Oxidative addition of organic halides to zerovalent palladium complexes containing rigid bidentate nitrogen ligands *

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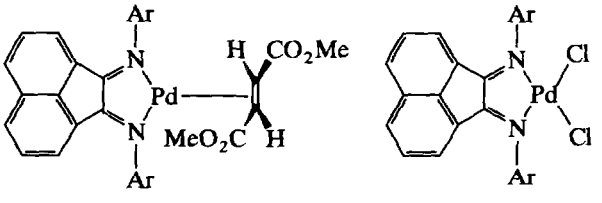
Abstract

Zerovalent complexes of the type Pd(Ar-BIAN)(alkene), *i.e.* complexes containing the rigid bidentate nitrogen ligands bis(arylimino)acenaphthene (Ar = *p*-Tol, *p*-$MeOC_6H_4$, *o*-Tol,*o*,*o*'-$Me_2C_6H_3$, *o*,*o*'-$^iPr_2C_6H_3$) and an electron-poor alkene have been shown to react with a variety of (organic) halides RX, including methyl, benzyl, aryl, acyl and allylic halides, to give the corresponding square planar divalent Pd(R)X(Ar-BIAN) or [Pd(η^3-allyl)(Ar-BIAN)]X complexes. The new complexes obtained have been fully characterized and their fluxional behaviour in solution studied by ^{1}H NMR spectroscopy. The rate of oxidative addition of iodomethane to Pd(*p*-Tol-BIAN)(alkene) complexes was found to decrease with increasing Pd–alkene bond strength, *i.e.* dimethyl fumarate > fumaronitrile, but oxidative addition to the fumaronitrile complex was accelerated by irradiation with a mercury lamp. Oxidative addition of allylic halides to Pd(*p*-Tol-BIAN)(alkene) complexes was instantaneous and independent of the coordinated alkene, whereas the analogous Pd(*o*,*o*'-$^iPr_2C_6H_3$-BIAN)(alkene) complexes react much more slowly. Mechanistic aspects are discussed on the basis of these observations. Some of organopalladium(II) complexes formed were treated with silver salts to give cationic complexes, *e.g.* [Pd(η^3-CH_2Ph)(*p*-Tol-BIAN)]SO_3CF_3. When reactive (organic) halides such as acetyl chloride, benzyl bromide or dihalogens were employed, further oxidative addition occurred. In the case of dibromine, the intermediate $Pd^{IV}Br_4$(*p*-Tol-BIAN) complex was observed by ^{1}H NMR spectroscopy; in the other cases, a $Pd^{II}X_2$(*p*-Tol-BIAN) complex was isolated together with the organic coupling products R_2.

Key words: Palladium; Imine; Oxidative addition; Fluxionality; Rigid ligands; Reductive elimination

1. Introduction

We previously reported the catalytic activity of zerovalent and divalent palladium complexes containing the rigid bidentate nitrogen ligand bis(phenylimino)-acenaphthene, Ph-BIAN [2*], in carbon–carbon cross-coupling reactions of organic halides with organometallic reagents [3]. We expected that complexes containing this type of ligand would have suitable properties for the catalysis of cross-coupling reactions owing to the particular electronic (good σ donor and good π acceptor) and steric (favouring chelating coordination) properties of these ligands.



Ar = C_6H_5
p-MeC_6H_4
p-$MeOC_6H_4$

The generally accepted mechanism of palladium-catalyzed cross-coupling reactions [4] involves initial oxidative addition of an organic halide to a zerovalent Pd(Ph-BIAN) complex through which the halide is activated towards reaction (Scheme 1).

Oxidative addition is a fundamental activation step in many catalytic processes, and as a consequence a

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* Reference numbers with asterisks indicate notes in the list of references.

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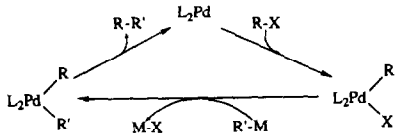


Scheme 1.

large number of reactions of organic halides with transition metal complexes have been reported [5]. A considerable amount of work has focused on zerovalent palladium and platinum complexes containing phosphine ligands, especially $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ [5]. Oxidative addition to palladium and platinum complexes containing bidentate nitrogen ligands such as bpy and phen as the stabilizing and activating ligands have also been reported but these mainly involved transitions between the M^{II} and M^{IV} oxidation states (M = Pd [6], Pt [7]), although some examples of oxidative addition to zerovalent M(NN)(alkene) complexes have been described [8].

Because the steric and electronic properties of Ar-BIAN ligands are markedly different from those of the more commonly used (unidentate) phosphine ligands, we studied reactions of Pd^0(Ar-BIAN) complexes with (organic) halides in detail, in order to gain an insight into their reactivity in oxidative addition. The type of zerovalent complex used was the same as that used for catalytic cross-coupling, *viz.* Pd(Ar-BIAN)(alkene) complexes containing electron-poor alkenes. These complexes can be easily synthesized [9], whereas other types of zerovalent complexes, such as $Pd(Ar\text{-}BIAN)_2$ are not readily accessible. Complexes of the type Pd(R)X(Ar-BIAN) obtained by oxidative addition are valuable starting materials for further mechanistic studies on the Pd(Ar-BIAN)-catalyzed cross-coupling reactions, *e.g.* in stoichiometric reactions with organometallic reagents [1,3(b)].

2. Experimental details

Reactions were performed in air, unless noted otherwise. ^1H NMR spectra were recorded on Bruker AMX 300 (300.13 MHz) and Bruker AC 100 (100.13 MHz) spectrometers 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 positive. ^{19}F NMR spectra were recorded on a Bruker AC 100 spectrometer (94.20 MHz), relative to $CFCl_3$ as external standard. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. $Pd(DBA)_2$ [10] (DBA = dibenzylideneacetone), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ [11], $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ [11], Ar-BIAN [12] and Pd(Ar-BIAN)(alkene) complexes [9] were synthesized by published literature procedures. $[Pd(\eta^3\text{-}PhC_3H_4)Cl]_2$ was made in the same way as $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and obtained in 80% yield.

2.1. Oxidative addition reactions

2.1.1. Pd(Me)I(p-Tol-BIAN) (1a)

Method A — To a solution consisting of 117.7 mg Pd(*p*-Tol-BIAN)(DMFU) (0.19 mmol) in 20 ml acetone was added 50 μl of iodomethane (0.80 mmol) and the mixture was stirred at 20°C for 2 h and the solvent then evaporated. The solid product was washed with diethyl ether (2 × 5 ml) and redissolved in 10 ml of dichloromethane and the solution filtered through Celite. The residue was washed with dichloromethane (2 × 5 ml) and the combined filtrate evaporated to about 1 ml. The product was precipitated by the addition of diethyl ether, washed with 10 ml of diethyl ether, and the product dried *in vacuo* to yield 105 mg (91%) of a dark red solid.

Method B — To a solution consisting of 0.68 g of $Pd(DBA)_2$ (1.18 mmol) and 0.45 g of *p*-Tol-BIAN (1.25 mmol) in 25 ml of acetone was added 100 μl of iodomethane (1.68 mmol). The mixture was stirred at 20°C for 2 h and the solvent then evaporated. The residue was washed with diethyl ether (3 × 10 ml) and purified by filtration through Celite as described above. The yield was 0.61 g (85%) of a dark red product. Analysis: Found: (Calc. for $C_{27}H_{23}IN_2Pd$): C, 53.14 (53.27); H, 3.88 (3.81); N, 4.65 (4.60)%. MS *m/z*: 608 (Calc. 608).

The other complexes were synthesized in the way described for Pd(Me)I(*p*-Tol-BIAN).

PdBr(CH_2Ph)(*p*-Tol-BIAN) (**2a**) was obtained after reaction at 20°C in acetone for 16 h or at 50°C in THF for 1 h, in 87% yield. Analysis: Found (Calc. for $C_{33}H_{27}BrN_2Pd$): C, 61.01 (62.14); H, 4.40 (4.27); N, 4.19 (4.39)%. MS *m/z*: 636/638 (Calc. 636/638).

PdBr($CH_2C_6H_4$-*p*-NO_2)(*p*-Tol-BIAN) (**3a**) was obtained after reaction at 20°C in THF for 30 min, in 79% yield. Analysis: Found (Calc. for $C_{33}H_{26}BrN_3O_2Pd$): C, 58.97 (58.04); H, 3.81 (3.84); N, 6.14 (6.15)%.

Pd(Ph)I(*p*-Tol-BIAN) (**4a**) and Pd(*p*-Tol)I(*p*-Tol-BIAN) (**5a**) were obtained after reaction at 20°C in acetone for 16 h, at 50°C in THF for 3 h or at 55°C in DMF for 15 min, in 70–80% yield. Compound **4a**: Analysis: Found (Calc. for $C_{32}H_{25}IN_2Pd$): C, 57.04 (57.29); H, 3.85 (3.76); N, 4.27 (4.18)%. Compound **5a**: Analysis: Found (Calc. for $C_{33}H_{27}IN_2Pd$): C, 57.41 (57.87); H, 3.90 (3.97); N, 4.10 (4.09)%. MS *m/z*: 684 (Calc. 684).

Pd(C_6H_4-*p*-NO_2)I(*p*-Tol-BIAN) (**6a**) and Pd(2-C_4H_3O)I(*p*-Tol-BIAN) (**7a**) were obtained by reaction

at 20°C in acetone or chloroform for 30 min, in 75–82% yield (2-C_4H_3O = 2-furyl). Compound **6a**: Analysis: Found (Calc. for $C_{32}H_{24}IN_3O_2Pd$): C, 53.92 (53.69); H, 3.47 (3.38); N, 5.75 (5.87)%. Compound **7a**: Analysis: Found (Calc. for $C_{30}H_{23}IN_2OPd$): C, 54.10 (54.53); H, 3.71 (3.51); N, 4.72 (4.24)%.

Pd(C(O)R)Cl(*p*-Tol-BIAN) (R = Me (**8a**), Et (**9a**), CH=CHMe (**10a**)) were obtained by reaction at 20°C in acetone or dichloromethane for 30 min, in 80–85% yield. Compound **8a**: Analysis: Found (Calc. for $C_{28}H_{23}ClN_2OPd$): C, 61.49 (61.67); H, 4.26 (4.25); N, 5.14 (5.14)%. Compound **9a**: Analysis: Found (Calc. for $C_{29}H_{25}ClN_2OPd$): C, 62.92 (62.27); H, 4.36 (4.51); N, 4.94 (5.01)%.

PdI_2(*p*-Tol-BIAN) (**11a**) was obtained by reaction at 20°C in acetone for 30 min, in 73% yield. MS *m/z*: 720 (Calc. for $C_{26}H_{20}I_2N_2Pd$, 720).

[Pd(allyl)(*p*-Tol-BIAN)]X complexes (**12–15a**) were obtained by reaction at 20°C in acetone for 45 min, in 78–86% yield. Compound **13a**: Analysis: Found (Calc. for $C_{29}H_{25}BrN_2Pd$); C, 58.69 (59.25); H, 4.38 (4.29); N, 4.72 (4.77)%. MS *m/z*: 507 (Calc. 507). Compound **14b**: Analysis: Found (Calc. for $C_{30}H_{27}ClN_2O_2Pd$): C, 61.01 (61.13); H, 4.68 (4.62); 4.93 (4.75)%. MS *m/z*: 553 (Calc. 553). Compound **15a**: Analysis: Found (Calc. for $C_{35}H_{30}ClN_2Pd$): C, 67.07 (67.75); H, 4.55 (4.88); N, 4.65 (4.51)%. MS *m/z*: 584 (Calc. 584).

[Pd(η^3-PhC_3H_4)(*p*-Tol-BIAN)]Br (**16a**) was synthesized via oxidative addition of 1-phenylallyl bromide in acetone at 20°C and formed in approximately 10% yield after 2 h, whereas complete conversion was achieved after 16 h (yield 72%).

2.1.2. Oxidative addition of allyl bromide at low temperature

To a solution consisting of 19.9 mg of Pd(*p*-Tol-BIAN)(DMFU) (0.034 mmol) in 0.30 ml of CD_2Cl_2 in an NMR tube, cooled to −78°C, was added 2.9 μl of allyl bromide (0.034 mmol). The tube was transferred to the probe of the NMR spectrometer, precooled to −80°C and the NMR spectrum recorded immediately at −80°C. The spectrum revealed the presence of [Pd(η^3-C_3H_5)(*p*-Tol-BIAN)]Br (**13a**) and uncoordinated DMFU as the sole products.

2.2. Reactions with silver salts

2.2.1. Preparation of [Pd(η^3-CH_2Ph)(p-Tol-BIAN)]SO_3CF_3 (17a)

To a solution consisting of 340.5 mg of PdBr(CH_2Ph)(*p*-Tol-BIAN), (**2a**) (0.53 mmol) in 50 ml of THF was added 142.5 mg $AgSO_3CF_3$ (0.55 mmol). The mixture was stirred in the dark at 20°C for 2 h and the solution was then filtered and evaporated to dryness. The product was redissolved in 30 ml of dichloromethane and the solution passed through Celite and the residue washed with 10 ml of dichloromethane. The combined filtrates were evaporated to about 3 ml and diethyl ether was added to precipitate the product, which was washed with 10 ml of diethyl ether and dried *in vacuo*, yielding 0.33 g of a red solid (88%). Analysis: Found (Calc. for $C_{34}H_{27}F_3N_2O_3PdS$): C, 57.49 (57.76); H, 3.94 (3.85); 4.04 (3.96)%.

[Pd(η^3-$CH_2C_6H_4$-*p*-NO_2)(*p*-Tol-BIAN)]SbF_6 (**18a**) was synthesized from **3a** and $AgSbF_6$ in 74% yield, while [Pd(η^3-C_3H_5)(*p*-Tol-BIAN)]SO_3CF_3 (**19a**) and [Pd(η^3-PhC_3H_4)(*p*-Tol-BIAN)]SO_3CF_3 (**20a**) were made from the halide complexes (**12**, **13a** and **15**, **16a**, respectively) and $AgSO_3CF_3$ by the method for the η^3-benzyl complex **17a**, yielding 84–91% of a yellow–orange solid. Compound **19a**: Analysis: Found (Calc. for $C_{30}H_{25}F_3N_2O_3PdS$): C, 54.00 (54.84); H, 4.34 (3.84); N, 4.03 (4.26)%.

2.3. Synthesis of Pd(allyl)(Ar-BIAN) complexes from [Pd(allyl)Cl]$_2$ dimers

[Pd(η^3-C_3H_5)(*p*-Tol-Bian)]Cl (**12a**) was obtained from a mixture of 80.1 mg of [Pd(η^3-C_3H_5)Cl]$_2$ (0.22 mmol) and 175.0 mg *p*-Tol-BIAN (0.49 mmol) in 10 ml of dichloromethane after stirring at 20°C for 1 h and filtering the solution through Celite. The residue was washed with dichloromethane (5 ml). The combined filtrate and washings were evaporated to ca. 1 ml, and 5 ml of diethyl ether was added to precipitate the product which was washed with diethyl ether (5 ml) and dried *in vacuo*, yielding 0.22 g of an orange–red product (92%).

[Pd(η^3-C_3H_5)(*p*-An-BIAN)]$^+$[Pd(η^3-C_3H_5)Cl_2]$^-$ (**21b**) was obtained by adding 132.4 mg of *p*-An-BIAN (0.34 mmol; *p*-An = *p*-$MeOC_6H_4$) to a solution of 123.4 mg of [Pd(η^3-C_3H_5)Cl]$_2$ (0.34 mmol) in 10 ml of dichloromethane. The mixture was stirred at 20°C for 1 h then filtered through Celite. The residue was washed with 5 ml of dichloromethane and the combined filtrate evaporated to dryness. The product was washed with diethyl ether (2 × 5 ml) and dried *in vacuo*, yielding 0.23 g of a red solid (90%). Analysis: Found (Calc. for $C_{32}H_{30}Cl_2N_2O_2Pd_2$): C, 51.13 (50.68); H, 3.96 (3.99); N, 3.84 (3.69).

[Pd(η^3-C_3H_5)(*o,o'*-$^i Pr_2C_6H_3$-BIAN)]$^+$[Pd(η^3-C_3H_5)Cl_2]$^-$ (**21c**) was synthesized in the same way. ^{1}H NMR ($CDCl_3$, −55°C) δ; 6.70 (d, J = 6.9 Hz, H_3); 7.62 (pst, H_4); 8.38 (d, J = 8.2 Hz, H_5); 7.41 (s, 6H, H_{10-12}); 3.13 (m, CH(^{i}Pr)); 1.33 (d); 1.02 (d, 6.3 Hz, CH_3 (^{i}Pr)); Pd(η^3-C_3H_5)(NN): 5.83 (br, CH); 3.68 (d, J = 6.8 Hz, H_{syn}); 3.27 (d, J = 12.9 Hz, H_{anti}); Pd(η^3-C_3H_5)Cl_2: 5.30 (br, CH); 4.00 (d, J = 6.2 Hz, H_{syn}); 2.89 (d, J = 11.8 Hz, H_{anti}) ppm.

2.4. Reactions of dinuclear allyl palladium complexes (21a,c) with p-An-BIAN

To a solution of 52.3 mg of **21b** (0.069 mmol) in 10 ml of dichloromethane was added 29.1 mg *p*-AnBIAN (0.074 mmol), and the mixture was stirred at 20°C. After 1 h, the solvent was removed *in vacuo* and the product washed with diethyl ether (2 × 5 ml) and dried *in vacuo*, yielding 70 mg of [Pd(*p*-An-BIAN)(η^3-C_3H_5)]Cl (**12b**) (yield 88%). The reaction of 67.5 mg [Pd(η^3-C_3H_5)(*o*,*o*'-^{i}Pr$_2$C$_6$H$_3$-BIAN)]$^+$[Pd(η^3-C_3H_5)Cl$_2$]$^-$ (**21c**, 0.078 mmol) with 31.2 mg of *p*-An-BIAN (0.079 mmol) was performed in the same way.

2.5. Reactions of divalent palladium complexes with (organic) halides

2.5.1. Benzyl bromide

A mixture consisting of 45.4 mg of PdBr(CH$_2$Ph)(*p*-Tol-BIAN) (**2a**) (0.071 mmol) and 0.20 ml of benzyl bromide (1.7 mmol) in 10 ml of THF was stirred at 50°C. After 16 h the solvent was evaporated and the product was shown by NMR spectroscopy to be a mixture of benzyl bromide (δ 4.50 ppm), bibenzyl (δ 2.90 ppm) and PdBr$_2$(*p*-Tol-BIAN) in a ratio of *ca.* 20:1:1.

2.5.2. Acetylchloride

Method a — to a suspension consisting of 0.10 g of Pd(DBA)$_2$ (0.17 mmol) and 65 mg of *p*-Tol-BIAN (0.18 mmol) in 10 ml of acetone or THF, was added 0.12 ml of acetyl chloride (1.7 mmol). The mixture was stirred at 20°C and samples (2 ml) were withdrawn from the reaction mixture at appropriate times (30 min to 16 h), evaporated to dryness and washed with diethyl ether (2 × 5 ml). Analysis of the products by ^{1}H NMR spectroscopy showed that Pd(C(O)Me)Cl(*p*-Tol-BIAN) was present in 95%–100% yield after 30 min and then decreased, with concomitant increase in the amount of PdCl$_2$(*p*-Tol-BIAN), until 100% of the latter was present after 16 h.

Method b — to a solution consisting of 30.4 mg of Pd(Me)I(*p*-Tol-BIAN) (**1a**) (0.050 mmol) in 10 ml of an acetone/dichloromethane (1:1) mixture were added three drops of acetylchloride (excess). The mixture was stirred at 20°C for 20 min and then evaporated to dryness. The product was washed with 5 ml of diethyl ether and dried *in vacuo*. The ^{1}H NMR spectrum indicates the presence of Pd(Me)I(*p*-Tol-BIAN) (**1a**) and Pd(C(O)Me)Cl(*p*-Tol-BIAN) (**8a**) in a ratio of 2.5:1, together with a small amount of a palladium complex containing neither methyl not acetyl ligands (probably PdClI(*p*-Tol-BIAN), 20%).

Method c — a solution consisting of 46.3 mg of Pd(Me)I(*p*-Tol-BIAN) (**1a**) (0.076 mmol) and 10 μl of acetyl chloride (0.14 mmol) in 10 ml of THF was stirred at 20°C and samples for IR spectroscopy were withdrawn at intervals. After 40 h the solvent was evaporated and the residue washed with 5 ml of diethyl ether and dried *in vacuo*. The IR monitoring revealed that the acetyl chloride (1810 cm^{-1}) slowly disappeared and that acetone (1730 cm^{-1}) was formed. ^{1}H NMR data for the final product ($CDCl_3$) δ: 8.20 (br, 2H); 8.03 (br, 1H); 7.53 (br, 2H); 7.36 (br d, 4H); 7.27 (br d, 4H); 6.72 (d, 1H, J = 7.2 Hz); 2.44 (s, 6H) ppm.

2.5.3. Dihalides

Method a — To an NMR tube containing a solution consisting of 20 mg of Pd(Me)I(*p*-Tol-BIAN) (**1a**) (0.033 mmol) in 0.60 ml of $CDCl_3$ cooled to −60°C was added 10 mg of diiodine (0.039 mmol). The tube was transferred to the probe of an NMR spectrometer precooled to −50°C and the spectrum recorded immediately. The only products present were PdI$_2$(*p*-Tol-BIAN) (**11a**) and iodomethane (2.17 ppm).

Method b — to a solution consisting of 19 mg of PdBr(CH$_2$Ph)(*p*-Tol-BIAN) (**2a**) (0.030 mmol) in 0.40 ml of $CDCl_3$ was added one drop of dibromine. The ^{1}H NMR spectrum recorded immediately after the addition of dibromine showed the presence of benzyl bromide and PdBr$_4$(*p*-Tol-BIAN).

Method c — To a solution consisting of 10 mg of PdBr$_2$(*p*-Tol-BIAN) (0.016 mmol) in 0.60 ml of $CDCl_3$ was added 20 μl of a 0.98 M solution of dibromine in $CDCl_3$ (0.020 mmol Br_2). The ^{1}H NMR spectrum immediately after addition of dibromine showed signals at (δ): 6.99 (d, J = 7.3 Hz, H_3); 7.63 (pst, H_4); 8.19 (d, J = 8.3 Hz, H_5); 7.48 (d, J = 8.1 Hz, H_9); 7.67 (d, J = 8.1 Hz, H_{10}); 2.52 (s, H_{12},) ppm. The spectrum recorded after 2 d showed the presence of acenaphthenequinone and *p*-toluidine. When the same reaction was carried out in dichloromethane the only product obtained after evaporation of the solution and drying of the product was PdBr$_2$(*p*-Tol-BIAN).

2.6. Assessment of the influence of added alkene on the rate of oxidative addition

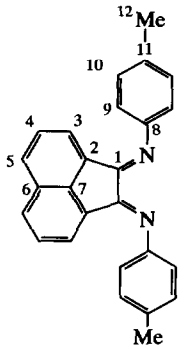
Two NMR tubes each containing 5.6 mg of Pd(*p*-Tol-BIAN)(DMFU) (0.009 mmol) in 0.50 ml of $CDCl_3$ were prepared, and to one of these 13 mg of DMFU (0.09 mmol, 10 equiv.) was added. After injection of 3.0 μl of rodomethane (0.05 mmol, 5 equiv.), the 300 MHz ^{1}H NMR spectra g each solution were recorded every 5 min for 45 min (16 scans each, approx. 1.5 min per spectrum) at 20°C. The integral of the product Pd–Me signal was monitored as a function of time as well as relative to the Me–C_6H_4 signals. The two reactions proceeded at the same rate.

3. Results

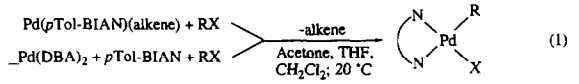
Zerovalent Pd(*p*-Tol-BIAN)(alkene) complexes react with a variety of (organic) halides to given neutral square planar organopalladium(II) complexes. The same products were also obtained by reaction of $Pd(DBA)_2$ with the halide in the presence of the Ar-BIAN ligand [eqn. (1)].

TABLE 1. ^{1}H NMR data for the oxidative addition products Pd(R)X(*p*-Tol-BIAN) [a]

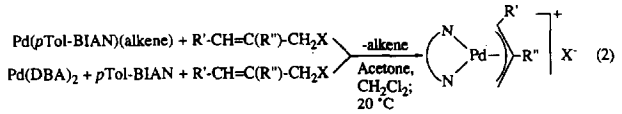
Complex	H_3	H_4	H_5	H_9	H_{10}	H_{12}	R
1a	7.00 d (7.2)	7.46 pst	8.06 d (8.3)	7.14 pst	7.40 d (7.9)	2.50 s	0.79 s (Me)
	6.68 d (7.3)	7.44 pst	8.01 d (8.3)		7.34 d (7.9)	2.47 s	
2a	6.81 d (7.2)	7.4 m (6H)	8.01 d (8.3)	7.16 d	7.4 m (6H)	2.52 s	3.40 s (CH_2)
							7.0 m (5H, Ph)
3a	6.69 vbr.	7.5 m (6H)	8.04 d (8.3)	7.16 d (8.0)	7.5 m (6H)	2.54 br	3.42 s (CH_2) [b]
4a	7.03 d (7.3)	7.47 pst	8.05 d (8.3)	7.24 d (8.2)	7.37 d (8.2)	2.48 s	6.99 m (H_o)
	6.82 d (7.3)	7.42 pst	8.02 d (8.2)	6.75 d (8.1)	6.97 d (8.1)	2.33 s	6.6 m (H_m)
							7.22 t (8.4, H_p)
5a	7.04 d (7.3)	7.5 m (2H)	8.05 d (8.4)	7.24 d (8.1)	7.37 d (8.1)	2.48 s	2.08 s (Me); 6.81 d
	6.88 d (7.3)		8.02 d (8.5)	6.74 d (8.1)	6.98 d (8.1)	2.33 s	6.42 d (8.0, C_6H_4)
6a	7.04 d (7.3)	7.4 m (6H)	8.08 d (8.5)	7.3 m (4H)	7.4 m (6H)	2.50 s	7.00 d, 6.75 d,
	6.86 d (7.3)		8.05 d (8.6)			2.29 s	(8.0, C_6H_4-*p*-NO_2)
7a	6.74 d (7.3)	7.48 pst	8.09 d (8.3)	7.21 d (8.2)	7.41 d (8.2)	2.50 s	7.90 d (7.7),
	7.0 m (3H)					2.45 s	7.0 m (3H; C_4H_3O)
8a	7.0 vbr.	7.47 pst	8.07 d (8.4)	7.17 d (8.4)	7.36 d (8.4)	2.47 s	2.17 s (C(O)Me)
9a	7.2–7.3 m	7.47 pst	8.04 d (8.1)	7.2–7.3 m	7.2–7.3 m	2.45 s	2.81 q, 0.67 t (7.2) (Et)
	(10H)			(10H)	(10H)		
10a	7.2–7.4 m	7.46 pst	8.04 d (8.2)	7.2–7.4 m	7.2–7.4 m	2.44 s	[c]
	(11H)			(11H)	(11H)		
11a [d]	6.52 d (7.3)	7.64 pst	8.29 d (8.0)	7.25 d (8.3)	7.47 d (8.3)	2.47 s	–
12a	7.04 d (7.1)	7.39 pst	7.97 d (8.2)	7.3 s (8H)	7.3 s (8H)	2.43 s	5.51 quin (9.2, CH)
							3.34 br. (CH_2)
13a	7.10 d (7.0)	7.4 m (6H)	7.98 d (8.1)	7.30 d (7.6)	7.4 m (6H)	2.46 s	5.48 quin (9.2, CH)
							3.39 br (CH_2)
14b	7.22 d (7.3)	7.46 pst	8.00 d (8.2)	7.06 d (8.7)	7.50 d (8.7)	3.91 s [e]	3.27 br (CH_2)
							1.96 s (Me)
15a	6.93 d (7.5)	7.35 pst	7.93 d (8.2)	7.1 m (13H)	7.1 m (13H)	2.42 s	7.1 m (13H, Ph) [f]
16a	6.85 d (7.1)	7.1–7.4 m	7.93 d (8.3)	7.1–7.4 m	7.1–7.4 m	2.38 s	7.1–7.4 m (15H, Ph) [b]
17a	6.73 d (7.4)	7.45 pst	8.06 d (8.3)	7.0 m (4H)	7.4 m (6H)	2.50 s	3.17 s (CH_2) [h]
18a	7.06 d (7.3)	7.4 m (6 H)	8.04 d (8.0)	6.84 d (8.1)	7.29 d (8.1)	2.52 s	3.33 s (CH_2)
	6.99 d (7.3)		8.02 d (8.0)	6.78 d (8.5)	7.70 d (8.5)	2.50 s	7.4 m (6H, C_6H_4)
19a	7.17 d (7.3)	7.52 pst	8.10 d (8.3)	7.39 s (8H)	7.39 s (8H)	2.49 s	5.85 m (CH) [i]
20a	6.9 pst (4H)	7.44 pst	8.04 d (8.3)	[j]	[j]	2.44 s	[j]
21b	7.09 d (7.3)	7.35 pst	8.07 d (8.3)	6.96 d (8.7)	7.48 d (8.7)	3.80 s [e]	5.72 quin (9.5, CH)
							3.50 d (9.5, CH_2) [k]



[a] Recorded at 300.13 MHz in $CDCl_3$ at 20°C, unless noted otherwise. Coupling constants (Hz) are shown in parentheses (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, ps = pseudo, br = broad, v = very). [b] 6.98 (d); 7.76 (d, J = 8.7 Hz, *p*-$NO_2C_6H_4$) ppm. [c] 7.2–7.4 (m, 11H, =C*H*Me); 5.46 (dd, J = 15.6, 1.5 Hz, C(O)-C*H*=); 1.77 (dd, J = 6.8, 1.5 Hz, =CH*Me*) ppm. [d] Recorded in DMSO-d_6. [e] *p*-MeO group of *p*-An-BIAN. [f] 5.88 (psq, C*H*=CH_2); 4.56 (d, J = 11.0 Hz, Ph-C*H*); 3.42 (d, J = 9.1 Hz, =CH_2) ppm. [g] 5.84 (psq, C*H*=CH_2); 4.70 (d, J = 11.0 Hz, Ph-C*H*); 3.41 (d, J = 9.1 Hz, =CH_2) ppm. [h] 7.4 (m, 6H); 7.0–7.1 (m, 3H, Ph) ppm. [i] 3.67 (d, J = 7.0 Hz, H_{syn}; 3.48 (d, J = 12.7 Hz, H_{anti}) ppm. [j] 6.9 (pst, 4H); 7.1–7.3 (m, 11H, H_3, H_9, H_{10}, *Ph*C_3H_4); 6.16 (psq, C*H*=CH_2); 4.87 (d, J = 11.9 Hz, Ph-C*H*); 3.72 (br d, =CH_2) ppm. [k] $[Pd(\eta^3\text{-}C_3H_5)Cl_2]^-$: 5.06 (m, CH); 3.72 (d, J = 6.6 Hz, H_{syn}); 2.62 (d, J = 12.0 Hz, H_{anti}) ppm.



1 MeI
2 $PhCH_2Br$
3 $pNO_2C_6H_4CH_2Br$
4 PhI
5 pTolI
6 $pNO_2C_6H_4I$
7 $2\text{-}C_6H_3O\text{-}I$
8 MeC(O)Cl
9 EtC(O)Cl
10 MeCH=CHC(O)Cl
11 I_2



12 R' = H, R" = H, X = Cl
13 R' = H, R" = H, X = Br
14 R' = H, R" = Me, X = Cl
15 R' = Ph, R" = H, X = Cl
16 R' = Ph, R" = H, X = Br

When allylic halides were added to the Pd(*p*-Tol-BIAN) complexes, four-coordinated cationic palladium(II) complexes were formed that contained a σ(N), σ(N')-chelating NN ligand and an η^3-coordinated allyl ligand [eqn. (2)]. The $[Pd(allyl)(Ar\text{-}BIAN)]^+$ complexes was also synthesized by the reaction of the appropriate Pd(allyl) dimer with 2 equiv. of the Ar-BIAN ligands (eqn. (3); Ar = *p*-Tol (**a**), *p*-$MeOC_6H_4$ (*p*-An, **b**), *o*, *o*'-$^i Pr_2C_6H_3$ (**c**)).

$$[Pd(allyl)Cl]_2 + 2\ Ar\text{-}BIAN \xrightarrow[CH_2Cl_2\ 20°C]{} 2\ [Pd(allyl)(Ar\text{-}BIAN)]^+Cl^- \quad (3)$$

The divalent palladium complexes synthesized are very stable in the solid state, and can be stored in air at 20°C without appreciable decomposition over several months. Most complexes are also very stable in solution and undergo no decomposition during several days in chloroform at 20°C in air. The complexes gave satisfactory analytical data and were characterized by ^1H and ^{13}C NMR spectroscopy (Tables 1 and 2).

In the account below, the oxidative addition reactions of the various (organic) halides will be discussed together with some reactions of the complexes and their fluxional behaviour on the NMR timescale.

3.1. Palladium–methyl complexes

Pd(*p*-Tol-BIAN)(DMFU) was found to react with a slight excess of iodomethane within 2 h to give Pd(Me)I(*p*-Tol-BIAN) (**1a**) as the sole product. The reaction may be performed in air, and there is no evidence for any reaction of the complex with oxygen or any influence of oxygen on the rate of reaction. Furthermore, the rate of oxidative addition is unaffected by the concentration of added DMFU. In contrast to the reactivity of Pd(*p*-Tol-BIAN)(DMFU), the reaction of Pd(*p*-Tol-BIAN)(FN) with iodomethane in acetone at 20°C required 15 d to go to completion (some decomposition occurred in this long reaction time). Heating the reaction mixture under reflux for 2 h led to the complete disappearance of the starting complex, but the amount of Pd(Me)I(*p*-Tol-BIAN) formed was low (25%) and the major product was uncoordinated *p*-Tol-BIAN (75%) owing to decomposition.

TABLE 2. ^{13}C NMR data for representative Pd(R)X(*p*-Tol-BIAN) complexes [a]

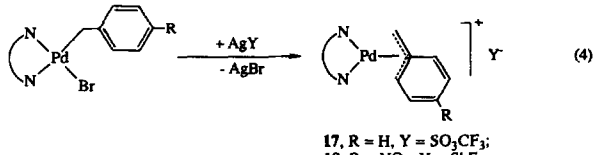
Complex	C_1	C_1	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	R
1a	171.5	126.5	125.0	128.4	130.9	131.1	144.3	144.0	122.2	130.3	137.2	21.1	−3.0
	167.2	126.1	124.8	128.3	130.3			143.1	121.1	129.3	136.7		
2a	n.o.	126.4	124.8	129.5	130.5	131.0	144.2	145.4	121.6	129.8	137.3	21.2	23.4 (CH_2) [b]
5a	170.8	127.0	125.7 br	130.3	131.7	131.8	145.2	144.7	122.2	130.1	137.6	21.9	21.0 (Me) [c]
	168.8	126.8		130.0	131.4			144.0	121.9	129.1	137.1	21.7	
8a	n.o.	126.8	125.6	n.o.	130.6	131.8	149.4	144.7	121.5	128.9	138.2	21.8	223.1 (C(O)); 33.7 (Me)
10a	n.o.	126.8	125.6	129.8	130.5	131.7	n.o.	144.7	121.7	129.0	138.1	21.8	18.6 (Me) [d]
12a	n.o.	127.9	125.0	128.5	130.8 [e]	131.6	n.o.	n.o.	120.3 br	130.8 [e]	n.o.	21.8	110.9 (CH); 60.8 (CH_2)
13a	n.o.	127.8	124.9	128.5	130.7 [e]	131.6	n.o.	n.o.	120.4 br	130.7 [e]	n.o.	21.8	110.5 (CH); 61.3 (CH_2)
14b	165.4	127.9	124.9	128.6	131.0	131.7	143.8	143.2	115.3	122.4	159.0	56.2 [f]	60.5 (CH_2); 23.6 (Me); C n.o.
15a	n.o.	127.7	124.9	128.5	131.0	131.5	146.2	143.7	120.3	130.5	138.2	21.8	[g]
17a	n.o.	124.9	125.3	128.4	131.9	131.0	n.o.	145.5	120.1	130.3	138.2	21.1	48.8 (CH_2) [h]
18a	n.o.	125.6	126.3	129.2 br	132.9	131.9	145.5	146.9	121.2	131.2	139.5	21.8	[i]
		125.3	126.2		132.6			146.7	119.8	131.1			
19a	171.1	124.9	125.4	128.4	131.9	131.1	146.3	145.9	120.3	130.4	138.4	21.1	119.5 (CH); 64.9 (CH_2)
20a	n.o.	128.5	126.2	129.1	132.3	131.8	150.2	143.8	120.3	130.9	138.0	21.8	[j]
21b	169.4	126.2	125.3	128.9	132.3	131.7	145.7	142.2	115.3	123.2	159.7	56.2 [f]	109.7 (CH); 61.2 (CH_2) [k]

[a] Recorded at 75.48 MHz in $CDCl_3$ at 20°C. See Table 1 for the adopted numbering scheme of *p*-Tol-BIAN. [b] *Ph*CH_2: 143.4 (C_i); 128.3, 127.6 ($C_{o,m}$); 123.6 (C_p) ppm. [c] *p*-MeC_6H_4: 131.9 (C_i); 136.0 (C_o); 127.7 (C_m); 138.9 (C_p) ppm. [d] MeCH=CHC(O): 217.8 (C=O); 147.9, 131.6 (CH=CH) ppm. [e] Accidentally overlapping. [f] *p*-MeO of *p*-An-BIAN. [g] PhC_3H_4: 59.4 (=CH_2); 78.2 (Ph–*C*H); 105.1 (*C*H=CH_2); 136.7 (C_i); 127.8 (C_o); 129.5 (C_m); 127.7 (C_p) ppm. [h] *Ph*CH_2: C_i n.o.; 106.7 (C_o); 134.0 (C_m); 130.1 (C_p) ppm. [i] *p*-$NO_2C_6H_4CH_2$: 144.0 (C_p); 130.1 (C_o or C_m) ppm; other signals were not observed. [j] PhC_3H_4: =CH_2 n.o.; 81.8 (Ph–*C*H); 113.6 (*C*H=CH_2); 135.8 (C_i); 128.4 (br, $C_{o,p}$); 129.5 (C_m) ppm. [k] $[Pd(\eta^3\text{-}C_3H_5)Cl_2]^-$: 117.4 (CH); 64.5 ($CH_2$) ppm.

The complex, Pd(Me)I(*p*-Tol-BIAN) did not react with FN (5 equiv.) at 20°C in acetone, which shows that the oxidative addition of iodomethane to Pd(*p*-Tol-BIAN) (FN) is not a reversible reaction with the equilibrium lying completely on the side of the zerovalent Pd(*p*-Tol-BIAN)(FN) complex. However, oxidative addition of iodomethane to Pd(*p*-Tol-BIAN)(FN) was complete in 2 h when the mixture was irradiated with a mercury lamp at 20°C. Use of a large excess of iodomethane gave the best results, since with smaller amounts (up to 50 equiv.) large quantities of metallic palladium separated from the reaction mixture. When the irradiation was carried out in the presence of toluene or styrene, Pd(Me)I(*p*-Tol-BIAN) was the only complex observed, and there was no indication of the formation of a Pd–CH_2Ph complex or of organic products arising from the presence of free radicals in solution [13*].

3.2. Palladium–benzyl complexes

Oxidative addition of benzyl bromide to Pd(*p*-Tol-BIAN)(DMFU) in acetone or chloroform was complete after 10 h at 20°C. Even when an excess of benzyl bromide was used, PdBr(CH_2Ph)(*p*-Tol-BIAN) (**2a**) was the sole product formed at 20°C. However, PdBr(CH_2Ph)(*p*-Tol-BIAN) reacted at 50°C in THF with benzyl bromide over 16 h to give $PdBr_2$(*p*-Tol-BIAN) and $(PhCH_2)_2$. The benzyl group in PdBr(CH_2Ph)(*p*-Tol-BIAN) is η^1-coordinated, but an η^3-coordinated benzyl moiety is formed by reaction with silver salts such as $AgSO_3CF_3$ [eqn. (4)]. The η^3-benzyl coordination in [Pd(CH_2Ph)(*p*-Tol-BIAN)]-SO_3CF_3 (**17a**) is clear from the ^{13}C NMR spectra, which show the methylene signal at δ 48.8 ppm (*cf.* δ 23.4 ppm for η^1-CH_2Ph in **2a** and δ *ca.* 60 ppm for the methylene C-atoms in the η^3-allyl fragment in complexes **12–15** and **19–21**). The trifluoromethanesulphonate anion is not coordinated to the palladium, as is indicated by the absence of stretching frequencies in the region 1200–1250 cm^{-1} and above 1300 cm^{-1} in the IR spectrum [14,15]. Palladium and platinum complexes containing η^3-coordinated benzyl groups are not common, but some have been described [16].



(4)

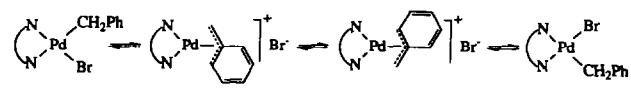
17, R = H, Y = SO_3CF_3;
18, R = NO_2, Y = SbF_6

The complex [Pd(η^3-CH_2Ph)(*p*-Tol-BIAN)]SO_3CF_3 (**17a**) was also formed together with Me_3SnBr in the reaction of PdBr(CH_2Ph)(*p*-Tol-BIAN) with $Me_3SnSO_3CF_3$. Reaction of PdBr(CH_2Ph)(*p*-Tol-BIAN) with other silver salts such as $AgSbF_6$ and $AgNO_3$ also gave [Pd(η^3-CH_2Ph)(*p*-Tol-BIAN)]Y, whereas reaction of [Pd(η^3-CH_2Ph)(*p*-Tol-BIAN)]-SO_3CF_3 with $NaBPh_4$ gave a mixture of products, among which were $PhCH_2Ph$ and $PhCH_2CH_2Ph$ (in a ratio of *ca.* 4:1), instead of those of simple anion exchange. Phenyl group transfer from BPh_4^- with carbon–carbon bond formation has previously been observed in the palladium–phosphine catalyzed phenylation of allyl acetates and in stoichiometric reactions of Pd(η^3-allyl)(NN) complexes (*vide infra*) [17]. However, the formation of bibenzyl in this case indicates intermolecular and/or radical reaction pathways.

Both PdBr(CH_2Ph)(*p*-Tol-BIAN) (**2a**) and [Pd(η^3-CH_2Ph)(*p*-Tol-BIAN)]SO_3CF_3 (**17a**) show fluxional behaviour on the NMR timescale. The observation of one signal for the methylene protons and one averaged signal for comparable protons on both halves of the ligand for the η^3-benzyl complex **17a** indicates site exchange and *syn–anti* exchange (similar to that observed for Pd(η^3-allyl) complexes [18]), which remain fast on the NMR timescale down to −80°C at 300 MHz. For the η^1-benzyl complex **2a**, fast site exchange of the bromine and benzyl ligand occurs at 20°C (at both 100 and 300 MHz), but at −50°C the limit of slow exchange is reached (100 MHz). The exchange probably involves an η^1–η^3–η^1 interconversion (Scheme 2).

The operation of such a mechanism is supported by the observation that the rate of site exchange decreases when an electron-withdrawing group is attached to the aromatic ring of the benzyl ligand: PdBr($CH_2C_6H_4$-*p*-NO_2)(*p*-Tol-BIAN) (**3a**) shows broad signals (*e.g.* of the Me groups) at 20°C, indicating an intermediate rate of site exchange. The electron-withdrawing nitro group decreases the electron density in the aromatic ring, reducing the ease of η^2-coordination of an aromatic double bond to the palladium, and as a consequence the rate of site exchange decreases. The *p*-nitrobenzyl ligand can, however, be converted into an η^3-benzyl ligand if the bromide is replaced by a weakly coordinating anion such as SbF_6.

The formation of a [Pd(η^3-CH_2Ph)(*p*-Tol-BIAN)]Br intermediate might also account for the facile reaction of PdBr(CH_2Ph)(*p*-Tol-BIAN) with $Me_3SnSO_3CF_3$,



Scheme 2.

which could be initiated by nucleophilic attack of the uncoordinated bromide at the Sn centre. However, an oxidative addition/reductive elimination sequence via Pd^{IV} intermediates cannot be ruled out.

3.3. Palladium–aryl complexes

Aromatic iodides were found to react with Pd(*p*-Tol-BIAN)(DMFU) to generate the aryl–palladium complexes Pd(Ar)I(*p*-Tol-BIAN) (Ar = Ph (**4a**), *p*-Tol (**5a**), *p*-$NO_2C_6H_4$ (**6a**), 2-C_4H_3O (2-furyl) (**7a**)) in good yield. The rate of reaction in *p*-iodotoluene depended on the solvent and increased in the order toluene < THF < DMF. Activated aromatics such as *p*-nitrophenyl iodide and 2-iodofuran reacted much faster, and oxidative addition was complete within 5 min at 20°C in chloroform. The same effects, *i.e.* increase in the rate of the reaction with increasing electrophilicity of the aromatic group and with increasing solvent polarity, were observed for similar reactions involving palladium–phosphine complexes [19].

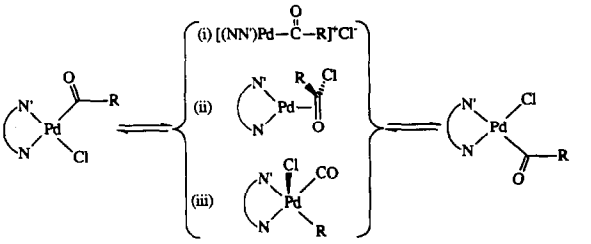
Reactions of aromatic bromides with Pd(*p*-Tol-BIAN)(DMFU) are much slower and are accompanied by considerable decomposition. Better results were obtained starting from $Pd(DBA)_2$ in the presence of *p*-Tol-BIAN and an excess of the aromatic bromide. Unfortunately, the complexes formed were not the simple oxidative addition products PdBr(Ar)(Ar-BIAN) [20*]. Chlorobenzene showed no tendency to bring about oxidative addition.

3.4. Palladium–acyl complexes

The oxidative addition of acyl chlorides, such as acetyl chloride, propionyl chloride and crotonyl chloride, to Pd(*p*-Tol-BIAN)(DMFU) occurred readily at 20°C in acetone and Pd(C(O)R)Cl(*p*-Tol-BIAN) (R = Me (**8a**), Et (**9a**), MeCH=CH (**10a**)) was formed as the sole product when 1 equiv. of the acyl chloride was used [21*].

The crotonyl moiety in Pd(C(O)CH=CHMe)Cl(*p*-Tol-BIAN) is coordinated in an η^1 fashion and there is no evidence for coordination of the double bond. When the complex is treated with $AgSO_3CF_3$ a considerable amount of decomposition is observed, whereas a stable complex would be expected if there were η^3 coordination of the crotonyl moiety (*cf.* the benzyl and allyl complexes **17–20**).

The Pd^{II}–acyl complexes all show fluxional behaviour on the NMR timescale. At 20°C there is fast site exchange between the chloride and the acyl group, leading to the observation of one averaged signal for the protons and C atoms on both halves of the ligand. At −40°C (100 MHz) two doublets are observed for H_5 and one doublet of H_3 appears at 6.6–6.7 ppm for all the complexes **8–10a**, indicating that exchange is



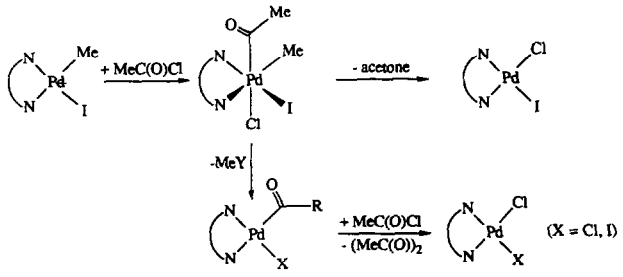
Scheme 3.

slowed down. The observed fluxional behaviour can in principle be explained in terms of (i) dissociation–association of the chloride (possibly aided by η^2 coordination of the acyl to palladium [22]), (ii) a reductive elimination/oxidative addition sequence or (iii) de-insertion of CO followed by site exchange in the five-coordinate intermediate and re-insertion (Scheme 3).

Dissociation of an imine N atom followed by ligand rotation is unlikely in view of the rigidity of the backbone of the Ar-BIAN ligand, but cannot be ruled out in view of the large *trans*-labilizing effect of the acyl ligand and the fact that unidentate coordination for the rigid phenanthroline ligand has been observed in the solid state in the complex $[PtCl(phen)(PEt_3)_2]\,BF_4$ [23].

When the oxidative addition of acetyl chloride was carried out with an excess MeC(O)Cl, apart from Pd(C(O)Me)Cl(*p*-Tol-BIAN), $PdCl_2$(*p*-Tol-BIAN) was formed [24*], especially when $Pd(DBA)_2$ was used as the starting zerovalent palladium complex. This product is probably formed by the oxidative addition of MeC(O)Cl to Pd(C(O)Me)Cl(*p*-Tol-BIAN) followed by reductive elimination of 2,3-butanedione, but when the reaction was performed in dry $CDCl_3$ in an NMR tube, no 2,3-butanedione was detected in the reaction mixture.

The reactivity of acetyl chloride towards organopalladium(II) complexes was demonstrated by the reaction with $PdMe_2$(*p*-Tol-BIAN) [15] and Pd(Me)I(*p*-Tol-BIAN). Reaction of acetyl chloride with Pd(Me)I(*p*-Tol-BIAN) at 20°C in dichloromethane/acetone for 30 min gave a mixture of $Pd^{II}Me$ and $Pd^{II}C(O)Me$ complexes (2.5 : 1) and a complex without Me or C(O)Me ligands (*ca.* 20%). Monitoring by IR spectroscopy of the reaction in THF showed slow disappearance of MeC(O)Cl with concomitant formation of acetone, which was complete after 2 d. The resulting palladium complex contained no Pd–Me nor Pd–C(O)Me groups and showed a set of (broadened) signals in the aromatic region, that pointed to a mixture of $PdCl_2$(*p*-Tol-BIAN), PdI_2(*p*-Tol-BIAN) and PdClI(*p*-Tol-BIAN) (Scheme 4).



Scheme 4.

3.5. Palladium–dihalide complexes

Reaction of Pd(*p*-Tol-BIAN)(DMFU) with 1–5 equiv. of diiodine in acetone at 20°C proceeded readily and PdI_2(*p*-Tol-BIAN) (**11a**) was obtained as the sole product [24*]. In contrast, reaction of Pd(*p*-Tol-BIAN)(DMFU) with 1 equiv. of dibromine gave $PdBr_2$(*p*-Tol-BIAN) [24*], whereas reaction with an excess of dibromine in $CDCl_3$ gave $PdBr_4$(*p*-Tol-BIAN). Reaction of dibromine with $PdBr(CH_2Ph)$(*p*-Tol-BIAN) gave benzyl bromide and $PdBr_4$(*p*-Tol-BIAN), and reaction with $PdBr_2$(*p*-Tol-BIAN) gave $PdBr_4$(*p*-Tol-BIAN). The palladium(IV) complex is rather unstable and attempts to isolate it by evaporation of the solvent resulted in the formation of $PdBr_2$(*p*-Tol-BIAN). When a solution of $PdBr_4$(*p*-Tol-BIAN) in $CDCl_3$ was kept at 20°C in the presence of excess dibromine, formation of acenaphthenequinone and *p*-toluidine was observed after 2 d; this must be ascribed to hydrolysis of the imine group by water from the solvent [25*]. The increased susceptibility of the imine group of the *p*-Tol-BIAN ligand towards nucleophilic attack is due to the high oxidation state of the palladium centre.

Diiodine also reacted with Pd^{II} complexes such as Pd(Me)I(*p*-Tol-BIAN), but in this case iodomethane and PdI_2(*p*-Tol-BIAN) were formed as the sole products. The reaction occurred instantaneously, even at −50°C in $CDCl_3$ in an NMR tube, and no Pd^{IV} intermediate was observed. The PdI_2(*p*-Tol-BIAN) formed did not react further with diiodine to give PdI_4(*p*-Tol-BIAN).

3.6. Palladium–allyl complexes

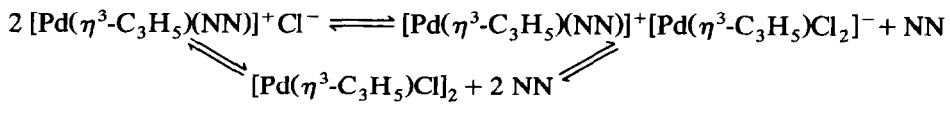
Allyl chloride and allyl bromide reacted instantaneously with Pd(*p*-Tol-BIAN)(alkene) complexes to give [Pd(η^3-C_3H_5)(*p*-Tol-BIAN)]X (**12, 13a**) and free alkene, irrespective of whether the alkene was DMFU, FN or MA. Even in dichloromethane at −80°C in an NMR tube the reaction took place immediately and no intermediate was observed. The reaction was also complete within 1 min when *p*-An-BIAN, *o*-Tol-BIAN and *o,o'*-$Me_2C_6H_3$-BIAN were coordinated to palladium, whereas the reaction with Pd(*o,o'*-$^i Pr_2C_6H_3$-BIAN) complexes was much slower (75% conversion after 2 h at 20°C).

Oxidative addition of 2-methylallyl chloride (C_4H_7Cl) or 3-phenylallyl chloride (3-PhC_3H_4Cl) to Pd(*p*-Tol-BIAN)(alkene) showed the same features, and was complete within 5 min at 20°C, but oxidative addition of 1-phenylallyl bromide required more than 2 h to go to completion.

As described for [Pd(allyl)(DAB)]$^+$ and [Pd(allyl)(Pyca)]$^+$ complexes [26], the [Pd(allyl)(Ar-BIAN)]X (X = Cl, Br) complexes are in equilibrium with dinuclear species and uncoordinated Ar-BIAN, as can be deduced from the observation of small signals attributable to [Pd(η^3-C_3H_5)Cl]$_2$ or [Pd(η^3-C_3H_5)(Ar-BIAN)]$^+$[Pd(η^3-C_3H_5)Cl_2]$^-$ and uncoordinated Ar-BIAN in the ^{1}H NMR spectrum of the mononuclear [Pd(η^3-C_3H_5)(Ar-BIAN)]$^+$ Cl^- complexes **12** (Scheme 5).

The dinuclear complex [Pd(η^3-C_3H_5)(*p*-An-BIAN)]$^+$[Pd(η^3-C_3H_5)Cl_2]$^-$ (**21b**) was synthesized independently by the reaction of [Pd(η^3-C_3H_5)Cl]$_2$ with 1 equiv. of *p*-An-BIAN. From the ^{1}H NMR spectra it is clear that the amount of [Pd(η^3-C_3H_5)Cl]$_2$ present in this mixture at 20°C decreases in the order *o,o'*-$^i Pr_2C_6H_3$-BIAN (50%) > *o,o'*-$Me_2C_6H_3$-BIAN (40%) > *o*-Tol-BIAN (20%) > *p*-Tol-BIAN ≈ *p*-An-BIAN (0–5%), *i.e.* with decreasing *ortho* substitution of the aromatic group of the Ar-BIAN ligand.

When the equilibrium mixture of [Pd(η^3-C_3H_5)Cl]$_2$ and 1 equiv. of *o,o'*-$^i Pr_2C_6H_3$-BIAN in $CDCl_3$ was cooled to −55°C, all the free ligand disappeared and only [Pd(η^3-C_3H_5)(*o,o'*-$^i Pr_2C_6H_3$-BIAN)]$^+$[Pd(η^3-C_3H_5)Cl_2]$^-$ (**21c**) was present in solution, in agreement with the observations for [Pd(η^3-C_4H_7)(Pyca)]$^+$ complexes [26(b)]. The low ability of *o,o'*-$^i Pr_2C_6H_3$-BIAN to coordinate to Pd–allyl complexes was also apparent from the reaction of [Pd(η^3-C_3H_5)(*o,o'*-$^i Pr_2C_6H_3$-BIAN)]$^+$[Pd(η^3-$C_3H_5Cl_2$]$^-$ (**21c**) with 1 equiv. of *p*-An-BIAN which gave only [Pd(η^3-C_3H_5)-(*p*-An-BIAN)]$^+$[Pd(η^3-C_3H_5)Cl_2)]$^-$ (**21b**) and uncoordinated *o,o'*-$^i Pr_2C_6H_3$-BIAN. Formation of the



Scheme 5.

monomer $[Pd(\eta^3\text{-}C_3H_5)(p\text{-An-BIAN})]^+Cl^-$ **(12b)** was observed in the reaction of $[Pd(\eta^3\text{-}C_3H_5)(p\text{-An-BIAN})]^+[Pd(\eta^3\text{-}C_3H_5)Cl_2]^-$ **(21b)** with 1 equiv. of *p*-An-BIAN [eqn. (5)].

$$\underset{\textbf{21b}}{[Pd(\eta^3\text{-}C_3H_5)(p\text{-An-BIAN})]^+[Pd(\eta^3\text{-}C_3H_5)Cl_2]^-} + p\text{-An-BIAN} \rightleftharpoons 2[Pd(\eta^3\text{-}C_3H_5)(p\text{-An-BIAN})]Cl \quad (5)$$

For the complexes $[Pd(\eta^3\text{-}C_4H_7)(p\text{-Tol-BIAN})]^+Cl^-$ **(14a)** and $[Pd(\eta^3\text{-}C_4H_7)(p\text{-An-BIAN})]^+Cl^-$ **(14b)** similar equilibria between mononuclear and dinuclear complexes were observed, but the amount of the $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ dimer was slightly larger (5–10% at 20°C) than for the allyl chloride analogues (**12**).

The halide counterion in [Pd(allyl)(*p*-Tol-BIAN)]X can be replaced by a weaker coordinating anion by reaction with $AgSO_3CF_3$, for example [Eqn. (6)]. In this case only mononuclear $[Pd(allyl)(p\text{-Tol-BIAN})]SO_3CF_3$ (**18**, **19a**) is present in solution, as observed for $[Pd(\eta^3\text{-}C_4H_7)(DAB)]^+$ and $[Pd(\eta^3\text{-}C_4H_7)(Pyca)]^+$ complexes with weakly coordinating anions [26]. Attempted anion exchange of $[Pd(\eta^3\text{-}C_3H_5)(p\text{-Tol-BIAN})]X$ with $NaBPh_4$ gave a mixture of products, containing *inter alia* allyl benzene, free *p*-Tol-BIAN and metallic palladium [eqn. (7)] analogous to observations for $Pd(\eta^3\text{-}C_4H_7)(NN)$ and $Pd(\eta^3\text{-}C_3H_5)(NN)$ complexes containing R-DAB, pyca, bpy and phen ligands [17(b)].

$$[Pd(allyl)(p\text{-Tol-BIAN})]X + AgSO_3CF_3 \xrightarrow[-AgX]{} [Pd(allyl)(p\text{-Tol-BIAN})]SO_3CF_3 \quad (6)$$

19a allyl = η^3-C_3H_5
20a allyl = η^3-PhC_3H_4

$$[Pd(allyl)(p\text{-Tol-BIAN})]SO_3CF_3 + NaBPh_4 \longrightarrow \text{allyl-Ph} + p\text{-Tol-BIAN} + Pd\downarrow \quad (7)$$

3.7. Fluxional behaviour of the Pd–allyl complexes

The $[Pd(\eta^3\text{-}C_3H_5)(p\text{-Tol-BIAN})]X$ complexes **12**, **13a** (X = Cl, Br) in $CDCl_3$ show fast site exchange of the *syn* and *anti* allyl protons at 20°C, whereas separate signals of H_{syn} [3.57(d, ^3J(H–H) = 6.3 Hz) ppm] and H_{anti} [3.38 (d, ^3J(H–H) = 11.4 Hz) ppm] are observed at −55°C. The same is observed in CD_2Cl_2 at −60°C, but the signals from the *anti* protons have shifted to 2.97 ppm, whereas those for the *syn* protons are almost at the same positions as in $CDCl_3$ (3.63 ppm). The rate of *syn–anti* exchange at several temperatures is influenced neither by a change in the concentration of the complex nor by the addition of *p*-Tol-BIAN or NEt_4Br, indicating *intra*molecular exchange. Similar observations were made for the analogous *p*-An-BIAN complexes **12**, **13b**.

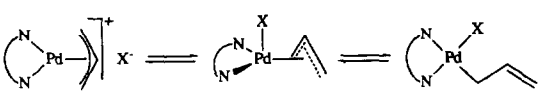
In contrast, the analogous $[Pd(\eta^3\text{-}C_3H_5)(p\text{-Tol-BIAN})]SO_3CF_3$ complex **19a** gives separate signals from H_{syn} (3.67 ppm) and H_{anti} (3.48 ppm) at 20°C in chloroform, and addition of a few drops of acetonitrile or methanol does not increase the rate of exchange (the only effect is a shift of the signal from the *anti* protons to 3.32 and 3.39 ppm, respectively, with the signal for the *syn* protons being hardly affected).

The complex $[Pd(\eta^3\text{-}C_4H_7)(p\text{-An-BIAN})]Cl$ **(14b)** behaves very like the allyl complexes **12**, **13**: at 20°C one broad signal is observed for the *syn* and *anti* protons, and this splits into two singlets at δ 3.44 and 3.18 ppm at 0°C. Upon further cooling, the signal at 3.18 ppm shifts to 3.37 ppm at −40°C, the signal at 3.44 ppm being unaffected. Comparison with the observed large influence of the solvent on the *anti* protons for $Pd(\eta^3\text{-}C_3H_5)$ complexes **12a** and **13a** (*vide supra*) suggests that the signal at 3.44 ppm comes from the *syn* protons and the low-frequency signal from the *anti* protons, in agreement with the fact that H_{syn} is usually found at higher frequency than the H_{anti} signal [27]. For the phenylallyl complexes, one doublet was observed for the *syn* and *anti* protons at all temperatures studied (20 to −55°C), for both $[Pd(\eta^3\text{-}PhC_3H_4)(p\text{-Tol-BIAN})]Cl$ **(15a)** and $[Pd(\eta^3\text{-}PhC_3H_4)(p\text{-Tol-BIAN})]SO_3CF_3$ **(20a)**.

The mechanism of *syn–anti* exchange has been studied extensively [18] and only brief comment will be made here. The influence of the anion on the rate of exchange suggests it is aided by coordination of the anion to the palladium centre (Scheme 6).

The observation that the addition of coordinating solvents such as methanol and acetonitrile does not increase the rate of *syn–anti* exchange is in agreement with our finding that these solvents coordinate only very weakly to Pd^{II}(*p*-Tol-BIAN) [21b] and Pt^{IV}(*p*-Tol-BIAN) complexes [15] and with the reported results for $[Pd(\eta^3\text{-}C_4H_7)(bpy)]SO_3CF_3$ [18(c)]. The faster exchange in the phenylallyl complexes reflects the weaker π-coordination properties of the phenylallyl moiety.

The dinuclear complex $[Pd(\eta^3\text{-}C_3H_5)(p\text{-An-BIAN})]^+[Pd(\eta^3\text{-}C_3H_5)Cl_2]^-$ **(21b)** shows in $CDCl_3$ one signal at 20°C for the *syn* and *anti* protons of the $Pd(\eta^3\text{-}C_3H_5)(p\text{-An-BIAN})$ part, whereas separate signals for H_{syn} and H_{anti} are observed for the $Pd(\eta^3$-



Scheme 6.

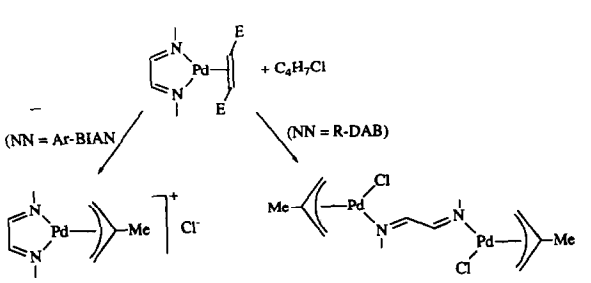
$C_3H_5)Cl_2$ part. At −55°C separate signals for the *syn* and *anti* protons of $Pd(\eta^3\text{-}C_3H_5)$(*p*-An-BIAN) are also observed. At 50°C the signals due to the two allyl groups of the $Pd(\eta^3\text{-}C_3H_5)$(*p*-An-BIAN) and the $Pd(\eta^3\text{-}C_3H_5)Cl_2$ entity coalesce, indicating that *intermolecular* exchange occurs. This intermolecular exchange is probably initiated by dissociation of the *p*-An-BIAN ligand from **21b** [eqn. (8)]. After formation of the $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ dimer, exchange occurs via reaction of the dimer with a $Pd(\eta^3\text{-}C_3H_5)$(*p*-An-BIAN) complex [18(a),(b)] or with free *p*-An-BIAN. An increase in the extent of dissociation of Ar-BIAN ligands from palladium in solution upon warming was also observed for $[Pd(\eta^3\text{-}C_3H_5)(o,o'\text{-}{}^iPr_2C_6H_3\text{-BIAN})][Pd(\eta^3\text{-}C_3H_5)Cl_2]$ (**21c**) (*vide supra*).

$$[Pd(\eta^3\text{-}C_3H_5)(p\text{-An-BIAN})]^+[Pd(\eta^3\text{-}C_3H_5)Cl_2]^- \rightleftharpoons [Pd(\eta^3\text{-}C_3H_5)Cl]_2 + p\text{-An-BIAN} \quad (8)$$

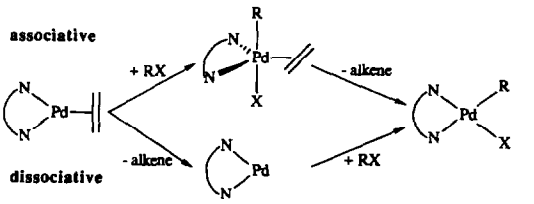
4. Discussion

Oxidative addition of organic halides to zerovalent Pd(Ar-BIAN)(alkene) complexes has given a variety of new divalent organopalladium complexes. The chelating coordination of Ar-BIAN ligands leads to the formation of complexes having the organic group and the halide in a mutual *cis* orientation, in contrast to the formation of *trans*-$[M(R)X(PR_3)_2]$ complexes upon oxidative addition to zerovalent palladium and platinum complexes containing unidentate phosphine ligands [5]. The rigidity of the Ar-BIAN ligands results in the formation of mononuclear cationic η^3-allylpalladium (Ar-BIAN) complexes upon oxidative addition of allylic halides, whereas similar reactions with complexes containing the flexible ^{t}Bu-DAB ligand give neutral binuclear complexes containing a *bridging* ^{t}Bu-DAB ligand [28] (Scheme 7).

In addition to the formation of organopalladium(II) complexes, formation of dihalide palladium(II) complexes was observed upon prolonged reaction with an excess of a reactive halide. These reactions probably involve oxidative addition of RX to Pd(R)X(Ar-BIAN)



Scheme 7.



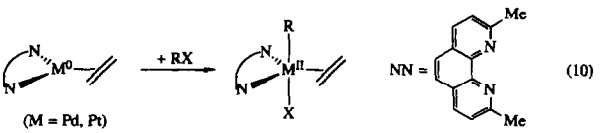
Scheme 8.

to give an intermediate Pd^{IV} complex from which reductive elimination occurs to yield PdX_2(Ar-BIAN) and R_2. The formation of the organic coupling product R_2 via such a 'double' oxidative addition, as was observed in the reaction of $PdBr(CH_2Ph)$(*p*-Tol-BIAN) at 50°C, could in principle account for the formation of bibenzyl in some Pd(Ar-BIAN) catalyzed cross-coupling reactions of benzyl bromide with organometallic reagents [3]. However, a detailed mechanistic study has shown that palladium(IV) intermediates do not play an important role in the formation of homocoupled products during Pd(Ar-BIAN) catalyzed cross-coupling reactions involving benzyl bromide [1].

Oxidative addition to zerovalent Pd(Ar-BIAN)(alkene) complexes may occur with loss of the coordinated alkene prior to or after oxidative addition (Scheme 8). The dissociative mechanism bears some similarity to the oxidative addition of organic halides to $M(PPh_3)_4$ (M = Pd, Pt), which is dissociated in solution to give free phosphine and $M(PPh_3)_3$ (major species in solution) and a small amount of $M(PPh_3)_2$, the latter being the reactive species in oxidative addition reactions [5(c),(h),(i);19(b),(c);29] [Eqn. (9)].

$$Pd(PPh_3)_4 \overset{-PPh_3}{\rightleftharpoons} Pd(PPh_3)_3 \overset{-PPh_3}{\rightleftharpoons} Pd(PPh_3)_2 \xrightarrow{+RX} Pd(R)X(PPh_3)_2 \quad (9)$$

However, oxidative addition to M(NN)(alkene) complexes (M = Pd, Pt; NN = bidentate nitrogen ligand) was suggested to occur via an associative mechanism because the five-coordinate M(R)X(NN)(alkene) complexes were obtained as products when appropriate nitrogen ligands were coordinated to the metal centre, *e.g.* 2,9-dimethylphenanthroline [eqn. (10)] [8(a),(b)].



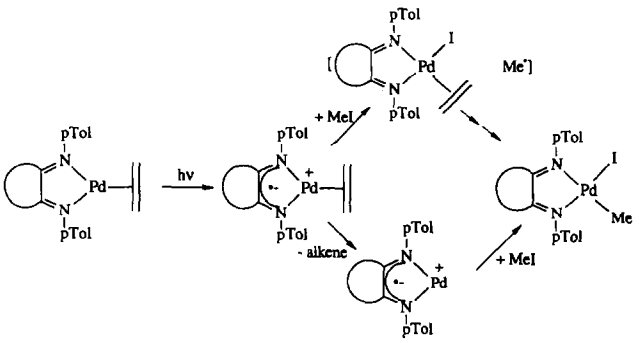
(10)

Our results are in agreement with an associative mechanism for oxidative addition to zerovalent Pd(Ar-BIAN)(alkene) complexes, as can be deduced from (i) the fact that added alkene (10 equiv. of DMFU) has no influence on the rate of oxidative addition (a significantly slower reaction would be expected if a route

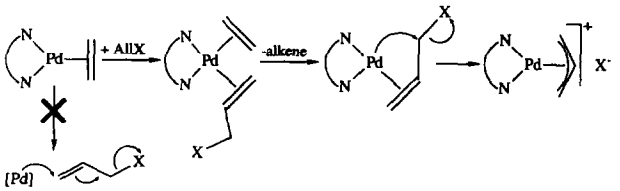
involving initial alkene dissociation were followed), and (ii) the observed order of reactivity, MeI ≫ EtI (no reaction), which is also the order of increased steric hindrance in the organic halide [30*]. These observations are in agreement with nucleophilic attack of a tricoordinate Pd^0(Ar-BIAN)(alkene) complex on the iodoalkane; the halide approaches the palladium centre from an apical position, resulting in steric interactions with the aromatic substituents of the Ar-BIAN ligand, which are orientated out of the coordination plane [9,12(c)] resulting in steric interference for larger alkyl halides. Finally, an associative mechanism is also in line with observations on Pd(2,9-Me_2phen)(alkene) complexes [eqn. (10)] [8] and with observations that other ML_2 (alkene) complexes react preferentially via associative pathways [31].

The observed acceleration of the reaction of iodomethane with Pd(*p*-Tol-BIAN)(FN) upon irradiation can be explained in several ways. The formation of free radicals in solution, by photochemical homolysis of the C–I bond of iodomethane, or the occurrence of a radical chain mechanism, can be ruled out because addition of toluene or styrene to the reaction mixture has no effect. Furthermore the homolysis of iodomethane would not give rise to the need to use a large excess of iodomethane to prevent deposition of palladium. A non-chain radical mechanism via a radical pair could be operative; in that case diffusion of radicals would not occur because recombination is much faster, prohibiting initiation of a radical chain reaction. Initiation of such a non-chain radical reaction can occur via iodine abstraction from iodomethane by the MLCT excited state of the Pd(*p*-Tol-BIAN)(FN), possibly preceded by electron transfer (from the reduced *p*-Tol-BIAN ligand) to iodomethane, followed by recombination to the oxidative addition product from which the alkene dissociates (Scheme 9). Abstraction of iodine from an iodoalkane by a metal complex in a MLCT excited state was reported for the photochemically initiated reaction of $PtMe_2$(phen) with 2-iodopropane [32]. Alternatively, irradiation might facilitate a dissociative reaction, since the Pd–alkene bond is weakened as a result of the lower electron density on the palladium centre in the MLCT excited state (Scheme 9).

In contrast to the observations made for iodomethane, the rate of oxidative addition of allylic halides to Pd(*p*-Tol-BIAN)(alkene) complexes is not influenced by the nature of the coordinated alkene (DMFU, FN, MA) in the zerovalent complex. This suggests that in this case dissociation of the alkene is assisted by η^2 coordination of the allylic halide to palladium prior to oxidative addition, and this is followed by intramolecular oxidative addition to give the Pd(allyl) complex (Scheme 10). η^2 Coordination of the allylic halide



Scheme 9.



Scheme 10.

before oxidative addition occurs has been proposed, but has never been observed owing to the high rate of the intramolecular oxidative addition [5e,33]. However, indirect evidence comes from the η^2 coordination of homoallyl halides CH_2=CH–$(CH_2)_n$–X ($n \geq 2$) prior to oxidative addition as revealed by low-temperature NMR spectroscopy [5(e)]. In agreement with such an associative mechanism for the oxidative addition of allylic halides, it was found that the reactions with Pd(*o*,*o*'-$^i Pr_2C_6H_3$-BIAN)(alkene) complexes are much slower than those with the analogous Pd(*p*-Tol-BIAN) complexes.

In the *o*,*o*'-$^i Pr_2C_6H_3$-BIAN complexes, η^2 coordination of the allylic halide to palladium is hindered by the isopropyl substituents, as observed for the alkene substitution reactions of Pd(*o*,*o*'-$^i Pr_2C_6H_3$-BIAN)(alkene) complexes [9]. Furthermore, the observation that 3-phenylallyl chloride and 3-phenylallyl bromide react faster than 1-phenylallyl bromide, which rules out a 1,3-substitution in the oxidative addition of allylic halides, is in agreement with the proposed coordination of the allylic halide prior to oxidative addition.

5. Conclusions

A variety of new divalent square planar organopalladium complexes of the type Pd(R)X(Ar-BIAN) is available via the facile oxidative addition of organic halides RX to zerovalent Pd(Ar-BIAN)(alkene) complexes. The complexes thus obtained are intermediates in the Pd(Ar-BIAN) catalyzed cross-coupling of organic halides with organometallic reagents [3], and are excel-

lent starting materials for further mechanistic studies of these cross-coupling reactions [1,3(b)] and other reactions, such as the (multiple) insertion of carbon monoxide and alkenes [21]. The observed loss of the coordinated alkene and the formation of a square planar Pd^{II} complex after oxidative addition is of importance for Pd(Ar-BIAN) catalyzed cross-coupling reactions because it means that use of either a zerovalent Pd(Ar-BIAN)(alkene) or a divalent $PdCl_2$(Ar-BIAN) catalyst precursor results in formation of the same species after oxidative addition of the organic halide [34*].

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2 The following abbreviations are used throughout the text: Ar-BIAN = bis(arylimino)acenaphthene; R-DAB = 1,4-diaza-1,3-butadiene, R–N=C(R′)–C(R″)=N–R; Pyca = pyridine-2-carbaldimine, C_5H_4N-2-C(R′)=N–R; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline; DMFU = dimethyl fumarate; FN = fumaronitrile; MA = maleic anhydride; DBA = dibenzylideneacetone; η^3-C_4H_7 = 2-methylallyl; η^3-PhC_3H_4 = 1-phenylallyl; Me = methyl; ^iP_r-isopropyl, Ph = phenyl; *p*-Tol = *p*-tolyl, *p*-MeC_6H_4; *p*-An = *p*-anisyl, *p*-$MeOC_6H_4$.

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