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ARTICLE

Exceptionally Efficient Catalytic Hydrodechlorination of Persistent Organic Pollutants: Application of New Sterically Shielded Palladium Carbene Complexes

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A new sterically shielded carbene with branched aromatic substituents (**9a**) and two palladium halogenide complexes (**11a,b**) have been prepared. The single crystal X-ray structures of free carbene **9a** and palladium carbene complexes **10b** and **11a** were determined. Very high catalytic efficiencies were evident for the sterically shielded palladium carbene complexes **10b** and **11a,b** when the latter complexes were employed as catalysts for hydrodechlorination of the chloroarenes *p*-dichlorobenzene and hexachlorobenzene. When optimized, the foregoing approach is significantly more effective than those of currently known transition metal carbene complexes. The most active catalysts were found to be the monocarbene complexes of palladium chloride and iodide, both of which feature highly branched aromatic substituents (**11a,b**).

Introduction

Haloarene compounds are members of a class of toxic waste that is commonly referred to as persistent organic pollutants (POPs). While haloarenes have useful applications in several important areas such as pesticides, pharmaceuticals, and some high-temperature fluids, these materials are highly toxic. Furthermore, haloarenes are resistant to environmental degradation and have accumulated in significant quantities throughout the world. The compounds that require particularly careful attention include DDT, hexachlorobenzene, dioxins, polychlorodibenzofurans, and polychlorobiphenyls.¹ Indeed, all of the foregoing compounds were included in the list of the 12 most hazardous persistent organic pollutants that was presented at the 2001 Stockholm Convention. Clearly, the safe management of these toxic POPs represents an environmental concern of paramount importance.

Several approaches have been developed for haloarene detoxification. Well established methods include combustion at high temperatures, oxidation in supercritical water, catalytic reduction with hydrogen, reduction by metals or nanometals, biodegradation, and microwave techniques.²⁻⁴ Among the foregoing methods, catalytic hydrodehalogenation offers the most promise as a cost effective solution for the neutralization of toxic POPs.

Several transition metal carbene complexes have been shown to be active with respect to hydrodehalogenation processes. In particular, palladium carbene complexes are well known to be suitable catalysts for the foregoing reactions. As an example, Nolan *et al.* demonstrated that an *in situ* generated palladium carbene catalyst based on Pd(dba)₂, potassium methoxide, and various imidazolium salts resulted in high yields of hydrodehalogenation products upon reaction in dioxane solution at 100 °C (TON up to 28–50, TOF up to 28–50 h⁻¹).⁵

As described in subsequent publications by Nolan *et al.*, complex **1** (Figure 1) was found to exhibit moderate catalytic efficiencies for the reactions of chlorobenzene at ambient temperature (TON 100, TOF 200 h⁻¹).⁶ Moreover, complex **2** was shown to be active for the hydrodehalogenation of *p*-dichlorobenzene at 60 °C (TON 194, TOF 111 h⁻¹).⁷ Interestingly, when microwave assistance was employed for the reaction with complex **2**, an even higher rate of reaction could be achieved at 120 °C. Using the latter approach, virtually quantitative yields for the hydrodechlorination of *p*-chlorotoluene and *p*-dichlorobenzene can be achieved in only 2 min (TON 4000, TOF 120000 h⁻¹ *p*-chlorotoluene; TON 3800, TOF 114000 h⁻¹ *p*-dichlorobenzene).⁷

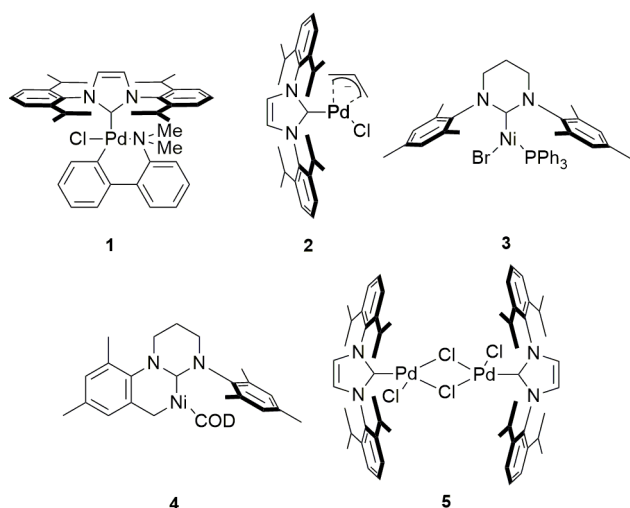


Figure 1. Palladium and nickel carbene catalysts used for hydrodehalogenation reactions

In addition to the three palladium carbene complexes discussed above, two nickel(I) complexes (Figure 1) have also been examined as potential catalysts for hydrodehalogenation processes. Unfortunately, however, the nickel(I) complex **3** proved to be ineffective for both the hydrodebromination of *p*-bromofluorobenzene and also for the hydrodechlorination of *p*-chlorofluorobenzene, both of which are activated haloarenes (TON 15–22 and TOF 4–44 h⁻¹ at 25 °C).⁸ Interestingly, however, the nickel(I) complex **4** was found to be active for the hydrodefluorination of fluorobenzenes.⁹ Taken collectively, complexes **1–4** were found to exhibit inadequate catalytic activities for the intended reactions.

Currently, the highest efficiency for the hydrodehalogenation of polyhalogenated arenes was obtained by using the dichloro-bridged dinuclear palladium carbene complex **5** that is displayed in Figure 1.¹⁰ This catalyst proved to be highly active for the hydrodehalogenation of either 1,2,4,5-tetrachlorobenzene or 2,2',3,3'-tetrachlorobiphenyl in isopropanol solution at 80 °C (TON 19650, TOF 819 h⁻¹ and TON 10000, TOF 417 h⁻¹, respectively).¹⁰

As evident from Figure 1, the existence of steric hindrance adjacent to a carbenic carbon atom plays an important role with respect to the reactivities of carbenes. With the overall objective of developing more efficient catalysts for use in the environmentally important haloarene hydrodehalogenation reaction, the present work is focused on the development of new highly sterically shielded palladium carbene complexes.

Results and Discussion

Syntheses of the stable, sterically shielded carbene **9a** and palladium carbene complexes **10b** and **11a,b**

The sterically shielded stable carbene **9a** that features branched aromatic N-substituents was synthesized in four steps as

outlined in Scheme 1. First, the sterically hindered 2,6-disubstituted aniline **6a** was prepared by treatment of 4-ethylaniline with benzhydrol in the presence of ZnCl₂ and concentrated aqueous HCl. The subsequent reaction of the bulky aniline **6a** with glyoxal in *n*-propanol solution in the presence of formic acid resulted in the formation of the corresponding diimine **7a**. In the next step, cyclization of the diimine **7a** was accomplished by treatment with paraformaldehyde in the presence of ZnCl₂ and concentrated aqueous HCl, thereby forming the 1,3-diarylimidazolium salt **8a**. Finally, treatment of the imidazolium salt **8a** with NaH in THF solution afforded the free sterically shielded stable carbene **9a** (see Supporting Information).

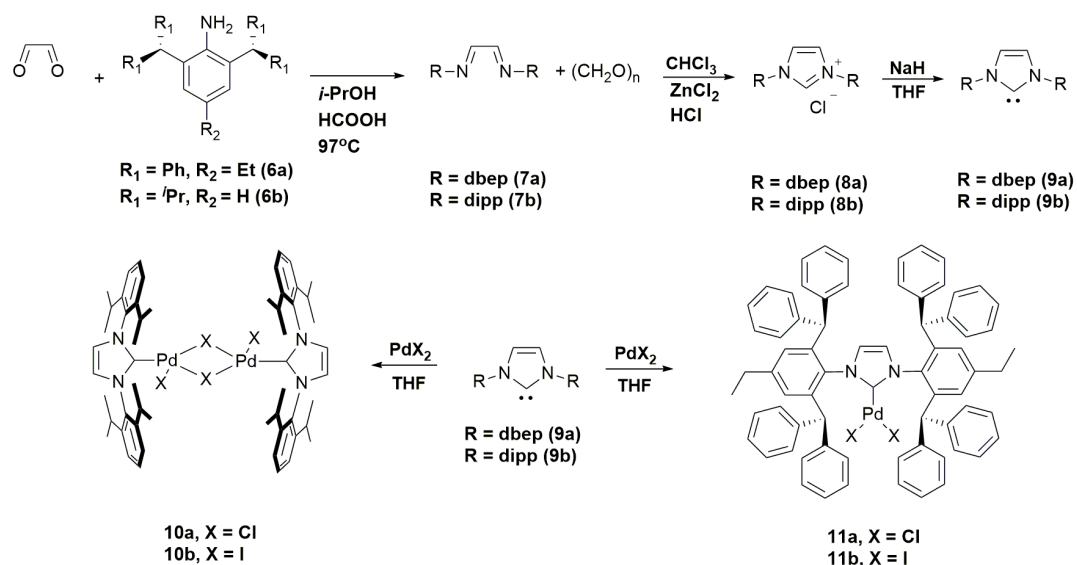
In principle, the procedure that was employed for the synthesis of the imidazolium salt **8a** is similar to that described by Marko *et al.*¹¹ The known carbene **9b** was generated from the imidazolium salt **8b** via reaction with potassium *tert*-butoxide in THF solution. The subsequent reactions of the foregoing carbenes with palladium(II) chloride or palladium(II) iodide were carried out using a 1:1 molar ratio in THF solution at room temperature according to the literature procedure.¹² The outcomes of these reactions were found to be dependent on the steric demands of the nitrogen substituents. On the one hand, the reaction of the more bulky dbep substituted carbene **9a** with palladium halogenides afforded the mononuclear carbene complexes **11a,b**. On the other hand, treatment of the less bulky dipp-substituted carbene **9b** with PdI₂ resulted in the formation of the diiodo-bridged dinuclear palladium carbene complex **10b**, and is reminiscent of the corresponding reaction with PdCl₂.¹²

Characterization of **6a–11b**

Compounds **6a–11b** were characterized by means of ¹H and ¹³C NMR spectroscopy and their compositions were established on the basis of elemental analyses. The crystal structures of **9a**, **10b**, and **11a** were determined by single crystal X-ray diffraction (see Supporting Information).

Single Crystal X-ray Diffraction Studies

Colorless single crystals of the free carbene **9a** were grown by slow evaporation of a benzene solution of **9a** and subsequently examined by X-ray diffraction. The free carbene **9a** crystallized in the P2₁/c space group of the monoclinic crystal system with two disordered benzene solvent molecules in the asymmetric unit. The crystal structure of **9a**, which is displayed in Figure 2, features a planar C(1)–N(1)–C(2)–C(3)–N(2) five-membered ring that is akin to those found for the majority of imidazol-2-ylidene rings. The plane of the central imidazol-2-ylidene moiety is oriented in an almost orthogonal fashion with respect to the planes of the flanking aryl substituents (86.24° and 87.97°). The bond angle at the carbene carbon atom is 101.5(2)°, and the existence of high bond orders of 1.61–1.63 for the C(1)–N(1) and C(1)–N(2) bonds and 1.50–1.53 for the



Scheme 1. Syntheses of sterically shielded carbenes and their respective palladium complexes (dbep = 2,6-dibenzhydryl-4-ethylphenyl)

C(2)-N(1) and C(3)-N(2) bonds imply a substantial amount of delocalization within the carbene ring structure. Interestingly, the C(2)-C(3) bond (Table 1) features a noticeably shortened bond length of 1.327(5) Å and a bond order of 2.051.

Dark red single crystals of **10b** were grown by slow vapor diffusion of hexanes into a chloroform solution of this compound. As displayed in Figure 2, complex **10b** possesses a diiodo-bridged dinuclear structure of the overall composition (LPdI₂)₂.

Complex **10b** crystallizes in the P-1 space group of the triclinic crystal system and features two diiodo-bridged

Table 1. Selected bond lengths (Å) for **9a**, **10b**, and **11a**.

Bond	9a (Å)	10b (Å)	11a (Å)
C(1)-N(1)	1.364(4)	1.347(6)	1.359(3)
C(1)-N(2)	1.368(4)	1.352(6)	
C(1)-N(1a)			1.359 (3)
C(2)-C(3)	1.327(5)	1.332 (7)	-
C(2)-C(2a)			1.340(5)
C(2)-N(1)	1.387(4)	1.378 (6)	1.394(3)
C(3)-N(2)	1.381(4)	1.387(6)	-
C(1)-Pd(1)	-	1.985(4)	1.961(4)

dinuclear structures in the asymmetric unit. Interestingly, complex **10b** exhibits a distorted I(2)-Pd(1)-I(3)-Pd(2) four-membered ring structure with a torsion angle of 157.522(16)°. Furthermore, the planes of the imidazolium and adjacent flanking dipp groups are oriented in an essentially orthogonal manner (82.0° and 86.5°).

Yellow single crystals of the palladium carbene complex **11a** were grown by slow evaporation of an acetonitrile solution and examined by single crystal X-ray diffraction. The

palladium carbene complex **11a** crystallized in the I2/a space group of the monoclinic crystal system. Complex **11a** also features a two-fold rotational axis that bisects the complex along the C(1)-Pd(1)-N(2) bond, hence only half of the complex is apparent in the asymmetric unit. In contrast to **10b**, complex **11a** possesses a mononuclear structure. The bond angle at the carbene carbon (105.4(3)°) is significantly larger than that exhibited by the free carbene **9a** (101.5(2)°). Moreover, the imidazol-2-ylidene bond lengths are similar to those measured for the free carbene **9a** (Table 1). Furthermore, the angle between the plane of the imidazol-2-ylidene ring and that of the flanking aryl substituent is more acute in **11a** (71.68°) than that in the free carbene **9a** (86.24° and 87.97°). In summary, palladium complexes **10b** and **11a** both adopt square planar geometries and feature strong Pd-C bonds and noticeably shortened Pd-Cl and Pd-I bonds (Supporting Information).

Catalytic Studies

The hydrodechlorination test reactions were performed by heating each reaction mixture containing the haloarene with potassium or sodium isopropoxide. The latter compounds had been generated from potassium or sodium *tert*-butoxide (or hydroxide) in the presence of the palladium catalyst in isopropanol solution at 80 °C. Each percent conversion was based on one chlorine atom and calculated according to the masses of the sodium or potassium chlorides. The most efficient catalysis trials were examined by means of gas chromatography. The catalytic efficiencies were estimated by using the TON and TOF values (the general procedure is described in the Supporting Information). A summary of the catalytic efficiencies of carbene complexes **10a,b** and **11a,b** with respect to the model compound *p*-dichlorobenzene and a variety of bases is presented in Table 2.

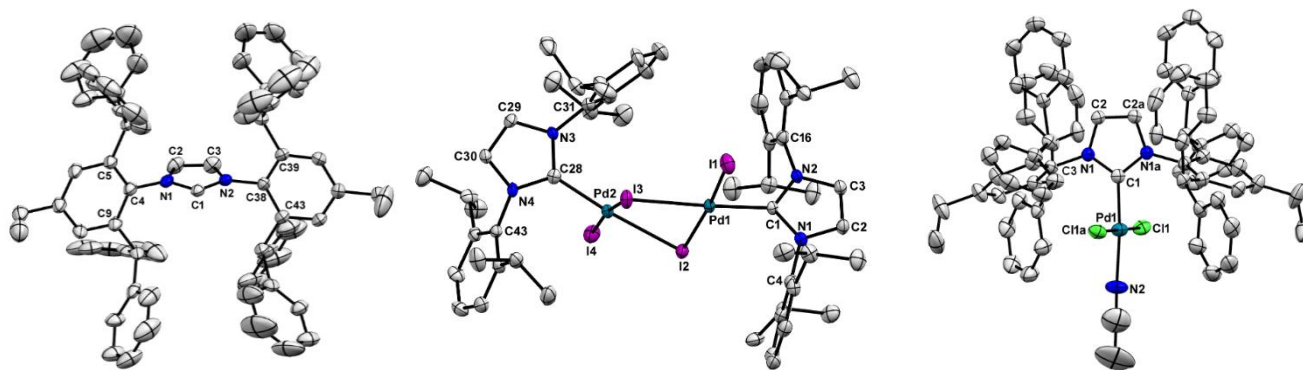


Figure 2. POV-Ray diagrams of the free carbene **9a** (left) and palladium carbene complexes **10b** (center) and **11a** (right) with thermal ellipsoids displayed at 50% probability. Compound **9a** crystallized with two disordered benzene solvent molecules and complex **10b** crystallized with two dinuclear species in the asymmetric unit, only one of which is displayed above. Complex **11a** crystallized with two disordered acetonitrile solvent molecules. All solvent molecules and hydrogen atoms have been omitted for clarity.

As evident from Table 2, the hydrodechlorination of *p*-dichlorobenzene with potassium *tert*-butoxide in the presence of catalysts **10a,b** and **11a,b** proceeded very efficiently.

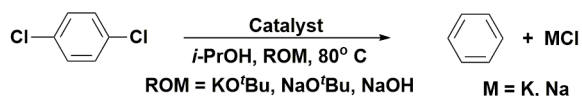


Table 2. Catalytic efficiencies of palladium catalysts **10a,b** and **11a,b** for the hydrodechlorination of *p*-dichlorobenzene

Cat.	Cat. loading (mol %)	Time (h)	Conversion (%)	TON (per Cl)	TOF (h ⁻¹)	ROM
10a	0.01	8	63	12600	1560	KO ^t Bu
10a	0.01	24	88	17600	734	KO ^t Bu
10a	0.01	24	32	6400	266	NaO ^t Bu
10a	0.01	24	96	19200	800	NaOH
10a	0.001	24	5	10000	416	NaOH
10b	0.01	24	100	20000	834	KO ^t Bu
10b	0.001	24	22	44000	1830	KO ^t Bu
10b	0.01	24	100	20000	834	NaO ^t Bu
10b	0.001	24	23	46000	1916	NaO ^t Bu
10b[*]	0.001	24	30	60000	2500	NaO ^t Bu
10b	0.01	24	100	20000	834	NaOH
10b	0.001	24	21	42000	1750	NaOH
10b[*]	0.001	24	30	60000	2500	NaOH
11a	0.001	24	70	140000	5833	KO ^t Bu
11b	0.001	24	90	180000	7500	KO ^t Bu

*The reaction was run in the presence of 1% LiO^tBu

The catalytic efficiencies of the diip-substituted complexes **10a,b** were examined initially. The known complex **10a**¹³ exhibited high TON and TOF values for the hydrodechlorination of *p*-dichlorobenzene (TON 17600, TOF 1560 h⁻¹). The catalytic efficiency increased when the known

chloride complex **10a** had been replaced by the palladium iodide complex **10b** (TON 44000, TOF 1830 h⁻¹). Upon changing the base that had been used in the reaction with sodium *tert*-butoxide (Table 2), a similar level of efficiency was evident for complex **10b** (TON 46000, TOF 1916 h⁻¹). However, the efficiency of **10b** significantly exceeded that observed for the palladium chloride complex **10a** (TON 6400, TOF 266 h⁻¹).

As the next step, the hydrodechlorination reactions of **10a,b** and **11a,b** were carried out in the presence of sodium hydroxide in an isopropanol solution. From the standpoint of haloarene neutralization, the use of the inexpensive base sodium hydroxide is of particularly importance with regard to applications in real world technology. It was found that the known complex **10a** was somewhat more effective for the reaction with sodium hydroxide (TON 19200, TOF 800 h⁻¹), than with either potassium or sodium *tert*-butoxide (TON 17600, TOF 734 h⁻¹ and TON 6400, TOF 266 h⁻¹, respectively). Moreover, complex **10b** (TON 42000, TOF 1750 h⁻¹) was significantly more effective than **10a** in the presence of NaOH.

Overall, the efficiency of **10b** is somewhat independent of the identity of the bases that were tested for use in this reaction. However, upon using 0.001 mol % of **10a**, a decrease in catalytic efficiency became evident (TON 10000, TOF 416 h⁻¹ vs. 19200 and 800 h⁻¹, respectively with 0.01 mol % of catalyst **10a**). The foregoing decrease in efficiency is possibly due to the equilibrium reaction of *i*-PrOH + NaOH ⇌ *i*-PrONa + H₂O that generates water and thereby deactivates this complex, particularly at lower catalyst concentrations. Interestingly, the catalytic efficiency of complex **10b** increased in the presence of a small quantity of lithium *tert*-butoxide (1 mol %) (TON 60000, TOF 2500 h⁻¹ vs. 42000 and 1750 h⁻¹ respectively for complex **10b** without the additive).

The sterically shielded palladium carbene complexes with branched aromatic N-substituents, **11a,b**, proved to be significantly more efficient than **10a,b**. The catalytic trials that

were carried out using **11a,b** with potassium *tert*-butoxide (Table 2) exhibited excellent efficiencies and increased TON values of 140000 and 180000 and TOF values of 5833 h⁻¹ and 7500 h⁻¹, respectively.

The most effective catalysts were found to be **10b** and **11a,b**, as determined on the basis of the model hydrodechlorination reactions with *p*-dichlorobenzene. Subsequently, **10b** and **11a,b** were examined for the hydrodechlorination of the known POP hexachlorobenzene. The pertinent catalytic data obtained in this study can be found in Table 3. The catalysts **10b** and **11a,b** displayed excellent efficiencies for the hydrodechlorination of hexachlorobenzene with TON and TOF values that ranged from 88000–318000 and 3667–13350 h⁻¹, respectively. Reactions that resulted in 100% conversion, as estimated by mass analysis of the metal halide precipitates, were confirmed by means of gas chromatography, which did not detect any intermediates or initial haloarenes.

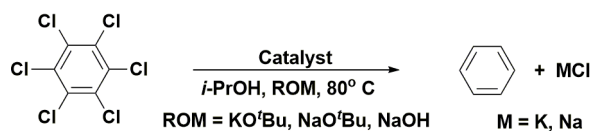
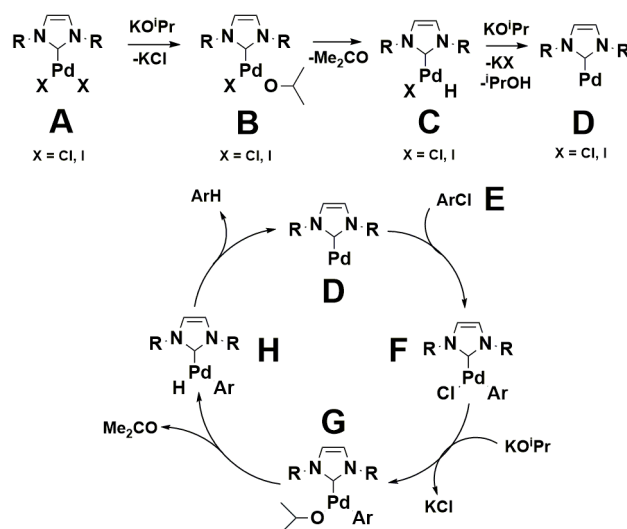


Table 3. Catalytic efficiencies of palladium catalysts **10a,b** and **11a,b** for the hydrodechlorination of hexachlorobenzene

Cat.	Cat. load. (mol %)	Time (h)	Conv. (%)	TON (per Cl)	TOF (h ⁻¹)	ROM
10b	0.01	24	100	60000	2500	KO ^t Bu
10b	0.01	24	66	39600	1650	NaOH
10b	0.003	24	44	88000	3667	KO ^t Bu
11a	0.001	24	35	210000	8750	KO ^t Bu
11a	0.005	24	100	120000	5000	KO ^t Bu
11b	0.001	24	53	318000	13350	KO ^t Bu
11b	0.004	24	100	150000	6250	KO ^t Bu

To the best of our knowledge, the catalytic efficiencies that were determined for complexes **11a,b** represent the highest efficiencies reported to date for the hydrodehalogenation of polyhaloarenes (TON 210000 – 318000, TOF 8750 – 13350 h⁻¹). Quantitative conversion per chlorine atom was achieved after 24 h with catalyst concentrations of 0.004 – 0.005 mol%. When comparing the efficiencies of **10b** and **11a,b** for the hydrodehalogenation of hexachlorobenzene, the best known catalyst (**10a**) was found to exhibit lower catalytic efficiencies for the reactions involving 1,2,4,5-tetrachlorobenzene (TON 19700, TOF 821 h⁻¹), 2,2',3,3'-tetrachlorobiphenyl (TON 10000, TOF 420 h⁻¹), and decachlorobiphenyl (TON 1000, TOF 42 h⁻¹).¹⁰ The best catalysts, **11a,b**, exceeded the maximum level of efficiency for **10a** by a factor of 10 – 16 times. Furthermore, catalysts **11a,b** required only a 0.001 – 0.005 mol percent concentration in order to function efficiently as compared with **10a** which is only active in the concentration range of 0.01–0.04 mol percent.

The proposed mechanism for the haloarene hydrodehalogenation reaction (Scheme 2)^{14, 15} involves initial reaction of the pre-catalyst **A** with potassium isopropoxide (that was generated from potassium or sodium *tert*-butoxide or hydroxide) to form the alkoxide derivative **B**. In the next step, the latter complex underwent β-hydride elimination, thereby releasing acetone and generating the hydridic palladium species **C**. The subsequent reaction of the hydridic species **C** with potassium *tert*-butoxide resulted in formation of the active palladium(0) complex **D**. Subsequent activation of the C–Cl bond in the haloarene compound **E** by complex **D** resulted in oxidative addition and the formation of complex **F**.



Scheme 2. Proposed mechanism for haloarene hydrodehalogenation

The reaction of complex **F** with potassium isopropoxide afforded the alkoxide complex **G**. Following this, an analogous β-hydride elimination step occurred, thereby generating the hydridic species **H**. Finally, reductive elimination resulted in formation of the protonated arene compound and regeneration of the active catalyst palladium(0) complex **D**.

Based on previous studies of related sterically shielded 1,2,4-triazol-5-ylidene systems,¹⁶ an important stage in the foregoing process may involve interaction of the initial precatalyst **A** with the metal isopropoxide. This reaction should be more facile for the iodide complexes than for the corresponding chloride analogues. As might be expected, the stabilities of these complexes depend on the extent of steric congestion.

In summary, it is noteworthy that highest catalytic activities for hydrodehalogenation to date have been achieved by the development of new palladium complexes with sterically shielded 1,3-diarylimidazol-2-ylidene ligands that feature two bulky, branched aromatic *N*-substituents, namely **11a,b**. A plausible reason for the dramatic increases in catalytic activities that were observed for the sterically shielded carbene complexes **11a,b** (in comparison with those of their dip-substituted counterparts **10a,b**) could be attributed to

stabilization of the Pd(0) complex **D** on account of the steric protection afforded by the bulky carbene ligand. Another important contributor to this enhancement of catalytic efficiency is the presence of iodide as the second ligand (**10b**, **11b**) (chloride ligands typically exhibit lower catalytic efficiencies than those of iodide-containing complexes). In summary, the excellent activities that were observed for **11a,b** at very low mol percent catalyst loadings imply that **11a,b** represent a realistic and efficient technology for the remediation of haloarene POPs.

Conclusions

A new sterically shielded stable carbene of the imidazole series with highly branched aromatic N-substituents (**9a**) has been synthesized and structurally authenticated by means of a single crystal X-ray diffraction study. The X-ray crystal structures of the palladium carbene complexes **10b** and **11a** were also determined. It was discovered that complexes **10b** and **11a,b** serve as highly efficient catalysts for the hydrodehalogenation of both hexachlorobenzene and *p*-dichlorobenzene. Moreover, each catalyst proved to be effective at very low mol percent catalyst loadings. Furthermore, the catalytic efficiencies of complexes **10b** and **11a,b** were found to be significantly superior for the hydrodehalogenation reaction of hexachlorobenzene than those of *p*-dichlorobenzene. In summary, complexes **11a,b** represent excellent candidates for the effective waste management of haloarene POPs. Finally, the sterically shielded imidazol-2-ylidene palladium iodide complex **11b** was found to exhibit the highest efficiency for the hydrodehalogenation reaction that has been reported to date and significantly exceeds the efficiencies of the current literature values of the known complex **10a** and its iodide analogue **10b**.

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References

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† Electronic Supplementary Information (ESI) available: Experimental procedures for the preparation of compounds **6a,7a,8a,9a,10b,11a,b** and for the catalytic reaction; ¹H and ¹³C NMR spectra; X-ray crystallographic data and CIF files for **9a**, **10b**, **11a**; CCDC 1009073 (**9a**), 1009074 (**10b**), 1009075 (**11b**).

- 1 T. I. Gorbunov, V. I. Saloutin, O. N. Chupakhin, *Rus. Chem. Rev.*, 2010, **79**, 565 (rus).
- 2 F. Alonso, I. Beletskaya, M. Yus, *Chem. Rev.*, 2002, **102**, 4009-4091.
- 3 C. L. Geiger, K. Carvalho-Knighton, S. Novaes-Card, P. Maloney, R. DeVor, In *Environmental Applications of Nanoscale and Microscale Reactive Metal Particles / ACS Symposium Series*; American Chemical Society: Washington, DC, 2010.
- 4 W. M. Czaplik, S. Grupe, M. Mayer, A. J. von Wangelin, *Chem. Commun.*, 2010, **46**, 6350.
- 5 M. S. Viciu, G. A. Grasa, S. P. Nolan, *Organometallics*, 2001, **20**, 3607.
- 6 O. Navarro, N. Marion, Y. Oonishi, R. A. Kelly, S. P. Nolan, *J. Org. Chem.*, 2006, **71**, 685.
- 7 O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan, *J. Org. Chem.*, 2004, **69**, 3173.
- 8 C. J. E. Davies, M. J. Page, C. E. Ellul, M. F. Mahon, M. K. Whittlesey, *Chem. Commun.*, 2010, **46**, 5151.
- 9 S. Kuhl, R. Schneider, Y. Fort, *Adv. Synth. Catal.* 2003, **345**, 341.
- 10 S. Akzinnay, F. Bisaro, C. S. J. Cazin, *Chem. Commun.*, 2009, **45**, 5752.
- 11 G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek, I. E. Marko, *Dalton Trans.*, 2010, **39**, 1444.
- 12 N. I. Korotkikh, V. Sh. Saberov, A. V. Kiselev, N. V. Glinyanaya, K. A. Marichev, T. M. Pekhtereva, G. V. Dudarenko, N. A. Bumagin, and O. P. Shvaika, *Chem. Heter. Comp.*, 2012, **47**, 1551.
- 13 M. S. Viciu, R. M. Kissling, E. D. Stevens, S. P. Nolan, *Org. Lett.*, 2002, **4**, 2229.
- 14 (a) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* 2007, **107**, 5606; (b) N-Heterocyclic Carbenes in Synthesis / Ed. by S. P. Nolan.– Weinheim: Wiley VCH Verlag GmbH & Co KgaA, 2006, 68; (c) J. Izquierdo, G. E. Hutson, D. T. Cohen, K. A. Scheidt, *Angew. Chem. Int. Ed.* 2012, **51**, 11686. (d) M. J. Fuchter, *Chem. Eur. J.* 2010, **16**, 12286; (e) P.-C. Chiang, J. Y. W. Bode, in *RSC Catalysis Series №. 6: N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools/ Edited by Silvia Díez-Gonzalez / Royal Society of Chemistry*, 2013, Chap. 14, 399.
- 15 N. I. Korotkikh, O. P. Shvaika, Carbene and carbene complex catalysis of organic reactions, Donetsk, DonNU, 2013, 372 p (ukr.).
- 16 N. V. Glinyanaya, V. Sh. Saberov, N. I. Korotkikh, A. H. Cowley, R. R. Butorac, D. A. Evans, T. M. Pekhtereva, A. F. Popov, O. P. Shvaika, *Dalton Trans.*, 2014 (accepted), DOI: 10.1039/c4dt01353k