



Review

On the behavior of amines in the presence of Pd⁰ and Pd^{II} species

Jacques Muzart*

Institut de Chimie Moléculaire de Reims, UMR 6229, CNRS - Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France

ARTICLE INFO

Article history:

Received 13 March 2009
 Received in revised form 5 May 2009
 Accepted 6 May 2009
 Available online 15 May 2009

Keywords:

Palladium
 Amines
 Catalysis
 Mechanism
 Cleavage
 Reduction
 Oxidation
 Hydrolysis

ABSTRACT

This review summarizes the different intrinsic reactions, with palladium, of amines having a C–H bond adjacent to the nitrogen atom. The proposed mechanisms are described with, in some cases, personal comments.

© 2009 Elsevier B.V. All rights reserved.

Contents

1. Introduction.....	15
2. Primary and secondary amines.....	15
3. Tertiary amines.....	17
4. Concluding remarks.....	23
Note added in proof.....	23
Acknowledgments.....	23
References.....	23

1. Introduction

Although an array of stable palladium complexes bearing nitrogen ligands have been isolated since more than 40 years [1], their use as catalysts has only emerged over the last 20 years [2]. Furthermore, various Pd-catalyzed reactions that require bases, appeal to tertiary amines [3,4], but the stability of these latter depends on the experimental conditions. This short review, that is not exhaustive, highlights the intrinsic reactions, in the presence of Pd⁰ and Pd^{II} species, of amines having, at least, a C–H bond adjacent to

the nitrogen atom. The synthesis of amine-coordinated palladium complexes and the intermolecular formation of C–N bonds, such as the Buchwald–Hartwig [5] and Tsuji–Trost reactions [6], are out of the scope of this review; they will be only mentioned when they support the proposed mechanisms.

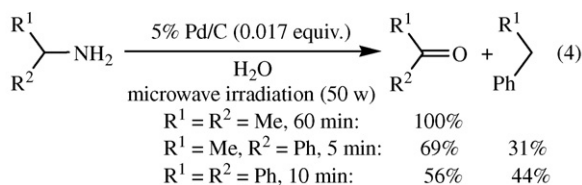
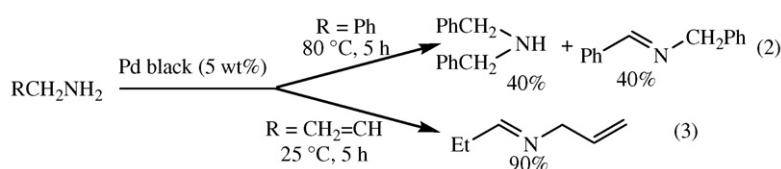
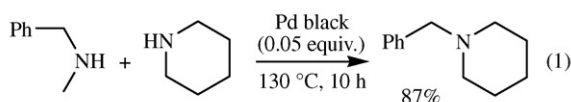
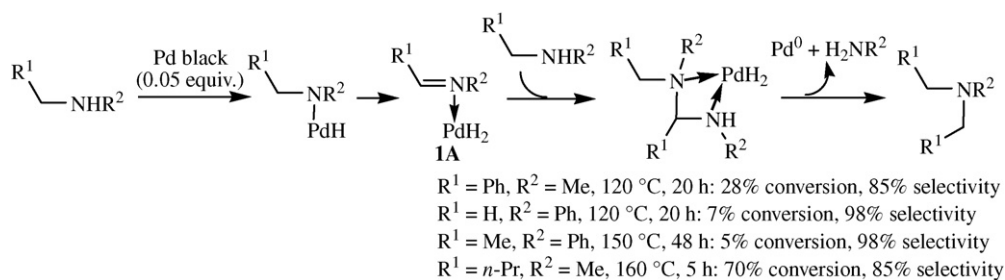
2. Primary and secondary amines

In 1973, Murahashi and co-workers disclosed the Pd black-catalyzed dehydrogenation, at 25–200 °C, of amines having hydrogens in α -position [7]. The formation of tertiary amines from secondary amines was explained by the addition of the substrate to the imine complex **1A** formed from the insertion of palladium into the N–H bond followed by a β -H elimination (Scheme 1). Comparison with the reduction of amidines led the authors to propose that the aminal thus formed, is coordinated to PdH₂, this allowing its hydrogenolysis [8]. The proposal of an imine as intermediate has been demonstrated from its trapping by a second amine (Eq. (1))

Abbreviations: Ar, aryl; BINAP, 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene; Bn, benzyl; cat., catalytic; Cy, cyclohexyl; dppp, 1,3-bis(diphenylphosphino) propane; equiv., equivalent; rt, room temperature; scCO₂, supercritical carbon dioxide; Tf, trifluoromethanesulfonyl; X, halogen.

* Fax: +33 3 2691 3166.

E-mail address: jacques.muzart@univ-reims.fr.



Scheme 1.

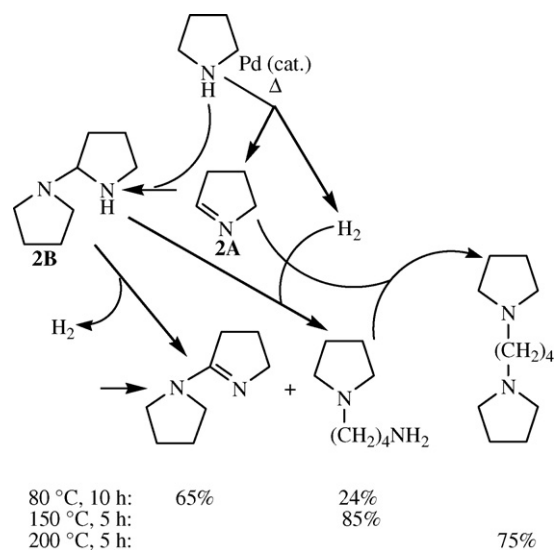
[7,8]. Primary amines lead to secondary amines and/or imines (Eqs. (2) and (3)) [7,8]. Miyazawa et al. have exploited these transformations for the effective synthesis, under microwave irradiation, of ketones from primary and secondary amines via the hydrolysis of their imines [9]. Under these conditions, the hydridopalladium species, in situ produced, cause the reduction of the aromatic ketones (Eq. (4)).

Murahashi's team has observed the influence of the temperature on the selectivity of the Pd-catalyzed reaction of pyrrolidine (Scheme 2): the increase of the temperature promotes the reductive cleavage of the NC–NH bond of **2B**, and then, the reaction of the corresponding primary amine with **2A**. Under similar experimental conditions, morpholine and *N*-methylpiperazine are *N*-formylated, the oxygen atom coming from the attack of the dimeric intermediate by the moisture (Scheme 3) [10].

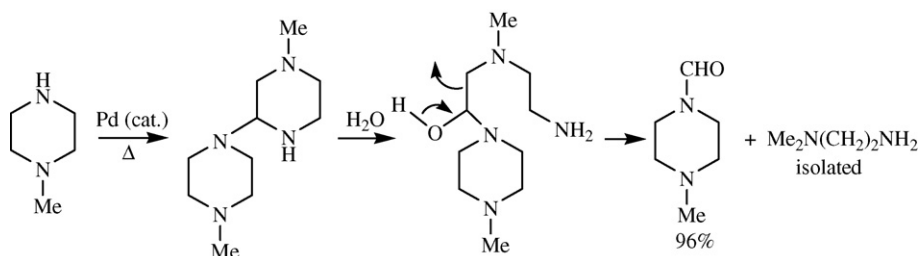
Primary and secondary amines having hydrogens in α -position can reduce ArPdX intermediates to afford ArH [11–13], the best efficiency being obtained with secondary amines [14]. The reduction occurs through complex **4A** derived from the insertion of the Pd^{II} species into the N–H bond (Scheme 4). β -H elimination from **4A** leads to an imine and ArPdH; this latter evolving into ArH and Pd⁰. Consistent with this mechanism, *N*-methyl-*N*-benzylideneamine has been detected when *N*-methylbenzylamine was used [11]. Nevertheless, phosphine ligands could be involved in the reduction of the corresponding ArPdX complexes.

For the reduction of (BINAP)Pd(OAc)₂ in C₆D₆ containing *t*-BuONa and benzylamine, it has been proposed the involvement

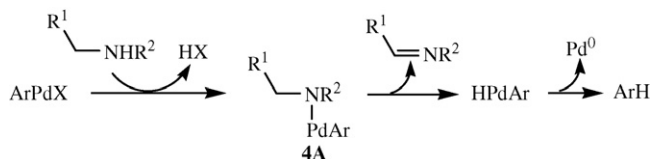
of both base and benzylamine in the formation of (BINAP)Pd⁰ (Scheme 5) [15]. At this level, it is necessary to point out that the reduction of Pd(OAc)₂ can be carried out with phosphines [16,17]. It has been nevertheless considered that the synthesis of Pd(P(OEt)₃)₄



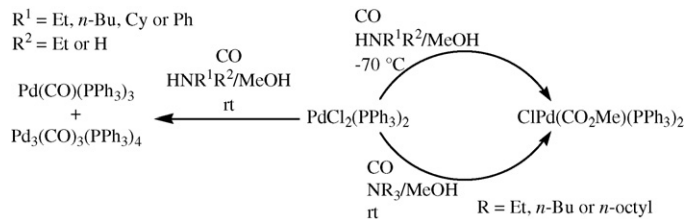
Scheme 2.



Scheme 3.



Scheme 4.



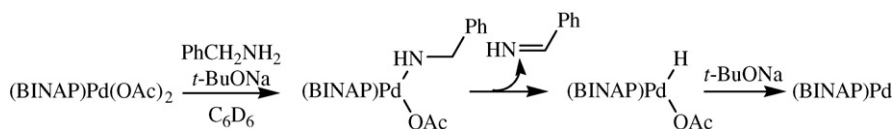
Scheme 6.

from a saturated aqueous solution of K₂PdCl₄ containing P(OEt)₃ and HNET₂ at 0 °C in MeOH [18] is due to the reducing properties of the amine [19]. Hidai et al. have observed the influence of the nature of the amine on the reaction of PdCl₂(PPh₃)₂ in MeOH under carbon monoxide atmosphere [20]. At room temperature, reduction of the complex occurred in the presence of primary and secondary amines, while tertiary amines led to CIPd(CO₂Me)(PPh₃)₂ (Scheme 6) [21]. This Pd^{II} complex is also obtained with primary and secondary amines when the reaction temperature was decreased to -70 °C (Scheme 6). These results indicate that the carbomethoxy complex is, at room temperature, easily converted into Pd⁰ species using CO/HNR¹R²/MeOH conditions, in contrast with its stability under CO/NR₃/MeOH conditions [20]. It remains however not obvious to determine the role of the amines in this Pd^{II} → Pd⁰ reaction, since such a reduction can also occur with alcohols [22] and carbon monoxide [23]. Moreover, palladium complexes such as PdCl₂(HNET₂)₂ [19] and PdCl₂(HNPhEt)₂ [24] have been isolated from CHCl₃ mixtures of the corresponding amines and PdCl₂(PhCN)₂ [19] or PdCl₂ [24]. Klabunde and co-workers have recently reported that the Pd^{II}-amine complexes obtained, at room temperature, from mixtures of Na₂PdCl₄ and primary

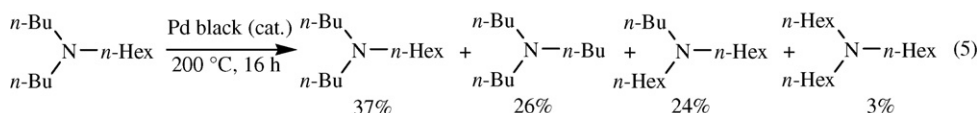
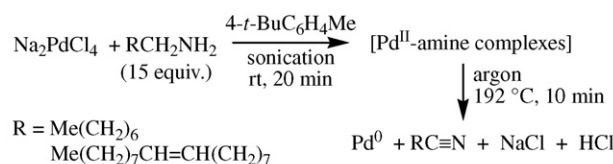
amines having hydrogens in α-position, evolved, at 192 °C, into Pd⁰ nanoparticles [25,26]. According to the IR spectra of the solutions, the amine ligands are oxidized to nitriles (Scheme 7) [25].

3. Tertiary amines

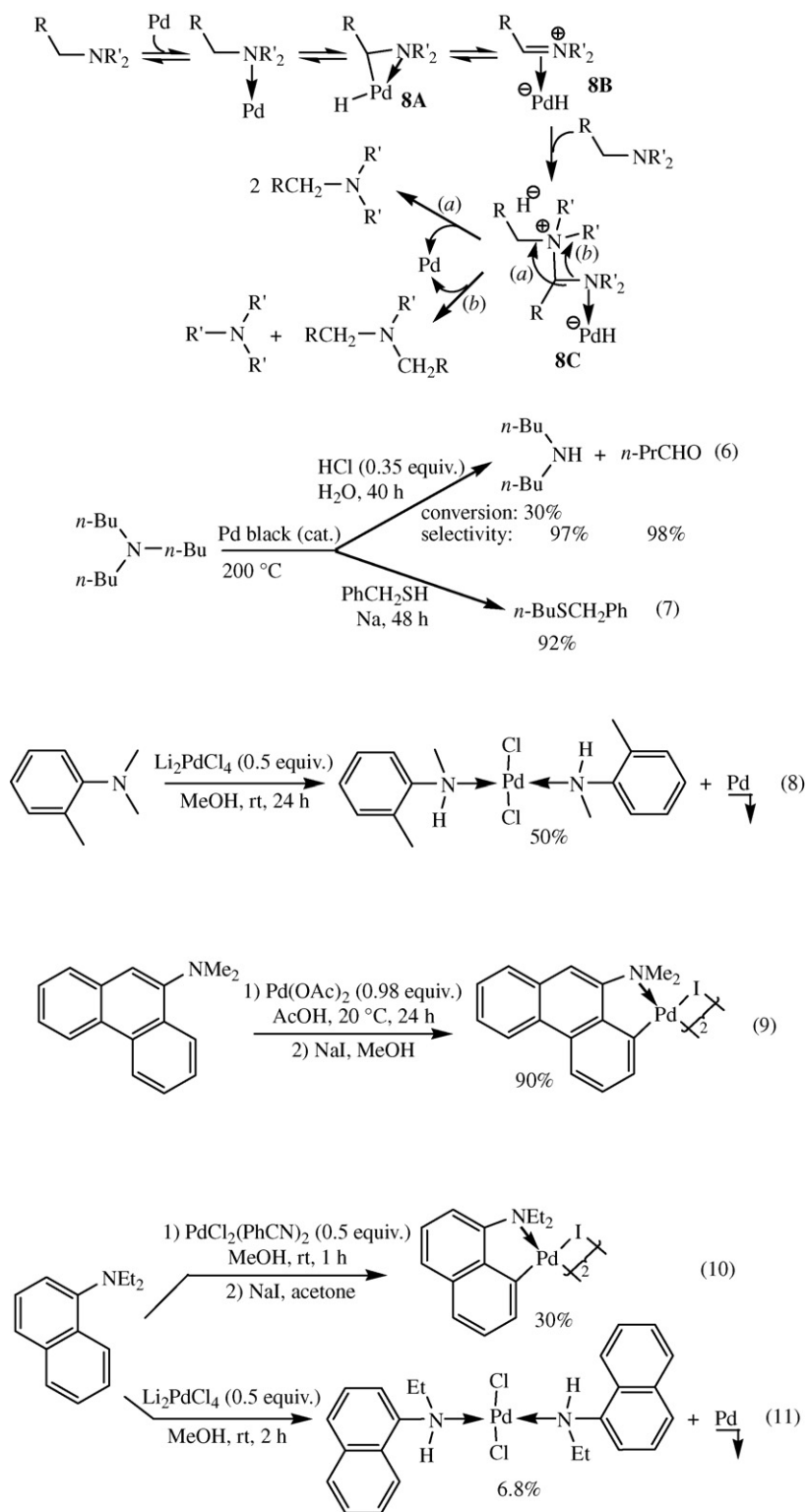
In 1978, Murahashi et al. reported Pd black-catalyzed intermolecular alkyl exchanges from aliphatic tertiary amines (Eq. (5)) [27]. Their interpretation of these exchanges was the coordination of palladium to nitrogen, followed by its reversible insertion into the adjacent C–H bond, affording **8A** which is in equilibrium with the iminium ion complex **8B** (Scheme 8). Attack of **8B** with a second molecule of the amine leads to **8C**, from which, alkyl exchanges occur. The Pd black-catalyzed racemization at 100–200 °C of (+)-*N,N*-dimethyl-*sec*-butylamine [27–29], the formation in acidified water of compounds corresponding to the hydrolysis of **8B** (Eq. (6)) [28], and the addition of thiolate anions to **8B** (Eq. (7)) [30], support this mechanistic scheme.



Scheme 5.



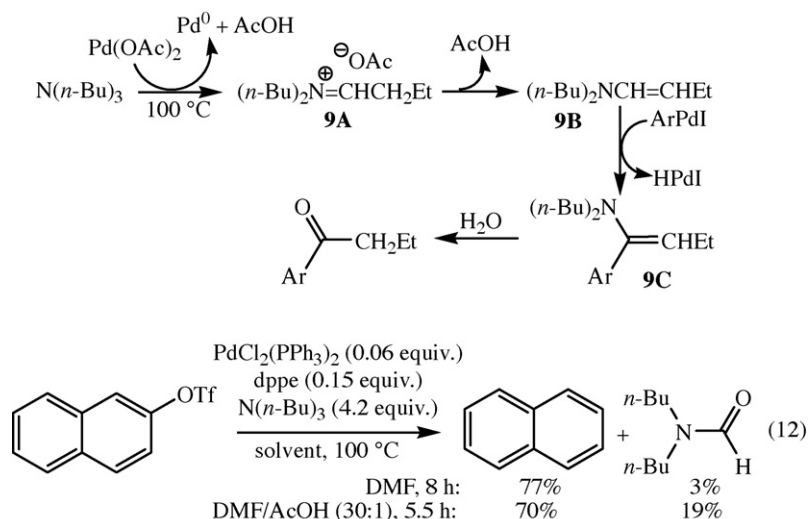
Scheme 7.



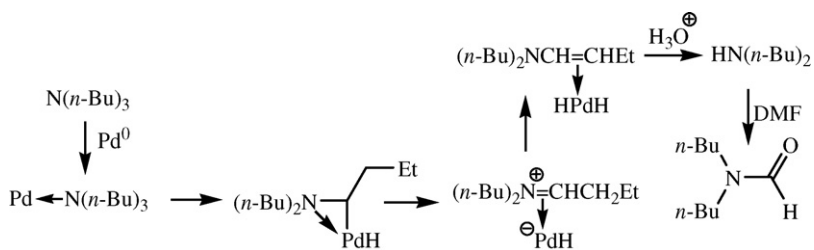
Scheme 8.

The Li_2PdCl_4 -mediated dealkylation, at room temperature in MeOH, of N,N -dialkylanilines yielding their corresponding complexes, as shown in Eq. (8), has been reported by Pfeffer and co-workers [31]. The mechanism of this dealkylation remains unclear; the concomitant precipitation of large amounts of Pd^0 leads to suspect a heterogeneous catalysis [32]. In our opinion, the methanolysis or hydrolysis, by traces of water, of in situ produced iminium ions is conceivable. Indeed, cleavage by ubiquitous water

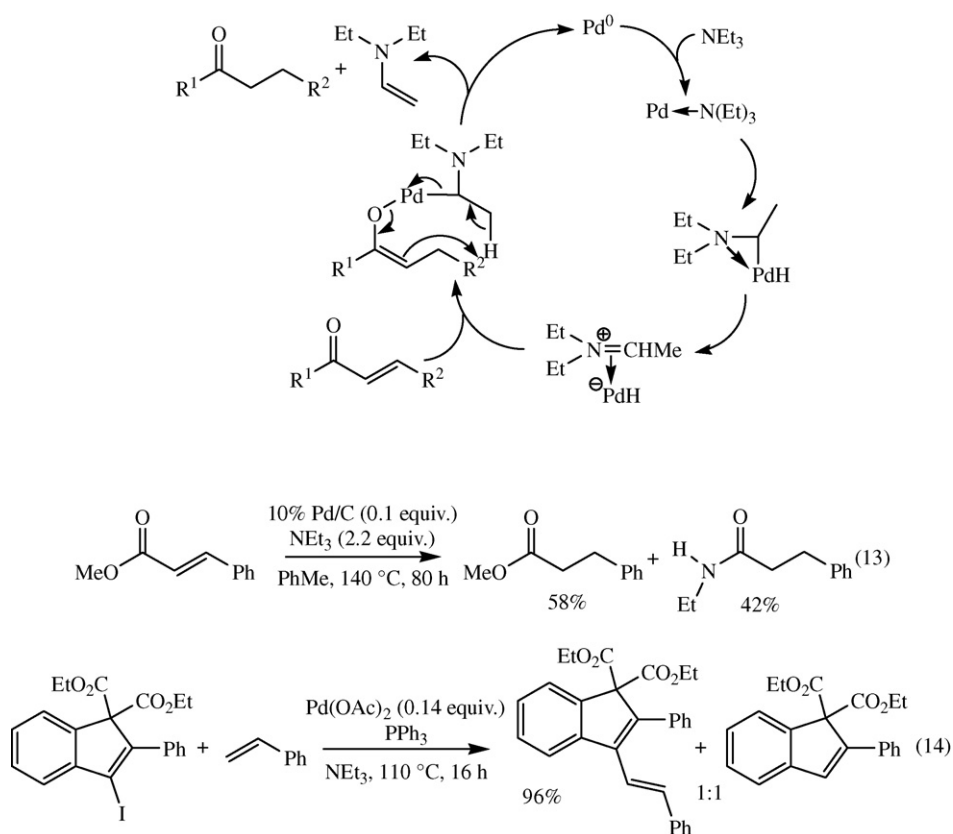
of N,N -diethylaniline leading to acetaldehyde has been reported, at room temperature in CDCl_3 , in the presence of $\text{PdCl}_2(\text{PhCN})_2$ [33]. Nevertheless, a more recent report from Pfeffer et al. highlights the difficulty to rationalize the dealkylation of tertiary arylamines [34]. Actually, palladation of 9-(dimethylamino)phenanthrene with Pd(OAc)_2 afforded effectively the corresponding cyclopalladated complex (Eq. (9)), while that of 9-(diethylamino)naphthalene was problematic: screening of different metallic agents and condi-



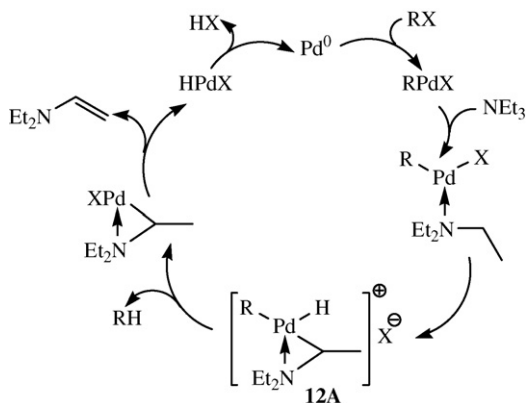
Scheme 9.



Scheme 10.



Scheme 11.



Scheme 12.

tions led to obtain the expected complex using $\text{PdCl}_2(\text{PhCN})_2$ in MeOH (Eq. (10)), while Li_2PdCl_4 yielded a dealkylated complex and metallic palladium (Eq. (11)). Besides, Aresta et al. have observed the deallylation with time of $\text{PdCl}_2(\text{PhNHallyl})_2$, this leading to $\text{PdCl}_2(\text{PhNH}_2)$, methylacetylene and allene [35].

In the course of the synthesis of biaryls from ArI, in presence of catalytic amounts of $\text{Pd}(\text{OAc})_2$ at 100°C in NEt_3 or $\text{N}(n\text{-Bu})_3$, Norman and co-workers have isolated ArCON-Pr as side-product in the latter solvent [36]. The mechanism adopted by this team, is a Heck-type addition to the enamine **9B** derived from the iminium ion **9A**. Hydrolysis of the corresponding adduct (**9C**) provides the isolated ketone (Scheme 9). The absence of ArCOMe when NEt_3 is the solvent, would be due to the lower susceptibility of this amine to oxidation [36,37].

According to Saá et al., the enamine (**9B**) can also be produced under Pd^0 catalysis [38]. In the course of their study of Pd-catalyzed reduction of aryl triflates in DMF in the presence of $\text{N}(n\text{-Bu})_3$, dibutylformamide has been isolated in a yield increasing with acetic acid as co-solvent (Eq. (12)). According to the authors, dibutylformamide is produced from the reaction of DMF with $\text{HN}(n\text{-Bu})_2$, this latter resulting from hydrolysis of the enamine (Scheme 10). In the absence of acid, the hydrogen donor leading to the reduction product would be $\text{N}(n\text{-Bu})_3$ through its protons on the α - and β -carbons [38,39].

The Pd^0 -catalyzed dehydrogenation of amines produces hydridopalladium species which can mediate the hydrogenation of C=C bonds (Scheme 11) and the isomerisation of secondary allylic alcohols into ketones [40,41]. The formation of hydrogenated ethyl amides as by-products of the Pd/C-catalyzed reduction of α,β -

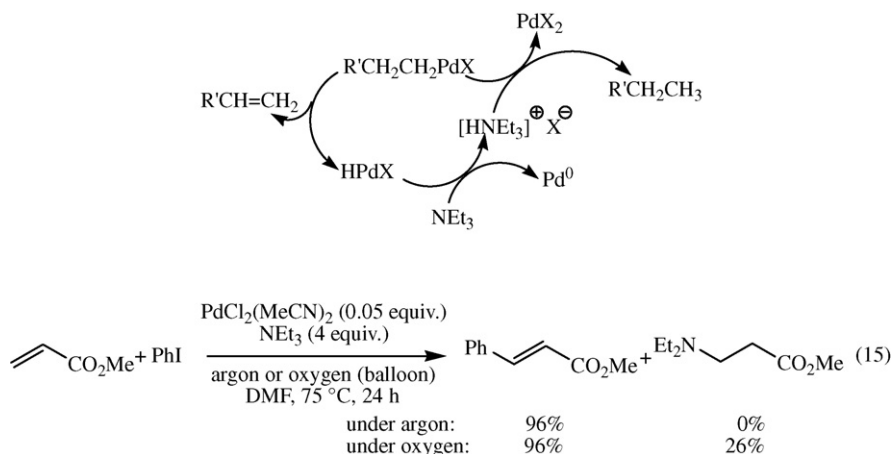
unsaturated esters with NEt_3 at 140°C in dry PhMe (Eq. (13)) suggests the in situ production of ethylamine [41]. Under these experimental conditions, a solution of NEt_3 affords a complex mixture containing volatile compounds and longer-chain alkyl amines [41].

The hydrogen donor capacity of tertiary amines having hydrogens in α -position has been used to reduce $\text{RPd}^{\text{II}}\text{X}$ intermediates, leading to Pd^0 species and RH [38,42–44]; a recent example is presented in Eq. (14) [45]. According to a proposal from Konopelski et al. [43], the reaction occurs via N-coordination to $\text{RPd}^{\text{II}}\text{X}$; this would allow a hydride transfer to the palladium atom to afford the cationic Pd^{IV} complex **12A**, reductive elimination from **12A** leading to RH (Scheme 12). In agreement with this mechanism, the use of $\text{N}(\text{CD}_2\text{CD}_2\text{CD}_3)_3$ instead of NEt_3 led to RD [44]. When a β -H elimination is possible from RPdX , both RH (Schemes 12 and 13) and $\text{R}(-\text{H})$ (Scheme 13) can be obtained, the former resulting from the reaction with either NEt_3 (Scheme 12), or the ammonium salt, HNEt_3X , in situ produced (Scheme 13) [46].

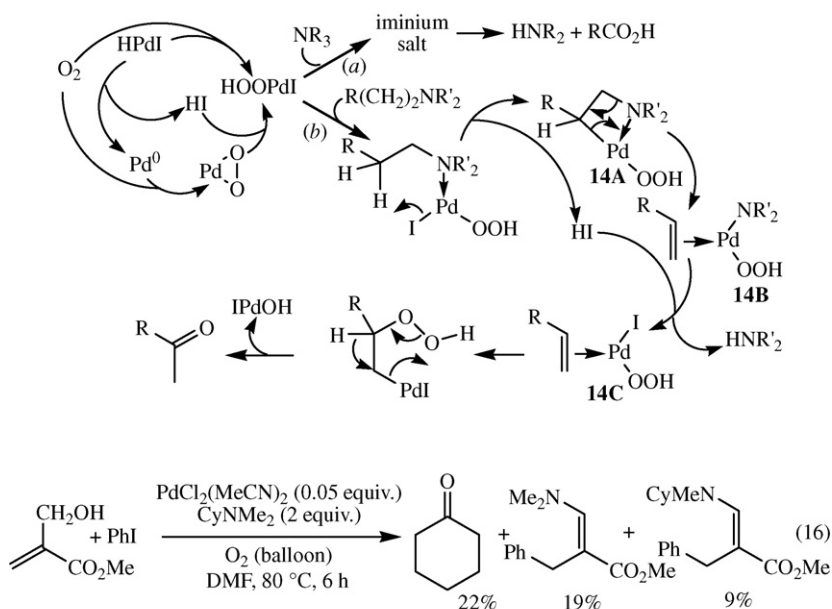
The unexpected dealkylation of triethylamine and cyclohexyldimethylamine has been observed, when they have been used as bases, for Heck reactions under an oxygen atmosphere (Eq. (15)) [47]. According to Hosokawa et al., the dealkylation could be mediated by hydroperoxy-iodopalladium species produced from either HPdI or PdO_2 [47,48]. The authors proposed that HOOPdI reacts with NR_3 to yield an iminium salt, which is involved in the formation of the HNR_2 (Scheme 14, path a). Since cyclohexanone has been isolated when cyclohexyldimethylamine was used as base under their experimental conditions (Eq. (16)), we suggest another mechanism (Scheme 14, path b). Coordination of the tertiary amine to Pd^{II} would mediate the activation of hydrogens in β -position of the nitrogen atom, leading to the formation of the palladacycle **14A** which suffers the $\beta\text{-NR}'_2$ elimination yielding **14B** [49]. Protonolysis of **14B** by HI delivers the secondary amine and **14C**. The carbonyl compound is produced from **14C** via the reaction pathway proposed by Roussel and Mimoun [50].

In 1983, McCrindle et al. disclosed the synthesis of η^1 -ylidic complexes from tertiary amines and $\text{PdCl}_2(\text{PhCN})_2$ (Eq. (17)) [51]. The authors suggest the dehydrogenation of the substrate and then, complexation of the enamine (Scheme 15) [33,51]. This cascade reaction would also produce HPdCl , the reaction of which with the amine leading to the corresponding ammonium salt and Pd^0 [51].

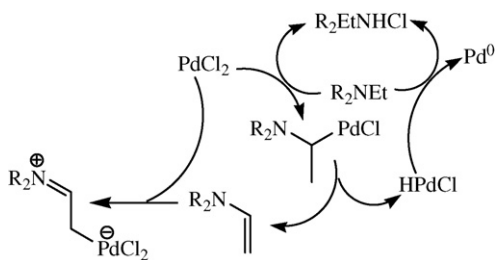
The reduction of $\text{PdCl}_2(\text{PPh}_3)_2$ and $\text{Pd}(\text{OAc})_2$ with NR_3 ($\text{R}=\text{Et}$ or $n\text{-Bu}$) is mentioned in 1988 Hegedus review [52], but, in 1993, Grushin and Alper reported the absence of reaction from the treatment of $\text{PdCl}_2(\text{PPh}_3)_2$ with dry NEt_3 , even at 80°C [53]. In contrast, the addition of water to this mixture entailed the precipitation



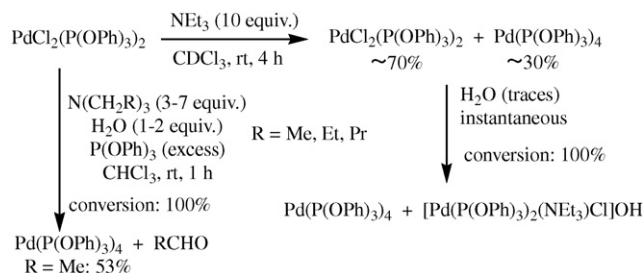
Scheme 13.



Scheme 14.



Scheme 15.

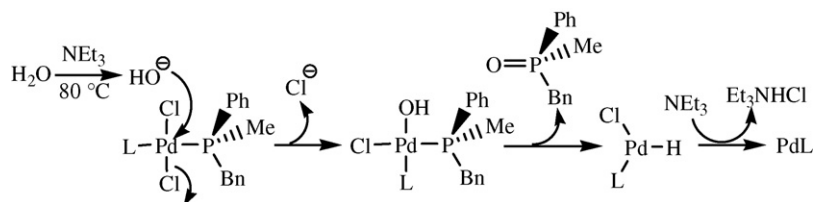


Scheme 17.

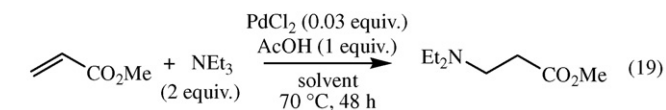
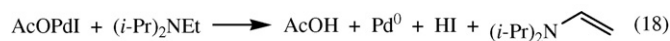
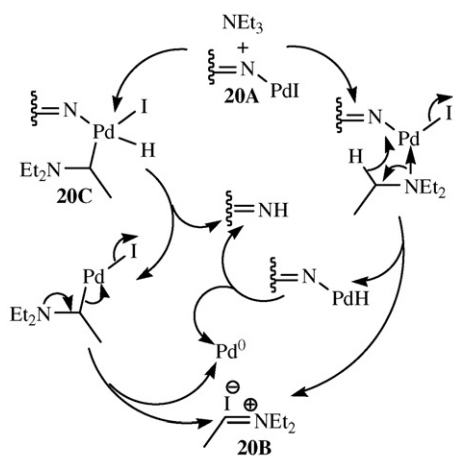
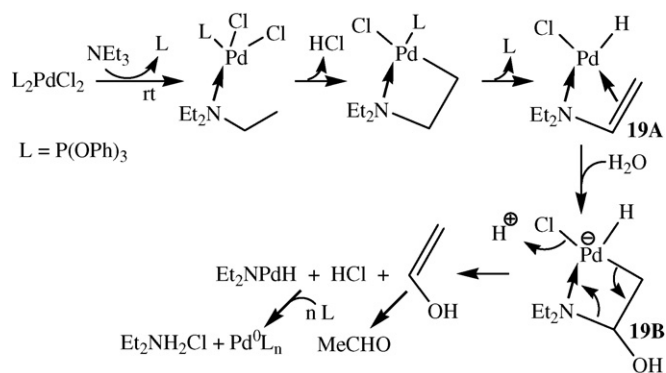
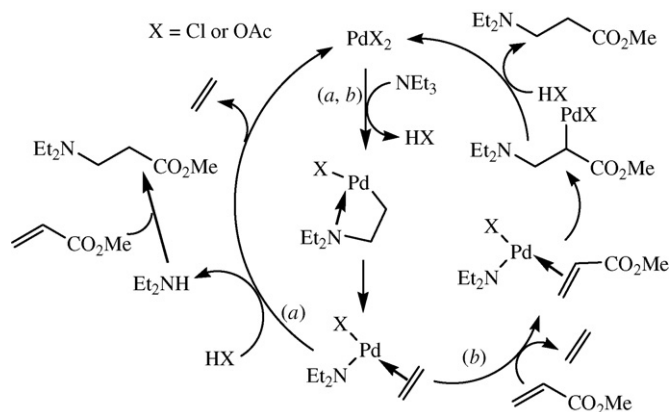
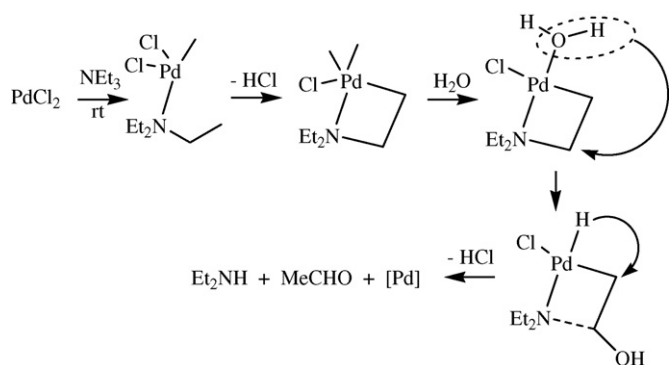
of palladium. According to these authors, the reduction is caused by the hydroxide anion formed from the reversible deprotonation of H_2O with NEt_3 . From the study of the reactivity of a palladium chloride complex bearing an optically active phosphine, a mechanism involving the substitution of Cl^- by OH^- and then, the reductive elimination of the phosphine oxide, has been proposed (Scheme 16). In agreement with this report, the addition of NEt_3 to a DMF solution of 1:10 $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ mixture has any detectable influence on the rate, at 25°C , of the $\text{Pd}^{\text{II}} \rightarrow \text{Pd}^0$ reaction [54,55]. The apathy or low reactivity of NEt_3 vis-à-vis the reduction of PdX_2

under anhydrous conditions, is also demonstrated with the synthesis of $\text{PdCl}_2(\text{NEt}_3)_2$ from a mixture of $\text{PdCl}_2(\text{PhCN})_2$ and NEt_3 [19].

Given Schemes 15 and 16, the formation of Pd^0 from HPdCl and NR_3 affords also the corresponding ammonium salt. Such a proposal is common in the literature. This reaction could be reversible, since Ling and co-workers have proposed that the reaction of triethylammonium iodide with $\text{Pd}(\text{OAc})_2$ and PPh_3 leads to $\text{HPdI}(\text{PPh}_3)_2$ and NEt_3 [56].



Scheme 16.



solvent: MeOH/scCO₂ (95%), EtOH/scCO₂ (26%), H₂O/scCO₂ (0%), MeCN (90%), THF (89%), DMF (86%), dioxane (73%), PhMe (37%)

Scheme 20.

In 2002, Ziólkowski and co-workers disclosed that the reduction of PdCl₂(P(OPh)₃)₂ with NR₃ (R = Et, *n*-Pr or *n*-Bu) requires addition of water to reach complete conversion of the Pd^{II} salt (Scheme 17) [57]. The low conversion, in the absence of added water, would be due to the minute amount of water present in the hygroscopic reagents. Aldehydes arising for the cleavage of the N–R bond have been isolated. Experiments using deuterated amines and/or D₂O have led the authors to propose the mechanism shown in Scheme 18, which differs completely from Scheme 16 but, both the starting complex and the reaction temperature, are also different. Actually, the differences of reactivity of NR₃ towards PdCl₂(P(OPh)₃)₂ and PdCl₂(PPh₃)₂ have been pointed out [19,57,58]. A mechanism involving the production, as intermediates, of enamine palladium complexes from the reaction of PdCl₂(P(OPh)₃)₂ with NR₃ has not been retained, because complexes similar to those disclosed by McCrindle et al. (Eq. (17)) [33] have not been observed [57]. Nevertheless, we propose that the transient enamine palladium complex **19A** can be considered (Scheme 19); activation of the C=C bond of the enamine, by coordination to Pd^{II}, would mediate the Wacker-type addition of H₂O leading to the anionic complex **19B**. This latter will suffer a β-NEt₂ elimination [49], liberating compounds that evolve towards Pd⁰, acetaldehyde and the ammonium salt.

A few months later, Larock and co-workers suggested two mechanisms for the reduction of iminopalladium^{II} species **20A** with NEt₃; both lead to the iminium salt **20B** and Pd⁰, but one of them involves the Pd^{IV} intermediate **20C** (Scheme 20) [59]. The authors did not comment upon the behavior of **20B**; this compound evolves probably towards Et₂NH₂I and MeCHO during the aqueous workup. Another possibility is the transformation of **20B** into the corresponding enamine and HI. Such a reaction has been proposed by Cacchi et al. to rationalize the reduction of AcOPdI with (*i*-Pr)₂NEt (Eq. (18)) [60].

Palladium nanoparticles have been isolated from heating, at 120 °C under vacuum, a mixture of PdCl₂ or Pd(OAc)₂, N(*n*-Bu)₃ and *n*-Bu₄NBr [61]. The mechanism of this Pd^{II} reduction remains unclear. As the ammonium salts are hygroscopic, the possible mediation of the process by traces of water cannot be discarded. Another possibility is the in situ formation of reducing radicals from *n*-Bu₄NBr, which act for the Pd^{II} → Pd⁰ reaction [62].

When studying the Pd-catalyzed acetalization of terminal olefins with methanol in the presence of NEt₃ using scCO₂ as the solvent [63], Jiang and co-workers have observed the possible Michael-type addition of the NEt₂ unit to the C=C bond of methyl acrylate. With AcOH as additive in the absence of oxygen, methyl 3-diethylaminopropionate is produced efficiently in various solvents, but water has a strong detrimental effect (Eq. (19)) [64]. With N(*n*-octyl)₃ instead of NEt₃, the formation of HN(*n*-octyl)₂, 1-octene and

1,1-dimethoxyoctane has been detected. Given these results, the authors have assumed that the Pd-catalyzed C–N bond cleavage of tertiary amines can occur in the absence of water. Two reaction pathways for which the oxidation state of palladium is preserved all along the catalytic cycle have been proposed (Scheme 21). Both proposed pathways involve, once more, a β - NET_2 elimination from a palladacycle [64,65]. The preservation of the Pd^{II} oxidation state is due to the protonolysis with AcOH of the N–Pd (path *a*) or C–Pd bond (path *b*).

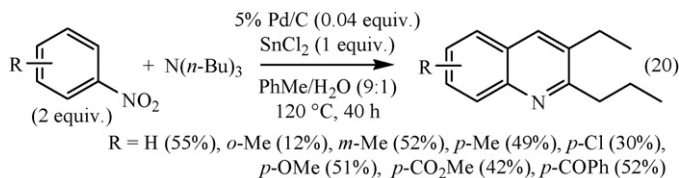
4. Concluding remarks

Although it is considered in some papers that PdX_2 reacts with tertiary amines to form Pd^0 species [19,47,52,58], it seems now admitted that the concomitant presence of H_2O is, under most experimental conditions, required to obtain active Pd^0 catalysts [66]. The reactivity of PdX_2 in the presence of H_2O /primary or secondary amines mixtures can be different, since complexes such as $\text{PdCl}_2(\text{HN}(\text{CH}_2\text{R})_2)_2$ have been isolated from reactions in aqueous media [67]. Besides, the reduction of ArPdX leading to ArH , Pd^0 and HX with primary, secondary or tertiary amines is a step of catalytic reactions which occur without apparent participation of water (Schemes 4 and 11).

The efficiency of some Pd-catalyzed reactions, in particular the telomerization of butadiene with alcohols, is increased by addition of tertiary amines [68–70]. It has been suggested that their role is to facilitate the reduction of Pd^{II} intermediates [68], but their coordination to key Pd^{II} species could be also involved [71]. In fact, the role of the added amine, towards the mechanism and the efficiency of Pd-catalyzed reactions, could be more subtle than usually considered, as pointed out by Amatore and Jutand for Heck reactions [72].

Note added in proof

Cho et al. have recently reported the Pd-catalyzed reductive alkyl group transfer from NR_3 ($\text{R} = n$ -butyl, n -hexyl, n -octyl) to nitroarenes [73]. The reaction occurs at 120°C in the presence of a stoichiometric amount of SnCl_2 , and leads to quinoleines Eq. (20) through an obscure mechanism. According to the proposal for a similar Ru-catalyzed reaction [74], an iminium ion complex corresponding to **8B** (Scheme 8) could be involved.



Acknowledgments

I thank Dr. G. Arsenault (Wellington Laboratories, Guelph, Canada), Dr. M. Pfeffer (Université Louis Pasteur, Strasbourg, France) and Pr. A.M. Trzeciak (University of Wrocław, Poland) for correspondence.

References

- [1] I. Omae, Chem. Rev. 79 (1979) 287–321.
- [2] A. Togni, L.M. Venanzi, Angew. Chem. Int. Ed. Engl. 33 (1994) 497–526; F. Fache, E. Schulz, M.L. Tommasino, M. Lemaire, Chem. Rev. 100 (2000) 2159–2231.
- [3] R.F. Heck, Palladium Reagents in Organic Syntheses, Acad. Press, London, 1985.
- [4] J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, 1995.
- [5] For reviews, see: D. Prim, J.-M. Campagne, D. Joseph, B. Andrioletti, Tetrahedron 58 (2002) 2041–2075; B. Schlummer, U. Scholz, Adv. Synth. Catal. 346 (2004) 1599–1626; J.F. Hartwig, Synlett (2006) 1283–1294; J.F. Hartwig, Acc. Chem. Res. 41 (2008) 1534–1544; For reevaluation of the mechanism, see: S. Shekhar, P. Ryberg, J.F. Hartwig, J.S. Mathew, D.G. Blackmond, E.R. Strieter, S.L. Buchwald, J. Am. Chem. Soc. 128 (2006) 3584–3591; For a recent example, see: A.C. Tadd, A. Matsuno, M.R. Fielding, M.C. Willis, Org. Lett. 11 (2009) 583–586.
- [6] For reviews, see: Ref. [4]; J. Muzart, Tetrahedron 61 (2005) 4179–4212; J. Muzart, Eur. J. Org. Chem. (2007) 3077–3089; For recent examples, see: G. Mora, O. Piechaczyk, X.F. Le Goff, P. Le Floch, Organometallics 27 (2008) 2565–2569; F. Benfatti, G. Cardillo, L. Gentilucci, E. Mosconi, A. Tolomelli, Org. Lett. 10 (2008) 2425–2428.
- [7] N. Yoshimura, I. Moritani, T. Shimamura, S.-I. Murahashi, J. Am. Chem. Soc. 95 (1973) 3038–3039.
- [8] S.-I. Murahashi, N. Yoshimura, T. Tsumiyama, T. Kojima, J. Am. Chem. Soc. 105 (1983) 5002–5011.
- [9] A. Miyazawa, K. Tanaka, T. Sakakura, M. Tashiro, H. Tashiro, G.K.S. Prakash, G.A. Olah, Chem. Commun. (2005) 2104–2106.
- [10] N. Yoshimura, I. Moritani, T. Shimamura, S.-I. Murahashi, J. Chem. Soc., Chem. Commun. (1973) 307–308.
- [11] A.S. Guram, R.A. Rennels, S.L. Buchwald, Angew. Chem. Int. Ed. Engl. 34 (1995) 1348–1350.
- [12] J.-F. Marcoux, S. Wagaw, S.L. Buchwald, J. Org. Chem. 62 (1997) 1568–1569; N. Kataoka, Q. Shelby, J.P. Stambuli, J.F. Hartwig, J. Org. Chem. 67 (2002) 5553–5566.
- [13] A.M. Zawisza, J. Muzart, Tetrahedron Lett. 48 (2007) 6738–6742.
- [14] M.S. Driver, J.F. Hartwig, J. Am. Chem. Soc. 118 (1996) 7217–7218.
- [15] J.P. Wolfe, S.L. Buchwald, J. Org. Chem. 65 (2000) 1144–1157.
- [16] C. Amatore, A. Jutand, M.A. M'Barki, Organometallics 11 (1992) 3009–3013; C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, G. Meyer, Organometallics 14 (1995) 5605–5614.
- [17] It has been argued that the formation of an active Pd^0 catalyst using this method is promoted by water: F. Ozawa, A. Kubo, T. Hayashi, Chem. Lett. (1992) 2177–2180; B.P. Fors, P. Krattiger, E. Strieter, S.L. Buchwald, Org. Lett. 10 (2008) 3505–3508; According to the Amatore/Jutand team, water is, on the best, only involved in a reaction occurring after the rate-determining step of the reduction: C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, Organometallics 14 (1995) 1818–1826; Water could convert an intermediate phosphonium salt into phosphine oxide: C. Amatore, A. Jutand, M.J. Medeiros, New J. Chem. 20 (1996) 1143–1148.
- [18] M. Meier, F. Basolo, R.G. Pearson, Inorg. Chem. 8 (1969) 795–801.
- [19] A.M. Trzeciak, J.J. Ziółkowski, Monatsh. Chem. 131 (2000) 1281–1291.
- [20] M. Hidai, M. Kokura, Y. Uchida, J. Organomet. Chem. 52 (1973) 431–435.
- [21] The effect of the nature of amine was not so distinct using $\text{PdCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CONHCMe}_2\text{CH}_2\text{SO}_3\text{Li})_2$ as substrate under similar conditions: A.M. Trzeciak, J.J. Ziółkowski, J. Mol. Catal. A: Chem. 154 (2000) 93–101.
- [22] J. Muzart, Tetrahedron 59 (2003) 5789–5816.
- [23] J. Tsuji, T. Mandai, Synthesis (1996) 1–24.
- [24] B. Bosnich, J. Chem. Soc. A (1966) 1394–1396.
- [25] Z. Yang, K.J. Klabunde, C.M. Sorensen, J. Phys. Chem. C 111 (2007) 18143–18147.
- [26] Z. Yang, K.J. Klabunde, J. Organomet. Chem. 694 (2009) 1016–1021.
- [27] S.-I. Murahashi, T. Hirano, T. Yano, J. Am. Chem. Soc. 100 (1978) 348–350.
- [28] S.-I. Murahashi, T. Watanabe, J. Am. Chem. Soc. 101 (1979) 7429–7430.
- [29] S.-I. Murahashi, T. Yano, J. Am. Chem. Soc. 102 (1980) 2456–2458.
- [30] S.-I. Murahashi, T. Yano, J. Chem. Soc., Chem. Commun. (1979) 270–271.
- [31] C. Mutet, M. Pfeffer, J. Organomet. Chem. 171 (1979) C34–C36; J. Dehand, C. Mutet, M. Pfeffer, J. Organomet. Chem. 209 (1981) 255–270.
- [32] M. Pfeffer, Personal communication, January 23, 2009.
- [33] R. McCrindle, G. Ferguson, G.J. Arsenault, A.J. McAlees, D.K. Stephenson, J. Chem. Res. (S) (1984) 360–361; R. McCrindle, G. Ferguson, G.J. Arsenault, A.J. McAlees, D.K. Stephenson, J. Chem. Res. (M) (1984) 3301–3344; G.J. Arsenault, Ph.D. thesis, Guelph University, 1986.
- [34] M. Pfeffer, N. Sutter-Beydoun, A. De Cian, J. Fischer, J. Organomet. Chem. 453 (1993) 139–146.
- [35] M. Aresta, C.F. Nobile, D. Petruzzelli, M.L. Tobe, J. Chem. Soc., Dalton Trans. (1977) 493–496.
- [36] F.R.S. Clark, R.O.C. Norman, C.B. Thomas, J. Chem. Soc., Perkin Trans. 1 (1975) 121–125.
- [37] H.B. Henbest, M.J.W. Stratford, Chem. Ind. (London) (1961) 1170–1171.
- [38] J.M. Saá, M. Dopico, G. Martorell, A. García-Raso, J. Org. Chem. 55 (1990) 991–995.
- [39] DMF could also, via its product decomposition, participate to the reduction of aryl triflates [13].
- [40] Y. Coquerel, P. Brémond, J. Rodriguez, J. Organomet. Chem. 692 (2007) 4805–4808.
- [41] Y. Coquerel, J. Rodriguez, Arkivoc XI (2008) 227–237.
- [42] W. Cabri, I. Candiani, S. DeBernardinis, F. Francalanci, S. Penco, R. Santo, J. Org. Chem. 56 (1991) 5796–5800; S. Laschat, F. Narjes, L.E. Overman, Tetrahedron 50 (1994) 347–358.
- [43] J.P. Konopelski, K.S. Chu, G.R. Negrete, J. Org. Chem. 56 (1991) 1355–1357.
- [44] G.E. Stokker, Tetrahedron Lett. 28 (1987) 3179–3182.
- [45] Z.A. Khan, T. Wirth, Org. Lett. 11 (2009) 229–231.

- [46] G.K. Friestad, B.P. Branchaud, *Tetrahedron Lett.* 36 (1995) 7047–7050.
- [47] T. Hosokawa, T. Kamiike, S.-I. Murahashi, M. Shimada, T. Sugafuji, *Tetrahedron Lett.* 43 (2002) 9323–9325.
- [48] For reviews concerning the interactions of HPdX and Pd0 with oxygen, see: K.M. Gligorich, M.S. Sigman, *Angew. Chem. Int. Ed.* 45 (2006) 6612–6615; J. Muzart, *Chem. Asian J.* 1 (2006) 508–515; For a recent study that agrees with our previous assumption (J. Muzart, J.-P. Pète, *J. Mol. Catal.* 15 (1982) 373–376) concerning the reaction of HPX with O₂, see: S. Chowdhury, I. Rivalta, N. Russo, E. Sicilia, *J. Chem. Theory Comput.* 4 (2008) 1283–1292; See also: J.M. Keith, W.A. Goddard, J. Oxgaard III., *J. Am. Chem. Soc.* 129 (2007) 10361–10369; B.V. Popp, S.S. Stahl, *Chem. Eur. J.* 15 (2009) 2915–2922.
- [49] For examples of β-heteroatom eliminations from Pd-intermediates, see: R.F. Heck, *J. Am. Chem. Soc.* 90 (1968) 5535–5538; A. Kasahara, T. Izumi, N. Fukuda, *Bull. Chem. Soc. Jpn.* 50 (1977) 551–552; I. Arai, G.D. Daves Jr., *J. Org. Chem.* 44 (1979) 21–23; K. Kikukawa, M. Naritomi, G.-X. He, F. Wada, T. Matsuda, *J. Org. Chem.* 50 (1985) 299–301; B.M. Choudary, M. Ravichandra Sarma, *Tetrahedron Lett.* 31 (1990) 1495–1496; Y. Kawamura, Y. Kawano, T. Matsuda, Y. Ishitobi, T. Hosokawa, *J. Org. Chem.* 74 (2009) 3048–3053.
- [50] M. Roussel, H. Mimoun, *J. Org. Chem.* 45 (1980) 5387–5390.
- [51] R. McCrindle, G. Ferguson, G.J. Arsenault, A.J. McAlees, *J. Chem. Soc., Chem. Commun.* (1983) 571–572.
- [52] L.S. Hegeudus, *Angew. Chem., Int. Ed. Engl.* 27 (1988) 1113–1126.
- [53] V.V. Grushin, H. Alper, *Organometallics* 12 (1993) 1890–1901.
- [54] C. Amatore, E. Carré, A. Jutand, M.A. M'Barki, *Organometallics* 14 (1995) 1818–1826.
- [55] See above for the reduction of Pd(OAc)₂ with phosphines and Ref. [17].
- [56] A. Jeevanandam, K. Narkunan, Y.-C. Ling, *J. Org. Chem.* 66 (2001) 6014–6020.
- [57] A.M. Trzeciak, Z. Ciunik, J.J. Ziólkowski, *Organometallics* 21 (2002) 132–137.
- [58] A.M. Trzeciak, H. Bartosz-Bechowski, K. Niesyty, Z. Ciunik, J.J. Ziólkowski, *Can. J. Chem.* 79 (2001) 752–759.
- [59] A.A. Pletnev, Q. Tian, R.C. Larock, *J. Org. Chem.* 67 (2002) 9276–9287.
- [60] S. Cacchi, G. Fabrizi, F. Gavazza, A. Goggiamani, *Org. Lett.* 5 (2003) 289–291.
- [61] J. Le Bras, D.K. Mukherjee, S. González, M. Tristany, B. Ganchehui, M. Moreno-Mañas, R. Pleixats, F. Hémin, J. Muzart, *New J. Chem.* 28 (2004) 1550–1553.
- [62] N.A. Dhas, A. Gedanken, *J. Mater. Chem.* 8 (1998) 445–450.
- [63] L. Jia, H. Jiang, J. Li, *Chem. Commun.* (1999) 985–986; Z.-Y. Wang, H.-F. Jiang, C.-R. Qi, Y.-G. Wang, Y.-S. Dong, H.-L. Liu, *Green Chem.* 7 (2005) 582–585; Z.-Y. Wang, H.-F. Jiang, X.-Y. Ouyang, C.-R. Qi, S.-R. Yang, *Tetrahedron* 62 (2006) 9846–9854.
- [64] B. Zou, H.-F. Jiang, Z.-Y. Wang, *Eur. J. Org. Chem.* (2007) 4600–4604.
- [65] In a subsequent report, path a has not been mentioned as possibility: H.-F. Jiang, Y.-X. Shen, Z.-Y. Wang, *Tetrahedron* 64 (2008) 508–514.
- [66] S.E. Denmark, R.C. Smith, *Synlett* (2006) 2921–2928.
- [67] C.-Y. Liao, K.-T. Chan, C.-Y. Tu, Y.-W. Chang, C.-H. Hu, H.M. Lee, *Chem. Eur. J.* 15 (2009) 405–417.
- [68] F. Vollmüller, W. Mägerlein, S. Klein, J. Krause, M. Beller, *Adv. Synth. Catal.* 343 (2001) 29–33.
- [69] B. Estrine, S. Bouquillon, F. Hémin, J. Muzart, *Eur. J. Org. Chem.* (2004) 2914–2922; R. Palkovits, I. Nieddu, C.A. Kruithof, R.J.M. Klein Gebbink, B.M. Weckhuysen, *Chem. Eur. J.* 14 (2008) 8995–9005.
- [70] For telomerizations carried out in aqueous biphasic systems, it has been recently reported that NEt₃ has a negative influence due to the increase of the catalyst leaching into the organic phase: A. Behr, J. Leschinski, C. Awungacha, S. Simic, T. Knoth, *Chem. Sus. Chem.* 2 (2009) 71–76.
- [71] C. Damez, B. Estrine, A. Bessmertnykh, S. Bouquillon, F. Hémin, J. Muzart, *J. Mol. Catal. A: Chem.* 244 (2006) 93–98.
- [72] C. Amatore, A. Jutand, *Acc. Chem. Res.* 33 (2000) 314–321.
- [73] C.S. Cho, T.G. Kim, H.W. Kim, *Catal. Commun.* 10 (2009) 1482–1485.
- [74] C.S. Cho, T.G. Kim, B.T. Kim, T.-J. Kim, S.C. Shim, *J. Organomet. Chem.* 650 (2002) 65–68.