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Notes

Oxidative Addition of Ligand-Chelated Palladium(0) to Aryl Halides: Comparison between 1,2-Bisthioethers and 1,2-Bisphosphines

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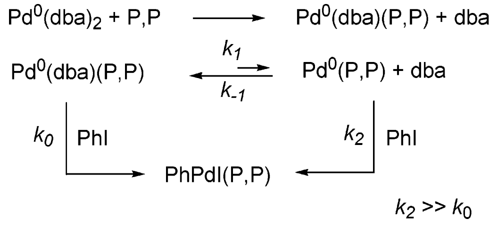
Summary: The kinetics of the oxidative addition of bidentate ligand-chelated Pd^0 complexes to phenyl iodide and bromide has been studied via cyclic voltammetry. The dibenzylideneacetone (dba) delivered by the palladium precursor $Pd(dba)_2$ was found to affect the concentration of the more reactive dba-free Pd^0 complex and consequently the kinetics of the overall oxidative addition. The complexes generated from $Pd(dba)_2$ and $PhSCH_2CH_2SPh$ (pte) were found to be considerably more reactive than those generated from $Pd(dba)_2$ and $Ph_2PCH_2CH_2PPh_2$ (dppe). The former complexes can react with PhBr at low temperatures.

Introduction

The field of catalysis is witnessing an ever-growing attention, and several highly efficient methods are currently known in the literature.[1] Despite these achievements, knowledge in this field is still partial and much effort will be needed to make this methodology comprehensive and well-established. In this context, the nature of the subsidiary ligands used for a given metal-catalyzed process is central, P- and N-based ligands occupying an unquestionable primary position.

On the other hand, despite the vast knowledge on sulfur−metal interactions in coordination chemistry,[2] the use of S-based ligands in catalysis is still rather underdeveloped.[3] Indeed, the thioether function, known to be less coordinating than an amine, an imine, or a phosphine, has been so far mainly exploited as the hemilabile part of mixed (P,S)[4] or (N,S) ligands.[5] On the other hand, ligands based exclusively on thioethers have been only sporadically reported.[6]

Scheme 1



Earlier works unambiguously established that interaction of $Pd^0(dba)_2$ with 1 equiv of a bidentate P,P ligand such as diop, binap, or dppf generates the two complexes Pd^0(dba)(P,P) and Pd^0(P,P) (Scheme 1). Although both the complexes are reactive toward PhI, the former and more abundant dba-ligated complex[7] is intrinsically less reactive than the minor dba-free one (Scheme 1).[8]

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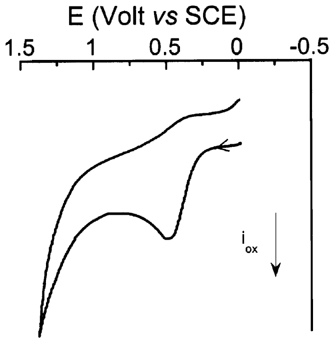


Figure 1. Cyclic voltammetry of $Pd^0(dba)(pte)$ generated from $Pd^0(dba)_2$ (2 mM) and pte (1.0 equiv) in DMF (containing $n Bu_4NBF_4$, 0.3 M) at a stationary gold disk electrode (d = 0.5 mm) with a scan rate of 0.5 V s^{-1}, at 20 °C.

It is known that, due to their acceptor character, phosphorus-based ligands can efficiently stabilize the transiently generated Pd(0) complex, whereas less acceptor ligands tend to bring about premature Pd(0) precipitation.[9] Furthermore, phosphorus-based ligands are known to electronically activate η^3-allyl Pd complexes toward nucleophilic additions. Nevertheless, ^{13}C spectroscopic measurements on η^3-allyl Pd complexes indicate that $Ph_2PCH_2CH_2PPh_2$ (dppe) and $PhSCH_2CH_2SPh$ (pte) do not differ substantially in their π-accepting properties.[10]

We report herein kinetic data on the reactivity of the Pd(0) complexes, generated by reacting $Pd^0(dba)_2$ with 1 equiv of the bidentate S,S ligand: pte, in oxidative addition with aryl halides in DMF. The kinetic data are compared with those obtained with the related P,P ligand dppe.

Results and Discussion

1. Characterization of the Complex Generated from $Pd^0(dba)_2$ and $PhSCH_2CH_2SPh$ (pte) in DMF. The Pd(0) complex generated by reacting $Pd^0(dba)_2$ (2 mM) with pte (1.0 equiv) was characterized by cyclic voltammetry performed in DMF containing $n Bu_4NBF_4$ (0.3 M). A single oxidation peak was observed at $E_{ox}{}^p = +0.495$ V vs SCE at a stationary gold disk electrode with a scan rate of 0.5 V s^{-1} (Figure 1). The oxidation peak of $Pd^0(dba)_2$ at +1.06 V (observed when alone) was no longer detected. A reduction peak characteristic of the reduction of 1 equiv of free dba was also observed.

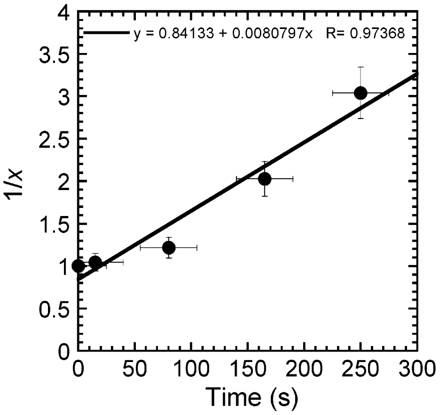
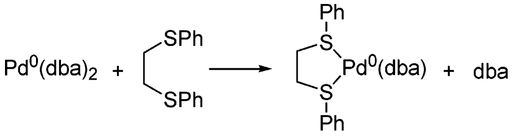


Figure 2. Kinetics of the oxidative addition of PhI (2 mM) with the palladium(0) complexes generated in situ from $Pd^0(dba)_2$ (2 mM) and pte (1.0 equiv) in DMF (containing $n Bu_4NBF_4$, 0.3 M) at 10 °C. Plot of 1/x (see text) versus time.

Scheme 2



The oxidation peak at +0.495 V was not modified upon addition of excess dba. Consequently, it characterizes the complex $Pd^0(dba)(pte)$ (Scheme 2). This result confirms that, despite the negligible back-donation properties of sulfur with respect to phosphorus, the bis-thioether ligand is able to stabilize a Pd(0) complex.[11]

The oxidation peak of $Pd^0(dba)(pte)$ disappeared upon addition of PhI (10 equiv), thereby attesting to the formation of reactive Pd(0) complexes generated from interaction between $Pd^0(dba)_2$ and pte. These results are then very similar to those obtained with P,P[7] or P,N[12] ligands. The major complex is still ligated by dba delivered from the precursor $Pd^0(dba)_2$. No oxidation peak due to the dba-free complex $Pd^0(pte)$ could be detected due to its very low concentration (vide infra).

2. Rate and Mechanism of the Oxidative Addition of Aryl Halides to the Pd(0) Complexes Generated from $Pd^0(dba)_2$ and pte in DMF. The reaction of PhI (2 mM) with the Pd(0) complexes generated from $Pd^0(dba)_2$ (2 mM) and pte (2 mM) in DMF was too fast to be followed by cyclic voltammetry at room temperature. At the lower temperature of 10 °C, the oxidative addition was still fast, but the kinetics could be followed by performing cyclic voltammetry versus time, exploiting the linear relation between the oxidation peak current of $Pd^0(dba)(pte)$ and its concentration. The plot of $1/x$ ($x = [Pd^0]_t/[Pd^0]_0 = i_t/i_0$; i_t, oxidation peak current of $Pd^0(dba)(pte)$ at t; i_0, initial oxidation peak current of $Pd^0(dba)(pte)$) versus time was linear (Figure 2), as expected for a reaction performed under stoichiometric conditions ($1/x = k_{obs}t + 1$) and attesting to a first-order reaction for the Pd(0) complex and PhI as well. However, the oxidative addition was too fast to get accurate data (low correlation coefficient). The half-life time was nevertheless estimated to be $t_{1/2} = 150 \pm 10$ s (DMF, $[PhI]_0$ = 2 mM, 10 °C).

In order to get more information on the mechanism of the oxidative addition, we then turned our attention to the reaction

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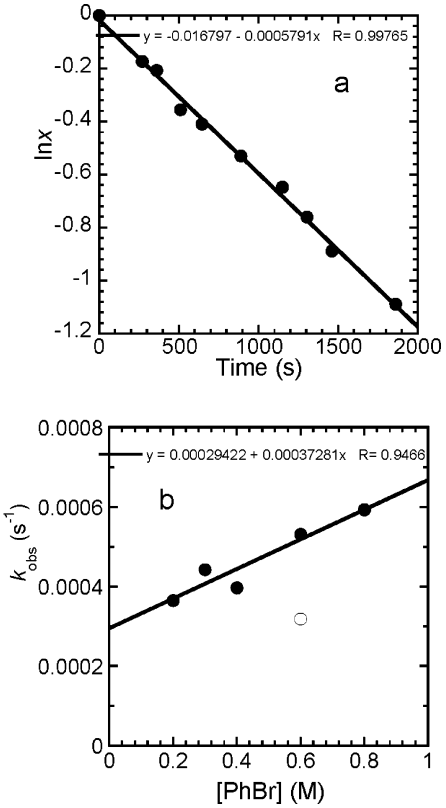
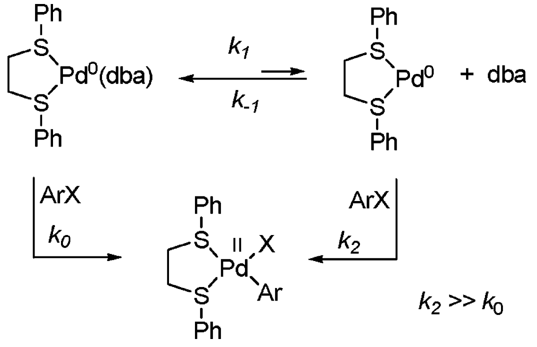


Figure 3. Kinetics of the oxidative addition of PhBr with the palladium(0) complexes generated in situ from $Pd^0(dba)_2$ (2 mM) and pte (1.0 equiv) in DMF (containing nBu_4NBF_4, 0.3 M) at 10 °C. (a) [PhBr] = 0.8 M. Plot of ln x (see text) versus time. $\ln x = -k_{obs}t$. (b) Determination of the reaction order of PhBr. Plot of k_{obs} versus PhBr concentration: (●) in absence of dba; (○) in presence of dba (20 mM).

Scheme 3



with bromobenzene, expected to be less reactive. The kinetics of the oxidative addition was still followed by cyclic voltammetry at 10 °C in the presence of excess PhBr. The plot of ln x ($x = [Pd^0]_t/[Pd^0]_0 = i_t/i_0$; i_t, oxidation peak current of Pd^0(dba)(pte) at t; i_0, initial oxidation peak current of Pd^0(dba)(pte)) against time was linear (Figure 3a) with $\ln x = -k_{obs}t$, attesting to a first-order reaction for the Pd(0) complex.

The kinetics of the oxidative addition was investigated at different PhBr concentrations, in the range 0.2−0.8 M. The plot of k_{obs} versus PhBr concentration gave a straight line with a positive intercept (Figure 3b): $k_{obs} = 0.00029422 + 0.00037281[PhBr]$. This means that two different Pd(0) species react concomitantly with PhBr (Scheme 3), as already observed for bidentate P,P ligands.[7] Moreover, the oxidative addition was slower in the presence of added dba (Figure 3b), attesting to the fact that Pd^0(pte) is intrinsically more reactive than Pd^0(dba)(pte). In the absence of spectroscopic characterization, this is an a posteriori proof that the major Pd(0) complex is indeed ligated by dba.

Table 1. Comparative Reactivity of Aryl Halides in Their Oxidative Addition to the Pd(0) Complexes Generated from $Pd^0(dba)_2$ and pte or dppe[a] in DMF at 10 °C

ligand	PhI (mM)	$t_{1/2}$ (s)	PhBr (mM)	$t_{1/2}$ (s)
pte	2	150	200	1830
dppe	200	8500	n.d.[b]	n.d.[b]

[a] $[Pd^0(dba)_2]$ = 2 mM; [pte] = 2 mM, [dppe] = 2 mM. [b] n.d. = not determined.

From the kinetic law, one has $k_{obs} = k_1 + k_0[PhBr]$.[7] This gives $k_1 = 3 \times 10^{-4}$ s^{-1}, $k_0 = 3.7 \times 10^{-4}$ M^{-1} s^{-1}, and $k_2 \gg 3.7 \times 10^{-4}$ M^{-1} s^{-1} (DMF, PhBr, 10 °C).

3. Comparative Reactivity of PhI and PhBr in Their Oxidative Addition with the Pd(0) Complexes Generated from $Pd^0(dba)_2$ and pte or dppe in DMF. From the half-life times collected in Table 1, the expected reactivity order is observed, PhI ≫ PhBr, when pte is the ligand of the Pd(0) complexes (first line in Table 1). The reaction of PhI (200 mM) with the Pd(0) complexes generated from $Pd^0(dba)_2$ (2 mM) and dppe (1.0 equiv) in DMF was very slow at 10 °C. The value of the half-life time given in Table 1 is compared to that obtained for pte. The Pd(0) complexes ligated by pte are thus considerably more reactive than those ligated by dppe in DMF at 10 °C.

Conclusion. The major Pd(0) complex formed in the reaction of $Pd(dba)_2$ with 1 equiv of $PhSCH_2CH_2SPh$ (pte) in DMF is still ligated by dba, Pd^0(dba)(pte), and is in equilibrium with Pd^0(pte). Both complexes are reactive toward oxidative addition. The oxidative addition of PhBr proceeds at 10 °C. Comparison with the related ligand dppe shows that the oxidative addition in the presence of pte is more rapid. This may be due either to the higher intrinsic reactivity of the (pte)-ligated Pd(0) complexes compared to (dppe)-ligated Pd(0) or/and to the fact that, in the case of the pte ligand, the equilibrium lies more in favor of the more reactive Pd(0)(pte) complex. In other words, the concentration of the Pd(0)(pte) would be higher than that of Pd(0)(dppe) in their respective equilibrium with the (dba)-ligated Pd(0) complexes. Once again, the dba delivered by the precursor appeared to be "noninnocent", as it controls the concentration and thus the reactivity of the more reactive complex Pd^0(pte).

Experimental Section

Chemicals. DMF was distilled from calcium hydride under vacuum and kept under argon. Dba and dppe were commercially available. $Pd(dba)_2$[13] and pte[14] were synthesized according to reported procedures.

Electrochemical Setup for Cyclic Voltammetry. Experiments were carried out in a three-electrode thermostated cell connected to a Schlenk line. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area. The reference was a saturated calomel electrode separated from the solution by a bridge filled with 3 mL of DMF containing nBu_4NBF_4 (0.3 M). The working electrode was a gold disk electrode (d = 0.5 mm).

Typical Procedure for the Characterization of the Pd(0) Complexes Generated from $Pd(dba)_2$ and pte and the Investigation of the Kinetics of the Oxidative Addition of Aryl Halides.

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Degassed DMF (15 mL) containing $n\mathrm{Bu_4NBF_4}$ (0.3 M) was charged into the electrochemical cell followed by 17.2 mg (30 μmol) of $\mathrm{Pd(dba)_2}$ and 7.4 mg (30 μmol) of pte. Cyclic voltammetry was performed at a scan rate of 0.5 V s^{-1} to characterize $\mathrm{Pd^0(dba)(pte)}$. Then 320 μL (3.03 mmol) of PhBr was then introduced, and the reaction was monitored by performing cyclic voltammetry from time to time at the same scan rate of 0.5 V s^{-1}, until total conversion. In other experiments, the amount of PhBr was varied and 70.3 mg (300 μmol) of dba was added before the introduction of PhBr. In another experiment, 3.4 μL (30 μmol) of PhI was added and the kinetics was monitored by cyclic voltammetry. A similar reaction was performed with the ligand dppe (11.94 mg, 30 μmol) and 674 μL (3 mmol) of PhI.

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