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

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The synthesis and characterization of divalent palladium and platinum complexes of the type PdX₂(Ar-BIAN) (X = Cl, Br, I, OC(O)Me), PdCl₂(Ph-BIC) and PtCl₂(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 o-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 PdCl₂(Ar-BIAN) complexes in THF or DMF occurs via two one-electron reductions and affords the complex PdCl₂(Ar-BIAN)⁺, which slowly produces some Pd²⁺(Ar-BIAN) complex. PdCl₂(Ar-BIAN)⁺ reacts with iodomethane, whereas with iodobenzene or bromobenzene no reaction was observed. PdCl₂(Ar-BIAN)⁺ reacts with free Ar-BIAN or the alkenes dimethyl furarate, dimethyl maleate, and methyl acrylate, giving complexes of the formulas PdCl₂(Ar-BIAN)²⁺ and PdCl₂(Ar-BIAN)(alkene)⁺, respectively. A two-electron reduction of the latter afforded Pd⁰(Ar-BIAN)₂ and Pd⁰(Ar-BIAN)(alkene)²⁻, respectively, whose further oxidation in two one-electron steps produces Pd⁰(Ar-BIAN) and Pd⁰(Ar-BIAN)(alkene). The Pd⁰(Ar-BIAN) complex which is slowly formed from PdCl₂(Ar-BIAN)⁺ reacts with alkene but directly affords the complexes Pd⁰(Ar-BIAN)(alkene)⁺ because Pd⁰(Ar-BIAN)(alkene) complexes are formed at a potential more negative than their first reduction potential. Reoxidation of Pd⁰(Ar-BIAN)(alkene)⁺ affords Pd²⁺(Ar-BIAN)(alkene) complexes. The results of the electrochemical experiments corroborate earlier mechanistic proposals of exchange of Ar-BIAN ligands in Pd⁰(Ar-BIAN)(alkene) complexes and homogeneous hydrogenation of electron-poor alkenes by Pd²⁺(Ar-BIAN)(alkene) complexes.

Introduction

Divalent palladium and platinum complexes are valuable catalyst precursors and have been used in a wide variety of reactions, including carbonolation of alkenes, organic halides, and nitroaromatic compounds. C=C cross coupling, allylic alkylation, and Heck type reactions. 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 Al(i-Bu)₂H₃ or Li₂(cyclooctatetraene) prior to further reactions has been reported. The formation of a Pd(0) complex from the Pd(OC(O)Me)₂/PPh₃ system has been elucidated by electrochemistry.

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 Pd₀(Ar-BIAN)(alkene). 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 Pd(Ar-BIAN)(alkene) species. Because of...
stereic 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. benzylic chloride and \(\beta\)-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 organonitrogen and -zinc reagents in the presence of 1 mol% of a PdCl\(_2\)(Ar-BIAN) catalyst,\(^{8a,b}\) as in the latter cases a transient reactive 14-electron Pd\(_0\)(Ar-BIAN) complex is formed in situ.

In view of the high reactivity of 14-electron zerovalent Pd\(_2\) complexes toward oxidative addition, we have investigated the possibility of in situ generation of low-coordinated Pd\(_0\)(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 aluminium compounds\(^{10}\) or with fluoride anion,\(^{11}\) (ii) photochemical extrusion of CO\(_2\) or N\(_2\) from M(II) complexes containing oxalate\(^{12}\) or azide\(^{13}\) 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 PdCl\(_2\)(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 PdX\(_2\)(Ar-BIAN) (\(X = \text{Cl, Br, I, OC(O)Me}\), PdCl\(_2\)(Ph-BIC) (Ph-BIC = bis-(phenylimino)camphane) and PtCl\(_2\)(Ar-BIAN) complexes 1–5 are described.

![Scheme 1](attachment:image.png)

**Experimental Section**

All syntheses were performed in air, unless noted otherwise. \(^1\)H NMR spectra were recorded on a Bruker AMX 300 (300.13 MHz) and a Bruker AC 100 (100.13 MHz) spectrometer and \(^13\)C 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. PdCl\(_2\)(PhCN)\(_2\), PdCl\(_2\)(PEt\(_2\)) and PtCl\(_2\)(SEt\(_2\)) were synthesized by following reported procedures. PdCl\(_2\)(MeCN)\(_2\) was synthesized in a similar way to that reported for PdCl\(_2\)(PhCN)\(_2\).

**PdCl\(_2\)(Ph-BIAN) (1a). Method A.** To a solution of 2.02 g of PdCl\(_2\)(PhCN)\(_2\) (5.3 mmol) (or 1.37 g (5.3 mmol) of PdCl\(_2\)(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.

![Image](attachment:image.png)

**References**

Dichloromethane layers were washed with water (3×) 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, washed with diethyl ether (3×30 mL), and dried in vacuo, yielding 2.81 g of an orange solid (76%).

**Method B.** A suspension of 1.28 g of PdCl2 (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 acetonitrile was added. The solid product was filtered off, washed with diethyl ether (3×30 mL), and dried in vacuo, yielding 2.56 g of PdCl2(Ph-BIAN) as an orange powder (95%).

11C NMR (ppm, DMSO-d6): C, 55.65 (56.55); H, 3.25 (3.16); N, 5.13 (5.05). IR (cm−1, KBr): 1610, ν(C=N); 348, ν(Pd−Cl). 13C NMR (ppm, DMSO-d6, the atom-numbering scheme is shown in Table 1): C1, not observed; C2, 124.8; C3, 128.9; C4, 133.2; C5, 132.0; C6, 147.1; C7, 141.2; C8, 140.4; C9, 124.8; C10, 129.7; C11, 30.2; CH1, 24.7, 24.2; CH2(i-Pr), 25.1, 24.2; CH3(i-Pr), 23.7, 23.5; CH3(-Pr2C6H3-BIAN) (4e).

**PdCl2(p-Tol-BIAN) (1b).** A red solution was evaporated to about 3 mL, 25 mL of hexane was added, and the mixture was cooled to 20 °C over 4 h, the solution was evaporated to dryness. The solid was obtained 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 purple-red product was obtained.

**PdCl2(p-Tol-BIAN) (3b).** A suspension of 1.28 g of PdCl2 (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 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 (calcld for C18H14Cl2N2Pd): C, 63.49 (63.77); H, 6.04 (5.95); N, 4.51 (4.34). IR (cm−1, KBr): 1616, ν(C=N); 345, ν(Pd−Cl). MS (m/z): 570 (calcld 570).

**PdCl2(o,o-MeOC6H4-BIAN) (1d).** The spectrum of the product formed was identical with that of 1a (method A) by addition of 0.95 equiv of p-Tol-BIAN to a filtered solution of PdCl2(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 (calcld for C26H20Cl2N2Pd): C, 58.95 (58.07); H, 3.86 (3.75); N, 4.99 (5.50). IR (cm−1, KBr): 1620, ν(C=N); 350, ν(Pd−Cl). MS (m/z): 538 (calcld 538).

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vacuo to yield 0.57 g of a brown-red solid (59%). Anal. Found (calcd for C_{24}H_{16}Cl_{2}N_{2}Pt): C, 48.17 (48.26); H, 2.70 (2.62); N, 4.68 (4.75). IR (cm\(^{-1}\), KBr): 1618 sh, ν(C=N); 348, ν(Pt-Cl). MS (m/z): 598 (calcd 598).

PtCl\(_2\)(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\(_2\)N\(_2\)Pt): C, 49.26 (49.85); H, 2.90 (2.88); N, 4.75 (4.68). IR (cm\(^{-1}\), KBr): 1630 sh, ν(C\(_\equiv\)N); 339, ν(Pt-Cl). MS (m/z): 626 (calcd 626).

**Electrochemical Setup and Procedure for Cyclic Voltammetry.** Cyclic voltammetry was performed as described previously.\(^{21}\) A home-built potentiostat equipped with a rotator for ohmic drop compensation was used. The reference electrode was an SCE (Tacussel) separated from the solution by a bridge (3 mL) filled with an n-Bu4NBF\(_4\) 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 PdCl\(_2\)(Ph-BIAN) (0.024 mmol) was dissolved in 12 mL of a solution of 1.48 g of n-Bu4-NBF\(_4\) (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, (0 to +2.0 V) followed by oxidation (+2.0 to +3.1 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(Ph-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 PdCl\(_2\)(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 PdCl\(_2\)(Ph-BIAN) (1a; 0.022 mmol, [Pd] = 1.83 mM) and 4.9 mg of ferrocene (Fe\(_2\)Pd\(_2\)(ty-BIAN)\(_2\)); 0.026 mmol, [Fe\(_2\)] = 2.16 mM) were dissolved in 12.0 mL of a 0.30 M solution of n-Bu4NBF\(_4\) in THF. The limiting current for the steady-state voltammetry, performed at a gold ultramicroelectrode (10 µm diameter) with a scan rate of 20 mV s\(^{-1}\), was i\(_{\text{lim,Fe}}\) = (0.175 V)G = 1.82 nA for 1a (where G = 10.44 nA V\(^{-1}\) is the gain of the potentiostat) and i\(_{\text{lim,Pd}}\) = (0.69 V)G = 7.20 nA for the ferrocene. Cyclic voltammetry at θ = 100 ms (E\(_{\text{lim,Pd}}\) = -0.58 V and E\(_{\text{lim,Fe}}\) = +0.75 V) performed at a gold electrode (0.5 mm diameter) revealed currents of i\(_{\text{Pd}}\) = (0.50 V)G = 2.62 µA for 1a (where G = 5.25 µA V\(^{-1}\) is the gain of the potentiostat) and i\(_{\text{Fe}}\) = (0.99 V)G = 5.19 µA for the ferrocene. At θ = 100 ms, i\(_{\text{Pd}}\) = (0.71 V)G = 3.72 µA for 1a and i\(_{\text{Fe}}\) = (1.36 V)G = 7.14 µA 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 = \(nFvC_{\text{D}}D^{1/2}t^{1/2}\) (S = electrode surface; \(\theta\) = step duration), so that

\[
\frac{i_{\text{lim,Pd}}}{i_{\text{lim,Fe}}} = \frac{n_{\text{Pd}}[\text{Pd}]D_{\text{Pd}}^{1/2}}{[\text{Fe}]D_{\text{Fe}}^{1/2}} = \frac{A}{B}
\]

From expressions A and B one gets

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

and thus:

\[
\frac{n_{\text{Pd}}}{{B}^2} = \frac{(i_{\text{lim,Pd}})^2(i_{\text{lim,Fe}})[\text{Fe}]}{(i_{\text{lim,Fe}})^2(i_{\text{lim,Pd}})[\text{Pd}]}
\]

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

\[
\frac{i_{\text{lim,Fe}}D_{\text{Fe}}}{i_{\text{lim,Pd}}D_{\text{Pd}}} = \frac{D_{\text{Fe}}}{D_{\text{Pd}}} = 2.16 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}
\]

Under these conditions, the characteristic time of the voltammetry at the ultramicroelectrode is \(T = r^2/D = 115 \text{ ms}\), 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(Ph-BIAN)palladium complexes 1 have been synthesized in good yields by substitution of weakly coordinating ligands from suitable precursors, such as PdCl\(_2\)(PhCN)\(_2\) and PdCl\(_2\)(MeCN)\(_2\) (eq 1). PdCl\(_2\)-

\[
PdCl_2(\text{PhCN})_2 + \text{Ar-BIAN} \rightarrow \text{CH}_2\text{Cl}_2, 20°C
\]

PdCl\(_2\) + Ar-BIAN \rightarrow MeCN, reflux

(COD) (COD = (Z,Z)-1,5-cyclooctadiene) could also be used as a precursor, but substitution of dimethyl sulfide ligands from PdCl\(_2\)(SM\(_2\)E\(_2\)) by Ar-BIAN ligands was only very slow. Alternatively, the same complexes were obtained by direct reaction of an Ar-BIAN ligand with PdCl\(_2\) in acetonitrile, via in situ formed PdCl\(_2\)(MeCN)\(_2\)). When the latter method is applied, metallic palladium and impurities from the PdCl\(_2\) 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. PdCl\(_2\)-(1)


(Ph-BIC) (1f) was obtained similarly to the PdCl2(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 PdCl2 in the presence of an excess of sodium bromide (about 10 equiv relative to palladium) or by reaction with PdBr2 (eq 2).

PdCl2 + Ar-BIAN \[\xrightarrow{\text{NaBr}}\] MeCN, 70 °C

PdBr2 + Ar-BIAN \[\xrightarrow{\text{MeCN, 70 °C}}\]

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 Pd(Ar-BIAN)(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 PdCl2(Ar-BIAN), PdI2(Ar-BIAN), and PdClI(Ar-BIAN).

Pd(OC(O)Me)2(o,o′-i-Pr2C6H3-BIAN)(4e) was obtained by reaction of o,o′-i-Pr2C6H3-BIAN with Pd(OC(O)Me)2 in acetonitrile. This complex reacted with aqueous concentrated hydrochloric acid to give quantitatively the dichloro complex 1e (eq 3).

\[\text{Pd(OC(O)Me)2}(o,o′-i-Pr2C6H3-BIAN) + 2\text{HCl(aq)} \rightarrow \text{PdCl2}(o,o′-i-Pr2C6H3-BIAN) + 2\text{MeCOOH}}\]

Synthesis of the dichloro(Ar-BIAN)platinum complexes 5 was achieved by reaction of K[PtCl2(C2H4)]·H2O with the appropriate Ar-BIAN ligand (eq 4). There was no evidence for the formation of any five-coordinate PtCl2(Ar-BIAN)(C2H4) complex22 under the conditions described here. No PtCl2(Ar-BIAN) complexes were obtained when Ar-BIAN was reacted with K2PtCl4, which was used for the synthesis of PtCl2(phen),23 cis-/trans-PtCl2(SEt2)2, and trans-PtCl2(MeCN)2.24 However, formation of PtCl2(Ph-BIAN) (5a) was achieved when the reaction of Ph-BIAN with PtCl2(SEt2)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 PtCl2(SEt2)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

### Table 1. 1H NMR Data for PdX2(Ar-BIAN) and PtCl2(Ar-BIAN) Complexes 1−5

<table>
<thead>
<tr>
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<th>H5</th>
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<td>1b</td>
<td>6.66 d</td>
<td>7.65 pst</td>
<td>8.30 d</td>
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<td>5b</td>
<td>7.05 d</td>
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</table>

* Recorded at 300.13 MHz in CDCl3 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 DMSO-δ6. c 1.50 s, OC(O)Me.

**References**

have shifted to higher frequency upon coordination, especially H2 and H3 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.\textsuperscript{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.\textsuperscript{19c,25} The perpendicular orientation of these aromatic rings in the complexes appears also from the observed low-frequency singlet at 1.55 ppm for the acetate moiety in Pd(OC(O)Me)2(0,0'-Pr2C6H3-I-Ar-BIAN) (4e), which must be ascribed to anisotropic shielding of this methyl group by the aromatic ring of the 0,0'-l-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-CH2-N-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 $^{13}$C NMR spectroscopy of some complexes, especially for the imine carbon C1 and the naphthene C atoms C3,4,5. Unfortunately, the solubility of most complexes is rather low, which precluded the collection of $^{13}$C NMR data for the entire series of complexes.

The IR spectra of the complexes (as KBr pellets) show a broadening of the C=O 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(N) complexes (M = Pd, Pt; NN = α-dilimine ligand) two close-lying M-Cl vibrations were reported.\textsuperscript{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.\textsuperscript{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 $^1$H NMR spectral data identical with the complexes obtained by the reaction of Pd(Me)Cl(COD) with Ar-BIAN.\textsuperscript{3c}

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 PdCl2(Ar-BIAN)(DMF)$^+$-Cl$^-$ species. In previous papers we described the necessity of strongly polar aprotic solvents such as DMF and HMPA (hexamethylphosphoramic triamide) in Pd(Ar-BIAN)(DMF)-catalyzed cross-coupling reactions of organic halides (RX) with organotin reagents (R'MeSn).\textsuperscript{8a,b} Probably, the Pd(R)(Ar-BIAN) complex formed after oxidative addition of RX to Pd(Ar-BIAN)(DMF) 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'MeSn, as compared to the neutral Pd(RX)(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'MeSn, 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.\textsuperscript{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).\textsuperscript{26} 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 electrons involved in the first reduction step of Pd$^{II}$Cl2(PH-BIAN) (1a) by using double-step chronoamperometry and

\[ \text{K[PdCl_2(C_2H_4)H_2O + Ar-BIAN] \rightarrow MeOH/CH_3Cl_2, 20^\circ C} \]

\[ \text{PtCl_2(SEt)_2 + Ar-BIAN} \rightarrow C_2H_4, \text{aceto/CH}_3\text{Cl}_2, 30^\circ C \]

\[ \text{5a Ar = C_6H_5} \]

\[ \text{5b Ar = p-MeC_6H_4} \]

\[ \text{[N\text{Cl}] Pd + SnMe_4 (excess) toluene, 60^\circ C} \]


(28) In DMF, an additional small reversible reduction peak was observed at about 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(Ar-BIAN). The most likely explanation is a thermal reaction of PdCl2(PH-BIAN) with DMF with formation of the cationic complex PdCl2(PH-BIAN)(DMF)$^+$-Cl$^-$ coordinated by DMF. In agreement with this assumption, we observed that the current of this peak decreased when n-Bu4NCI (5–60 equiv relative to the palladium complex) was added to the solution.
assume that the first reduction at R1 is located on the orbital of the diimine ligand.19c,31

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>Epc(R0)/Epd(O0) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph-BIAN</td>
<td></td>
</tr>
<tr>
<td>PdCl2(Ph-BIAN) (1a)</td>
<td></td>
</tr>
<tr>
<td>PdCl2(Ph-BIAN) (1a)b</td>
<td></td>
</tr>
<tr>
<td>PdCl2(p-Tol-BIAN) (1b)</td>
<td></td>
</tr>
<tr>
<td>PdCl2(p-Tol-BIAN) (1b)b</td>
<td></td>
</tr>
<tr>
<td>PdCl2(p-MeOC6H4-BIAN) (1c)</td>
<td></td>
</tr>
<tr>
<td>Epc(R1)/Epd(O1) (V)</td>
<td></td>
</tr>
<tr>
<td>Epc(R0)/Epd(O0) (V)</td>
<td></td>
</tr>
<tr>
<td>Epc(R1)/Epd(O3) (V)</td>
<td></td>
</tr>
<tr>
<td>Epc(R0)/Epd(O4) (V)</td>
<td></td>
</tr>
</tbody>
</table>

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.

The cyclic voltammogram of solely the ligand Ph-BIAN 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). 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)²⁹a, similar to the reduction reported for PtCl2(α-dimine) complexes.³⁰ Furthermore, it is expected that the LUMO of complexes of the type dis-MCl2(dimine) (M = Pd, Pt) is the π*-orbital of the dimine ligand.²⁹c,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:

PdCl2(Ph-BIAN)²⁻ + 2e⁻ → PdCl2(Ph-BIAN)²⁻ + Cl⁻ or

PdCl2(Ph-BIAN)²⁻ + 2e⁻ → PdCl2(Ph-BIAN)²⁻ + (2 - x)Cl⁻

x = 0 - 2

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

Volts vs SCE

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:

\[ \text{PdCl}_2(\text{Ph-BIAN}) + \text{e}^- \rightarrow \text{PdCl}_2(\text{Ph-BIAN})^- \] (6)

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

The cyclic voltammogram of solely the ligand Ph-BIAN 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). 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)²⁹a, similar to the reduction reported for PtCl2(α-dimine) complexes.³⁰ Furthermore, it is expected that the LUMO of complexes of the type dis-MCl2(dimine) (M = Pd, Pt) is the π*-orbital of the dimine ligand.²⁹c,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:

\[ \text{PdCl}_2(\text{Ph-BIAN})^- + \text{e}^- \rightarrow \text{PdCl}_2(\text{Ph-BIAN})^{2-} \]

\[ \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \rightarrow \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \]

\[ \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \rightarrow \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \]

\[ \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \rightarrow \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \]

\[ \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \rightarrow \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \]

\[ \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \rightarrow \text{PdCl}_2(\text{Ph-BIAN})^{2-} + \text{Cl}^- \]

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.


(32) In this case the reduction afforded three chloride-ligated palladium(0) complexes involved in fast equilibrium: \[ \text{Pd(PPh3)_2Cl}_3 \] depending on the chloride ion and palladium concentration (n = 1, x = 1; n = 2, x = 2).¹⁴
the reduction of the zerovalent complexes Pd(p-Tol-BIAN)(DMFU) (DMFU = dimethyl fumarate) and Pd(p-Tol-BIAN)(MA)\(^{(23)}\) (MA = maleic anhydride) have been collected in Table 2. All palladium complexes showed two reversible reduction peaks at R3 and R4 involving one electron each (Figure 2). For these two complexes, the first reduction is located on the Ar-BIAN ligand, as in PdCl\(_2\)(Ar-BIAN) complexes, whereas the second reduction is located on the alkene ligand, as reported for comparable M\(^0\)(α-diimine)(alkene) complexes (M = Pd, Pt).\(^{(33)}\)

\[
Pd(p\text{-Tol-BIAN})(DMFU) + e^- \rightarrow Pd(p\text{-Tol-BIAN})(DMFU)^{2-} \quad R_3/O_3 \quad (7)
\]

\[
Pd(p\text{-Tol-BIAN})(DMFU)^{2-} + e^- \rightarrow Pd(p\text{-Tol-BIAN})(DMFU)^{3-} \quad R_4/O_4 \quad (8)
\]

The equations for the reduction of Pd(p-Tol-BIAN)-(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 Pd(p-BIAN)-(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 R3 and R4 of Pd(p-Tol-BIAN)(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 PdCl\(_2\)(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 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 (in the presence of the alkene) and 4 (in the presence of Ph-BIAN). In all cases, when PdCl\(_2\)(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 R1 and R2 of the PdCl\(_2\)(Ar-BIAN) complex (which remained similar to those observed in the absence of alkene), two additional reduction peaks at R5 and R6. 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 PdCl\(_2\)(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 R5), two oxidation peaks were observed at O4 and O3 (Figures 3a,c and 4a). By performing successive cyclic scans, we observed that the oxidation peak O3 was reversible (Figures 3a and 4a). We also observed that peak R5, which is the reverse peak of O4, was located at a slightly less negative potential than that observed for peak R3 (Figures 3a and 4a).

A detailed investigation of the mechanism could be achieved in the case of the reduction of PdCl\(_2\)(p-Tol-BIAN) in the presence of DMFU, since an authentic sample of Pd(p-Tol-BIAN)(DMFU) was available (Table 2). By comparison of the electrochemical data from Tables 2 and 3, we noticed that the second reduction peak R3 of Pd(p-Tol-BIAN)(DMFU) was not observable when PdCl\(_2\)(p-Tol-BIAN) was reduced in the presence of DMFU, demonstrating that Pd(p-Tol-BIAN)(DMFU) was not formed. Indeed, the reduction potential observed at R3 (−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).
for R4 (−1.28 V) for the reduction of PdCl₂(p-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 R₂; (c) reduction of PdCl₂(Ph-BIAN) (2 mM) in the presence of DMM (2 mM) and so the peak current of R₂ 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 PdCl₂(p-Tol-BIAN) (DMFU) at R₄ was never observed on the first reduction scan.

A second hypothesis would be that the two-step reduction of PdCl₂(p-Tol-BIAN) at R2 affords the monovalent palladium complex PdᴵCl(p-Tol-BIAN)− (reaction 9), which reacts with the olefin to produce the complex PdᴵCl(p-Tol-BIAN)(DMFU)•−, which is reduced at R₅.

Note that in this framework, the peak R₅ must involve the exchange of two electrons because it yields the dianion oxidized at O₄. However, its magnitude is less than that of R₂ (1e) because reaction 10 is not quantitative, as indicated by the presence of the free olefin reduced at R₆. Therefore, the complex Pd⁰(p-Tol-BIAN)(DMFU)•− is generated at R₅, and on the reverse scan one can observe its two reversible sequential oxidations:

\[
Pd⁰(p-Tol-BIAN)(DMFU)•− + 2e− → PdCl₂(p-Tol-BIAN) + 2Cl− (9)
\]

\[
PdCl₂(p-Tol-BIAN) + 2e− → Pd⁰(p-Tol-BIAN)(DMFU)•− + Cl− (10)
\]

A first hypothesis, i.e., that the reduction of PdCl₂(p-Tol-BIAN) affords directly and quantitatively the zerovalent palladium complex Pd⁰(p-Tol-BIAN)(DMFU)•− or Pd⁰(p-Tol-BIAN)Clₓ−; x = 1, 2, which could react with DMFU to afford Pd⁰(p-Tol-BIAN)(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 R₂. This would imply that the second reduction peak of the bivalent complex Pd³⁺Cl₂(p-Tol-BIAN) at R₂ should involve two electrons

\[
Pd⁰(p-Tol-BIAN)(DMFU)•− + 1e− O₃/R₃ (8′)
\]

However, for a given scan rate, when the scan direction was reversed at −1.2 V, i.e. after the reduction at R₂ but before the reduction at R₃, the oxidation peak O₃ 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 R₅) (compare parts a and b of Figure 3). This shows that some complex Pd⁰(p-Tol-BIAN)(DMFU)•− has been generated during the time required to scan the potential
between peaks R2 and O3. We have demonstrated above (by ruling out the first hypothesis) that the complex Pd0-(p-Tol-BIAN) was not produced directly and quantitatively at R2. Therefore, PdCl(p-Tol-BIAN)\(^{--}\), which is quantitatively produced at R2, slowly affords Pd0(p-Tol-BIAN):

\[
PdCl(p-Tol-BIAN)^{--} \rightarrow \ \ \ \ \ \ \ Pd^0(p-Tol-BIAN) + Cl^- \ \ \ \text{slow (12)}
\]

Its reaction with DMFU affords the complex Pd0(p-Tol-BIAN)(DMFU), which is immediately reduced to Pd0-(p-Tol-BIAN)(DMFU)\(^{--}\), since the first reduction potential of Pd0(p-Tol-BIAN)(DMFU) is located at R3, i.e. before the potential R2 where it starts to be produced:

\[
Pd^0(p-Tol-BIAN) + DMFU + 1e^- \rightarrow \ \ \ \ \ \ \ Pd^0(p-Tol-BIAN)(DMFU)^{--} \ \ \ \text{R2 (13)}
\]

However, this overall process is slow. The time elapsed between R2 and R3 is very short compared to that elapsed between R2 and O3. Hence, the complex Pd0(p-Tol-BIAN)(DMFU)\(^{--}\) cannot be formed in appreciable quantity during such a short time, which is the reason that we do not observe its reduction peak R4 and also that the reduction peak R2 always involves nearly one electron and not two.

In the case of the reduction of PdIICl2(Ph-BIAN) in the presence of Ph-BIAN (1 equiv) reported in Figure 4, the reduction at R5 was necessary to produce the Pd0-(Ph-BIAN)\(^{2-}\) complex oxidized at O4 and O3 (by reactions similar to reactions 10 and 11), since the current of O3 decreased drastically when the scan direction was reversed at \(-1.1 \text{ V}\) just after R2 instead of \(-2 \text{ V}\) (compare parts a and b of Figure 4). However, when the potential was held at \(-1.1 \text{ V}\) for a while, just before inversion, the oxidation peak O3 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:

\[
PdCl(Ph-BIAN)^{--} \rightarrow \ \ \ \ \ \ \ Pd^0(Ph-BIAN) + Cl^- \ \ \ \text{slow (12')} \n\]

\[
Pd^0(Ph-BIAN) + Ph-BIAN + 1e^- \rightarrow \ \ \ \ \ \ \ Pd^0(Ph-BIAN)^{2-} \ \ \ \text{(13')}\n\]

\[
Pd^0(Ph-BIAN)^{2-} \rightarrow \ \ \ \ \ \ \ Pd^0(Ph-BIAN) + 1e^- \ \ \ \text{O3/R3 (7'')}\n\]

These results show that the reaction of Pd0(Ar-BIAN) with Ar-BIAN is slower than that with the alkenes. Therefore, we can assume that the reduction of PdII-Cl2(Ar-BIAN)\(^{--}\) afforded the monovalent palladium species PdCl(Ar-BIAN)\(^{--}\) with one electron still located on the ligand. The zerovalent palladium complex Pd0(Ph-BIAN) (or Pd0(Ph-BIAN)Cl\(^{x-}\)) is not produced directly from the reduction of PdIICl2(Ph-BIAN)\(^{--}\) but is formed from the PdCl(Ph-BIAN)\(^{--}\) complex\(^{35}\) by a slow intramolecular reaction in which the electron is transferred from the ligand to the palladium(I). The overall reduction of PdIICl2(Ph-BIAN) might be summarized as in Scheme 2.

The general mechanism of the reactions of alkenes (or Ph-BIAN) with the low-valent palladium complexes generated from the reduction of the bivalent PdIICl2-(Ar-BIAN) can be summarized as in Scheme 3.

In Situ Reaction of Organic Halides with the Palladium Complexes Formed upon Reduction of PdIICl2(Ar-BIAN) Complexes. The cyclic voltammogram of the reduction of PdIICl2(Ar-BIAN) remained

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\(^{35}\) The PdCl(Ph-BIAN)\(^{--}\) 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.
peak at R4 (see Tables 2 and 3). In contrast, an additional reduction peak was observed at R5 partially overlapping with peak R2 (Figure 5a) that might result from the oxidative addition of PdICl(p-Tol-BIAN)− to MeI.

\[ \text{PdCl}(\text{p-Tol-BIAN})^- + \text{MeI} \rightarrow \text{MePd}^{II}\text{Cl}(\text{p-Tol-BIAN})^- \] (14)

\[ \text{MePd}^{III}\text{Cl}(\text{p-Tol-BIAN})^- + 1e \rightarrow \text{MePd}^{II}\text{Cl}(\text{p-Tol-BIAN})^- + \text{I}^- \text{ at } R_5 \] (15)

or

\[ \text{MePd}^{III}\text{Cl}(\text{p-Tol-BIAN})^- + 2e \rightarrow \text{MePd}^{II}\text{Cl}(\text{p-Tol-BIAN})^2^- + \text{I}^- \text{ at } R_5 \] (16)

When the scan direction was reversed after R5, 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 MePdIII(p-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 MePdIIICl(p-Tol-BIAN)− is expected to occur at a more negative potential than that of MePdII(p-Tol-BIAN)−.\(^{26}\) Were reaction 16 operating, it would imply that MePdIIICl(p-Tol-BIAN)2− would be produced at R5 (−1.02 V), i.e. at a less negative potential than −1.4 V at which MePdIII(p-Tol-BIAN)2− is formed. Moreover, the oxidation peak O4 of MePdIIICl(p-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 R5 most probably corresponds to reaction 15.

**Implications to Catalytic and Stoichiometric Reactions of Pd0(Ar-BIAN) Complexes.** The in situ observation of complexes of the type Pd0(Ar-BIAN), 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 Pd0(Ar-BIAN)(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 Pd0(Ar-BIAN)(Ar′-BIAN) complex, which loses one of the two Ar-BIAN ligands to generate the new Pd0(Ar′-BIAN)(MA) complex or to regenerate the starting complex.\(^{37}\) Furthermore, the observation of zerovalent Pd0(Ar-BIAN)(alkene) complexes containing DMM and MeAc, complexes which could not be isolated from reaction of Pd0(DBA)2 or Pd2(TTAA)3 (DBA = dibenzylideneacetone, TTAA = tritoluylideneacetylacetone) with Ar-BIAN in the presence of these alkenes, shows that these alkenes are able to stabilize Pd0(Ar-BIAN)\(^{38}\) fragments in solution. Similar species are expected to be formed in solution during the hydrogenation of these alkenes by Pd0(Ar-BIAN)(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 Pd0(Ar-BIAN)(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 PdCl2(Ar-BIAN) complexes show interesting electrochemical behavior. The two one-electron reductions of PdCl2(Ar-BIAN) complexes result in the formation of PdCIPdCl(Ar-BIAN) complexes, which are able to react with alkenes, Ar-BIAN ligands, and MeI but not with ary1 halides during the time scales investigated. The PdCl(Ar-BIAN)− complexes slowly afford some Pd0(Ar-BIAN) complex which coordinates alkenes or Ar-BIAN, giving Pd0(Ar-BIAN)(alkene) and Pd0(Ar-BIAN)2 complexes.

\(^{26}\) The reduction peak potentials of ArPdX(PPh3)2 complexes are in the following order: 1 < Br < Cl.\(^{14d}\) The same order was found for Pd0(PPh3)2.\(^{14c}\)

\(^{25}\) 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 Pd(Ar-BIAN)(Ar-BIAN)(alkene) complex in which two Ar-BIAN ligands are (monodentate) coordinated.

\(^{37}\) Complexes of the formula “Pd0(Ar-BIAN)” are expected to be extremely reactive toward oxidative addition, due to the coordinative unsaturation and the bent geometry of the complex.\(^{15b}\)

supporting the proposed mechanisms for ligand exchange reactions and homogeneous alkene hydrogenation reactions. In neither case can the complexes \( \text{Pd}^0(\text{Ar-BIAN})(\text{alkene}) \), \( \text{Pd}^0(\text{Ar-BIAN})_2 \), and \( \text{MePd}^{II}(\text{Ar-BIAN}) \) 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 \( \text{Pd}^{II}\text{Cl}_2(\text{PPh}_3)_2 \), which affords quantitatively the zerovalent complex \( \text{Pd}^0(\text{PPh}_3)_2 \) ligated by chloride anions, the reduction of \( \text{Pd}^{II}\text{Cl}_2(\text{Ar-BIAN}) \) 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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