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Preliminary communication

Stabilization of bis(triphenylphosphine)palladium(0) by chloride ions. Electrochemical generation of highly reactive zerovalent palladium complexes

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Abstract

"$Pd^0(PPh_3)_2$" has been generated by electroreduction of $Cl_2Pd(PPh_3)_2$ in the absence of PPh_3. Its structure is consistent with $[Cl_xPd^0(PPh_3)_2]_n^{nx-}$, with values of x and/or n depending on the chloride ion concentration. The half-lives of its reactions with PhI or PhBr have been determined, and found to be 350 and 100 times, respectively, as large as those for $Pd(PPh_3)_4$.

Zerovalent palladium complexes are effective catalysts for cross-coupling reactions [1,2,3]. For example $Pd^0(PPh_4)_4$ is able to activate the carbon–halogen bond of aromatic halides through an oxidative addition in which the low coordinated $Pd^0(PPh_3)_2$ is regarded as the effective reagent [2,4,5]. Negishi et al. [6] recently described the first synthesis and characterization of such a low coordinative zerovalent palladium complex stabilized by chloride anions, obtained by the reaction of organolithium reagents with $Cl_2Pd(PPh_3)_2$, and assigned to it the structure $[Li_xCl_xPd^0(PPh_3)_2]_n$ ($x = 1$ or 2?, $n \geqslant 1$?). We report here that similar complexes can be obtained by electrochemical reduction of $Cl_2Pd(PPh_3)_2$ in the absence of Li^+, and that they are much more reactive towards carbon–halogen bond than the more stable related species $Pd^0(PPh_3)_3$ and $Pd^0(PPh_3)_4$.

Electrochemical generation of bis(triphenylphosphine)palladium(0) in the presence of chloride ions.

Figure 1a shows the voltammogram of $Cl_2Pd(PPh_3)_2$ at a steady gold disk electrode. This bivalent palladium complex is electroreducible via a single reduction

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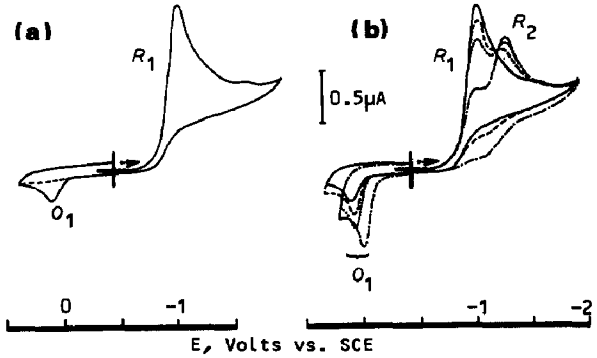

Fig. 1. Cyclic voltammetry of $Cl_2Pd(PPh_3)_2$, 2 mM, in THF, n-Bu_4NBF_4, 0.3 M, at a gold steady disk electrode (ϕ 0.5 mm). (a) $Cl_2Pd(PPh_3)_2$ alone (solid curve) or in the presence of PhI, 20 mM, (dashed curve), without purposely added chloride ions; (b) $Cl_2Pd(PPh_3)_2$, in absence of PhI as in (a) but in the presence of various amounts of n-Bu_4NCl: (———) 0, (------) 10, (······) 38, (·—·—·) 200 mM. v 0.2 V s^{-1}. T 20 °C. Potentials are referred to the SCE.

wave R_1 involving two electrons [5b,7] at E^{p}_{R1} − 1.0 V vs. SCE.

$$Cl_2Pd^{II}(PPh_3)_2 + 2\,e^- \xrightarrow{R_1} \text{“}Pd^0(PPh_3)_2\text{”} \qquad (1)$$

The electrogenerated low coordinated zerovalent palladium complex is electro-oxidable at wave O_1, E^{p}_{01} 0.1 V vs. SCE. Double step chronoamperometry [8] (first step on wave R_1 and second on wave O_1) shows that the zerovalent palladium formed at wave R_1 is quantitatively oxidized at wave O_1, demonstrating that this low coordinated zerovalent palladium is relatively stable, and does not undergo rapid chemical reaction to give, e.g., metallic palladium:

$$Cl_2Pd^{II}(PPh_3)_2 \xrightarrow{2\,e^-} \text{“}Pd^0(PPh_3)_2\text{”} \not\rightarrow Pd\downarrow \qquad (2)$$

When chlorides are added to a solution containing $Cl_2Pd(PPh_3)_2$, the voltammetric reduction of $Cl_2Pd(PPh_3)_2$ involves two waves (E^{p}_{R1} − 1 V and E^{p}_{R2} − 1.25 V vs. SC, Fig. 1b), with relative magnitudes dependent on the chloride concentration. At high chloride concentration the two waves have identical current peaks, corresponding to one electron each. It appears then that chlorides are able to stabilize the monovalent palladium electrogenerated at the first wave R_1.

$$Cl_2Pd^{II}(PPh_3)_2 \xrightarrow[R_1]{1e + Cl^-} \text{“}Pd^{I}(PPh_3)_2\text{”} \xrightarrow[R_2]{1e + Cl^- \text{”}} \text{“}Pd^0(PPh_3)_2\text{”} \qquad (3)$$

At the same time, a single oxidation wave O_1 of the “$Pd^0(PPh_3)_2$” electrogenerated at wave R_2 is observed but with a peak potential which becomes less anodic when the chloride concentration is increased (Fig. 1b). This means that the electrogenerated zerovalent palladium complex involves chloride anions as ligands, and can be tentatively described as $[(n\text{-}Bu_4N)_x,Cl_xPd^0(PPh_3)_2]_n$, since n-$Bu_4NBF_4$ is the supporting electrolyte. Such electrogenerated complexes are similar to Negishi's complexes $Li_xCl_xPd^0(PPh_3)_2$ [6], but our results show that they have to be viewed as free anions. This indicates that the countercation effect observed by Negishi is not related to intrinsic stabilities but rather to ion-pairing effects.

The above results based upon cyclic voltammetry were further confirmed by preparative scale electrolysis. Thus an electrolysis (conducted in a divided cell;

cathode: gold gauze; anode: lithium rod; catholyte: $Cl_2Pd(PPh_3)_2$, 0.5 mmol, in 30 ml of THF containing n-Bu_4NBF_4, 0.2 M as supporting electrolyte) at a controlled potential of −1.2 V vs. SCE, yielded, after the consumption of 2 Faraday per mol, an orange solution. The ^{31}P NMR spectrum (400 MHz, THF) of the solution showed three signals, at 23.15, 25.22 and 27.14 ppm relative to H_3PO_4 (the relative heights of the three peaks were: 1/0.71/0.62). These three signals, the ratios of which are a function of the chloride concentration, can be assigned to three differently stabilized zerovalent palladium complexes $[x(\text{n-Bu}_4\text{N}),\text{Cl}_x\text{Pd}^0(\text{PPh}_3)_2]_n$. In the light of the electrochemical data in Fig. 1, where a single oxidation wave O_1 appears, these three species must be regarded as being in rapid equilibrium [8] on the cyclic voltammetry time scale. Similar data obtained at higher scan rates reveal that these equilibria can be considered as extremely fast even on a time-scale of a few tens of microseconds. The ^{31}P NMR spectra do not show any characteristic peaks of $Pd^0(PPh_3)_3$ at 20.5 ppm [6], $Pd^0(PPh_3)_4$ at 15.8 ppm [6] or of the starting complex $Cl_2Pd(PPh_3)_2$ at 24.26 ppm. Furthermore when 3 mmol of n-Bu_4NCl are added to an identical solution immediately before the electrolysis, the ^{31}P NMR spectra show a main signal at 22.98 ppm, similar to that reported by Negishi [6].

Comparison of the reactivity of $[x(\text{n-Bu}_4\text{N}),\text{Cl}_x\text{Pd}^0(\text{PPh}_3)_2]_n$ and $Pd^0(PPh_3)_4$ with PhI

Figure 1a also shows that in the absence of added chloride ions, wave O_1 disappears when the voltammetry of $Cl_2Pd(PPh_3)_2$ is performed in the presence of 10 equivalents of PhI. Similarly the chloride-dependent wave O_1, observed in the presence of added chloride ions (see above and Fig. 1b), disappears when PhI is introduced into the solution. This demonstrates that all the various species $[x(\text{n-Bu}_4\text{N}),\text{Cl}_x\text{Pd}^0(\text{PPh}_3)_2]_n$ react with PhI, while remaining in rapid equilibrium.

$$\frac{1}{n}\left[x(\text{n-Bu}_4\text{N}),\text{Cl}_x\text{Pd}^0(\text{PPh}_3)_2\right]_n + \text{PhI} \rightarrow \text{PhPdI}(\text{PPh}_3)_2 + x\text{n-Bu}_4\text{NCl} \tag{4}$$

The formation of $PhPdI(PPh_3)_2$ was established by ^{31}P NMR spectroscopy. Thus when 10 equivalents of PhI are added to an electrolyzed solution of $PdCl_2(PPh_3)_2$ in the presence or absence of added chloride (see above), the ^{31}P NMR signals of the various zerovalent palladium complexes disappear, to be replaced by a signal at 24.79 ppm characteristic of $PhPdI(PPh_3)_2$ [6]. (An intermediate signal is observed at 34 ppm, and disappears with time to be replaced by the characteristic peak of $PhPdI(PPh_3)_2$ mentioned above). $PhPdI(PPh_3)_2$ was isolated from the solution and further characterized by its ^1H NMR spectrum (250 MHz, $CDCl_2$): 6.25 ppm (t J 7.5 Hz 2H); 6.36 ppm (t J 7.5 Hz 1H); 6.63 ppm (d J 7.5 Hz 2H); 7.3 ppm (m 18H); 7.54 ppm (m 12H); the data are identical to those for $PhPdI(PPh_3)_2$ made by a published procedure [4].

Transient cyclic voltammetry of the systems in Fig. 1 permits assessment of the relative reactivities towards PhI of $[x(\text{n-Bu}_4\text{N}),\text{Cl}_x\text{Pd}^0(\text{PPh}_3)_2]_n$, $Pd^0(PPh_3)_3$, and $Pd^0(PPh_3)_4$. Thus at fast scan rates, the wave O_1 is restored even in the presence of PhI. Figure 2 shows the variations of its current peak, normalized to that observed under identical conditions but in the absence of PhI, as a function of the scan rate. Although, a quantitative description of the kinetics must await further investigations, the data indicate a value of ca. 80 ms for the half life of $[x(\text{n-Bu}_4\text{N}),\text{Cl}_x\text{Pd}^0(\text{PPh}_3)_2]_n$, 2 m$M$, in the presence of 1 equivalent PhI under the

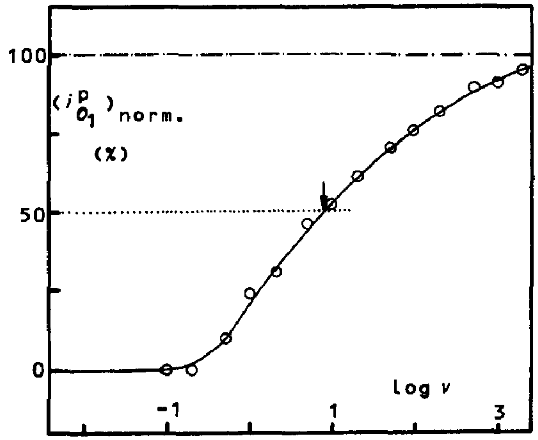

Fig. 2. Variations of the normalized current peak of wave $O_1((i^{p}_{O1})_{norm} = 100 \times i^{p}_{O1}{}^{[(PhI)]}/i^{p}_{O1}{}^{[(PhI)=0]})$ as a function of the scan rate, υ (in V s^{-1}), in the cyclic voltammetry (identical conditions as in Fig. 1) of a 2 m*M* $Cl_2Pd(PPh_3)_2$ solution in THF, in the presence of PhI, 2 m*M*. The arrow indicates the value of the scan rate, $\upsilon_{1/2}$ in V s^{-1}, corresponding to the half life of Pd^0: $t_{1/2}(s) \approx 1.50/\upsilon_{1/2}$.

conditions relevant to Fig. 2. This $t_{1/2}$ value compares with that of ca. 30s for $Pd^0(PPh_3)_4$ under the same conditions. This indicates that these anionic complexes are ca. 350 times as reactive than the chemically stable $Pd^0(PPh_3)_4$. Similar experiments with PhBr as the organic halide shows that the reactivity in this case is ca. 100 times greater than that of $Pd^0(PPh_3)_4$.

Conclusion

Low coordinated zerovalent palladium complexes can be readily generated by electrochemical reduction of $Cl_2Pd(PPh_3)_2$. These complexes are stabilized by chloride anions and they appear to be of the type $[x(n\text{-}Bu_4N),Cl_xPd^0(PPh_3)_2]_n$, analogous to the $LiClPd^0(PPh_3)_n$ intermediates recently postulated to be the effective agent in the catalysis of cross-coupling reactions [9]. The use of $n\text{-}Bu_4NBF_4$ as the supporting electrolyte shows that these species can exist in the form of "free" anions, and do not require stabilization by a strong interaction with a small countercation such as Li^+ (compare ref. 6).

All the various species are in rapid equilibrium and undergo oxidative addition with PhI to afford $PhPdI(PPh_3)_2$. The rate of oxidative addition of PhI to these low coordinated complexes is much greater than that to $Pd(PPh_3)_3$ or $Pd(PPh_3)_4$ [5a,7]. This may account for the greater efficiency of such low ligated zerovalent palladium species over saturated complexes in cross-coupling reactions, in which the rate determining step is generally considered to be the oxidative addition of the organic halide to the zerovalent palladium [10]. Further kinetic studies are in progress to elucidate the nature of the different species $[x(n\text{-}Bu_4N),Cl_xPd^0(PPh_3)_2]_n$ and their respective roles in the mechanism of the oxidative addition. Although these species are sufficiently stable in solution to allow their spectroscopic or electrochemical characterization, all attempts to isolate them were unsuccessful, as was found previously for comparable species [6].

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