same organics and the $\text{Pd}_3(\text{X})^+$ adducts ($\text{X} = \text{I}$ and Br). However for MeI, the major inorganic product is the A-frame $\text{Pd}_2(\text{dppm})_2(\text{Me})_2\text{I}^+$ binuclear complex. For BzBr, the corresponding A-frame complex $\text{Pd}_2(\text{dppm})_2(\text{Bz})_2\text{Br}^+$ could not be detected. The spin-trap agents, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and 5,5'-dimethyl-1-pyrroline *N*-oxide (DMPO), have been used

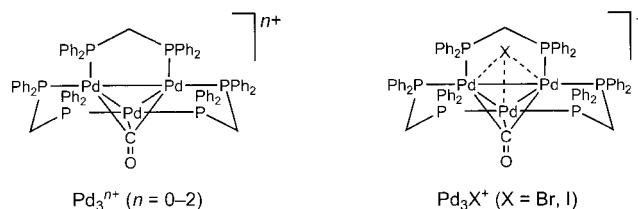
to demonstrate the intermediacy of the radical $\text{Bz}^\cdot$. The catalytic generation of "Bz" was performed using two methods, i.e. 1) using a copper anode as the working electrode [$\text{Pd}_3(\text{Br})^+ + \text{Cu} - \text{e}^- \rightarrow \text{Pd}_3^{2+} + \text{CuBr}(\text{s})$] and 2) using a carbon cathode as the working electrode [$\text{Pd}_3(\text{Br})^+ + 2\text{e}^- \rightarrow \text{Pd}_3^0 + \text{Br}^-$]. The chemical yields for Bz_2 vary between 50 and 56 % and the Faradic yield is of the order of 90 % for method 1 and between 52 and 59 % for method 2 [taking into account the quantity of electricity necessary to reduce the catalyst $\text{Pd}_3(\text{Br})^+$]. The X-ray structure of $\text{Pd}_3(\text{dppm})_3(\text{CO})(\text{Br})^+$ is presented and the following parameters were recorded: monoclinic space group $P2_1/n$, $a = 10.6546(2)$, $b = 37.1091(7)$, $c = 21.2714(7)$ Å, $\beta = 91.55(1)^\circ$, $V = 8407.3(4)$ Å³, $Z = 4$, $R_1 = 0.0581$ [$I > 2\sigma(I)$], $wR_2 = 0.1478$ (all data).

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Introduction

The C–X bond activation is an important process in organic synthesis.^[1–7] In this respect, our groups have investigated numerous thermal and electrochemical reactions between $\text{Pd}_3(\text{dppm})_3(\text{CO})^{2+}$ (**1**; Pd_3^{2+})^[8–10] and halocarbons (RX) and some important electrochemically induced organic catalyses have been reported.^[11–13] The direct thermal reaction ($\text{Pd}_3^{2+} + \text{RX}$) quantitatively produces the corresponding adducts $\text{Pd}_3(\text{X})^+$ and "R⁺".

The elucidation of the mechanism of C–X bond cleavage for alkyl halides and acid chlorides has been studied in some detail.^[14] However, whereas the reactivity of Pd_3^{2+} towards RX has been fully investigated under both stoichiometric and catalytic conditions, the corresponding reduced



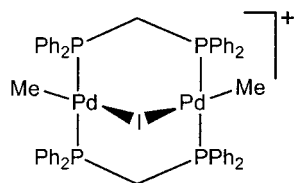
species Pd_3^+ and Pd_3^0 have only been briefly studied under catalytic conditions.

We now wish to report the reactivity of the Pd_3^+ and Pd_3^0 species under stoichiometric conditions towards MeI and BzBr and evidence for the slow formation of the $\text{d}^8\text{--d}^8$ A-frame $\text{Pd}_2(\text{dppm})_2(\text{Me})_2\text{I}^+$ complex during the $\text{Pd}_3^0 + \text{MeI}$ reactions has been obtained for the first time, indicating the presence of a parallel process which may explain the catalyst poisoning in some cases.

The use of BzBr was made since the presence of the potential Bz^+ and $\text{Bz}^\cdot$ intermediates can easily be deduced from the lesser volatile products, hence providing key information on the mechanism. Similarly, the MeI substrate is well known to undergo facile oxidative addition with Pd species in the low oxidation states, often resulting in the

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formation of a Pd–Me bond.^[15–18] Finally, the efficient catalytic generation of “Bz” was examined.

Results and Discussion

Stoichiometric Reactivity of Pd₃⁺

As reported earlier,^[11,14,19] Pd₃⁺ can be quantitatively obtained from a 1-electron reduction of the corresponding dicationic compound. Its RDE voltammogram is depicted in Figure 1 (trace a) and exhibits two closely spaced waves for oxidation and reduction labelled A₁' and A₂, respectively [*E*_{1/2} (A₁') = –0.24 V and *E*_{1/2} (A₂) = –0.51 V vs. SCE]. Line 1b results from the addition of an excess of methyl iodide to Pd₃⁺. The disappearance of waves A₁' and A₂ can be observed, demonstrating that the Pd₃⁺ complex has completely reacted. On the other hand, the current waves A₃ and A₄ indicate the formation of the previously known iodide coordination cluster Pd₃(I)⁺ [*E*_{1/2} (A₃) = –0.80 V and *E*_{1/2} (A₄) = –1.25 V vs. SCE] which was confirmed by ³¹P NMR spectroscopic analysis of the reaction solution in which only the signal of Pd₃(I)⁺ can be seen (*δ* = –6.4 ppm).^[20–22]

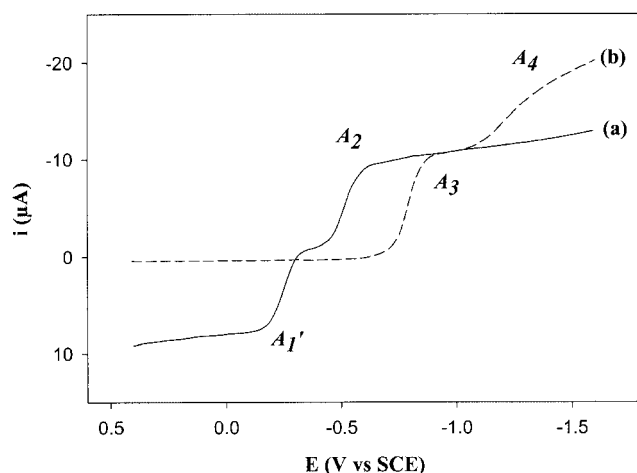
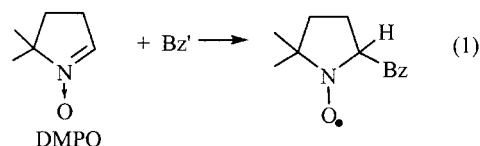


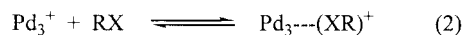
Figure 1. RDE voltammogram of Pd₃⁺ (0.81 mM) in THF with 0.2 M Bu₄NPF₆: (a) alone, (b) immediately after addition of 1.1 molar equiv. of CH₃I.

Addition of BzBr (1.1 equiv.) to Pd₃⁺ produces Pd₃(Br)⁺ as confirmed by the comparison of the electrochemical [*E*_{1/2} = –0.7 V (A₃)] and ³¹P NMR spectroscopic data (*δ* = –6.14 ppm in [D₆]acetone) as well as the formation of Bz₂ (44% based upon GCMS data) and PhMe.^[23] During the course of this investigation, crystals of Pd₃(Br)⁺ suitable for X-ray analysis were obtained and investigated (see below). The organic products indicate a radical-type reactivity in-

volving the “Bz” species which produces Bz₂ by homo-coupling and PhMe by hydrogen abstraction from the solvent.^[24] The addition of an excess of the spin trap agent 5,5'-dimethyl-1-pyrroline *N*-oxide (DMPO, 10 equiv.) to the Pd₃⁺/BzBr reaction yields the stable Bz-DMPO spin adduct as readily observed by EPR spectroscopy which exhibits the expected 6-line signal:^[25] *a*_B^H = 20.66 G, *a*^N = 14.16 G.^[26,27] The absence of Bz₂ in reaction (1) suggests a quantitative reaction.



The two possible mechanisms for the production of the organic radical [Pd₃⁺ + RX → Pd₃(X)⁺ + R·] are 1) an outer-sphere electron transfer from Pd₃⁺ to RX, followed by X[–] elimination from the intermediate R–X[–] (X[–] is then trapped by the resultant Pd₃²⁺) or 2) a halide abstraction process occurring within a host-guest Pd₃···(RX)⁺ assembly in which the homolytic C–X bond cleavage takes place, as described by reactions (2) and (3).



The driving force in reaction (3) is the formation of the very stable Pd₃(X)⁺ adduct. The former outer-sphere mechanism is highly unlikely since the oxidation (*E*_{1/2} = –0.29 V) and reduction potentials (*E*_{1/2} ≈ –2.5 V vs. SCE)^[28,29] for Pd₃⁺ and R–X, respectively, are not thermodynamically favourable for such a process. On the other hand, the second proposal is more likely to occur based upon the well-established mechanism reported for the Pd₃²⁺ cluster [Pd₃²⁺ + RX → Pd₃···(XR)²⁺ → Pd₃(X)⁺ + “R⁺”].^[11–14]

Going back to the Pd₃⁺/MeI reaction, the absence of observed organics is due to their high volatility and, based on the observation made for the Pd₃⁺/BzBr reaction, one can suggest that these are Me₂ and MeH.

Reactivity with Pd₃⁰

The 2-electron reduction of Pd₃²⁺ leads to Pd₃⁰ quantitatively. Addition of an excess of MeI to the electrochemically generated Pd₃⁰-containing solution monitored by RDE voltammetry (Figure 2) results in the complete disappearance of the two 1-electron oxidation waves of the Pd₃⁰ species (waves A₁' and A₂') and the appearance of waves A₃ and B₁ (–1.18 V vs. SCE) which are due to the anticipated Pd₃–(I)⁺ species and the known dinuclear d⁸–d⁸ A-frame complex Pd₂(dppm)₂(Me)₂I⁺, respectively.^[30] Based upon the current amplitudes of waves A₃ and B₁ and the relative intensity of the corresponding ³¹P NMR signals (at –6.40 and +19.76 ppm), the relative proportions are ≈ 20–25% and ≈ 80–75%, respectively. This result is different from that of Pd₃⁺ for which no A-frame complex was observed and

suggests the presence of oxidative addition of MeI to Pd_3^0 as a parallel pathway.

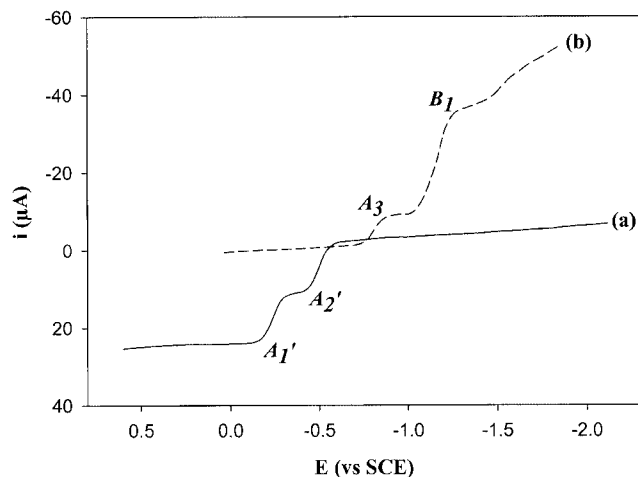


Figure 2. RDE voltammogram of Pd_3^0 (1.2 mM) in THF with 0.2 M Bu_4NPF_6 : (a) alone, (b) immediately after addition of an excess (4 molar equiv.) of CH_3I .

The addition of BzBr (2 equiv.) to a Pd_3^0 -containing solution leads to a slower reaction with respect to that of a similar reaction with Pd_3^+ (as monitored by the RDE method; Figure 3) but the presence of Bz_2 (GC-MS yields $\approx 44\%$) and PhMe as organic products could be detected in about the same relative amount.

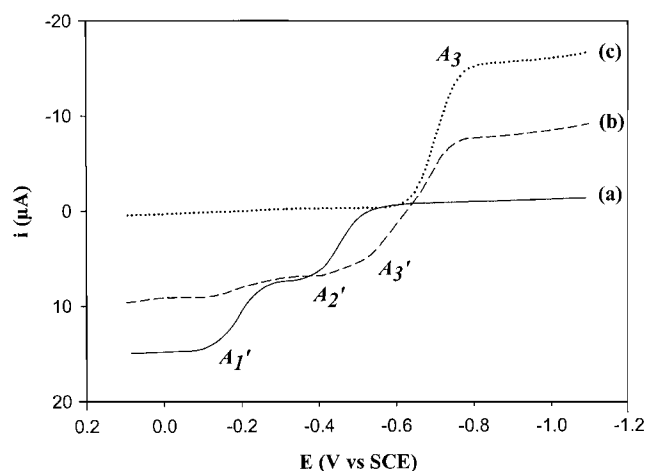
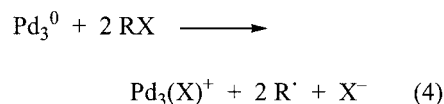
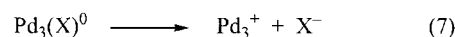
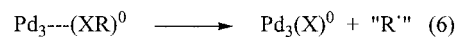


Figure 3. RDE voltammogram of Pd_3^0 (0.75 mM) in THF with 0.2 M Bu_4NPF_6 : (a) alone, (b) immediately after addition of 2 molar equiv. of PhCH_2Br , (c) after 15 min at room temperature.

On the other hand, $\text{Pd}_3(\text{Br})^+$ was quantitatively obtained and no trace of the $\text{d}^8\text{--d}^8$ $\text{Pd}_2(\text{dppm})_2(\text{Bz})_2\text{Br}^+$ complex was detected on this occasion (see below). The addition of DMPO to the solution prior to reaction leads to the same spin adduct as described above and no Bz_2 was observed, also suggesting completion of the spin-trap reaction. The overall reaction for the radical formation can be written as in reaction (4).

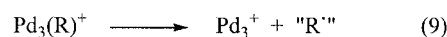
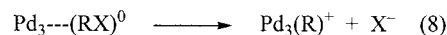


A similar mechanism to that for Pd_3^+ can be proposed; see reaction (7).



The halocarbon molecule penetrates inside the cluster cavity forming a transient reactive host-guest complex $\text{Pd}_3\cdots(\text{XR})^0$ [reaction (5)], in which a homolytic C–X bond cleavage takes place, giving the corresponding alkyl radical “R” [reaction (6)]. The resultant $\text{Pd}_3(\text{X})^0$ intermediate is unstable and eliminates X^- to form Pd_3^+ [reaction (7)]. This latter process is well known and has been previously established for $\text{X}^- = \text{Br}^-$ and I^- .^[8,22] Finally, the paramagnetic Pd_3^+ cluster undergoes reactions (2) and (3).

A second mechanism can also be considered and this involves the heterolytic C–X bond cleavage of the species $\text{Pd}_3\cdots(\text{RX})^0$ followed by the reductive elimination of “R”; see reactions (8) and (9).



Again, Pd_3^+ undergoes reactions (2) and (3). Reaction (8), which differs from reaction (6), finds its driving force from the electrostatic attraction of a potential carbocation “R⁺” with the electron-rich Pd_3^0 centre. However, reactions 8 and 9 are both unlikely. The postulated $\text{Pd}_3(\text{R})^+$ intermediate exhibits a Pd_3^{2+} centre and a carbanion which follows the octet rule similar to the Pd_3X^+ adducts. Its dissociation into Pd_3^+ and “R” [reaction (9)] would be far too high in energy. In addition, the formation of the $\text{Pd}_3(\text{R})^+$ species would prove difficult since the approach of the Pd_3^0 cluster towards the alkyl carbon atom in BzBr is sterically encumbered. Finally, such alkyl adducts of Pd_3^{2+} have never been observed and appear highly reactive.^[31]

In order to support this hypothesis, DFT computations were performed on the model compounds $\text{Pd}_3(\text{H}_2\text{PCH}_2\text{PH}_2)_3(\text{CO})(\text{Me})^+$ and $\text{Pd}_3(\text{H}_2\text{PCH}_2\text{PH}_2)_3(\text{CO})(\text{Br})^+$. The first observation is that the computed total energies are -17067.91 and -19590.39 a. u. (arbitrary units), respectively, indicating the greater stability of the $\text{Pd}_3(\text{Br})^+$ species. The second observation pointing in the same direction is that the computed energies for individual MOs are systematically higher for the $\text{Pd}_3(\text{Me})^+$ species. As an example, a partial comparative MO diagram for the LUMO and HOMO is presented in Figure 4. The MO's have been described previously elsewhere and this is not within the scope of this work.^[32,33] In conclusion, DFT supports the hypothesis that $\text{Pd}_3(\text{Me})^+$ is a less stable species than $\text{Pd}_3(\text{Br})^+$, Br^- or Pd_3^{2+} .

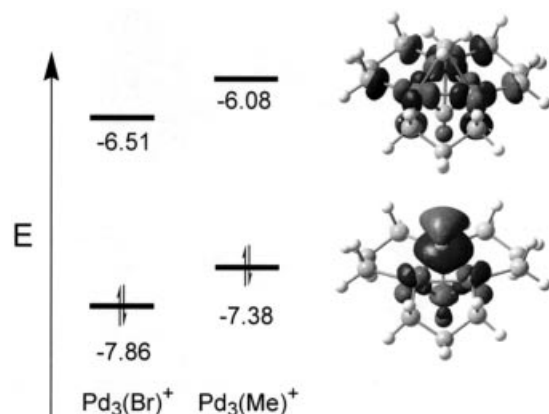
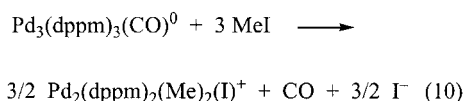


Figure 4. Left: Partial MO diagram of the HOMO and LUMO of the model compounds $\text{Pd}_3(\text{H}_2\text{PCH}_2\text{PH}_2)_3(\text{CO})(\text{Me})^+$ and $\text{Pd}_3(\text{H}_2\text{PCH}_2\text{PH}_2)_3(\text{CO})(\text{Br})^+$. Right: MO drawing for the HOMO and LUMO for $\text{Pd}_3(\text{H}_2\text{PCH}_2\text{PH}_2)_3(\text{CO})(\text{Me})^+$.

Two new questions now arise. Firstly, why can the radical $\text{Bz}^\cdot$ intermediate be observed in quantitative amounts (based upon observed Bz_2 and PhMe) for both Pd_3^0 and Pd_3^+ species and, secondly, why can two inorganic products be observed for the Pd_3^0/MeI reaction (Pd_3 adduct and A-frame) while the Pd_3^+/MeI reaction leads to only one inorganic product (Pd_3 adduct)? These observations imply that another competitive process must occur which can be formalised as shown in reaction (10).



The answer to the first question can be found in the considerable stability of the $\text{Pd}_3(\text{X})^+$ adducts^[22] [reaction (3)] which readily drives the reactions. Thus, the same driving force may be present in the case of Pd_3^+ . The answer to the second question can be found in the synthesis of Pd_3^0 itself.^[34] The reduction of $\text{Pd}(\text{dppm})\text{Cl}_2$ or $\text{Pd}_2(\text{dppm})_2\text{Cl}_2$ leads to the zero-valent " $\text{Pd}_2(\text{dppm})_2$ " species. In the presence of a source of CO, this very reactive binuclear complex provides Pd_3^0 .^[35,36] On the other hand, the synthesis of $\text{Pd}_2(\text{dppm})_2(\text{Me})_2(\text{I})^+$ can be performed by addition of MeI to $\text{Pd}_2(\text{dppm})_3$ ^[37] and the latter can dissociate into " $\text{Pd}_2(\text{dppm})_2$ " and dppm .^[38] These previous results suggest that Pd_3^0 should dissociate to form the highly reactive species " $\text{Pd}_2(\text{dppm})_2$ " which would react with MeI.

On the other hand, the absence of reactivity in the case of BzBr, to form the A-frame product, suggests an important difference between the rates of the $\text{Pd}_3^0/\text{BzBr}$ and " $\text{Pd}_2(\text{dppm})_2$ "/BzBr reactions which would favour the first reaction. It should be noted that the A-frame product $\text{Pd}_2(\text{dppm})_2(\text{Bz})_2(\text{Br})^+$ has been previously reported in the literature^[39] but the synthesis was not through the BzBr oxidative addition pathway as for MeI. This method was attempted but with no success which is consistent with our results. The preferred route was the reaction between $\text{Pd}(\text{dppm})\text{Br}_2$ and the Grignard reagent BzMgBr .

Some questions remain such as how does the structure of the halogenated substrate affect the occurrence of the A-frame product? What is the main factor between the halogen and the alkyl group? In order to address these points, Pd_3^0 was treated with a slight excess of BzI in a cross experiment. This led to quantitative formation of $\text{Pd}_3(\text{I})^+$ meaning that reaction (4) proceeds solely.

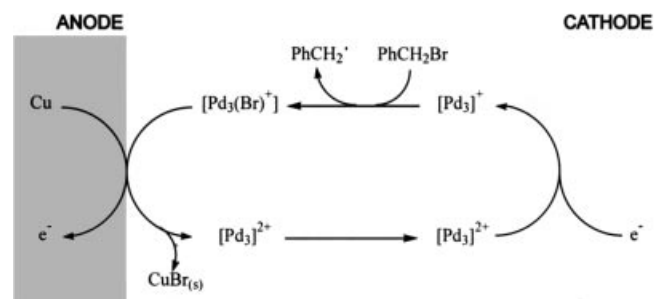
Thus, the steric hindrance of the alkyl group is likely playing an important role in the oxidative addition of RX to Pd_3^0 . In order to confirm this proposal, a series of alkyl iodides, RI , were tested in the reaction with Pd_3^0 ($\text{R} = \text{Et}$, $i\text{Pr}$, $t\text{Bu}$). In no case was the A-frame product observed and $\text{Pd}_3(\text{I})^+$ was always the sole inorganic product. Hence, reaction (10) may be extremely sensitive to the steric encumbrance of the alkyl group since it operates only when $\text{R} = \text{Me}$.

Catalytic Formation of "Bz" Radicals

The chemistry of free radicals has experienced an important growth in recent years^[40,41] but the use of organotin compounds such as R_3SnH remains the first choice for radical generation.^[42] However, because their use must be stoichiometric, their toxicity has encouraged chemists to find alternate and more environmentally friendly methods.^[43] Thus, the indirect reduction of RX using an electron transfer catalyst mediating the RX conversion to " $\text{R}^\cdot$ " is appealing.^[44]



In an attempt to render the stoichiometric reactions for "Bz" described above catalytic, two methodologies were examined. The first involves $\text{Pd}_3(\text{Br})^+$ as a precatalyst in a single compartment electrochemical cell equipped with a copper anode as the controlled-potential working electrode, a platinum cathode as the counter-electrode and CH_2Cl_2 as the solvent. The electrolysis proceeds as shown in Scheme 1. The 1-electron oxidation at the copper anode produces CuBr(s) and Pd_3^{2+} from $\text{Pd}_3(\text{Br})^+$. Pd_3^{2+} diffuses towards the cathode where it is reduced to Pd_3^+ which itself diffuses in the solution and reacts with BzBr to generate $\text{Pd}_3(\text{Br})^+$ and "Bz". Bz_2 is the sole organic product observed and no PhMe is formed. The reason is that, unlike THF, CH_2Cl_2 is not an H-donor. Table 1 summarises the results (entry



Scheme 1.

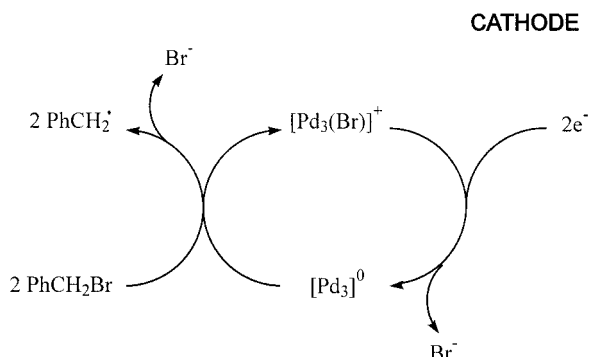
Table 1. Controlled-potential electrolysis of $\text{Pd}_3(\text{Br})^+$ in the presence of BzBr .

Entry	Working electrode (WE)	E_{WE} (V vs. SCE)	Solvent ^[a]	Molar ratio $\text{BzBr}/\text{cluster}$	Q (F per mol of BzBr)	Spin trap	Product(s)	% Chemical yield	% Faradic yield ^[b]
1	Cu anode ^[c]	+0.6	CH_2Cl_2	25	0.84	none	dibenzyl	76 ^[d]	90
2	C cathode ^[c]	−0.9	THF	14	1.24	none	dibenzyl	70 ^[d]	56
3	C cathode ^[c]	−1.3	THF	14	1.21	none	dibenzyl	60 ^[d]	50
4	C cathode ^[c]	−0.9	THF	14	1.14	DMPO ^[f]	spin adduct ^[g]	42 ^[d]	38
5	C cathode ^[c]	−0.9	THF	14	1.09	TEMPO ^[f]	dibenzyl spin Adduct	30 ^[h]	28

[a] In the case of entry 1, CH_2Cl_2 was used as the solvent and no PhMe was observed; for entries 2–5, THF was used and PhMe was detected by GC–MS but not quantified because of strong overlap with the solvent peak in the chromatogram. [b] Faradic yield = Chemical Yield/ Q . [c] The platinum counter-electrode was not separated, being directly immersed in the solution in order for it to electrolyse. [d] Measured by gas chromatography. [e] Standard assembly with an isolated platinum counter-electrode located in a separate compartment. [f] Quantity = 1 molar equivalent with respect to BzBr . [g] Only observed by ESR with no quantification. [h] Isolated yield.

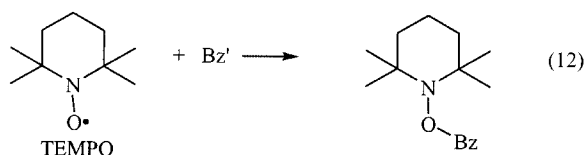
1). Both the chemical (76%) and Faradic (90%) yields are good.

The second method involves the use of a carbon cathode where the single 2-electron reduction of $\text{Pd}_3(\text{Br})^+$ in Pd_3^0 (at about −1 V vs. SCE) occurs in THF. The catalytic cycle is shown in Scheme 2 based on the findings of the stoichiometric reactions above. This method leads to slightly lower chemical yields of Bz_2 and the presence of PhMe was noted. The data are summarised in Table 1.



Scheme 2.

The addition of the spin trap DMPO to the solution during catalysis (entry 4) leads to the formation of the spin adduct as shown in reaction (1). On the other hand, addition of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) ^[45–48] (entry 5) leads to a partial trapping where Bz_2 and the diamagnetic spin adduct can be observed [reaction (12)].



X-ray Structure of $\text{Pd}_3(\text{Br})^+$

This compound completes the series for $\text{Pd}_3(\text{X})^+$ (Figure 5 and Table 2) where $\text{X} = \text{Cl}$ ^[49,50] and I . ^[21] A comparison of the skeleton (Table 3) indicates a fairly robust core in which the nature of the halide does not perturb the bond distances within the experimental uncertainties. In all cases,

the $\text{Pd}-\text{X}$ distances indicate strong ionic interactions and vary as expected ($\text{Cl} < \text{Br} < \text{I}$).

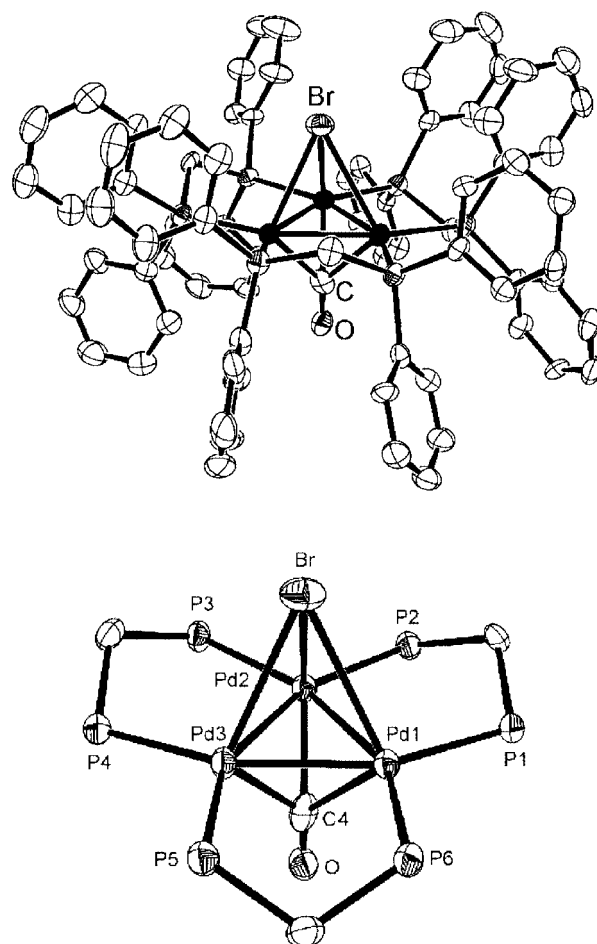


Figure 5. Top: ORTEP representation of $\text{Pd}_3(\text{Br})^+$. The PF_6^- counter-anion, crystallisation toluene molecules and H-atoms are not shown for clarity. The ellipsoids are shown at the 50% probability level. Bottom: Drawing showing the skeleton of the cluster and the atom numbering.

Conclusions

The stoichiometric reactivity toward halocarbons of the Pd_3^+ and Pd_3^0 species has been investigated for the first

Table 2. Selected bond distances [Å] and angles [°] for Pd₃(Br)⁺.

Distances		Angles	
Pd(1)–C(4)	2.143(10)	Pd(1)–Pd(2)–Pd(3)	59.63(2)
Pd(2)–C(4)	2.139(10)	Pd(1)–Pd(3)–Pd(2)	60.26(2)
Pd(3)–C(4)	2.145(9)	Pd(2)–Pd(1)–Pd(3)	60.11(2)
Pd(1)–Br	3.027(9)	O–C(4)–Pd(1)	132.7(9)
Pd(2)–Br	2.8276(10)	O–C(4)–Pd(2)	141.0(9)
Pd(3)–Br	2.9666(11)	O–C(4)–Pd(3)	132.9(10)
Pd(1)–Pd(2)	2.5991(8)	C(4)–Pd(1)–P(1)	114.8(2)
Pd(1)–Pd(3)	2.5826(8)	C(4)–Pd(1)–P(6)	112.3(2)
Pd(2)–Pd(3)	2.5950(8)	C(4)–Pd(2)–P(2)	115.2(2)
Pd(1)–P(1)	2.315(2)	C(4)–Pd(2)–P(3)	118.4(2)
Pd(1)–P(6)	2.314(2)	C(4)–Pd(3)–P(4)	113.6(2)
Pd(2)–P(2)	2.315(2)	C(4)–Pd(3)–P(5)	112.1(2)
Pd(2)–P(3)	2.311(2)	P(1)–Pd(1)–P(6)	109.55(7)
Pd(3)–P(4)	2.309(2)	P(2)–Pd(2)–P(3)	108.44(7)
Pd(3)–P(5)	2.305(2)	P(4)–Pd(3)–P(5)	108.97(7)
C(4)–O	1.104(10)	P(1)–Pd(1)–Br	104.46(6)
		P(6)–Pd(1)–Br	113.22(6)
		P(2)–Pd(2)–Br	104.95(6)
		P(3)–Pd(2)–Br	98.83(6)
		P(5)–Pd(3)–Br	113.85(6)
		P(4)–Pd(3)–Br	104.09(6)

Table 3. Comparison of selected bond distances [Å] for the Pd₃(X)⁺ clusters.

Average distance ^[a]	X = Cl ^[49]	X = Cl ^[50]	X = Br (this work)	X = I ^[21]
d(Pd–Pd)	2.595(17)	2.591(11)	2.592(10)	2.596(5)
d(Pd–P)	2.311(30)	2.310(11)	2.311(6)	2.314(9)
d(Pd–C)	2.103(10)	2.133(50)	2.142(3)	2.163(29)
d(Pd–X)	2.861	2.899	2.940	3.022

[a] The uncertainties are based on the maximum difference between the average value and experimental data.

time and has allowed the discovery of a new reactivity, particularly with respect to the inorganic products evolved from the Pd₃⁰ species. The resultant A-frame product is stable since its reduction potential is higher than that for Pd₃⁺ and Pd₃⁰. Although there is no evidence in this work, the parallel pathway leading to the A-frame product may cause catalyst poisoning. Moreover, the catalytic generation of free radicals has been performed in good yields and the electrochemical methods may represent interesting alternatives to other stoichiometric reagents such as R₃SnH which may exhibit some undesired toxicity. Applications of such species in organic syntheses, especially those relative to C–X bond activation, are many. Due to the nature of the radical-type reactions that these species lead to, many other applications should be possible.

Experimental Section

Materials: The [Pd₃(dppm)₃(CO)](PF₆)₂ complex was prepared according to the literature.^[20,51] Dichloromethane was distilled under Ar over P₂O₅ and tetrahydrofuran (THF) was distilled under Ar over Na (Aldrich). Benzyl bromide (BzBr), methyl iodide (MeI) and the spin trap agents TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) and DMPO (5,5'-dimethyl-1-pyrroline N-oxide) were purchased from Aldrich and used as received. Benzyl iodide (BzI) was prepared according to a literature method.^[52] The Bu₄NPF₆ salt

was synthesized by mixing stoichiometric amounts of Bu₄NOH (40% in water) and HPF₆ (60% in water). After filtration, the salt was recrystallised twice from ethanol and dried at 80 °C for at least two days.

Apparatus: NMR spectra were measured on a Bruker WM 300 spectrometer (³¹P NMR: 121.497 MHz). The chemical shifts are reported with respect to H₃PO₄ (³¹P NMR). The GC–MS data were collected on a Hewlett–Packard 6890 Series instrument. EPR measurements were carried out on a Bruker ESP 300 spectrometer; field calibration was made with DPPH (*g* = 2.0037).

Electrochemical Experiments: All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon. The supporting electrolyte was degassed under vacuum before use and then dissolved to a concentration of 0.2 M. For cyclic voltammetry experiments, the concentration of the analyte was almost 10^{−3} M. Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel PJT24–I potentiostat connected to a Tacussel GSTP4 waveform generator. The reference electrode was a saturated calomel electrode (SCE) 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 (*φ* = 3 mm). Under these conditions, when operating in THF, the formal potential for the ferrocene^{+/−} couple was found to be +0.56 V versus the SCE. The controlled potential electrolysis was performed with an Amel 552 potentiostat coupled with an Amel 721 electronic integrator. High scale electrolyses were performed in a cell with three compartments separated with fritted glasses of medium porosity. Carbon gauze was used as the working electrode, a platinum plate as the counter-electrode and a saturated calomel electrode as the reference electrode. The electrolyses corresponding to the copper method were performed with a copper plate as the working electrode (anode), a platinum plate as the counter-electrode (cathode) and a saturated calomel electrode as the reference electrode, the latter being separated from the others in a two-compartment cell.

Procedures for the Electrochemical Experiments. Conventional High-Scale Electrolysis: The [Pd₃(dppm)₃(CO)](PF₆)₂ cluster (12.5 mg, 7 × 10^{−3} mmol, 6 mol-% per mol of BzBr) and BzBr (12.45 μL, 0.105 mmol) were added to the cathodic compartment of the cell containing a 0.2 M solution of Bu₄NPF₆ in THF (10 mL). The anodic compartment and the reference electrode compartment were filled with the Bu₄NPF₆–THF solution. The potential was set to −0.9 V vs. SCE. The electrolysis was stopped after the current had dropped to less than 0.5 mA. After filtration of the mixture, the solvent was removed and the residue extracted with diethyl ether (3 × 5 mL). The internal standard method was used to measure the GC yields of the products. These were identified by comparison of the GC–MS spectra and GC retention times with those of available authentic samples. The electrolysis was also performed in the presence of TEMPO (in an equimolar amount to BzBr) which led to the isolation of the spin adducts Bz–DMPO (30%) and Bz₂ (42%). These were separated by column chromatography (solvent: CH₂Cl₂) and identified by mass spectrometry, ¹H NMR spectroscopy and by comparison with literature data.^[53]

High-Scale Electrolysis. The Copper Method: Pd₃²⁺ cluster (11.6 mg, 6.5 × 10^{−3} mmol, 4 mol-% per mol of BzBr) and BzBr (20 μL, 0.168 mmol) were added to the anodic compartment containing a 0.2 M solution of Bu₄NPF₆ in CH₂Cl₂ (10 mL). The Bu₄NPF₆–CH₂Cl₂ solution (10 mL) was poured into the reference electrode compartment. The copper anode potential was set to +0.6 V vs. SCE and the electrolysis was stopped after one Faraday

per mol of BzBr had passed. The quantification procedure was the same as described above.

Theoretical Computations: The Density Functional Theory calculations (DFT) were performed using the commercially available Gaussian 98^[54] software and a Pentium 4 (1.6 GHz) computer. The computations were performed at the RB3LYP level [Becke's three parameter hybrid functional^[55] using the LYP (Lee–Yang–Parr) correlation functional].^[56,57] The basis set for the polarisation and diffuse function was the 3-21G* set.^[58–60] To save computation time, $\text{H}_2\text{PCH}_2\text{PH}_2$ was selected instead of dppm . In order to test the methodology, the computed bond distances and angles of the model cluster $\text{Pd}_3(\text{H}_2\text{PCH}_2\text{PH}_2)_3(\text{CO})(\text{Br})^+$ were checked against those of the crystal structure of $\text{Pd}_3(\text{dppm})_3(\text{CO})(\text{Br})^+$ [denoted as $\text{Pd}_3(\text{Br})^+$ in the text]. The comparison was satisfactory.

X-ray Structure of $[\text{Pd}_3(\text{dppm})_3(\text{CO})\text{Br}](\text{PF}_6)$: Single crystals of Pd_3Br^+ (as its PF_6^- salt) were obtained from acetone/toluene/hexane, mounted in inert oil and transferred to the cold gas stream (110 K) of a Nonius Kappa CCD diffractometer located at the Université de Bourgogne. The structure was solved by the heavy atoms method (SHELXS-97) and refined by full-matrix least-squares methods (SHELXL-97)^[61] with the aid of the WINGX program.^[62] The capping CO molecule and the capping Br atom were found to be slightly disordered (inversion of both ligands with respect to the Pd_3 plane), the occupancies converged to 0.93/0.07.

Table 4. Crystallographic data.

	$[\text{Pd}_3(\text{dppm})_3(\text{CO})\text{Br}]\text{PF}_6 \cdot 2.5\text{toluene}$
Empirical formula	$\text{C}_{76}\text{H}_{66}\text{BrF}_6\text{OP}_7\text{Pd}_3 \cdot 2.5\text{C}_7\text{H}_8$
F_w	1955.52
Description	red prism
Crystal size [mm]	$0.3 \times 0.1 \times 0.1$
Temperature [K]	110(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	10.6546(2)
b [Å]	37.1091(7)
c [Å]	21.2714(7)
α [°]	90
β [°]	91.55(1)
γ [°]	90
V [Å ³]	8407.3(4)
Z	4
ρ (calcd.) [g cm ⁻³]	1.545
Scan mode	ω and φ
$F(000)$	3948
$\mu(\text{Mo-K}\alpha)$ [mm ⁻¹]	1.305
θ -range [°]	2.96–23.77
Limiting indices	$-11 \leq h \leq 11$ $-42 \leq k \leq 32$ $-24 \leq l \leq 24$
Reflections collected	15640
Independent reflections	11002
Data/restraints/parameters	11002/25/949
Goodness-of-fit on F^2	1.038 ^[c]
Final R indices [$I > 2\sigma(I)$]	$R_1^{[a]} = 0.0581$ $wR_2^{[b]} = 0.1325$
R indices (all data)	$R_1^{[a]} = 0.0816$ $wR_2^{[b]} = 0.1479$
Largest diff. peak and hole (e Å ⁻³)	1.14 –1.12

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [F_o^4])^{1/2}$. [c] Goodness of fit = $[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$. Weight for $[\text{Pd}_3(\text{dppm})_3(\text{CO})\text{Br}]\text{PF}_6 \cdot 2.5\text{toluene} = 1/(\sigma^2(F_o^2) + (0.051 \times P)^2 + 54.0 \times P)$ where $P = [\text{Max}(F_o^2, 0) + 2 \times F_c^2] / 3$.

The minor component of the disorder was isotropically refined with some least-squares restraints to ensure equivalent geometrical parameters for both components. Among the three toluene solvate molecules, only one was anisotropically refined, the others were each refined with an overall isotropic thermal parameter and one of them, close to an inversion centre, was refined with an occupancy of 0.5. All other non-hydrogen atoms were anisotropically refined and the hydrogen atoms were included using a riding model. Crystallographic data are reported in Table 4.

CCDC-243382 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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