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Stereo and regioselectivity in the phenylation of cationic allylpalladium(II) α -diimine complexes by tetraphenylborate anion

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Abstract

The reaction of the cationic complex $[\text{Pd}(\text{4-methoxy-1,3-}\eta^3\text{-cyclohexenyl})(\text{py-2-CH=NC}_6\text{H}_4\text{OMe-4})]^+$ (1) with BPh_4^- in the presence of fumaronitrile yields *trans*-3-methoxy-6-phenylcyclohexene (2a) and *trans*-4-methoxy-3-phenylcyclohexene (2b), in ca. 1:1 molar ratio. The *trans* stereochemistry of these products implies that the phenylation of the allyl ligand involves prior transfer of a phenyl group from BPh_4^- to the metal, followed by reductive coupling of the organic moieties. In the reactions of $[\text{Pd}(\eta^3\text{-1,1-}\text{R}_1\text{,}\text{R}_2\text{-C}_3\text{H}_3)(\text{N-N}')^+]$ (3) [$\text{N-N}' = 4\text{-MeOH}_4\text{C}_6\text{N-CH=CH=NC}_6\text{H}_4\text{OMe-4}$; py-2-CH=NR ($\text{R} = \text{C}_6\text{H}_4\text{OMe-4}$, Me, or CMe_3), 2,2'-bipyridine (bipy); $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Ph}$, Me; $\text{R}_1 = \text{R}_2 = \text{Me}$] with BPh_4^- in the presence of activated olefins, both regioisomers $\text{PhCH}_2\text{-CH=CR}_1\text{R}_2$ (4a) and $\text{CH}_2\text{=CH-CR}_1\text{R}_2\text{Ph}$ (4b) are formed with a relative ratio which depends essentially on the allylic substituents: $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Ph}$, 4a > 98%; $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Me}$, 4a 75–67%; $\text{R}_1 = \text{R}_2 = \text{Me}$, 4a 64–58%. The regioisomer distribution is very little affected by the nature of the α -diimine, of the activated olefin, and of the solvent. For $\text{R}_1 = \text{H}$ and $\text{R}_2 = \text{Ph}$, Me, the olefinic product 4a has a *trans* (*E*) geometry. These results have been interpreted in terms of reductive elimination occurring in the intermediate $[\text{PdPh}(\eta^3\text{-1,1-}\text{R}_1\text{,}\text{R}_2\text{-C}_3\text{H}_3)(\text{N-N}')]^+$ with a $\sigma\text{-N}$ monodentate α -diimine ligand.

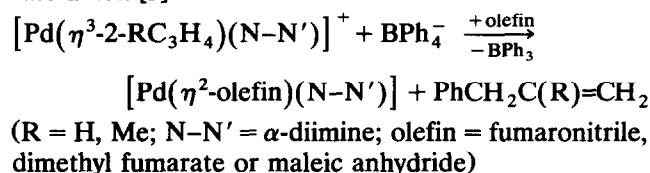
1. Introduction

η^3 -Allylpalladium complexes are used as intermediates in organic synthesis, either for stoichiometric or catalytic reactions involving nucleophilic attack at the terminal allylic carbons by a variety of carbon, oxygen, and nitrogen nucleophiles [1,2]. In particular, the reactions with carbon nucleophiles have been widely studied for their importance in the formation of new C–C bonds [1–4]. From a stereochemical point of view, it has been found that stabilized carbon nucleophiles, such as dimethyl sodiomalonate, attack the η^3 -allyl ligand from the side opposite to palladium, whereas magnesium, lithium, mercury and tin organometallic reagents attack the η^3 -allyl ligand from the same side as palladium. In the latter case, the mechanism in-

volves initial attack of the nucleophile at the central metal, followed by reductive elimination.

On the other hand, in these reactions the regioselectivity depends on a balance of steric and electronic factors of the entering nucleophile, allyl substituents and ancillary ligands on the metal. An increasing steric hindrance to approach of the nucleophile generally favours the attack at the less substituted allyl carbon, whereas an increasing electron demand of the metal promotes the reaction at the more substituted position.

In a recent paper, we reported a mechanistic study of the phenylation of cationic η^3 -allylpalladium complexes, containing α -diimine ligands, by tetraphenylborate anion [5].



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TABLE 1. Regioisomer distribution in reaction (3)

α -Diimine N-N'	Allyl substituents		Olefinic products		Activated olefin	Solvent
	R ₁	R ₂	4a (%) ^a	4b (%) ^a		
py-2-CH=NC ₆ H ₄ OMe-4 ^b	H	Ph	> 98	–	fn	CD ₂ Cl ₂
py-2-CH=NC ₆ H ₄ OMe-4 ^b	H	Me	71	29	fn	CDCl ₃
py-2-CH=NCMe ^b	H	Me	67	33	fn	CDCl ₃
py-2-CH=NCMe ₃ ^b	H	Me	67	33	fn	CDCl ₃
4-MeOC ₆ H ₄ N=CH-CH=NC ₆ H ₄ OMe-4 ^c	H	Me	67	33	fn	(CD ₃) ₂ CO
bipy ^b	H	Me	74	26	fn	CDCl ₃
py-2-CH=NC ₆ H ₄ OMe-4 ^b	Me	Me	58	42	fn	CD ₂ Cl ₂
py-2-CH=NC ₆ H ₄ OMe-4 ^b	Me	Me	62	38	fn	CDCl ₃
py-2-CH=NC ₆ H ₄ OMe-4 ^b	Me	Me	64	36	fn	(CD ₃) ₂ CO
py-2-CH=NC ₆ H ₄ OMe-4 ^b	Me	Me	60	40	dmf	CDCl ₃
py-2-CH=NC ₆ H ₄ OMe-4 ^b	Me	Me	60	40	nq	CDCl ₃
py-2-CH=NCMe ₃ ^b	Me	Me	58	42	fn	CDCl ₃
4-MeOC ₆ H ₄ N=CH-CH=NC ₆ H ₄ OMe-4 ^c	Me	Me	58	42	fn	(CD ₃) ₂ CO
bipy ^b	Me	Me	59	41	fn	CDCl ₃

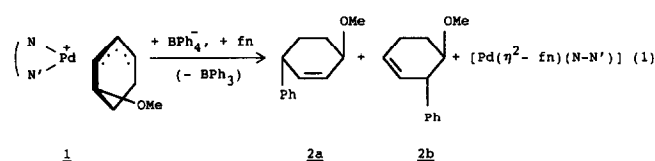
^a Evaluated from integration of the ¹H NMR spectra of the reaction mixtures; ^b cationic complex 3 as tetraphenylborate salt; ^c cationic complex 3 as perchlorate salt.

The proposed mechanism involves extensive ion pairing between the cationic substrate and the BPh₄[–] anion, followed by rate-determining phenyl transfer to the palladium centre to form a reactive intermediate [Pd(2-RC₃H₄)Ph(N-N')], which undergoes fast reductive elimination of allylbenzenes.

In order to gain more information about the phenyl transfer step, the nature of the intermediate, and the subsequent coupling of the phenyl and allyl groups, we have studied the stereo and regiochemistry of the above reaction, using cyclic and/or asymmetrically substituted allyl ligands. NaBPh₄ has been recently used as a phenylating agent in the palladium-catalyzed substitution of allylic chlorides [6] and acetates [7].

2. Results and discussion

The stereochemistry of phenylation was determined by examination of cyclohexenes **2a** and **2b** prepared from the cationic 4-methoxy-1-3 η^3 -cyclohexenyl complex **1** in which the palladium is *trans* to the methoxy group [8] (eqn. (1)),



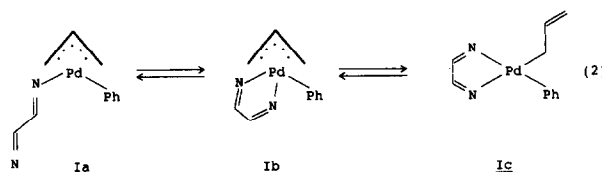
(N-N' = py-2-CH=NC₆H₄OMe-4; fn = fumaronitrile)

Both regioisomers **2a** and **2b** were obtained in a molar ratio of *ca.* 1:1. The *trans* configuration of **2a** was assigned by comparing its ¹H NMR spectrum with that of an authentic sample prepared by a different method [9]: also of diagnostic value was the large

separation between the two CH₂–CH₂ multiplets centered at 2.13 and 1.60 ppm, respectively [10]. The *trans* stereochemistry of **2b** was not obvious from its ¹H NMR spectrum. However, **2b** was hydrogenated to the corresponding methoxy-2-phenylcyclohexane, which exhibited the same ¹H NMR spectrum as an authentic sample prepared from *trans*-hydroxy-2-phenylcyclohexane (see Experimental Section).

The stereochemical course of reaction (1) confirms the proposed mechanism for the phenylation of cationic allylpalladium(II) α -diimine complexes [5], as it involves transfer of a phenyl group from BPh₄[–] to the metal followed by reductive coupling of the organic moieties to form the *trans* disubstituted cyclohexenes **2a** and **2b**.

Due to the flexible bonding properties of α -diimine [11] and allyl [12] ligands, the reactive intermediate containing the phenyl and allyl groups simultaneously linked to palladium may give rise to the following equilibria.



Reductive elimination of allylbenzenes was found to occur for complexes [Pd(η^3 -allyl)(Ar)(L)] (L = triarylphosphine), analogous to intermediate **Ia**, and also, but at lower rates, for complexes [Pd(η^1 -allyl)(Ar)(diphos)] with a chelating diphosphine Ph₂PCH₂CH₂PPh₂ or Z-Ph₂PCH=CHPPh₂, analogous to intermediate **Ic**, [13,14]. In the reaction of the latter compounds, no five-coordinate intermediate of type **Ib** was

observed, whereas such a species was detected in solution for the corresponding nickel(II) derivatives [14]. On the other hand, five-coordinate complexes of the type $[\text{PdCl}(\text{Me})(\eta^2\text{-ol})(\text{N}-\text{N}')]^+$ could be obtained only when the N-N' ligand was the rigid and sterically crowded 2,9-dimethyl-1,10-phenanthroline [15]. Thus in our case the reductive coupling step is likely to

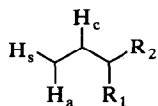
involve either the η^3 -allyl **1a** or the η^1 -allyl **1c** species, or even both.

Clearly, the nature of the reactive intermediate affects the regiochemistry of the olefinic products. It is known that η^1 -allyl ligands are predominantly linked to d^8 metals through the less hindered terminal carbon atom [16]. Accordingly, in the case of the intermediacy

TABLE 2. Selected ^1H NMR data for the cationic complexes $[\text{Pd}(\eta^3\text{-all})(\text{N}-\text{N}')]^+\text{X}^-$ ^a

Complex	α -Diimine protons ^b			Allyl protons ^c				
	H-C=N	H(6)	H(3)	R ₁	R ₂	H _c	H _a	H _s
$[\text{Pd}(\text{N}-\text{N}')(\eta^3\text{-1,1-}R_1R_2\text{C}_3\text{H}_3)]\text{ClO}_4$ N-N' = py-2-CH=NC ₆ H ₄ OMe-4								
R ₁ = H, R ₂ = Ph	8.68 s	mk	8.12 m	4.87 d $^3J(\text{H}-\text{H}_c) = 11.8$	–	6.28 dt $^3J(\text{H}_c-\text{H}_s) = 7.2$ $^3J(\text{H}_c-\text{H}_a) = 12.6$	3.59 d	4.07 d(br)
R ₁ = H, R ₂ = Me	8.78 s	8.73 m	8.25 m ^d	4.20 dq $^3J(\text{H}-\text{H}_c) = 12.4$	1.37 d(br) $^3J(\text{H}-\text{Me}) = 6.3$	5.62 dt $^3J(\text{H}_c-\text{H}_s) = 6.8$ $^3J(\text{H}_c-\text{H}_a) = 12.4$	3.34 d	4.10 d
R ₁ = Me, R ₂ = Me ^e	8.82 s	8.65 m	8.36 m	1.32 s	1.48 s(br)	5.42 dd $^3J(\text{H}_c-\text{H}_s) = 8.2$ $^3J(\text{H}_c-\text{H}_a) = 13.0$	3.58 d	3.97 d
N-N' = 4-MeOC ₆ H ₄ N=CH-CH=NC ₆ H ₄ OMe-4								
R ₁ = H, R ₂ = Me	8.51 s	–	–	4.20 dq $^3J(\text{H}-\text{H}_c) = 12.4$	0.95 d $^3J(\text{H}-\text{Me}) = 6.2$	5.57 dt $^3J(\text{H}_c-\text{H}_s) = 6.7$ $^3J(\text{H}_c-\text{H}_a) = 12.4$	3.50 d	3.95 d
R ₁ = Me, R ₂ = Me ^e	8.50 s	–	–	0.92 s	1.20 s	5.26 dd $^3J(\text{H}_c-\text{H}_s) = 7.4$ $^3J(\text{H}_c-\text{H}_a) = 12.1$	3.47 d	3.74 d
$[\text{Pd}(\text{N}-\text{N}')(\eta^3\text{-1,1-}R_1R_2\text{C}_3\text{H}_3)]\text{BPh}_4$ N-N' = py-2-CH=NCMe ₃								
R ₁ = H, R ₂ = Me	8.19 s	8.36 m	< 7.5 ^f	4.07 dq $^3J(\text{H}-\text{H}_c) = 12.3$	1.52 d $^3J(\text{H}-\text{Me}) = 6.3$	5.51 dt $^3J(\text{H}_c-\text{H}_s) = 7.2$ $^3J(\text{H}_c-\text{H}_a) = 12.5$	3.16 d	4.25 d
R ₁ = Me, R ₂ = Me	8.16 s	8.40 m	< 7.5 ^f	1.30 s	1.66 s	5.30 dd $^3J(\text{H}_c-\text{H}_s) = 7.5$ $^3J(\text{H}_c-\text{H}_a) = 13.1$	3.44 d	4.24 d
$[\text{Pd}(\text{bipy})(\eta^3\text{-1,1-}R_1R_2\text{C}_3\text{H}_3)]\text{BPh}_4$ R ₁ = H, R ₂ = Me								
R ₁ = H, R ₂ = Me	–	8.49 m	7.91 m	4.03 dq $^3J(\text{H}-\text{H}_c) = 11.6$	1.57 d $^3J(\text{H}-\text{Me}) = 6.4$	5.65 dt $^3J(\text{H}_c-\text{H}_s) = 8.1$ $^3J(\text{H}_c-\text{H}_a) = 11.6$	3.32 d d(br)	3.9 (br) ^g
R ₁ = Me, R ₂ = Me	–	8.53 m	7.89 m	1.37 s	1.72 s	5.47 dd $^3J(\text{H}_c-\text{H}_s) = 7.4$ $^3J(\text{H}_c-\text{H}_a) = 12.8$	3.61 d	3.85 d
$[\text{Pd}(\text{N}-\text{N}')(\eta^3\text{-C}_6\text{H}_8\text{OMe})]\text{ClO}_4$ ^{e,h} N-N' = py-2-CH=NC ₆ H ₄ OMe-4								
R ₁ = H, R ₂ = Me	8.75 s	8.84 m	8.20 m ^d	–	5.41 d(br) $^3J(\text{H}-\text{H}_c) = 6.2$	5.88 dd $^3J(\text{H}_c-\text{H}_s) = 6.6$	–	5.13 d(br)

^a In CD₂Cl₂ unless otherwise stated; satisfactory integration values were obtained; coupling constants in Hz; mk = masked, s = singlet, d = doublet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad; the spectra of BPh₄[–] derivatives were recorded immediately after dissolution; for the py-2-CH=NR derivatives time-overaged spectra were obtained, due to a fast dynamic process involving α -diimine ligand site exchange [21]; ^b H(6) and H(3) refer to protons at position 6 and 3 respectively, on the pyridine ring; ^c allyl numbering scheme:



^d overlapping with the H(4) pyridine signals; ^e in CDCl₃ solution; ^f masked by the phenyl proton resonances of BPh₄[–] anion; ^g overlapping with R₁ signal; ^h $\eta^3\text{-C}_6\text{H}_8\text{OMe}$ = 4-methoxy-1-3- η^3 -cyclohexenyl group.

^a Spectra recorded in CDCl₃; coupling constants evaluated from decoupling experiments.

Thus, in the phenylation at the less substituted allylic carbon, the R_1 and R_2 groups do not exchange their position (a process that would require a fast $Ia \rightleftharpoons Ic$ interchange prior to the reductive elimination step). This result lends further support to formation of intermediate Ia , which decays very rapidly to the final products as soon as it is produced in the phenyl transfer step.

3. Experimental section

The chloro-bridged dimers $[PdCl(\eta^3\text{-all})]_2$ (all = 4-methoxy-1-3- η^3 -cyclohexenyl, 1-phenylallyl, 1-methylallyl, 1,1-dimethylallyl) [8,16,19] and the α -diimines $RN=CH-CH=NR$ ($R = C_6H_4OMe-4$), $py-2-CH=NR$ ($R = C_6H_4OMe-4$, Me, CM_e_3) [20] were prepared by published methods. The cationic complexes $[Pd(\eta^3\text{-all})(N-N')X^+]$ [$N-N' = RN=CH-CH=NR$ ($R = C_6H_4OMe-4$), $X^- = ClO_4^-$; $N-N' = py-2-CH=NR$ ($R = C_6H_4OMe-4$, Me, CM_e_3), $X^- = ClO_4^-$, BPh_4^- ; $N-N' = bipy$, $X^- = BPh_4^-$] were prepared in high yields (70–90%) by standard procedures [5,21], and were characterized in solution by 1H NMR spectroscopy (Table 2).

All other chemicals and solvents were reagent grade, and were used without further purification.

The 1H NMR spectra were run on Bruker AM400 and Bruker WP80SY spectrometers at 25°C and 30°C respectively, using tetramethylsilane as an internal standard. The IR spectra were recorded on a Perkin-Elmer 983 G instrument, using Nujol mulls and CsI plates.

Thin-layer chromatography was performed on glass sheets covered with silica gel 60F-254 (0.25 mm) (Merck). Column chromatography was performed on silica gel 60 (Merck 70–230 mesh).

3.1. Reaction of the cationic complexes $[Pd(\eta^3\text{-all})(N-N')]^+$ with BPh_4^- in the presence of activated olefins (ol)

3.1.1. All = 4-methoxy-1-3- η^3 -cyclohexenyl; $N-N' = py-2-CH=NC_6H_4OMe-4$; ol = fumaronitrile

The cationic complex **1** as the tetraphenylborate salt (24.7 mg, 3.3×10^{-2} mmol) was dissolved in CD_2Cl_2 (1 ml) in the presence of fumaronitrile (3.1 mg, 4.0×10^{-2} mmol). After 30 min, the yellow microcrystals of the sparingly soluble $[Pd(\eta^3\text{-fn})(py-2-CH=NC_6H_4OMe-4)]$ [5] were filtered off. The 1H NMR spectrum of the solution indicated the formation of *trans* cyclohexenes **2a** and **2b** (eqn. (1)) in a ca. 1:1 molar ratio [from integration of the $\delta(OMe)$ singlets at 3.38 ppm (**2a**) and 3.24 ppm (**2b**)], as phenylation products.

For stereochemical studies, **2a** and **2b** were isolated and characterized in the following manner. The complex **1** as BPh_4^- salt (2.34 g, 3.12 mmol) was dissolved

in CH_2Cl_2 (80 ml) in the presence of fumaronitrile (0.293 g, 3.75 mmol). After 1 h, the yellow solid was filtered out, and the solution was concentrated at reduced pressure (in a rotary evaporator) to leave a yellowish oily residue. Chromatography on a silica gel column (petroleum ether 40–70/ Et_2O 95:5 v/v) gave **2a** ($R_F = 0.4$, 0.08 g) and **2b** ($R_F = 0.5$, 0.10 g).

1H NMR ($CDCl_3$, 400 MHz): **2a**, δ 7.30–7.15 (5H, m, C_6H_5), 5.95–5.80 (2H, m, $CH=CH$), 3.94–3.88 (1H, m, $CH-OMe$), 3.46–3.40 (1H, m, $CH-Ph$), 3.41 (3H, s, OCH_3), 2.20–2.05 (2H, m, CH_2-CH_2) 1.70–1.50 (2H, m, CH_2-CH_2); **2b**, δ 7.35–7.20 (5H, m, C_6H_5), 5.90–5.55 (2H, m, $CH=CH$, $J = 10.0$ Hz), 3.46–3.40 (1H, m, $CH-Ph$), 3.38–3.33 (1H, m, $CH-OMe$), 3.28 (3H, s, OCH_3), 2.30–1.60 (4H, m, CH_2-CH_2).

The 1H NMR spectrum of **2a** in CCl_4 (80 MHz) exhibits an upfield shift for all signals of ca. 0.1 ppm, and matches that reported for *trans*-3-methoxy-6-phenylcyclohexene [9]. The 1H NMR spectrum of *cis*-3-methoxy-6-phenylcyclohexene differs from that of the *trans* isomer particularly in the CH_2-CH_2 region, where the four protons resonate as a multiplet in the narrow range 1.75–2.00 ppm [9]. The 1H NMR spectrum of **2a** in $CDCl_3$ is also in good agreement with that of the homologous *trans*-3-hydroxy-6-phenylcyclohexene in the same solvent [17].

For **2b**, spin decoupling experiments gave coupling constants of 10.0 Hz between the olefinic protons, 6.0 Hz between the $Ph-CH$ and the $MeOCH$ protons, 8.4 and 2.8 Hz between $MeO-CH$ and the protons of the adjacent methylene group, which did not allow an unambiguous structural assignment. Compound **2b** (0.04 g) dissolved in $EtOH$ (7 ml) was hydrogenated with H_2 (30 atm) in the presence of Pd/C catalyst (10%, 0.02 g). After 12 h, the suspension was filtered off, and the clear solution was evaporated under reduced pressure to give the crude cyclohexane derivative, which was purified by chromatography on a silica gel column (petroleum ether 40–70/ Et_2O 9:1 v/v) ($R_F = 0.8$, 0.02 g). Comparison of the 1H NMR spectrum of this product with that of an authentic sample of *trans*-methoxy-2-phenylcyclohexane prepared by methylation of *trans*-2-phenylcyclohexanol [22], gave identical results: 1H NMR ($CDCl_3$, 400 MHz): 7.33–7.17 (5H, m, C_6H_5), 3.30 (1H, dt, $J = 10.1$, 4.5 Hz, $CHOMe$) 3.14 (3H, s, OCH_3), 2.56 (1H, ddd, $J = 12.0$, 10.1, 4.1 Hz, $CH-Ph$), 2.33–2.25 m, 1.96–1.87 m, 1.82–1.73 m, 1.59–1.25 m (8H, $-CH_2-$).

3.1.2. All = 1-methylallyl, 1,1-dimethylallyl; $N-N' = 4-MeOC_6H_4N=CH-CH=NC_6H_4OMe-4$; ol = fumaronitrile

The cationic complex **3** as perchlorate salt (3.3×10^{-2} mmol) and $NaBPh_4$ (11.3 mg, 3.3×10^{-2} mmol)

were dissolved in $(\text{CD}_3)_2\text{CO}$ (1 ml) in the presence of fumaronitrile (3.1 mg, 4.0×10^{-2} mmol). After 2 h, the orange-brown solid $[\text{Pd}(\eta^2\text{-fn})(4\text{-MeOC}_6\text{H}_4\text{N}=\text{CH}-\text{CH}=\text{NC}_6\text{H}_4\text{OMe-4})]$ [5] was filtered off. The ^1H NMR spectrum of the solution showed the complete disappearance of the starting compound **3** and formation of both regioisomers **4a** and **4b** (eqn. (3)) in the molar ratios reported in Table 1. The characteristic resonances of the olefins **4a** and **4b** are listed in Table 3.

3.1.3. *All* = 1-phenylallyl, 1-methylallyl, 1,1-dimethylallyl; *N-N'* = *py*-2- $\text{CH}=\text{NR}$ ($R = \text{C}_6\text{H}_4\text{OMe-4}$, *Me*, *CMe*₃), *bipy*; *ol* = fumaronitrile, dimethylfumurate, 1,4-naphthoquinone

The cationic complex **3** as BPh_4^- salt (3.3×10^{-2} mmol) and the activated olefin (4.0×10^{-2} mmol) were dissolved in 1 ml of the deuterated solvent (CDCl_2 , CDCl_3 , $(\text{CD}_3)_2\text{CO}$). After 1 h (*py*-2- $\text{CH}=\text{NR}$) or 12 h (*bipy*) the sparingly soluble complex $[\text{Pd}(\eta^2\text{-ol})(\text{N-N}')]$ was filtered out, and the solution was examined by ^1H NMR spectroscopy. In every case, the reaction involved the complete disappearance of **3** to yield both regioisomers **4a** and **4b** (eqn. (3)) in the molar ratios of Table 1, evaluated from integration of their characteristic signals (Table 3).

3.2. Preparation and characterization of $[\text{Pd}(\eta^2\text{-nq})(\text{py-2-CH}=\text{NC}_6\text{H}_4\text{OMe-4})]$

The cationic complex $[\text{Pd}(\eta^3\text{-1,1-Me}_2\text{C}_3\text{H}_3)(\text{py-2-CH}=\text{NC}_6\text{H}_4\text{OMe-4})]\text{BPh}_4$ (0.35 g, 0.5 mmol) and 1,4-naphthoquinone (0.095 g, 0.6 mmol), were dissolved in CH_2Cl_2 (50 ml) with stirring. After 1 h, Et_2O (50 ml) was added to complete the precipitation of the red-brick product (0.19 g). This compound was characterized by elemental analysis (Found: C, 58.3; H, 3.9; N, 5.7. $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2\text{Pd}$ calcd.: C, 57.93; H, 3.80; N, 5.88%), and IR spectra [$\nu(\text{C}=\text{O})$ at 1625 and 1573 cm^{-1} ; cf. the $\nu(\text{C}=\text{O})$ band of uncoordinated 1,4-naphthoquinone at 1650 cm^{-1}].

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References

- 1 B. M. Trost, *Tetrahedron*, **33** (1977) 2615; B. M. Trost, *Acc. Chem. Res.*, **13** (1980) 385; B. M. Trost and T. R. Verhoeven, *Comp. Organomet. Chem.*, **8** (1982) 799; B.M. Trost, *Angew. Chem. Int. Ed. Engl.*, **28** (1989) 1173.
- 2 J. Tsuji, *Organic Synthesis with Palladium Compounds*, Springer, Berlin, 1980; J. Tsuji, *Tetrahedron*, **42** (1986) 4361; J. Tsuji and I. Minami, *Acc. Chem. Res.*, **20** (1987) 140.
- 3 J. S. Temple, M. Riediker and J. Schwartz, *J. Am. Chem. Soc.*, **104** (1982) 1310.
- 4 T. Hayashi, M. Konishi and M. Kumada, *J. Chem. Soc., Chem. Commun.*, (1984) 107.
- 5 B. Crociani, F. Di Bianca, P. Uguagliati and L. Canovese, *J. Chem. Soc., Dalton Trans.*, (1991) 71.
- 6 H. Kurosawa, S. Ogoshii, Y. Kawasaki, S. Muray, M. Miyoshi and I. Ikeda, *J. Am. Chem. Soc.*, **112**, (1990) 2813.
- 7 J. Y. Legros and J. C. Fiaud, *Tetrahedron Lett.*, **31** (1990) 7453.
- 8 J. E. Bäckvall, R. E. Nordberg, K. Zetterberg and B. Åkermark, *Organometallics*, **2** (1983) 1625.
- 9 J. H. P. Utley and G. B. Yates, *J. Chem. Soc., Perkin Trans. II*, (1978) 395.
- 10 J. E. Bäckvall, R. E. Nordberg and D. Wilhelm, *J. Am. Chem. Soc.*, **107** (1985) 6892.
- 11 G. van Koten and K. Vrieze, *Adv. Organomet. Chem.*, **21** (1982) 151.
- 12 P. M. Maitlis, P. Espinet and M. J. H. Russel, *Comp. Organomet. Chem.*, **6** (1982) 385.
- 13 H. Kurosawa, M. Emoto, H. Ohnishi, K. Miki, N. Kasai, K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.*, **109** (1987) 6333.
- 14 H. Kurosawa, H. Ohnishi, M. Emoto, Y. Kawasaki and S. Murai, *J. Am. Chem. Soc.*, **110** (1988) 6272.
- 15 A. De Renzi, G. Morelli, A. Panunzi and A. Vitagliano, *Gazz. Chim. Ital.*, **117** (1987) 445.
- 16 J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, (1967) 1839; S. Numata, R. Okawara and H. Kurosawa, *Inorg. Chem.*, **16** (1977) 1737.
- 17 D. R. Tueting, A. M. Echavarren and J. K. Stille, *Tetrahedron*, **45** (1989) 979.
- 18 J. Keijsper, H. van der Poel, L.H. Polm, G. van Koten, K. Vrieze, P. F. A. Seignette, R. Varenhorst and C. Stam, *Polyhedron*, **2** (1983) 1111.
- 19 W. T. Dent, R. Long and A. J. Wilkinson, *J. Chem. Soc.*, (1964), 1585; M. C. Ashraf, T. G. Burrowes and W. R. Jackson, *Aust. J. Chem.*, **29** (1976) 2643.
- 20 H. tom Dieck and I. W. Renk, *Chem. Ber.*, **104** (1971) 110; G. Matsubayashi, M. Okunaka and T. Tanaka, *J. Organomet. Chem.*, **56** (1973) 215.
- 21 B. Crociani, T. Boschi and P. Uguagliati, *Inorg. Chim. Acta*, **48** (1981) 9; B. Crociani, F. Di Bianca, A. Giovenco and T. Boschi, *Inorg. Chim. Acta*, **127** (1987) 169.
- 22 R. L. Letsinger and E. Bobko, *J. Am. Chem. Soc.*, **75** (1953) 2649.