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Divalent Palladium and Platinum Complexes Containing Rigid Bidentate Nitrogen Ligands and Electrochemistry of the Palladium Complexes¹

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The synthesis and characterization of divalent palladium and platinum complexes of the type $\text{PdX}_2(\text{Ar-BIAN})$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OC}(\text{O})\text{Me}$), $\text{PdCl}_2(\text{Ph-BIC})$ and $\text{PtCl}_2(\text{Ar-BIAN})$ is described. These complexes contain the rigid bidentate nitrogen ligands bis(arylimino)acenaphthene (Ar-BIAN; Ar = Ph, *p*-MeC₆H₄, *p*-MeOC₆H₄, *o,o'*-Me₂C₆H₃, *o,o'*-*i*-Pr₂C₆H₃) or bis(phenylimino)camphane (Ph-BIC), which act as σ -donor ligands to the metal center, as was deduced from the observed shifts in the IR and NMR spectra of the complexes. Electrochemical reduction of $\text{PdCl}_2(\text{Ar-BIAN})$ complexes in THF or DMF occurs via two one-electron reductions and affords the complex $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})^{\bullet-}$, which slowly produces some $\text{Pd}^0(\text{Ar-BIAN})$ complex. $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})^{\bullet-}$ reacts with iodomethane, whereas with iodobenzene or bromobenzene no reaction was observed. $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})^{\bullet-}$ reacts with free Ar-BIAN or the alkenes dimethyl fumarate, dimethyl maleate, and methyl acrylate, giving complexes of the formulas $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})_2^{\bullet-}$ and $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})(\text{alkene})^{\bullet-}$, respectively. A two-electron reduction of the latter afforded $\text{Pd}^0(\text{Ar-BIAN})_2^{2-}$ and $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})^{2-}$, respectively, whose further oxidation in two one-electron steps produces $\text{Pd}^0(\text{Ar-BIAN})_2$ and $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$. The $\text{Pd}^0(\text{Ar-BIAN})$ complex which is slowly formed from $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})^{\bullet-}$ reacts with alkene but directly affords the complexes $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})^{\bullet-}$ because $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$ complexes are formed at a potential more negative than their first reduction potential. Reoxidation of $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})^{\bullet-}$ affords $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$ complexes. The results of the electrochemical experiments corroborate earlier mechanistic proposals of exchange of Ar-BIAN ligands in $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$ complexes and homogeneous hydrogenation of electron-poor alkenes by $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$ complexes.

Introduction

Divalent palladium and platinum complexes are valuable catalyst precursors and have been used in a wide variety of reactions, including carbonylation of alkenes, organic halides, and nitroaromatic compounds,² C–C cross coupling,³ allylic alkylation,⁴ and Heck type reactions.⁵ A general feature of most of these reactions is

the in situ reduction of the catalyst precursor, leading to a formal 14-electron zerovalent complex which undergoes oxidative addition of one of the reacting substrates. In situ reduction of Pd(II) precursors by $\text{Al}(\text{i-Bu})_2\text{H}^{3h}$ or $\text{Li}_2(\text{cyclooctatetraene})^6$ prior to further reactions has been reported. The formation of a Pd(0) complex from the $\text{Pd}(\text{OC}(\text{O})\text{Me})_2/\text{PPh}_3$ system has been elucidated by electrochemistry.⁷

We have recently demonstrated the activity of divalent palladium complexes containing the rigid bidentate nitrogen ligands bis(arylimino)acenaphthene (Ar-BIAN) in catalytic cross coupling reactions of organic halides with organomagnesium and -zinc compounds, whereas similar reactions employing organotin reagents were more effectively catalyzed by zerovalent complexes of the type $\text{Pd}(\text{Ar-BIAN})(\text{alkene})$.⁸ The use of such zerovalent catalyst precursors limits the applicability of the coupling reaction, as now the first step of the reaction is oxidative addition of the organic halide to a 16-electron $\text{Pd}(\text{Ar-BIAN})(\text{alkene})$ species. Because of

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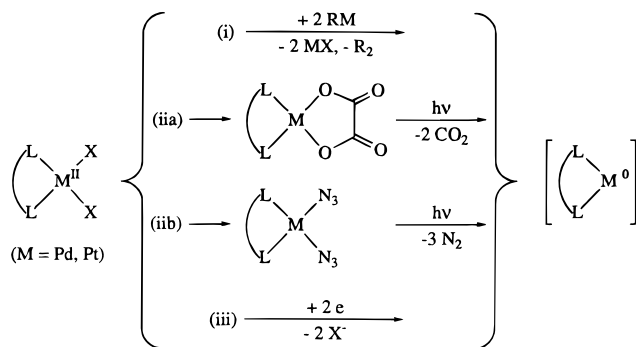
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Scheme 1

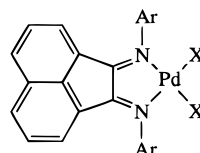
steric and electronic reasons, such a complex can be anticipated to be much less reactive than an in situ generated Pd(Ar-BIAN) complex and cross coupling is only observed for relatively reactive organic halides,^{8a,b} which are able to undergo the oxidative addition reaction.⁹ This is evidenced by our observations that e.g. benzyl chloride and β -bromostyrene do not give appreciable conversion in the Pd(Ar-BIAN)-catalyzed cross coupling with organotin reagents. On the other hand, ready conversion of these substrates was achieved with organomagnesium and -zinc reagents in the presence of 1 mol % of a PdCl₂(Ar-BIAN) catalyst,^{8a,b} as in these latter cases a transient reactive 14-electron Pd⁰(Ar-BIAN) complex is formed in situ.

In view of the high reactivity of 14-electron zerovalent PdL₂ complexes toward oxidative addition, we have investigated the possibility of in situ generation of low-coordinated Pd⁰(Ar-BIAN) complexes and subsequent reactions of such species. Available methods for the in situ generation of these complexes are (Scheme 1) (i) chemical reduction of divalent palladium or platinum complexes, e.g. with organolithium or -aluminum compounds¹⁰ or with fluoride anion,¹¹ (ii) photochemical extrusion of CO₂ or N₂ from M(II) complexes containing oxalate¹² or azide¹³ ligands, respectively, and (iii) electrochemical reduction of the divalent halide complexes.^{14,15}

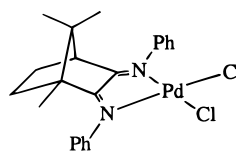
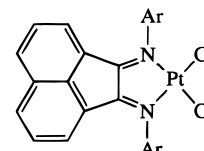
We have used electrochemistry to generate and study reduced Pd(Ar-BIAN) complexes, as this method has several important advantages as compared to the other methods. First, the palladium dihalide complexes which are conveniently synthesized in high yields can be used directly, whereas for photochemical reduction of Pd-oxalate or Pd-azide complexes additional synthetic modifications are required.^{12,13} Second, the potential of the reduction can be controlled and the formation and

subsequent reaction(s) of the complexes monitored by cyclic voltammetry. Furthermore, only the palladium complex and the reacting species are present during the reaction, whereas in the case of chemical reduction always several reagents are present, which might give rise to side reactions.

In this paper we report the results of our studies on the electrochemical behavior of PdCl₂(Ar-BIAN) complexes and the reactivity of the complexes formed after reduction toward alkenes, free Ar-BIAN, and some organic halides. Furthermore, the synthesis and characterization of these and related PdX₂(Ar-BIAN) (X = Cl, Br, I, OC(O)Me), PdCl₂(Ph-BIC) (Ph-BIC = bis(phenylimino)camphane) and PtCl₂(Ar-BIAN) complexes **1–5** are described.



- 1 X = Cl
2 X = Br
3 X = I
4 X = OC(O)Me

**1f****5**

Experimental Section

All syntheses were performed in air, unless noted otherwise. ¹H NMR spectra were recorded on a Bruker AMX 300 (300.13 MHz) and a Bruker AC 100 (100.13 MHz) spectrometer and ¹³C NMR spectra on a Bruker AMX 300 spectrometer (75.48 MHz). Chemical shift values are in ppm relative to TMS as external standard with high-frequency shifts denoted as positive. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Mass spectra were obtained on a Varian MAT 711 double-focusing spectrometer and were performed by the Institute for Mass Spectroscopy, Universiteit van Amsterdam, and all obtained data agreed well with simulated spectra of the respective complexes. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. PdCl₂(PhCN)₂,¹⁶ PtCl₂(SEt)₂,¹⁷ K[PtCl₃(C₂H₄)]·H₂O,¹⁸ and Ar-BIAN and Ph-BIC¹⁹ were synthesized by following reported procedures. PdCl₂(MeCN)₂ was synthesized in a way similar to that reported for PdCl₂(PhCN)₂.

PdCl₂(Ph-BIAN) (1a). Method A. To a solution of 2.02 g of PdCl₂(PhCN)₂ (5.3 mmol) (or 1.37 g (5.3 mmol) of PdCl₂(MeCN)₂) in 100 mL of dichloromethane was added 1.81 g of Ph-BIAN (5.4 mmol), and the mixture was stirred at 20 °C. After 1 h the suspension was evaporated and the resulting product washed subsequently with methanol (2 × 10 mL) and diethyl ether (3 × 20 mL). The product was dried in vacuo,

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giving 2.56 g of $\text{PdCl}_2(\text{Ph-BIAN})$ as an orange powder (95%). Analytically pure samples were obtained by recrystallization from dichloromethane/hexane.

Method B. A suspension of 1.28 g of PdCl_2 (7.2 mmol) in 100 mL of acetonitrile was warmed to 70 °C, to give a red solution. Then 2.60 g of Ph-BIAN (7.8 mmol) was added and the mixture refluxed for 1 h. After the mixture was cooled to 20 °C, the solvent was evaporated to about 10 mL and 50 mL of diethyl ether was added. The solid product was filtered off and washed with diethyl ether (3 × 30 mL). Then the product was redissolved in dichloromethane, this solution was filtered through Celite filter aid to remove metallic palladium, and the filtrate was evaporated to 5 mL. After addition of hexane the solid was filtered out and dried in vacuo, yielding 2.81 g of an orange solid (76%).

Anal. Found (calcd for $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{N}_2\text{Pd}$): C, 55.65 (56.55); H, 3.25 (3.16); N, 5.13 (5.50). IR (cm^{-1} , KBr): 1630, $\nu(\text{C}=\text{N})$; 348, $\nu(\text{Pd}-\text{Cl})$. ^{13}C NMR (ppm, DMSO- d_6 ; the atom-numbering scheme is shown in Table 1): C₁, not observed; 128.3, C₂; 124.8, C₃; 128.9, C₄; 132.1, C₅; 130.9, C₆; 145.1, C₇; 155.3, C₈; 122.6, C₉; 129.2, C₁₀; 125.1, C₁₁. MS (m/z): 510 (calcd 510).

$\text{PdCl}_2(p\text{-Tol-BIAN})$ (1b); orange-brown) was synthesized in the same way as **1a** (method A) by addition of 0.95 equiv of $p\text{-Tol-BIAN}$ to a filtered solution of $\text{PdCl}_2(\text{PhCN})_2$ in dichloromethane (87% yield). The product obtained in this way is analytically pure but may be recrystallized by slow evaporation of a solution of **1b** in DMF to give orange-brown plates. Anal. Found (calcd for $\text{C}_{26}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Pd}$): C, 58.95 (58.07); H, 3.86 (3.75); N, 4.99 (5.21). IR (cm^{-1} , KBr): 1620, $\nu(\text{C}=\text{N})$; 350, $\nu(\text{Pd}-\text{Cl})$. MS (m/z): 538 (calcd 538).

$\text{PdCl}_2(p\text{-MeOC}_6\text{H}_4\text{-BIAN})$ (1c); red) was synthesized and purified in the same way as **1b**, in 88% yield. Anal. Found (calcd for $\text{C}_{26}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_2\text{Pd}$): C, 54.84 (54.81); H, 3.65 (3.54); N, 4.75 (4.92). IR (cm^{-1} , KBr): 1620 sh, $\nu(\text{C}=\text{N})$; 360, $\nu(\text{Pd}-\text{Cl})$. MS (m/z): 570 (calcd 570).

$\text{PdCl}_2(o,o'\text{-Me}_2\text{C}_6\text{H}_3\text{-BIAN})$ (1d); orange) was synthesized in 80% yield as described in method B. Anal. Found (calcd for $\text{C}_{26}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Pd}$): C, 59.39 (59.44); H, 4.29 (4.28); N, 4.99 (4.95). IR (cm^{-1} , KBr): 1618, $\nu(\text{C}=\text{N})$; 345, $\nu(\text{Pd}-\text{Cl})$.

$\text{PdCl}_2(o,o'\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{-BIAN})$ (1e) was synthesized via method B as a yellow-orange solid (84%). Anal. Found (calcd for $\text{C}_{36}\text{H}_{40}\text{Cl}_2\text{N}_2\text{Pd}$): C, 63.60 (63.77); H, 6.04 (5.95); N, 4.51 (4.13). IR (cm^{-1} , KBr): 1617, $\nu(\text{C}=\text{N})$; 342, $\nu(\text{Pd}-\text{Cl})$. ^{13}C NMR (ppm, CDCl_3): C_{1,2,6,7,8}, not observed; 125.7, C₃; 129.1, C₄; 132.3, C₅; 139.8, C₉; 124.1, C₁₀; 128.9, C₁₁; 29.4, CH ($i\text{-Pr}$); 23.7, 23.5, CH₃ ($i\text{-Pr}$).

$\text{PdCl}_2(\text{Ph-BIC})$ (1f) was synthesized from PdCl_2 in 77% yield via method B and recrystallized from DMF to yield yellow needles. Anal. Found (calcd for $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{N}_2\text{Pd}$): C, 53.93 (53.52); H, 4.65 (4.90); N, 5.80 (5.67). IR (cm^{-1} , KBr): 1657, 1634, $\nu(\text{C}=\text{N})$; 345, $\nu(\text{Pd}-\text{Cl})$. ^1H NMR (ppm, DMSO- d_6): 7.2–7.4 m (10 H), Ph; 1.02 s, 0.85 s, 0.41 s, H_{8,9,10}; other signals overlapped by the signals of H₂O and DMSO.

$\text{PdBr}_2(p\text{-Tol-BIAN})$ (2b). **Method C.** To a solution of 0.21 g of PdCl_2 (1.2 mmol) and 1.22 g of NaBr (11.9 mmol) in 20 mL of acetonitrile, warmed to 70 °C, was added 0.46 g of $p\text{-Tol-BIAN}$ (1.3 mmol), and the mixture was stirred at 70 °C. After 1 h the mixture was evaporated, and the solid product was extracted with dichloromethane (3 × 30 mL). The combined dichloromethane layers were washed with water (3 × 25 mL), dried on MgSO_4 , and filtered through Celite filter aid. After evaporation of the solvent to approximately 3 mL, 25 mL of hexane was added. The product was filtered off, washed with 10 mL of hexane, and dried in vacuo, to yield 0.56 g (75%) of a red product.

Method D. A solution of 0.25 g of PdBr_2 (0.94 mmol) and 0.35 g of $p\text{-Tol-BIAN}$ (0.97 mmol) in 20 mL of acetonitrile was stirred at 70 °C. After 30 min the solution was evaporated to dryness and the product washed with diethyl ether (2 × 10 mL). The product was redissolved in 50 mL of dichloromethane, this solution was filtered through Celite filter aid, and the residue was washed with dichloromethane (2 × 20

mL). The combined filtrates were evaporated to about 5 mL, 15 mL of hexane was added, and the mixture was cooled to –20 °C. After several hours the product was filtered off and dried in vacuo, giving 0.50 g of a red product (85%).

Anal. Found (calcd for $\text{C}_{26}\text{H}_{20}\text{Br}_2\text{N}_2\text{Pd}$): C, 49.58 (49.83); H, 3.13 (3.22); N, 4.41 (4.47). IR (cm^{-1} , KBr): 1617, $\nu(\text{C}=\text{N})$.

$\text{PdBr}_2(o,o'\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{-BIAN})$ (2e); orange) was synthesized in the same way as **2b** in 78% (method C) or 81% (method D) yield. Anal. Found (calcd for $\text{C}_{36}\text{H}_{40}\text{Br}_2\text{N}_2\text{Pd}$): C, 56.41 (56.38); H, 5.32 (5.26); N, 3.73 (3.65). IR (cm^{-1} , KBr): 1620, $\nu(\text{C}=\text{N})$. ^{13}C NMR (ppm, CDCl_3): 176.0, C₁; 125.6, C₂; 126.5, C₃; 129.7, C₄; 133.1, C₅; 132.0, C₆; 147.1, C₇; 142.2, C₈; 140.4, C₉; 124.8, C₁₀; 129.7, C₁₁; 30.2, CH ($i\text{-Pr}$); 24.7, 24.2, CH₃ ($i\text{-Pr}$).

$\text{PdI}_2(\text{Ph-BIAN})$ (3a). To an orange solution of 15.1 mg of $\text{PdCl}_2(\text{Ph-BIAN})$ (**1a**) (0.025 mmol) in 10 mL of dichloromethane was added a solution of 0.15 g of NaI (1.0 mmol) in 5 mL of acetone, and the solution immediately turned dark red. After it was stirred at 20 °C over 4 h, the solution was evaporated to dryness. The solid was extracted at 0 °C with dichloromethane (2 × 10 mL), and the extracts were evaporated to dryness. After washing of the solid with 5 mL of diethyl ether and drying in vacuo, a dark purple-red product was obtained.

$\text{PdI}_2(p\text{-Tol-BIAN})$ (3b) was obtained as a dark red product in the same way as **3a**. MS (m/z): 720 (calcd for $\text{C}_{26}\text{H}_{20}\text{I}_2\text{N}_2\text{-Pd}$: 720).

$\text{Pd}(\text{OC}(\text{O})\text{Me})_2(o,o'\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{-BIAN})$ (4e). A 0.26 g amount of $o,o'\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{-BIAN}$ (0.52 mmol) was added to a solution of 0.11 g of $\text{Pd}(\text{OC}(\text{O})\text{Me})_2$ (0.49 mmol) in 15 mL of acetonitrile, and the mixture was heated to 70 °C. After 1 h the brown-red solution was evaporated to dryness and the product washed with diethyl ether (2 × 10 mL). The resulting product was dissolved in 50 mL of dichloromethane and filtered through Celite filter aid. The filtrate was evaporated to about 3 mL, and 20 mL of hexane was added. The product was obtained as an orange-brown solid in 70% yield (0.25 g) by filtration and drying in vacuo. Anal. Found (calcd for $\text{C}_{40}\text{H}_{46}\text{N}_2\text{O}_4\text{Pd}$): C, 66.90 (66.25); H, 6.76 (6.40); N, 3.95 (3.86). IR (cm^{-1} , KBr): 1629, $\nu(\text{C}=\text{O})$. ^{13}C NMR (ppm, CDCl_3): 174.8, C₁; 125.2, C₂; 126.5, C₃; 129.7, C₄; 133.2, C₅; 132.0, C₆; 147.4, C₇; 140.8, C₈; 141.2, C₉; 125.0, C₁₀; 129.6, C₁₁; 29.9, CH ($i\text{-Pr}$); 25.1, 24.2, CH₃ ($i\text{-Pr}$); 177.4, $\text{OC}(\text{O})\text{Me}$; 22.8 $\text{OC}(\text{O})\text{Me}$.

Reaction of $\text{Pd}(\text{OC}(\text{O})\text{Me})_2(o,o'\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{-BIAN})$ (4e) with HCl. To an orange solution of 22.3 mg of **4e** (0.031 mmol) in 0.5 mL of CDCl_3 was added 1 drop of concentrated aqueous hydrochloric acid (excess), and the mixture was vigorously shaken for a few seconds. The yellow CDCl_3 solution was removed from the biphasic system, filtered, and analyzed directly by ^1H NMR spectroscopy without isolation. The spectrum of the product formed was identical with that of **1e** obtained by the reaction of $o,o'\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{-BIAN}$ with PdCl_2 as described above.

$\text{PtCl}_2(\text{Ph-BIAN})$ (5a). **Method E.** A solution of 0.29 g of Ph-BIAN (0.87 mmol) in 30 mL of dichloromethane was added to a solution of 0.32 g of $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\cdot\text{H}_2\text{O}$ (0.83 mmol) in 10 mL of methanol. After the mixture was stirred at 20 °C for 15 min, charcoal was added; this mixture was stirred for 5 min and subsequently filtered. The residue was washed with 10 mL of dichloromethane, and the filtrates were evaporated to dryness. The product was washed with diethyl ether (2 × 5 mL), and after drying in vacuo 0.32 g of a brown-red product was obtained (65%).

Method F. To a suspension of 0.72 g of $\text{PtCl}_2(\text{SET}_2)_2$ (1.6 mmol) and 0.61 g of Ph-BIAN (1.8 mmol) in 30 mL of acetone was added approximately 5 mL of dichloromethane, and a clear solution was obtained. This solution was transferred to a stainless steel autoclave, pressurized with ethene (5 bar), and stirred at 30 °C. After 16 h the ethene pressure was released and the reaction mixture concentrated to ca 5 mL in vacuo. The product was precipitated by the addition of 15 mL of hexane, washed with diethyl ether (2 × 10 mL), and dried in

vacuo to yield 0.57 g of a brown-red solid (59%). Anal. Found (calcd for $C_{24}H_{16}Cl_2N_2Pt$): C, 49.26 (48.17); H, 2.61 (2.70); N, 4.75 (4.68). IR (cm^{-1} , KBr): 1618 sh, $\nu(C=N)$; 348, $\nu(Pt-Cl)$. MS (m/z): 598 (calcd 598).

PtCl₂(*p*-Tol-BIAN) (5b); brown-red) was obtained in the same way as described for **5a** (method A) in 87% yield. Anal. Found (calcd for $C_{26}H_{20}Cl_2N_2Pt$): C, 48.42 (49.85); H, 2.90 (3.22); N, 4.12 (4.47). IR (cm^{-1} , KBr): 1630 sh, $\nu(C=N)$; 339, $\nu(Pt-Cl)$. MS (m/z): 626 (calcd 626).

Electrochemical Setup and Procedure for Cyclic Voltammetry. Cyclic voltammetry was performed as described previously.¹⁴ A home-built potentiostat equipped with positive feedback for ohmic-drop compensation was used.²⁰ The reference electrode was an SCE (Tacussel) separated from the solution by a bridge (3 mL) filled with an *n*-Bu₄NBF₄ solution identical with that used in the cell. All potentials given here refer to this reference electrode. All the experiments were performed at 20 °C under an atmosphere of argon. Solvents were distilled (THF from sodium benzophenone ketyl and DMF from calcium hydride) and degassed prior to use.

In a typical procedure 12.2 mg of PdCl₂(Ph-BIAN) (0.024 mmol) was dissolved in 12 mL of a solution of 1.48 g of *n*-Bu₄NBF₄ (4.5 mmol) in 15 mL of THF (0.30 M; 3 mL of the latter solution was introduced into the bridge compartment of the reference SCE electrode). Under standard conditions, cyclic voltammograms were obtained at a scan rate of 0.2 V/s, reduction first (0 to -2.0 V) followed by oxidation (-2.0 to +1.0 V) and finally reduction (to 0 V), unless noted otherwise in the text. After cyclic voltammograms of the starting complex were recorded, reagents were added to the cell and voltammograms recorded (reduction first), to monitor the reaction(s) of the electrogenerated Pd(Ar-BIAN) complex with the added reagents. Experiments on the influence of the scan rate on the voltammograms were all performed for scan rates between 0.1 and 100 V/s.

Determination of the Number of Electrons Involved in the First Reduction of PdCl₂(Ph-BIAN) (1a). Electron consumption in transient electrochemistry was determined by following a method previously described, which combines the use of chronoamperometry and steady-state voltammetry at an ultramicroelectrode.²¹ Thus, 11.4 mg of PdCl₂(Ph-BIAN) (**1a**; 0.022 mmol, [Pd] = 1.83 mM) and 4.9 mg of ferrocene (Fe(η^5 -C₅H₅)₂; 0.026 mmol, [Fe] = 2.16 mM) were dissolved in 12.0 mL of a 0.30 M solution of *n*-Bu₄NBF₄ in THF. The limiting current for the steady-state voltammetry, performed at a gold ultramicroelectrode (10 μ m diameter) with a scan rate of 20 mV s⁻¹, was $i_{lim,Pd}^{\text{red}} = (0.175 \text{ V})G = 1.82 \text{ nA}$ for **1a** (where $G = 10.44 \text{ nA V}^{-1}$ is the gain of the potentiostat) and $i_{lim,Fe}^{\text{red}} = (0.69 \text{ V})G = 7.20 \text{ nA}$ for the ferrocene. Chronoamperometry at $\theta = 200 \text{ ms}$ ($E^{\text{red}}_{Pd} = -0.58 \text{ V}$ and $E^{\text{ox}}_{Fe} = +0.75 \text{ V}$) performed at a gold electrode (0.5 mm diameter) revealed currents of $i_{Pd} = (0.50 \text{ V})G = 2.62 \text{ }\mu\text{A}$ for **1a** (where $G = 5.25 \text{ }\mu\text{A V}^{-1}$ is the gain of the potentiostat) and $i_{Fe} = (0.99 \text{ V})G = 5.19 \text{ }\mu\text{A}$ for the ferrocene. At $\theta = 100 \text{ ms}$, $i_{Pd} = (0.71 \text{ V})G = 3.72 \text{ }\mu\text{A}$ for **1a** and $i_{Fe} = (1.36 \text{ V})G = 7.14 \text{ }\mu\text{A}$ for ferrocene (all data are the average of two or three independent determinations).

At an ultramicroelectrode, at low scan rate, the expression for the current is $i^{\text{lim}} = 4rFnCD$ (r = radius of the electrode; C = concentration of the species; n = number of electrons; D : diffusion coefficient of the species). Therefore, one has $i^{\text{lim}}_{Pd} = 4rFn_{Pd}[Pd]D_{Pd}$ for **1a** and, since $n_{Fe} = 1$ $i^{\text{lim}}_{Fe} = 4rF[Fe]D_{Fe}$ for the ferrocene, so that

$$\frac{i^{\text{lim}}_{Pd}}{i^{\text{lim}}_{Fe}} = \frac{n_{Pd}[Pd]D_{Pd}}{[Fe]D_{Fe}} = A$$

The expression for the current of the chronoamperometry is $I = nFSC\pi^{-1/2}D^{1/2}\theta^{-1/2}$ (S = electrode surface; θ = step duration), so that

$$\frac{i_{Pd}}{i_{Fe}} = \frac{n_{Pd}[Pd]D_{Pd}^{1/2}}{[Fe]D_{Fe}^{1/2}} = B$$

From expressions A and B one gets

$$\frac{B^2}{A} = \frac{n_{Pd}[Pd]}{[Fe]}$$

and thus:

$$n_{Pd} = \frac{B^2[Fe]}{A[Pd]} = \frac{(i_{Pd})^2(i^{\text{lim}}_{Fe})[Fe]}{(i_{Fe})^2(i^{\text{lim}}_{Pd})[Pd]}$$

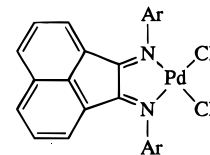
On the basis of the chronoamperometric value at $\theta = 200 \text{ ms}$, one obtains $n_{Pd} = 1.2 \pm 0.2$ and $n_{Pd} = 1.2 \pm 0.2$ when $\theta = 100 \text{ ms}$. The diffusion coefficient, D_{Pd} , for **1a** can be determined from the value of the diffusion coefficient for the ferrocene, $D_{Fe} = 7.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$,²¹ as follows:

$$\frac{i^{\text{lim}}_{Pd}[Fe]D_{Fe}}{i^{\text{lim}}_{Fe}[Pd]n_{Pd}} = D_{Pd} = 2.16 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

Under these conditions, the characteristic time of the voltammetry at the ultramicroelectrode is $T = r^2/D = 115 \text{ ms}$,²¹ a value which fits the gap examined by chronoamperometry. From these results, one concludes that the first reduction of **1a** involves one electron.

Results and Discussion

Synthesis and Characterization of the Complexes 1–5. Dichloro(Ar-BIAN)palladium complexes **1** have been synthesized in good yields by substitution of weakly coordinating ligands from suitable precursors, such as PdCl₂(PhCN)₂ and PdCl₂(MeCN)₂ (eq 1). PdCl₂-



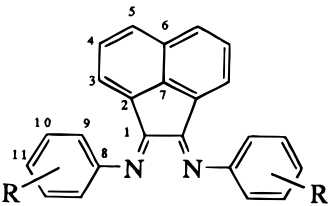
(1)

- 1a** Ar = C₆H₅
1b Ar = *p*-MeC₆H₄
1c Ar = *p*-MeOC₆H₄
1d Ar = *o,o'*-Me₂C₆H₃
1e Ar = *o,o'*-iPr₂C₆H₃

(COD) (COD = (*Z,Z*)-1,5-cyclooctadiene) could also be used as a precursor, but substitution of dimethyl sulfide ligands from PdCl₂(SMe₂)₂ by Ar-BIAN ligands was only very slow. Alternatively, the same complexes were obtained by direct reaction of an Ar-BIAN ligand with PdCl₂ in acetonitrile, via in situ formed PdCl₂(MeCN)₂. When the latter method is applied, metallic palladium and impurities from the PdCl₂ are easily removed by dissolution of the product in dichloromethane and filtration through Celite filter aid. This method was less suitable for the synthesis of **1b** and **1c**, as these complexes did not dissolve well enough in common organic solvents to allow further purification. PdCl₂-

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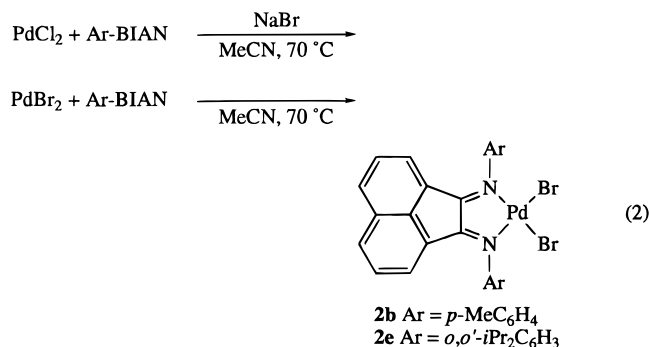
Table 1. ^1H NMR Data for $\text{PdX}_2(\text{Ar-BIAN})$ and $\text{PtCl}_2(\text{Ar-BIAN})$ Complexes **1–5**^a


	H ₃	H ₄	H ₅	H _{9,10,11}	R
1a	6.81 d 7.2	7.3–7.7 m (12 H)	8.13 d 8.4	7.3–7.7 m (12 H)	
1b ^b	6.66 d 7.1	7.65 pst	8.30 d 8.2	7.43 d, 7.30 d 8.4	2.44 s, <i>p</i> -Me
1c ^b	6.76 d 7.0	7.65 pst	8.30 d 8.0	7.38 d, 7.14 d 8.1	3.88 s, <i>p</i> -MeO
1d	6.62 d 7.3	7.52 dd 7.3, 8.3	8.15 d 8.3	7.3 m (6 H)	2.44 s, <i>o,o'</i> -Me ₂
1e	6.54 d 7.3	7.5 m (4 H)	8.13 d 8.3	7.5 m (4 H), H ₁₁ 7.37 d (7.7 Hz), H ₁₀	3.53 sep (6.8 Hz), CH (<i>i</i> -Pr) 1.52 d, 0.99 d (6.8 Hz), CH ₃ (<i>i</i> -Pr)
2b	6.81 d 7.3	7.50 pst	8.11 d 8.3	7.38 d, 7.26 d 8.1	2.48 s, <i>p</i> -Me
2e	6.48 d 7.3	7.5 m (4 H)	8.14 d 8.3	7.5 m (4 H), H ₁₁ 7.38 d (7.6 Hz), H ₁₀	3.51 sep (6.8 Hz), CH (<i>i</i> -Pr) 1.50 d, 0.96 d (6.8 Hz), CH ₃ (<i>i</i> -Pr)
3a	6.66 d 7.5	7.3–7.7 m (12 H)	8.08 d 8.6	7.3–7.7 m (12 H)	
3b	6.74 d 7.2	7.49 pst	8.09 d 8.3	7.42 d, 7.21 d 8.0	2.50 s, <i>p</i> -Me
4e ^c	6.63 d 7.3	7.5 m (4 H)	8.11 d 8.3	7.5 m (4 H), H ₁₁ 7.34 d (7.6 Hz), H ₁₀	3.71 sep (6.8 Hz), CH (<i>i</i> -Pr) 1.57 d, 0.93 d (6.8 Hz), CH ₃ (<i>i</i> -Pr)
5a	6.96 d 7.3	7.3–7.6 m (12 H)	8.27 d 8.1	7.3–7.6 m (12 H)	
5b	7.05 d 7.1	7.4–7.7 m (10 H)	8.26 d 8.1	7.4–7.7 m (10 H)	2.50 s, <i>p</i> -Me

^a Recorded at 300.13 MHz in CDCl_3 at 20 °C, unless indicated otherwise. Coupling constants (Hz) are given below the chemical shifts. Abbreviations used: s = singlet, d = doublet, dd = doublet of doublets, pst = pseudo triplet, sep = septet, m = multiplet. ^b In $\text{DMSO}-d_6$. ^c 1.50 s, OC(O)Me.

(Ph-BIC) (**1f**) was obtained similarly to the $\text{PdCl}_2(\text{Ar-BIAN})$ analogues **1a–e**.

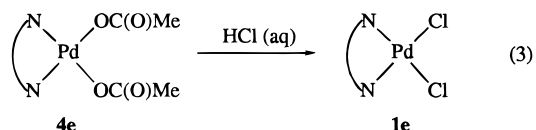
The dibromo(Ar-BIAN)palladium complexes **2** were synthesized in a comparable way, either by reaction of Ar-BIAN with PdCl_2 in the presence of an excess of sodium bromide (about 10 equiv relative to palladium) or by reaction with PdBr_2 (eq 2).



The diiodo complexes **3** were obtained by halogen metathesis of the dichloro complexes **1** with sodium iodide, and the complexes obtained show the same spectral data as those obtained by oxidative addition of diiodine to $\text{Pd}(\text{Ar-BIAN})(\text{alkene})$ complexes.⁹ The best results were obtained when the reactions were performed on a small scale (10–50 mg of Pd complex) with a large excess of NaI (≥ 20 equiv relative to Pd), since otherwise mixtures of complexes were obtained, most likely $\text{PdCl}_2(\text{Ar-BIAN})$, $\text{PdI}_2(\text{Ar-BIAN})$, and $\text{PdClI}(\text{Ar-BIAN})$.

$\text{Pd}(\text{OC}(\text{O})\text{Me})_2(o,o'\text{-i-Pr}_2\text{C}_6\text{H}_3\text{-BIAN})$ (**4e**) was obtained by reaction of *o,o'*-*i*-Pr₂C₆H₃-BIAN with $\text{Pd}(\text{OC}(\text{O})\text{Me})_2$

in acetonitrile. This complex reacted with aqueous concentrated hydrochloric acid to give quantitatively the dichloro complex **1e** (eq 3).



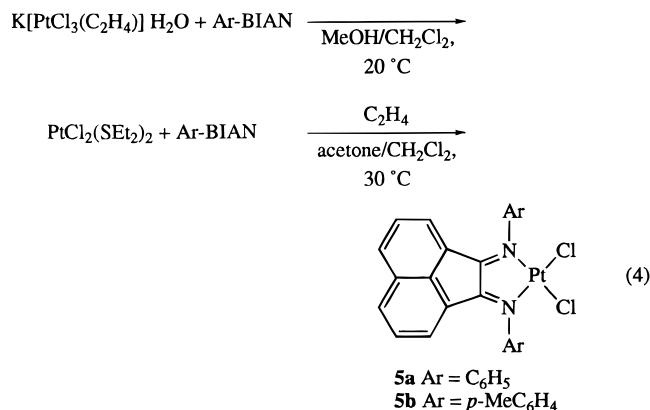
Synthesis of the dichloro(Ar-BIAN)platinum complexes **5** was achieved by reaction of $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ with the appropriate Ar-BIAN ligand (eq 4). There was no evidence for the formation of any five-coordinate $\text{PtCl}_2(\text{Ar-BIAN})(\text{C}_2\text{H}_4)$ complex²² under the conditions described here. No $\text{PtCl}_2(\text{Ar-BIAN})$ complexes were obtained when Ar-BIAN was reacted with K_2PtCl_4 , which was used for the synthesis of $\text{PtCl}_2(\text{phen})$,²³ *cis*-/*trans*- $\text{PtCl}_2(\text{SET}_2)_2$, and *trans*- $\text{PtCl}_2(\text{MeCN})_2$.²⁴ However, formation of $\text{PtCl}_2(\text{Ph-BIAN})$ (**5a**) was achieved when the reaction of Ph-BIAN with $\text{PtCl}_2(\text{SET}_2)_2$ was carried out under ethene pressure (eq 4), probably via an in situ formed Pt(ethene) complex. Addition of dimethyl fumarate (DMFU) to a mixture of Ph-BIAN and $\text{PtCl}_2(\text{SET}_2)_2$ did not lead to the formation of **5a**, and only starting materials were recovered after 6 h at 20 °C.

From the ^1H NMR data of the complexes **1–5** (Table 1) it appears that the signals of the Ar-BIAN ligands

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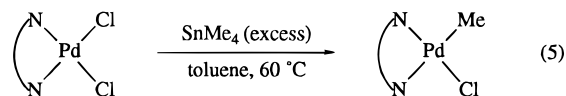
have shifted to higher frequency upon coordination, especially H₄ and H₅, by about 0.1–0.3 ppm for Pd and 0.1–0.4 ppm for Pt. This observation is consistent with donation of electron density from the Ar-BIAN ligand to the metal center, similar to the observations made for Pd(Ar-BIAN)(alkene) complexes.²⁵ The effect of coordination on the chemical shift of H₃ is less clear, which might be due to the combined effect of coordination to the metal center, inducing a shift to higher frequency, and reorientation of the aromatic ring due to the presence of the halide ligands in the coordination plane, leading to increased anisotropic shielding of H₃ and a concomitant low-frequency shift.^{19c,25} The perpendicular orientation of these aromatic rings in the complexes appears also from the observed low-frequency singlet at 1.50 ppm for the acetate moiety in Pd(OC(O)Me)₂(*o,o'*-*i*-Pr₂C₆H₃-BIAN) (**4e**), which must be ascribed to anisotropic shielding of this methyl group by the aromatic ring of the *o,o'*-*i*-Pr₂C₆H₃ substituent. For complexes bearing ligands with ortho-substituted aromatic groups on the Ar-BIAN ligands, i.e. **1d**, **1e**, **2e**, and **4e**, the observed shift of the *o*-CHR₂-Ar (R = H, Me) resonance by 0.3–0.7 ppm to higher frequency seems to indicate that there is some interaction between the halide or acetate ligand and this proton.

Shifts to higher frequency have also been observed in the ¹³C NMR spectroscopy of some complexes, especially for the imine carbon C₁ and the naphthene C atoms C_{3,4,5}. Unfortunately, the solubility of most complexes is rather low, which precluded the collection of ¹³C NMR data for the entire series of complexes.

In the IR spectra of the complexes (as KBr pellets) the C=N stretching vibration is observed at 1620–1660 cm⁻¹, i.e. shifted by 10–30 cm⁻¹ to lower frequency as compared to the free ligands. For the dichloro complexes **1** and **5** one M-Cl stretching vibration is observed in the region 340–360 cm⁻¹. The broadness of this signal is probably due to two overlapping M-Cl vibrations, as for related *cis*-MCl₂(NN) complexes (M = Pd, Pt; NN = α -diimine ligand) two close-lying M-Cl vibrations were reported.²⁶

Transmetalation Reactions. Attempted substitution of one or two of the halide atoms by organic groups in PdCl₂(Ar-BIAN) (**1a**) or PtCl₂(Ar-BIAN) (**5a**) by

reaction with organolithium, -magnesium, or -zinc reagents failed. In all cases mixtures of unknown products were formed, which is most likely due to a combination of reactions at the metal center and at the ligand and decomposition. It has been reported before that reaction of PtCl₂(bpy) (bpy = 2,2'-bipyridine) with MeLi was not an efficient route for the synthesis of Pt-methyl complexes.²⁷ Only in the case of the reaction of PdCl₂(Ar-BIAN) with an excess of tetramethyltin at 60 °C in toluene was conversion to Pd(Me)Cl(Ar-BIAN) observed (eq 5). At 20 °C no reaction occurred, and at



60 °C excess SnMe₄ (≥ 5 equiv) and reactions lasting several hours (≥ 4 h) were necessary to obtain complete conversion. The products synthesized in this way show ¹H NMR spectral data identical with the complexes obtained by the reaction of Pd(Me)Cl(COD) with Ar-BIAN.^{8c}

At this point it becomes clear that the observed behavior of the PdCl₂(Ar-BIAN) complexes, when dissolved in DMF, can be ascribed to the formation of a [PdCl(Ar-BIAN)(DMF)]⁺Cl⁻ species. In previous papers we described the necessity of strongly polar aprotic solvents such as DMF and HMPA (hexamethylphosphoric triamide) in Pd(Ar-BIAN)(DMFU)-catalyzed cross-coupling reactions of organic halides (RX) with organotin reagents (R'₄Sn).^{8a,b} Probably, the Pd(R)X(Ar-BIAN) complex formed after oxidative addition of RX to Pd(Ar-BIAN)(DMFU) is partially solvated in DMF solution to give [Pd(R)(Ar-BIAN)(DMF)]⁺X⁻, which accelerates the rate-determining transmetalation step. The faster reaction of the ionic [Pd(R)(Ar-BIAN)(DMF)]⁺ complex with R'₄Sn, as compared to the neutral Pd(R)X(Ar-BIAN) complex, can be explained by invoking (i) the increased accessibility of palladium, (ii) the increased electrophilicity of palladium, facilitating attack at the tin bound C atom in R'₄Sn, and (iii) the presence of a noncoordinating halide anion, which, by precoordination to tin, might facilitate the transfer of an organic group from tin to palladium.^{8b}

Electrochemical Behavior of Pd^{II}Cl₂(Ar-BIAN) Complexes 1a–c. In the cyclic voltammogram of Pd^{II}-Cl₂(Ar-BIAN) complexes **1a–c**, 2 mM in THF (or DMF), two reduction peaks were observed, a reversible one at *ca.* -0.4 V vs SCE (R₁) and an irreversible one at about -1.1 V (R₂) (Figure 1a, Table 2).²⁸ After reduction of the complex at R₂, a weak oxidation peak was observed on the reverse scan that might be ascribed to species generated during the two-step reduction of PdCl₂(Ar-BIAN) complexes, i.e. Cl⁻ or a low-valent palladium complex. Determination of the number of electrons²¹ involved in the first reduction step of Pd^{II}Cl₂(Ph-BIAN) (**1a**) by using double-step chronoamperometry and

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(28) In DMF, an additional small reversible reduction peak was observed at -0.70 V (10–20% relative to R₁). As the ratio of this signal did not increase at lower scan rates, it is not due to a species formed upon the first reduction of PdCl₂(Ph-BIAN). The most likely explanation is a thermal reaction of PdCl₂(Ph-BIAN) with DMF with formation of the cationic complex PdCl(Ph-BIAN)(DMF)⁺Cl⁻ coordinated by DMF. In agreement with this assumption, we observed that the current of this peak decreased when *n*-Bu₄NCl (5–60 equiv relative to the palladium complex) was added to the solution.

Table 2. Electrochemical Data for Pd(Ar-BIAN) Complexes and Ph-BIAN^a

	$E_{pc}(R_0)/E_{pc}(O_0)$ (V)	
Ph-BIAN	-1.27/-1.14 $O_0/-0.93$	
	$E_{pc}(R_1)/E_{pc}(O_1)$ (V)	$E_{pc}(R_2)$ (V) irr
PdCl ₂ (Ph-BIAN) (1a)	-0.38/-0.29	-1.03
PdCl ₂ (Ph-BIAN) (1a) ^b	-0.46/-0.39	-1.11
PdCl ₂ (<i>p</i> -Tol-BIAN) (1b)	-0.41/-0.31	-1.09
PdCl ₂ (<i>p</i> -Tol-BIAN) (1b) ^b	-0.40/-0.35	-1.14
PdCl ₂ (<i>p</i> -MeOC ₆ H ₄ -BIAN) (1c) ^b	-0.50/-0.42	-1.19
	$E_{pc}(R_3)/E_{pc}(O_3)$ (V)	$E_{pc}(R_4)E_{pc}(O_4)$ (V)
Pd(<i>p</i> -Tol-BIAN)(DMFU)	-0.79/-0.71	-1.28/-1.19
Pd(<i>p</i> -Tol-BIAN)(MA)	-0.66/-0.58	-1.18/-1.10
Pd(Me)I(<i>p</i> -Tol-BIAN)	-0.74/-0.59	-1.40/-1.32

^a The mechanisms of the reduction of the different complexes are similar. For simplification, their respective first and second reduction potential peaks have the same notation, although their potentials differ. All peaks were reversible except when stated otherwise (irr = irreversible). Oxidation and reduction peak potentials were determined versus SCE. Recorded as 2.0 mM solutions in THF at a scan rate of 0.2 V s⁻¹, at a gold-disk electrode (i.d. = 5 mm) at 20 °C unless otherwise noted. ^b Recorded in DMF under the same conditions.

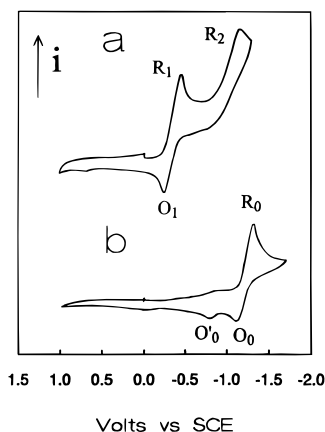
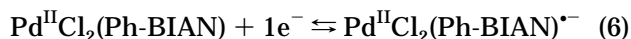


Figure 1. Cyclic voltammetry performed in THF (0.3 M *n*-Bu₄NBF₄) at a stationary gold-disk electrode (i.d. = 0.5 mm) with a scan rate of 0.2 V s⁻¹, at 20 °C: (a) PdCl₂(Ph-BIAN) (2 mM); (b) Ph-BIAN (2 mM).

steady-state voltammetry at a ultramicroelectrode revealed that one electron was involved in this step. Since the reduction peak was reversible, the first reduction step affords a radical anion:

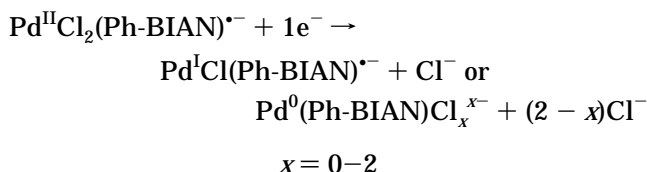


$$E_{pc}(R_1) = -0.41 \text{ V}$$

The cyclic voltammogram of solely the ligand Ph-BIAN¹⁹ in solution exhibited one reduction peak at -1.27 V, which was partially reversible at the scan rate of 0.2 V s⁻¹ (Table 2, Figure 1b).^{29a} Therefore, we can assume that the first reduction at R₁ is located on the Ph-BIAN ligand (which is therefore more easily reduced when ligated to the palladium^{29b}), similar to the reduction reported for Pt^{II}Cl₂(α-diimine) complexes.³⁰ Furthermore, it is expected that the LUMO of complexes of the type *cis*-M^{II}Cl₂(diimine) (M = Pd, Pt) is the π*-orbital of the diimine ligand.^{19c,31}

The current of the second irreversible reduction peak was comparable to that of the first one. Since the diffusion coefficients are expected to be close for the neutral and the monoreduced complexes, the second reduction also involves one electron. This reduction may afford several different species by cleavage of one or two Pd-Cl bonds. Further experiments reported

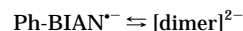
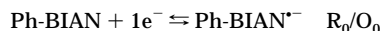
below allow to discriminate between these species:



The observation of two reduction peaks contrasts with that made for PdCl₂(PPh₃)₂ under similar conditions,^{14a-c} where only one irreversible reduction peak involving two electrons was detected with generation of chloride-ligated palladium(0) complexes.³²

Electrochemical Properties of Pd⁰(Ar-BIAN)-(alkene) Complexes. In order to investigate the role of α-diimine-ligated palladium(0) complexes in the catalytic hydrogenation of alkenes, the electrochemical properties of some Pd⁰(Ar-BIAN)(alkene) complexes have been studied. The electrochemical data concerning

(29) (a) The reduction peak was not completely reversible, since on the reverse scan the two oxidation peaks O₀ and O_{0'} were observed (Table 1). The oxidation current peak of O₀ was found to be smaller relative to that of O_{0'} when the scan rate was increased; i.e., the reduction peak was less reversible at high scan rate. This is characteristic of an electron transfer that affords a species involved in an equilibrium:



For an example of reversible dimerization, see: Smith, C. R.; Utley, J. H. P.; *J. Chem. Res., Synop.* **1982**, 18. (b) The reduction of the ligand Ph-BIAN on the palladium is fully reversible, whereas it was not for the free ligand.^{29a} When ligated on the palladium, the ligand Ph-BIAN^{•-} cannot be involved in the equilibrium reported above in ref 29a.

(30) (a) Braterman, P. S.; Song, J. I.; Vogler, C.; Kaim, W. *Inorg. Chem.* **1992**, 31, 222. (b) Braterman, P. S.; Song, J. I.; Wimmer, F. M.; Wimmer, S.; Kaim, W.; Klein, A.; Peacock, R. D. *Inorg. Chem.* **1992**, 31, 5084. (c) Vogler, C.; Schwederski, B.; Klein, A.; Kaim, W. *J. Organomet. Chem.* **1992**, 436, 367. (d) Klein, A.; Hausen, H. D.; Kaim, W. *J. Organomet. Chem.* **1992**, 440, 207.

(31) (a) Martin, M.; Krogh-Jespersen, M. B.; Hsu, M.; Tewksbury, J.; Laurent, M.; Viswanath, K.; Patterson, H. *Inorg. Chem.* **1983**, 22, 647. (b) Kamath, S. S.; Uma, V.; Srivastava, T. S. *Inorg. Chim. Acta* **1989**, 161, 49.

(32) In this case the reduction afforded three chloride-ligated palladium(0) complexes involved in fast equilibrium $[\text{Pd}^0(\text{PPh}_3)_2\text{Cl}]_n^{\bullet-}$, depending on the chloride ion and palladium concentration ($n = 1, x = 1, 2; n = 2, x = 2$).¹⁴

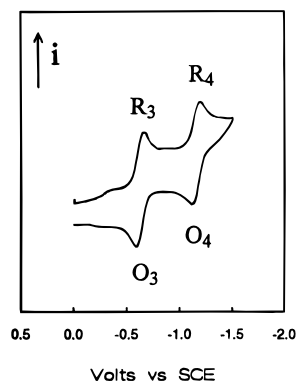
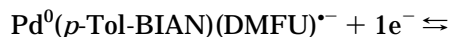
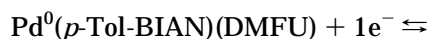


Figure 2. Cyclic voltammetry of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{MA})$ (2 mM) in THF (0.3 M $n\text{-Bu}_4\text{NBF}_4$) at a stationary gold-disk electrode (i.d. = 0.5 mm) with a scan rate of 0.2 V s^{-1} , at 20°C .

the reduction of the zerovalent complexes $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$ (DMFU = dimethyl fumarate) and $\text{Pd}^0(p\text{-Tol-BIAN})(\text{MA})$ ²⁵ (MA = maleic anhydride) have been collected in Table 2. All palladium complexes showed two reversible reduction peaks at R_3 and R_4 involving one electron each (Figure 2). For these two complexes, the first reduction is located on the Ar-BIAN ligand, as in $\text{Pd}^{\text{II}}\text{Cl}_2(\text{Ar-BIAN})$ complexes, whereas the second reduction is located on the alkene ligand, as reported for comparable $\text{M}^0(\alpha\text{-diimine})(\text{alkene})$ complexes ($\text{M} = \text{Pd}, \text{Pt}$).³³



The equations for the reduction of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{MA})$ are similar. The less negative reduction potential observed for the coordinated ligand as compared to free Ar-BIAN can be ascribed to donation of charge density from the Ar-BIAN ligand to the palladium and concomitant lowering of the ligand-centered LUMO, which is in agreement with the observation that the reduction potentials for the complex containing the more electron-withdrawing alkene (MA) are less negative than those of the DMFU complex.

No oxidation peaks of the complexes $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$ were observed up to +1.5 V.

In the presence of excess DMFU, neither the potential nor the current of the reduction of peaks R_3 and R_4 of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$ was affected. In the presence of MA, substitution of DMFU by MA was observed, and in the presence of DMM (dimethyl maleate) no changes in the cyclic voltammogram were observed, as was expected on the basis of earlier results.²⁵

In Situ Reaction of Alkenes or Ph-BIAN with the Low-Valent Palladium Complexes Formed upon Reduction of $\text{Pd}^{\text{II}}\text{Cl}_2(\text{Ar-BIAN})$ Complexes. The reduction of complexes **1a** and **1b** has been performed in the presence of 1 equiv of either alkenes (DMFU, DMM, MeAc (methyl acrylate)) or Ph-BIAN. The corresponding electrochemical data are collected in Table 3 (for simplification, all reduction or oxidation peaks

Table 3. Electrochemical Data for Complexes Obtained upon Reduction of $\text{PdCl}_2(\text{Ar-BIAN})$ (1a**, **b**) in the Presence of Iodomethane, Alkenes, and Ph-BIAN^a**

reacn	direct scan		reverse scan	
	$E_{\text{pc}}(R_5)$ (V)	$E_{\text{pc}}(R_6)/E_{\text{pc}}(O_6)$ (V)	$E_{\text{pc}}(O_4)$ (V)	$E_{\text{pc}}(O_3)/E_{\text{pc}}(R_3)$ (V)
1a + MeI	−1.37			
1a + DMFU	−1.24	−1.44/−1.30	−1.13	−0.80/−0.69
1a + DMFU ^b	−1.38		−1.23	n.d./−0.70
1a + DMM	−1.21	−1.59/−1.46	−1.12	−0.79/−0.68
1a + DMM ^b	−1.40	−1.70/−1.50	−1.30	n.d./−0.70
1a + MeAc	−1.28	n.d.	−1.18	−0.87/−0.78
1a + MeAc ^b	−1.31		−1.24	n.d./−0.80
1a + Ph-BIAN	−1.30		−1.15	−0.78/−0.80
1b + MeI	−1.02			
1b + DMFU ^b	−1.31	−1.42/−1.34	−1.19	−0.80/−0.71
1b + DMFU ^b	−1.32		−1.25	n.d./−0.71

^a For simplification, the first and second reduction potential peaks have the same notation, although their potentials differ. All peaks were reversible except when stated otherwise. Oxidation and reduction peak potentials were determined versus SCE. Recorded as 2.0 mM solutions in THF at a scan rate of 0.2 V s^{-1} , at a gold-disk electrode (i.d. = 5 mm) at 20°C unless stated otherwise. ^b Recorded in DMF under the same conditions.

corresponding to similar reactions but different complexes have the same notation in every column, although their respective potential values are different). Typical cyclic voltammograms are represented in Figures 3 (reduction in the presence of the alkene) and 4 (reduction in the presence of Ph-BIAN). In all cases, when $\text{Pd}^{\text{II}}\text{Cl}_2(\text{Ar-BIAN})$ was reduced in the presence of an alkene or Ph-BIAN, the corresponding cyclic voltammogram exhibited, besides the two one-electron-reduction peaks R_1 and R_2 of the $\text{PdCl}_2(\text{Ar-BIAN})$ complex (which remained similar to those observed in the absence of alkene), two additional reduction peaks at R_5 and R_6 . The latter was due to the reduction of the free alkene.³⁴ Since some free alkene could be detected on the cyclic voltammogram, it implies that the reaction of the palladium complexes generated by the reduction of $\text{Pd}^{\text{II}}\text{Cl}_2(\text{Ar-BIAN})$ with the alkene was not quantitative within the time scale of the cyclic voltammetry. When the scan direction after reduction was reversed at a potential more negative than −1.4 V (after peak R_6), two oxidation peaks were observed at O_4 and O_3 (Figures 3a,c and 4a). By performing successive cyclic scans, we observed that the oxidation peak O_3 was reversible (Figures 3a and 4a). We also observed that peak R_4 , which is the reverse peak of O_4 , was located at a slightly less negative potential than that observed for peak R_5 (Figures 3a and 4a).

A detailed investigation of the mechanism could be achieved in the case of the reduction of $\text{PdCl}_2(p\text{-Tol-BIAN})$ in the presence of DMFU, since an authentic sample of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$ was available (Table 2). By comparison of the electrochemical data from Tables 2 and 3, we noticed that the second reduction peak R_4 of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$ was not observable when $\text{PdCl}_2(p\text{-Tol-BIAN})$ was reduced in the presence of DMFU, demonstrating that $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$ was not formed. Indeed, the reduction potential observed at R_5 (−1.31 V) was different from that observed

(34) The reduction peak potentials (in THF) of the alkenes employed in this work are (corresponding oxidation peak potentials in parentheses): MA, −0.82 V (irr); DMFU, −1.44 V (−1.30 V); DMM, −1.55 V (−1.41 V); MeAc, −2.21 V (irr).

(33) Ito, N.; Saji, T. Aoyagui, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2323.

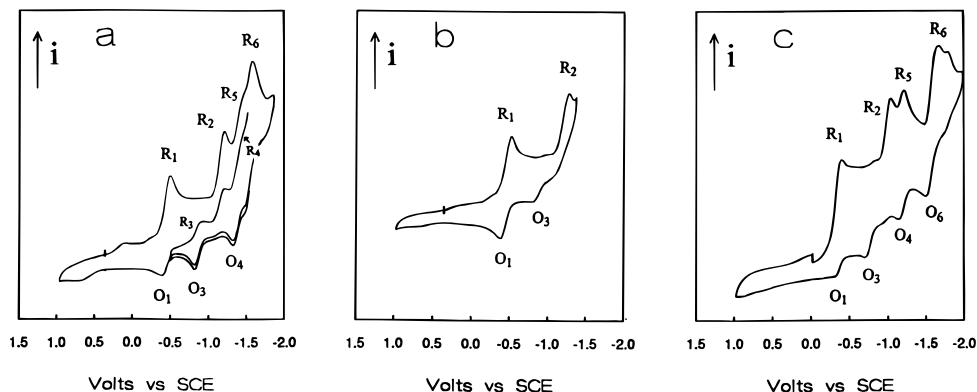


Figure 3. Cyclic voltammetry performed in THF (0.3 M $n\text{-Bu}_4\text{NBF}_4$) at a stationary gold-disk electrode (i.d. = 0.5 mm) with a scan rate of 0.2 V s^{-1} , at 20°C : (a) reduction of $\text{PdCl}_2(p\text{-Tol-BIAN})$ (2 mM) in the presence of DMFU (2 mM); (b) same experiment as in (a) but the scan direction after reduction was reversed at -1.4 V , just after R_2 ; (c) reduction of $\text{PdCl}_2(\text{Ph-BIAN})$ (2 mM) in the presence of DMM (2 mM).

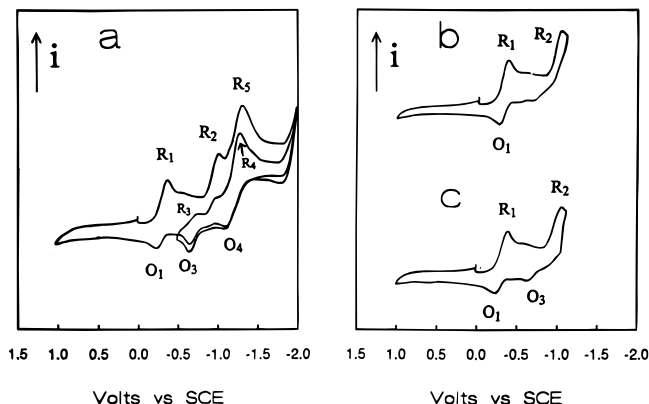


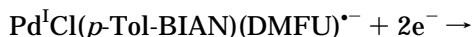
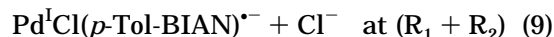
Figure 4. Cyclic voltammetry performed in THF (0.3 M $n\text{-Bu}_4\text{NBF}_4$) at a stationary gold-disk electrode (i.d. = 0.5 mm) with a scan rate of 0.2 V s^{-1} , at 20°C : (a) reduction of $\text{PdCl}_2(\text{Ph-BIAN})$ (2 mM) in the presence of Ph-BIAN (2 mM); (b) same experiment as in (a) but the scan direction after reduction was reversed at -1.1 V , just after R_2 ; (c) same experiment as in (b) but the potential was held for a while at -1.1 V .

for R_4 (-1.28 V) for the reduction of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$. However, on the reverse scan we observed two oxidation peaks at -1.19 and -0.80 V (Table 3) that correspond to the oxidation peaks O_4 (-1.19 V) and O_3 (-0.80 V) of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})^{2-}$ (Table 2, reactions 7 and 8). Furthermore, the oxidation peak O_3 was reversible (Figure 3a) as in the case of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$ at $R_3 = -0.71 \text{ V}$ (Tables 2 and 3). The fact that the oxidation peaks characteristic of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})^{2-}$ were observed on the reverse scan demonstrates that the complex $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$ has been generated during the reduction of $\text{PdCl}_2(p\text{-Tol-BIAN})$ in the presence of DMFU. This second conclusion seems to be in contradiction with that mentioned above.

A first hypothesis, i.e., that the reduction of $\text{PdCl}_2(p\text{-Tol-BIAN})$ affords directly and quantitatively the zerovalent palladium complex $\text{Pd}^0(p\text{-Tol-BIAN})$ (or $\text{Pd}^0(p\text{-Tol-BIAN})\text{Cl}_x^{x-}$; $x = 1, 2$), which could react with DMFU to afford $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$, can be easily rejected. Indeed, the first reduction of the latter occurs at -0.79 V , i.e. at a potential less negative than that where it would be produced at R_2 . This would imply that the second reduction peak of the bivalent complex $\text{Pd}^{\text{II}}\text{Cl}_2(p\text{-Tol-BIAN})$ at R_2 should involve two electrons

and so the peak current of R_2 should have a double magnitude in the presence of DMFU. This was not observed for DMFU (Figure 3a), for DMM (Figure 3c), or for Ph-BIAN (Figure 4a). Moreover, as mentioned above, the second reduction peak of $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})$ at R_4 was never observed on the first reduction scan.

A second hypothesis would be that the two-step reduction of $\text{PdCl}_2(p\text{-Tol-BIAN})$ at R_2 affords the monovalent palladium complex $\text{Pd}^{\text{I}}\text{Cl}(p\text{-Tol-BIAN})^{\bullet-}$ (reaction 9), which reacts with the olefin to produce the complex $\text{Pd}^{\text{I}}\text{Cl}(p\text{-Tol-BIAN})(\text{DMFU})^{\bullet-}$, which is reduced at R_5 .

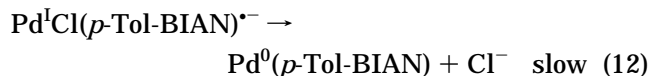


Note that in this framework, the peak R_5 must involve the exchange of two electrons because it yields the dianion oxidized at O_4 . However, its magnitude is less than that of R_2 (1e) because reaction 10 is not quantitative, as indicated by the presence of the free olefin reduced at R_6 . Therefore, the complex $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})^{2-}$ is generated at R_5 , and on the reverse scan one can observe its two reversible sequential oxidations:

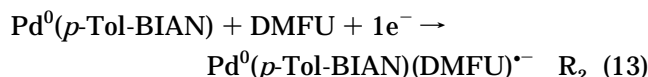


However, for a given scan rate, when the scan direction was reversed at -1.2 V , i.e. after the reduction at R_2 but before the reduction at R_5 , the oxidation peak O_3 was already observed but its magnitude was much lower as compared to the situation where the scan direction was reversed at -1.7 V (i.e. after the reduction at R_5) (compare parts a and b of Figure 3). This shows that some complex $\text{Pd}^0(p\text{-Tol-BIAN})(\text{DMFU})^{\bullet-}$ has been generated during the time required to scan the potential

between peaks R_2 and O_3 . We have demonstrated above (by ruling out the first hypothesis) that the complex Pd^0 -(*p*-Tol-BIAN) was not produced directly and quantitatively at R_2 . Therefore, $Pd^I Cl(p\text{-Tol-BIAN})^{\bullet-}$, which is quantitatively produced at R_2 , slowly affords $Pd^0(p\text{-Tol-BIAN})$:

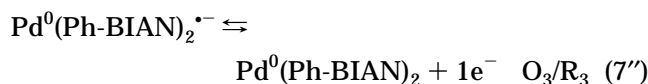
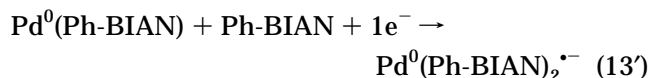
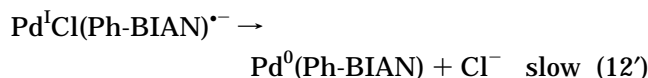


Its reaction with DMFU affords the complex $Pd^0(p\text{-Tol-BIAN})(DMFU)$, which is immediately reduced to Pd^0 -(*p*-Tol-BIAN)(DMFU) $^{\bullet-}$, since the first reduction potential of $Pd^0(p\text{-Tol-BIAN})(DMFU)$ is located at R_3 , i.e. before the potential R_2 where it starts to be produced:



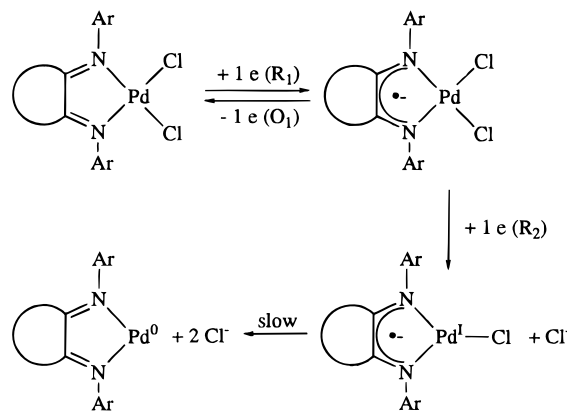
However, this overall process is slow. The time elapsed between R_2 and R_5 is very short compared to that elapsed between R_2 and O_3 . Hence, the complex $Pd^0(p\text{-Tol-BIAN})(DMFU)^{\bullet-}$ cannot be formed in appreciable quantity during such a short time, which is the reason that we do not observe its reduction peak R_4 and also that the reduction peak R_2 always involves nearly one electron and not two.

In the case of the reduction of $Pd^{II}Cl_2(Ph\text{-BIAN})$ in the presence of Ph-BIAN (1 equiv) reported in Figure 4, the reduction at R_5 was necessary to produce the Pd^0 -(Ph-BIAN) $_2^{2-}$ complex oxidized at O_4 and O_3 (by reactions similar to reactions 10 and 11), since the current of O_3 decreased drastically when the scan direction was reversed at -1.1 V just after R_2 instead of -2 V (compare parts a and b of Figure 4). However, when the potential was held at -1.1 V for a while, just before inversion, the oxidation peak O_3 was observed with a higher magnitude on the reverse scan (Figure 4c). During the duration of the potential hold, the following reactions had time to proceed:

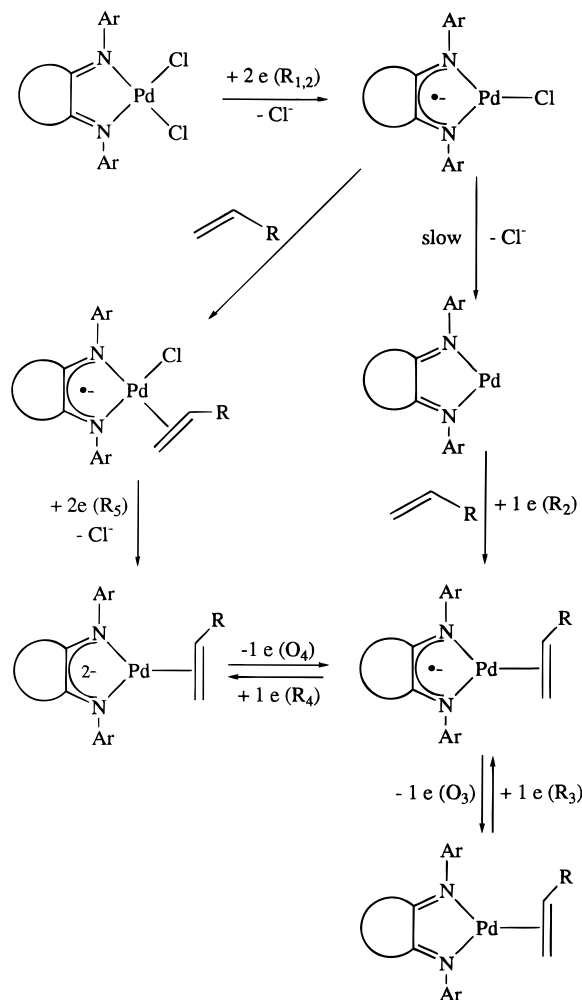


These results show that the reaction of $Pd^0(Ar\text{-BIAN})$ with Ar-BIAN is slower than that with the alkenes. Therefore, we can assume that the reduction of $Pd^{II}Cl_2(Ph\text{-BIAN})^{\bullet-}$ afforded the monovalent palladium species $Pd^I Cl(Ph\text{-BIAN})^{\bullet-}$ with one electron still located on the ligand. The zerovalent palladium complex $Pd^0(Ph\text{-BIAN})$ (or $Pd^0(Ph\text{-BIAN})Cl_x^{\bullet-}$) is not produced directly from the reduction of $Pd^{II}Cl_2(Ph\text{-BIAN})^{\bullet-}$ but is formed from the $Pd^I Cl(Ph\text{-BIAN})^{\bullet-}$ complex³⁵ by a slow intramolecular reaction in which the electron is transferred from the ligand to the palladium(I). The overall reduction of $Pd^{II}Cl_2(Ph\text{-BIAN})$ might be summarized as in Scheme 2.

Scheme 2



Scheme 3



The general mechanism of the reactions of alkenes (or Ph-BIAN) with the low-valent palladium complexes generated from the reduction of the bivalent $Pd^{II}Cl_2$ -(Ar-BIAN) can be summarized as in Scheme 3.

In Situ Reaction of Organic Halides with the Palladium Complexes Formed upon Reduction of $Pd^{II}Cl_2(Ar\text{-BIAN})$ Complexes. The cyclic voltammogram of the reduction of $Pd^{II}Cl_2(Ar\text{-BIAN})$ remained

(35) The $Pd^I Cl(Ph\text{-BIAN})_2^{\bullet-}$ complex contains two paramagnetic entities but could not be characterized by ESR spectroscopy. Indeed, the complex was produced during a short time, i.e., during the voltammetric scan. In order to observe electrogenerated species in the cavity of an ESR instrument, special equipment is required, which is not available in our institutes.

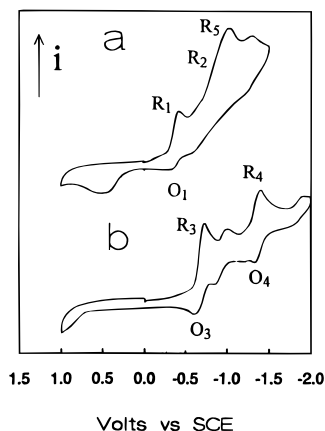
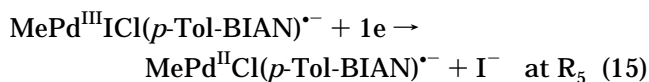
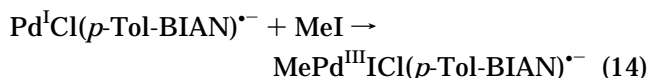
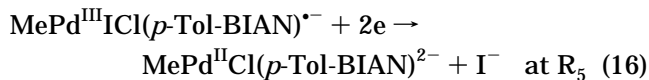


Figure 5. Cyclic voltammetry performed in THF (0.3 M $n\text{-Bu}_4\text{NBF}_4$) at a stationary gold-disk electrode (i.d. = 0.5 mm) with a scan rate of 0.2 V s⁻¹, at 20 °C: (a) reduction of $\text{PdCl}_2(p\text{-Tol-BIAN})$ (2 mM) in the presence of MeI (2 mM); (b) Reduction of $\text{MePdI}(p\text{-Tol-BIAN})$ (2 mM).

unchanged in the presence of 1 equiv of PhBr or PhI, demonstrating that no reaction occurred with either $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})^{\bullet-}$ or $\text{Pd}^0(\text{Ar-BIAN})$ during the time scale of the cyclic voltammetry. This poor reactivity contrasts with that of $\text{Pd}^0(\text{PPh}_3)_2$ generated from the reduction of $\text{Pd}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2$, which was found to be very reactive with PhI and a little less with PhBr.^{14c} However, a reaction was observed with methyl iodide, a more reactive organic halide. The cyclic voltammogram of the reduction of $\text{Pd}^{\text{II}}\text{Cl}_2(p\text{-Tol-BIAN})$ in the presence of 1 equiv of MeI is given in Figure 5a. By comparison with the cyclic voltammogram of $\text{MePd}^{\text{III}}\text{I}(p\text{-Tol-BIAN})^9$ given in Figure 5b, we can conclude that the latter was not formed, since we did not observe its second reduction peak at R_4 (see Tables 2 and 3). In contrast, an additional reduction peak was observed at R_5 partially overlapping with peak R_2 (Figure 5a) that might result from the oxidative addition of $\text{Pd}^{\text{I}}\text{Cl}(p\text{-Tol-BIAN})^{\bullet-}$ to MeI.



or



When the scan direction was reversed after R_5 , an oxidation peak was observed at +0.485 V, featuring the oxidation of iodide ions liberated in reaction 15 or 16. The two reduction steps of $\text{MePd}^{\text{III}}\text{I}(p\text{-Tol-BIAN})$ were found to be reversible and of course did not produce any iodide anion, the oxidation of the latter being not observed on the reverse scan (compare parts a and b of Figure 5).

The reduction of the complex $\text{MePd}^{\text{II}}\text{Cl}(p\text{-Tol-BIAN})^{\bullet-}$ is expected to occur at a more negative potential than that of $\text{MePd}^{\text{III}}\text{I}(p\text{-Tol-BIAN})^{\bullet-}$.³⁶ Were reaction 16 operating, it would imply that $\text{MePd}^{\text{II}}\text{Cl}(p\text{-Tol-BIAN})^{2-}$ would be produced at R_5 (−1.02 V), i.e. at a less negative

potential than −1.4 V at which $\text{MePd}^{\text{III}}\text{I}(p\text{-Tol-BIAN})^{2-}$ is formed. Moreover, the oxidation peak O_4 of $\text{MePd}^{\text{II}}\text{Cl}(p\text{-Tol-BIAN})^{2-}$ should then be observed on the reverse scan, but it was not (Figure 5a). Therefore, we can discriminate between reactions 15 and 16 and consider that the reduction peak R_5 most probably corresponds to reaction 15.

Implications to Catalytic and Stoichiometric Reactions of $\text{Pd}^0(\text{Ar-BIAN})$ Complexes. The in situ observation of complexes of the type $\text{Pd}^0(\text{Ar-BIAN})_2$, which could not be synthesized or isolated in any other way, lends support to our proposed mechanism for the substitution of a coordinated Ar-BIAN ligand in a $\text{Pd}^0(\text{Ar-BIAN})(\text{MA})$ complex for another Ar'-BIAN ligand as detailed elsewhere.²⁵ This reaction may occur via initial dissociation of the alkene and formation of a $\text{Pd}^0(\text{Ar-BIAN})(\text{Ar'-BIAN})$ complex, which loses one of the two Ar-BIAN ligands to generate the new $\text{Pd}^0(\text{Ar'-BIAN})(\text{MA})$ complex or to regenerate the starting complex.³⁷ Furthermore, the observation of zerovalent $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$ complexes containing DMM and MeAc, complexes which could not be isolated from reaction of $\text{Pd}^0(\text{DBA})_2$ or $\text{Pd}^0_3(\text{TTAA})_3$ (DBA = dibenzylideneacetone, TTAA = tritoluylideneacetylacetone) with Ar-BIAN in the presence of these alkenes, shows that these alkenes are able to stabilize $\text{Pd}^0(\text{Ar-BIAN})^{38}$ fragments in solution. Similar species are expected to be formed in solution during the hydrogenation of these alkenes by $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$ complexes, a reaction which was shown to be homogeneous for alkenes containing at least one electron-withdrawing substituent.³⁹ For the isolation of zerovalent complexes of the type $\text{Pd}(\text{Ar-BIAN})(\text{alkene})$, strongly electron-withdrawing alkenes such as DMFU, MA, fumaronitrile, and tetracyanoethylene were necessary, whereas for alkenes containing less electron-withdrawing substituents starting materials and/or decomposition products were recovered after attempted isolation. The electrochemical results show that such complexes can be formed in solution, although they are not isolable.

Conclusion

A series of divalent palladium and platinum complexes containing the rigid Ar-BIAN and Ph-BIC ligands has been synthesized and characterized; the $\text{Pd}^{\text{II}}\text{Cl}_2(\text{Ar-BIAN})$ complexes show interesting electrochemical behavior. The two one-electron reductions of $\text{Pd}^{\text{II}}\text{Cl}_2(\text{Ar-BIAN})$ complexes result in the formation of $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})^{\bullet-}$ complexes, which are able to react with alkenes, Ar-BIAN ligands, and MeI but not with aryl halides during the time scales investigated. The $\text{Pd}^{\text{I}}\text{Cl}(\text{Ar-BIAN})^{\bullet-}$ complexes slowly afford some $\text{Pd}^0(\text{Ar-BIAN})$ complex which coordinates alkenes or Ar-BIAN, giving $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$ and $\text{Pd}^0(\text{Ar-BIAN})_2$ complexes,

(36) The reduction peak potentials of $\text{ArPdX}(\text{PPh}_3)_2$ complexes are in the following order: $\text{I} < \text{Br} < \text{Cl}$.^{14d} The same order was found for $\text{PdX}_2(\text{PPh}_3)_2$.^{14c}

(37) In view of some current studies involving Ar-BIAN and similar rigid ligands we cannot, however, exclude the possibility that one nitrogen of the Ar-BIAN dissociates, followed by addition of another Ar'-BIAN molecule, generating as an intermediate a $\text{Pd}(\text{Ar-BIAN})(\text{Ar'-BIAN})(\text{alkene})$ complex in which two BIAN ligands are (monodentate) coordinated.

(38) Complexes of the formula " $\text{Pd}^0(\text{Ar-BIAN})$ " are expected to be extremely reactive toward oxidative addition, due to the coordinative unsaturation and the bent geometry of the complex.^{15b}

(39) van Asselt, R.; Elsevier, C. J. *J. Mol. Catal.* **1991**, *65*, L13.

supporting the proposed mechanisms for ligand exchange reactions²⁵ and homogeneous alkene hydrogenation reactions.³⁹ In neither case can the complexes $\text{Pd}^0(\text{Ar-BIAN})(\text{alkene})$, $\text{Pd}^0(\text{Ar-BIAN})_2$, and $\text{MePd}^{\text{II}}(\text{Ar-BIAN})$ be obtained directly by reduction in cyclic voltammetry, because they are all generated at a potential which is more negative than their first reduction step. In all cases they are then generated in a state corresponding to their first or second reduction. Nevertheless, electrochemistry has provided evidence that species which cannot be generated via synthetic routes, such as $\text{Pd}^0(\text{Ar-BIAN})(\text{MeAc})$ and $\text{Pd}^0(\text{Ar-BIAN})_2$, are indeed accessible. In contrast to the reduction of $\text{Pd}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_2$, which affords quantitatively the zerovalent complex $\text{Pd}^0(\text{PPh}_3)_2$ ligated by chloride anions, the reduction of $\text{Pd}^{\text{II}}\text{Cl}_2(\text{Ar-BIAN})$ complexes does not afford

directly and quantitatively $\text{Pd}^0(\text{Ar-BIAN})$ complexes. This is due to the ability of the Ar-BIAN ligand to accept one electron, whereas this is not the case for the triphenylphosphine ligand, where the electrons are not transferred to the ligand but remain on the palladium center.

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