Synthesis, Structure, and Reductive Elimination Reactions of the First (*σ*-Aryl)palladium Complex Stabilized by IPr N-Heterocyclic Carbene†

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Summary: The first (σ-aryl)palladium complex stabilized with one IPr N-heterocyclic carbene and one PPh_3 ligand has been synthesized via a novel method, structurally characterized, and found to undergo remarkably facile C−C reductive elimination of the 2-phenylimidazolium cation via phosphine predissociation.

Nucleophilic N-heterocyclic carbenes (NHC)[1] represent a new class of ligands which have already demonstrated exceptional utility in catalysis with metal complexes.[2] Among numerous successful applications of NHC ligands are highly efficient Pd-catalyzed amination, Heck olefin arylation, and coupling (Stille, Kumada, and Suzuki) reactions of chloroarenes.[2−4] As has been demonstrated by Nolan and co-workers,[4,5] *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) is particularly efficient for important Pd-catalyzed transformations of most unreactive aryl chlorides. At the same time, the catalysis-related mechanistic organometallic chemistry of NHC-stabilized Pd aryls still remains in its early infancy, mostly due to the lack of efficient methods to prepare such complexes.[6] The synthesis of NHC Ar−Pd species usually employs oxidative addition of haloarenes to NHC-stabilized Pd(0). These oxidative addition reactions normally require elevated temperatures, at which the desired organopalladium products most often undergo partial or complete decomposition.[6b,c] In this communication, we report a new, totally different approach to the synthesis of (*σ*-aryl)- and (*σ*-alkyl)-palladium NHC complexes under mild conditions.

Arylpalladium complexes with NHC = IPr have not been reported,[7] although studying their structure and reactivity might bear important implications for catalysis. Most active catalysts are obtained at a Pd to IPr ratio of 1,[4,5] indicating that the catalytic reactions are mediated by *mono*carbene Pd species. Thus, after the Ar−Cl oxidative addition step the key Pd(II) aryl intermediate should contain one IPr ligand in addition to the Ar and Cl on the metal. Herein we describe the synthesis, structure, and solution behavior of the first IPr chloro Pd aryl species, [(IPr)Pd(PPh_3)(Ph)Cl] (**1**), and its unexpectedly facile C−C reductive elimination of $[IPrPh]^+Cl^-$ via PPh_3 predissociation.

We found that *N*,*N*′-bis(2,6-diisopropylphenyl)imidazolium chloride ($[IPrH]^+Cl^-$) reacted with $[(Ph_3P)_2Pd_2(Ph)_2(\mu\text{-}OH)_2]$ in benzene to give **1**,[8] which was isolated as a 1:1 benzene solvate in 66% yield (eq 1). A *σ*-methyl analogue of **1**, [(IPr)Pd(PPh_3)(Me)Cl] (**2**),[9] was prepared similarly in 47% yield from $[(Ph_3P)_2Pd_2(Me)_2(\mu\text{-}OH)_2]$ and $[IPrH]^+Cl^-$. Reaction 1 represents a novel method for the synthesis of (*σ*-organo)palladium NHC complexes. It formally involves substitution of the hydroxo ligands on Pd with the Cl^-, followed by deprotonation of the imidazolium cation with the OH^- released to generate the carbene that coordinates to the metal. Possibly, NHC complexes of other transition metals may be prepared using the same approach, from the corresponding hydroxo or alkoxo species.

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(6) (a) There has been one, very recent literature example of a fully characterized NHC-stabilized arylpalladium complex, $[(NHC)_2Pd(4\text{-}CH_3C_6H_4)Cl]$, where NHC = *N*,*N*′-di-*tert*-butylimidazol-2-ylidene (no reactivity/stability data reported).[6b] Another NHC Pd aryl, $[(tmiy)_2Pd(Ph)I]$ (tmiy = 1,3,4,5-tetramethylimidazolin-2-ylidene), has been characterized in a mixture of products but never isolated pure.[6c] A structurally characterized *non*-NHC carbene (σ-C_6F_5)Pd complex has been described.[6d] (b) Caddick, S.; Cloke, F. G. N.; Hitchcock, P. B.; Leonard, J.; Lewis, A. K. d. K.; McKerrecher, D.; Titcomb, L. R. *Organometallics* **2002**, *21*, 4318. (c) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596. (d) Albéniz, A. C.; Espinet, P.; Manrique, R.; Pérez-Mateo, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 2363.

(7) For two structurally characterized IPr *non*-aryl Pd complexes, $[(IPr)_2Pd_2Cl_2(\mu\text{-}Cl)_2]$ and [(IPr)Pd(allyl)Cl], see refs 5h and 5i, respectively.

(8) NMR data for **1**. ^1H NMR (C_6D_6, ppm): δ 0.8 (d, 6.8 Hz, 3H, CH_3), 0.9 (d, 6.8 Hz, 3H, CH_3), 1.2 (d, 6.8 Hz, 3H, CH_3), 1.7 (d, 6.8 Hz, 3H, CH_3), 2.7 (sept, 6.8 Hz, 2H, *i*-Pr CH), 4.3 (sept, 6.8 Hz, 2H, *i*-Pr CH), 6.2−7.8 (m, 28H, arom H). ^{31}P NMR (C_6D_6, ppm): δ 23.9 (s). ^1H NMR (CD_2Cl_2, ppm): δ 0.7 (d, 6.8 Hz, 3H, CH_3), 0.9 (d, 6.8 Hz, 3H, CH_3), 1.2 (d, 6.8 Hz, 3H, CH_3), 1.6 (d, 6.8 Hz, 3H, CH_3), 2.6 (sept, 6.8 Hz, 2H, *i*-Pr CH), 3.9 (sept, 6.8 Hz, 2H, *i*-Pr CH), 6.1 (m, 4H, Ph *o*,*m*-H), 6.3 (m, 1H, Ph *p*-H), 7.0−7.7 (m, 23H, arom H). ^{31}P NMR (CD_2Cl_2, ppm): δ 24.3 (s). Anal. Calcd for $C_{51}H_{56}ClN_2PPd$: C, 70.4; H, 6.5; N, 3.2. Found: C, 70.2; H, 6.6; N, 3.2.

(9) NMR data for **2**. ^1H NMR (C_6D_6, ppm): δ −0.1 (d, 7.2 Hz, 3H, Pd−CH_3), 0.9 (br d, 6.6 Hz, 3H, CH_3), 1.0 (br d, 6.6 Hz, 3H, CH_3), 1.1 (br d, 6.6 Hz, 3H, CH_3), 1.7 (br d, 6.6 Hz, 3H, CH_3), 3.0 (br m, 2H, *i*-Pr CH), 4.0 (br m, 2H, *i*-Pr CH), 6.6−7.7 (m, 23H, arom H). ^{31}P NMR (C_6D_6, ppm): δ 30.5 (s). Anal. Calcd for $C_{46}H_{54}ClN_2PPd$: C, 68.4; H, 6.7; N, 3.5. Found: C, 68.0; H, 6.7; N, 3.5.

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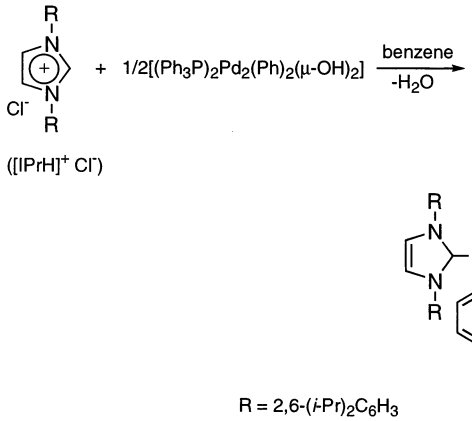


The formation of **1** (eq 1) occurred via a Pd phosphine intermediate, whose formation and eventual disappearance could be followed by ^{31}P NMR (s, 25.1 ppm). Intermediate-enriched solutions in C_6D_6 (at early stages of the reaction) were analyzed by ^{1}H, ^{13}C, and ^{31}P NMR in order to elucidate the structure of this species. It was established that the intermediate is not [$(Ph_3P)_2$Pd(Ph)Cl], which exhibits characteristic ^{1}H NMR signals from the σ-phenyl ligand.[10] The presence of a sharp *singlet* at ca. −3 ppm in the ^{1}H NMR spectrum allowed for tentative formulation of the intermediate as [(IPr)Pd(PPh_3)(Ph)(OH)]. No intermediate was detected during the preparation of the σ-methyl complex **2** using the same protocol.

The structure of **1** was established by X-ray diffraction (Figure 1).[11] The deviations from the mean plane defined by Pd1−C2−C6−P1−Cl1 are considerable, being 0.006, −0.170, 0.169, 0.184, and −0.189 Å, respectively. This distortion from the expected square-planar geometry toward tetrahedral is likely due to the presence of the bulky IPr ligand. As in a series of complexes of the type [(NHC)(PR_3)PdI_2][12] and [(carbene)(PR_3)Pd(C_6F_5)X] (X = Br, Cl)[6d] the IPr and the second bulkiest ligand (PPh_3) on Pd in **1** are mutually trans.

In an attempt to prepare the iodo analogue of **1**, reaction 1 was repeated with [IPrH]$^+$I$^-$ (obtained by precipitation with KI from a warm aqueous solution of [IPrH]$^+$Cl$^-$). Unlike reaction 1, the reaction of [IPrH]$^+$I$^-$ was not selective and the desired complex [(IPr)Pd(PPh_3)(Ph)I] was not isolated. After several hours a solid began to precipitate, which was isolated and identified (Figure 2) as 2-phenyl-IPr iodide ([IPrPh]$^+$I$^-$),[13] i.e., the product of C−C reductive elimination from the presumably generated [(IPr)Pd(PPh_3)(Ph)I]. Furthermore, it was also found that, while being stable in benzene, **1** readily undergoes C−C reductive elimination in dichloromethane at 20 °C to give 2-phenyl-IPr chloride, [IPrPh]$^+$Cl$^-$ (eq 2). This is the first example of C−C

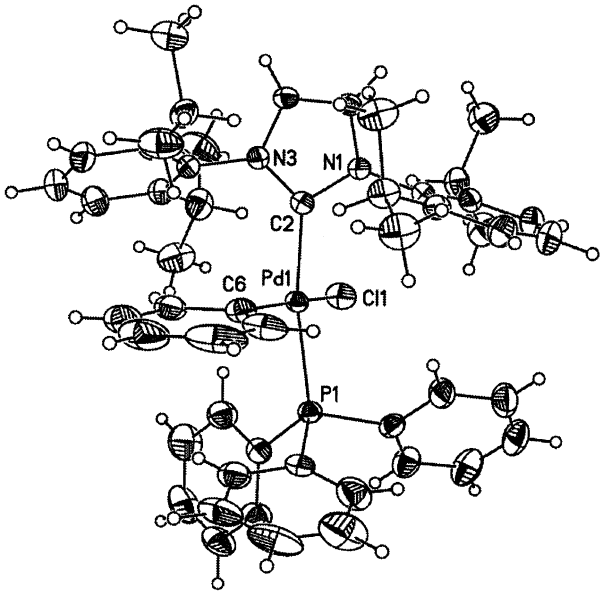
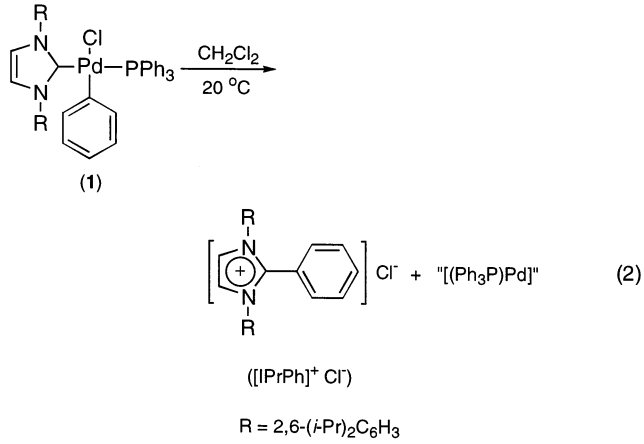


Figure 1. ORTEP drawing of [(IPr)(Ph_3P)Pd(Ph)Cl] (**1**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pd−C(2) = 2.057(2), Pd−C(6) = 2.008(2), Pd−Cl = 2.404(1), Pd−P = 2.307(1); C(2)−Pd−C(6) = 94.34(8), C(6)−Pd−P = 90.98(6), C(2)−Pd−Cl = 88.54(5), P−Pd−Cl = 87.66(2), C(2)−Pd−P = 169.96(5), C(6)−Pd−Cl = 169.99(7).

reductive elimination of a phenyl and an NHC ligand from a well-defined individual Pd complex. A few Ar−NHC reductive elimination reactions from Pd species that were not isolated but rather generated in situ have been reported.[6b,c]



A series of preliminary ^{1}H NMR experiments were carried out to follow the decomposition of **1** in CD_2Cl_2 by the appearance and change in the intensity of the *i*-Pr resonances[8,13] from the [IPrPh]$^+$ cation vs those

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(11) Crystal data for **1**·C_6H_6: Bruker SMART 1K CCD diffractometer, M_r = 947.91, monoclinic, *C*2/*c*, a = 19.216(3) Å, b = 13.443(3) Å, c = 39.187(7) Å, β = 104.164(6)°, V = 9815(3) Å^3, Z = 8, D_c = 1.283 Mg m^{-3}, T = 173(1) K, μ = 0.50 mm^{-1}, 71 009 reflections measured (3.74 < 2θ < 56.56°), 12 018 independent (R_{int} = 0.0392), SADABS correction, R1 = 0.0342 (for 12 018 reflections with $I > 4\sigma(I)$) and 0.050 (all data), wR2 = 0.0805 for 567 parameters with no restraints. The structure has been deposited with the Cambridge Crystallographic Data Center (CCDC reference number: 200331).

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(13) ^{1}H NMR data for [IPrPh]$^+$I$^-$ (CD_2Cl_2, ppm): δ 1.1 (d, 6.8 Hz, 6H, CH_3), 1.3 (d, 6.8 Hz, 6H, CH_3), 2.5 (sept, 6.8 Hz, 4H, *i*-Pr CH), 7.0 (d m, 2H, Ph *o*-H), 7.3 (t, 2H, Ph *m*-H), 7.4 (d, 7.9 Hz, 4H, *i*-$Pr_2C_6H_3$ *m*-H), 7.5 (tm, 1H, Ph *p*-H), 7.65 (t, 7.9 Hz, 2H, *i*-$Pr_2C_6H_3$ *p*-H), 8.1 (s, 2H, imid H). Crystal data for [IPrPh]$^+$I$^-$: Rigaku RU300 diffractometer, M_r = 592.58, triclinic, $P\bar{1}$, a = 10.171(2) Å, b = 10.632(2) Å, c = 16.599(3) Å, α = 83.11(3)°, β = 104.164(6)°, γ = 61.63(3)°, V = 1568.1(5) Å^3, Z = 2, D_c = 1.255 Mg m^{-3}, T = 173(1) K, μ = 1.04 mm^{-1}, 8900 reflections measured (2.48 < 2θ < 48.20°), 4570 independent (R_{int} = 0.0464), R1 = 0.0349 (for 4570 reflections with $I > 4\sigma(I)$), 0.0374 (all data), wR2 = 0.0969 for 334 parameters with no restraints. The structure has been deposited with the Cambridge Crystallographic Data Center (CCDC reference number: 200332).

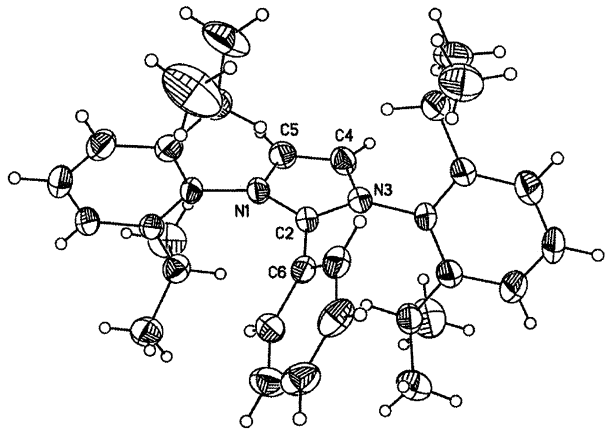

Figure 2. ORTEP drawing of $[IPrPh]^+I^-$ (cation only) with thermal ellipsoids drawn at the 50% probability level.

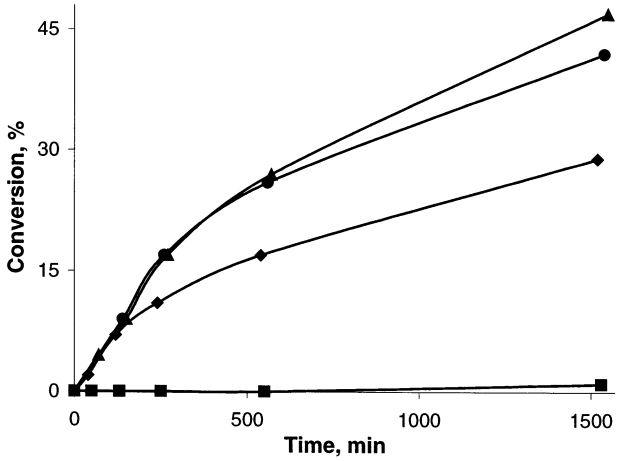

Figure 3. Reductive elimination of $[IPrPh]^+Cl^-$ from $[(Ph_3P)(IPr)Pd(Ph)Cl]$ (**1**) in CD_2Cl_2 at 20 °C: (◆) [**1**] = 2.3 × 10^{-3} M; (■) [**1**] = 2.3 × 10^{-3} M + $[PPh_3]$ = 4.6 × 10^{-3} M; (●) [**1**] = 2.3 × 10^{-3} M + [PPN-Cl] = 4.6 × 10^{-3} M; (▲) [**1**] = 0.4 × 10^{-3} M.

from **1** (Figure 3). As seen from Figure 3, reaction 2 occurred faster at a lower concentration of **1** and was almost completely inhibited in the presence of 2 equiv of PPh_3. These observations provided strong evidence for phosphine dissociation from **1** prior to the C−C reductive elimination. In sharp contrast, the Me-tmiy reductive elimination from cationic $[(PR_3)_2Pd(tmiy)(Me)]^+$ (tmiy = 1,3,4,5-tetramethylimidazolin-2-ylidene) has been reported to occur *without* phosphine predissociation.[14] On the other hand, the closely related reductive elimination of $[Ph_4P]^+X^-$ from $[(Ph_3P)_2Pd(Ph)X]$ (X = I, Br, Cl) does involve dissociation of one of the two phosphines.[15,16]

The accelerating effect of [PPN]Cl (Figure 3) is likely due to an increase in the ionizing power of the reaction medium, which lowers the activation energy barrier to the polar transition state.[16] Indeed, the solvent effect on the rate of reaction 2 follows the well-pronounced trend $C_6H_6 \ll CH_2Cl_2 < CH_2Cl_2$/[PPN]Cl. Another remarkable similarity in the reductive elimination of $[IPrPh]^+$ and $[Ph_4P]^+$ from the Pd centers is that both reactions occur more readily for the iodo than for the chloro complexes: i.e., $[(IPr)Pd(PPh_3)(Ph)I]$ vs $[(IPr)Pd(PPh_3)(Ph)Cl]$ (see above) and $[(Ph_3P)_2Pd(Ph)I]$ vs $[(Ph_3P)_2Pd(Ph)Cl]$.[16] This halide effect is best rationalized in terms of the longer Pd−P bonds in, and hence more facile phosphine dissociation from, the iodo rather than chloro Pd complexes.[16]

In conclusion, the first (σ-aryl)palladium complex containing the IPr ligand, $[(IPr)Pd(PPh_3)(Ph)Cl]$ (**1**), has been synthesized by a novel method and fully characterized in the solid state and in solution. Evidence has been obtained for phosphine dissociation from **1** prior to facile C−C reductive elimination, which may be considered as an important route to catalyst deactivation.

Supporting Information Available: Full details of the X-ray crystallographic studies of **1**·C_6H_6 and $[IPrPh]^+I^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

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