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

Bruno Crociani and Simonetta Antonaroli

Dipartimento di Scienze e Tecnologie Chimiche, II University of Rome, Via O. Raimondo, 00173 Roma (Italy)

Francesca Di Bianca and Alberta Fontana

Dipartimento di Chimica Inorganica, University of Palermo, Palermo (Italy)

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Abstract

The reaction of the cationic complex [Pd(4-methoxy-1,3-η^3-cyclohexenyl)(py-2-CH=NC_6H_4OMe-4)]$^+$ (**1**) with BPh_4^- in the presence of fumaronitrile yields *trans*-3-methoxy-6-phenylcyclohexene (**2a**) and *trans*-4-methoxy-3-phenyl-cyclohexene (**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 [Pd(η^3-1,1-R_1,R_2-C_3H_3)(N–N′)]$^+$ (**3**) [N–N′ = 4-MeOH_4C_6N=CH–CH=NC_6H_4OMe-4; py-2-CH=NR (R = C_6H_4OMe-4, Me, or CMe_3), 2,2′-bipyridine (bipy); R_1 = H, R_2 = Ph, Me; R_1 = R_2 = Me] with BPh_4^- in the presence of activated olefins, both regioisomers $PhCH_2$–CH=CR_1R_2 (**4a**) and CH_2=CH–CR_1R_2Ph (**4b**) are formed with a relative ratio which depends essentially on the allylic substituents: R_1 = H, R_2 = Ph, **4a** > 98%; R_1 = H, R_2 = Me, **4a** 75–67%; R_1 = R_2 = 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 R_1 = H and R_2 = 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 [PdPh(η^3-1,1-R_1,$R_2C_3H_3$)(N–N′)] with a σ-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 involves 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].

$$[Pd(\eta^3\text{-}2\text{-}RC_3H_4)(N\text{–}N')]^+ + BPh_4^- \xrightarrow[-BPh_3]{+\text{olefin}} [Pd(\eta^2\text{-olefin})(N\text{–}N')] + PhCH_2C(R)=CH_2$$

(R = H, Me; N–N′ = α-diimine; olefin = fumaronitrile, dimethyl fumarate or maleic anhydride)

Correspondence to: Professor B. Crociani.

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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_2Cl_2
py-2-CH=NC$_6$H$_4$OMe-4 [b]	H	Me	71	29	fn	$CDCl_3$
py-2-CH=NMe [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	$(CD_3)_2CO$
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_2Cl_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	$(CD_3)_2CO$
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	$(CD_3)_2CO$
bipy [b]	Me	Me	59	41	fn	$CDCl_3$

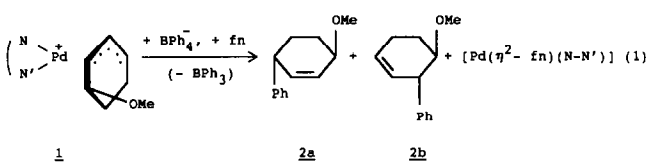
[a] Evaluated from integration of the ^{1}H NMR spectra of the reaction mixtures; [b] cationic complex **3** as tetraphenylborate salt; [c] cationic complex **3** as perchlorate salt.

The proposed mechanism involves extensive ion pairing between the cationic substrate and the BPh_4^- anion, followed by rate-determining phenyl transfer to the palladium centre to form a reactive intermediate [Pd(2-RC$_3$H$_4$)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. $NaBPh_4$ 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)),



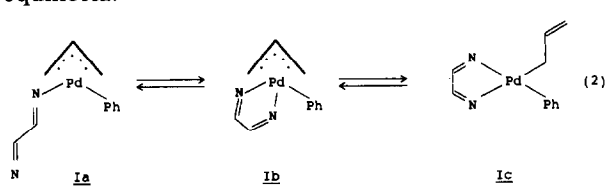
1 **2a** **2b**

(N–N′ = py-2-CH=NC$_6$H$_4$OMe-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 ^{1}H 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 CH_2–CH_2 multiplets centred at 2.13 and 1.60 ppm, respectively [10]. The *trans* stereochemistry of **2b** was not obvious from its ^{1}H NMR spectrum. However, **2b** was hydrogenated to the corresponding methoxy-2-phenylcyclohexane, which exhibited the same ^{1}H 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 BPh_4^- 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.



Ia Ib Ic

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 $Ph_2PCH_2CH_2PPh_2$ or *Z*-Ph_2PCH=$CHPPh_2$, analogous to intermediate **Ic**, [13,14]. In the reaction of the latter compounds, no five-coordinate intermediate of type **Ib** was

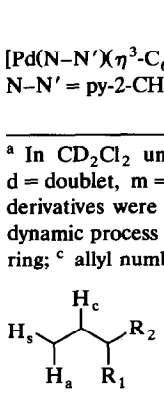
observed, whereas such a species was detected in solution for the corresponding nickel(II) derivatives [14]. On the other hand, five-coordinate complexes of the type [PdCl(Me)(η^2-ol)(N–N′)] could be obtained only when the N–N′ ligand was the rigid and sterically crowded 2,9-dimethyl-1,10-phenanthroline [15]. Thus in our case the reductive coupling step is likely to involve either the η^3-allyl **Ia** or the η^1-allyl **Ic** 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 ^{1}H NMR data for the cationic complexes [Pd(η^3-all)(N–N′)]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
[Pd(N–N′)(η^3-1,1-R_1,$R_2C_3H_3$)]ClO_4								
N–N′ = py-2-CH=NC_6H_4OMe-4								
R_1 = H, R_2 = Ph	8.68 s	mk	8.12 m	4.87 d ^3J(H–H_c) = 11.8	–	6.28 dt ^3J(H_c–H_s) = 7.2 ^3J(H_c–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(H–H_c) = 12.4	1.37 d(br) ^3J(H–Me) = 6.3	5.62 dt ^3J(H_c–H_s) = 6.8 ^3J(H_c–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(H_c–H_s) = 8.2 ^3J(H_c–H_a) = 13.0	3.58 d	3.97 d
N–N′ = 4-MeOC_6H_4N=CH–CH=NC_6H_4OMe-4								
R_1 = H, R_2 = Me	8.51 s	–	–	4.20 dq ^3J(H–H_c) = 12.4	0.95 d ^3J(H–Me) = 6.2	5.57 dt ^3J(H_c–H_s) = 6.7 ^3J(H_c–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(H_c–H_s) = 7.4 ^3J(H_c–H_a) = 12.1	3.47 d	3.74 d
[Pd(N–N′)(η^3-1,1-R_1,$R_2C_3H_3$)]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(H–H_c) = 12.3	1.52 d ^3J(H–Me) = 6.3	5.51 dt ^3J(H_c–H_s) = 7.2 ^3J(H_c–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(H_c–H_s) = 7.5 ^3J(H_c–H_a) = 13.1	3.44 d	4.24 d
[Pd(bipy)(η^3-1,1-R_1,$R_2C_3H_3$)]BPh_4								
R_1 = H, R_2 = Me	–	8.49 m	7.91 m	4.03 dq ^3J(H–H_c) = 11.6	1.57 d ^3J(H–Me) = 6.4	5.65 dt ^3J(H_c–H_s) = 8.1 ^3J(H_c–H_a) = 11.6	3.32 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(H_c–H_s) = 7.4 ^3J(H_c–H_a) = 12.8	3.61 d	3.85 d
[Pd(N–N′)(η^3-C_6H_8OMe)]ClO_4 [e,h]								
N–N′ = py-2-CH=NC_6H_4OMe-4	8.75 s	8.84 m	8.20 m [d]	–	5.41 d(br) ^3J(H–H_c) = 6.2	5.88 dd ^3J(H_c–H_s) = 6.6	–	5.13 d(br)

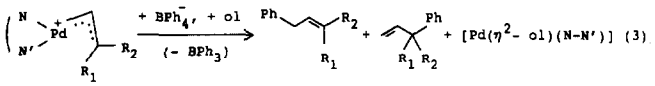
[a] In CD_2Cl_2 unless otherwise stated; satisfactory integration values were obtained; coupling constants in Hz; mk = masked, s = singlet, d = doublet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad; the spectra of BPh_4^- derivatives were recorded 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 $CDCl_3$ solution; [f] masked by the phenyl proton resonances of BPh_4^- anion; [g] overlapping with R_1 signal; [h] η^3-C_6H_8OMe = 4-methoxy-1-3-η^3-cyclohexenyl group.

by **Ic**, one would expect an increasing phenylation at the less substituted carbon by increasing the number of substituents on the other allyl terminus. This was indeed observed in the palladium-catalyzed coupling of organostannanes with vinyl epoxides, for which a mechanism *via* η^1-allyl intermediates, similar to **Ic**, was proposed [17].

We have therefore examined the distribution of regioisomers **4a** and **4b** in reaction (3) carried out with the cationic complexes **3** containing unsymmetrically substituted η^3-allyl ligands, in different deuterated solvents and in the presence of various activated olefins in order to stabilize the product [(Pd(η^2-ol)(N–N′)]:



3 4a 4b

[N–N′ = 4-MeOH$_4$C$_6$N=CH–CH=NC$_6$H$_4$OMe-4; py-2-CH=NR (R = C$_6$H$_4$OMe-4, Me, CMe$_3$), 2,2′-bipyridine; R_1 = H, R_2 = Ph, Me; R_1 = R_2 = Me; ol = fumaronitrile (fn), dimethylfumarate (dmf), 1,4-naphthoquinone (nq)].

The ^{1}H NMR spectra of the reaction mixtures show that the olefinic derivatives **4a** and **4b** are formed with the relative percentages listed in Table 1.

As can be seen, the regiochemistry of reaction **3** is essentially influenced by the allyl substituents R_1 and R_2, with a slight dependence on the natures of the solvent, of the activated olefin and of the α-diimine ligand. For R_1 = H and R_2 = Ph, the phenylation occurs almost regiospecifically at the less substituted terminal carbon with formation of E-1,3-diphenylpropene (**4a**: R_1 = H, R_2 = Ph, > 98%) and trace amount of a second product (possibly **4b**), whose ^{1}H NMR signals are so weak as to prevent any unambiguous assignment. For R_1 = H and R_2 = Me, the yield of **4a** (*E*-1-phenyl-2-butene) decreases to 67–75%. In this case, the regioisomer 3-phenyl-1-butene (**4b**: R_1 = H, R_2 = Me) is clearly observed and identified in the ^{1}H NMR spectra (Table 3). For R_1 = R_2 = Me, the increased substitution brings about a further decrease in the yield of **4a** (2-methyl-4-phenyl-2-butene) to 58–64%, with a concomitant increase of **4b** (3-methyl-3-phenyl-1-butene).

These results point to a reductive coupling occurring predominantly through intermediate **Ia**, without participation of either the solvent or the activated olefin.

The small influence of the steric properties of the α-diimine is also understood if it acts as a σ-N monodentate ligand, with a planat *trans* N=C–C=N skeleton perpendicular to the coordination plane [18]. In this configuration, the steric interactions of the nitrogen substituents with the allyl and/or phenyl ligand are much reduced compared with those which would occur if the N–N′ ligands were σ,σ-N,N′ chelated to the palladium centre (as in **Ic**).

The stereochemistry of the phenylation products **4a** (R_1 = H; R_2 = Ph, Me) reflects the stereochemistry of the starting η^3-allyl complexes **3**, in which the R_2 group assumes a *syn* configuration relative to the central allylic proton, as is clearly indicated by the coupling constant of *ca.* 12 Hz between the latter proton and R_1 (see Table 2).

As can be inferred from the large coupling constant values between the olefinic protons (*ca.* 15 Hz, see Table 3), the products **4a** (R_1 = H; R_2 = Ph, Me) are formed with a *trans* geometry around the double bond.

TABLE 3. ^{1}H NMR spectra of the olefinic products **4a** and **4b** in reaction (3) [a]

Compound	Ph	=CH	R_1	R_2	$-CH_2-$	$=CH_2$
4a						
R_1 = H; R_2 = Ph E-1,3-diphenylpropene	8.0–7.1 m	6.6–6.1 m ^3J(CH–CH$_2$) = 4.7	6.6–6.1 m ^3J(CH=CH) = 15.2	8.0–7.1 m	3.55 m	–
R_1 = H; R_2 = Me E-1-phenyl-2-butene	7.4–7.1 m	5.59 m ^3J(CH–CH$_2$) = 6.25	5.51 m ^3J(CH=CH) = 15.4	1.70 d ^3J(CH–CH$_3$) = 5.8	3.32 d	–
R_1 = Me; R_2 = Me 2-methyl-4-phenyl-2-butene	7.4–7.1 m	5.34 tm ^3J(CH–CH$_2$) = 7.4	1.72 s(br)	1.72 s(br)	3.30 d	–
4b						
R_1 = H; R_2 = Me 3-phenyl-1-butene	7.4–7.1 m	6.01 m	3.47 dq ^3J(CH–CH) = 6.5	1.37 d ^3J(CH–CH$_3$) = 6.5	–	5.1–5.0 m
R_1 = Me; R_2 = Me 3-methyl-3-phenyl-1-butene	7.4–7.1 m	6.2–5.9 m	1.40 s	1.40 s	–	5.2–4.9 m

[a] Spectra recorded in $CDCl_3$; 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** ⇌ **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, CMe_3) [20] were prepared by published methods. The cationic complexes $[Pd(\eta^3\text{-all})(N\text{–}N')]X$ [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, CMe_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 $[Pd(\eta^3\text{-all})(N\text{–}N')]^+$ 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$_6$H$_4$OMe-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 $[Pd(\eta^2\text{-fn})(py\text{-}2\text{-}CH{=}NC_6H_4OMe\text{-}4)]$ [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 δ(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, C*H*=C*H*), 3.94–3.88 (1H, m, C*H*–OMe), 3.46–3.40 (1H, m, C*H*–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, C*H*=C*H*, *J* = 10.0 Hz), 3.46–3.40 (1H, m, C*H*–Ph), 3.38–3.33 (1H, m, C*H*–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–C*H* and the MeOC*H* protons, 8.4 and 2.8 Hz between MeO–C*H* 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, C*H*OMe) 3.14 (3H, s, OCH_3), 2.56 (1H, ddd, *J* = 12.0, 10.1, 4.1 Hz, C*H*–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$_6$H$_4$N=CH–CH=NC$_6$H$_4$OMe-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 $(CD_3)_2CO$ (1 ml) in the presence of fumaronitrile (3.1 mg, 4.0×10^{-2} mmol). After 2 h, the orange-brown solid [Pd(η^2-fn)(4-MeOC$_6$H$_4$N=CH–CH=NC$_6$H$_4$OMe-4)] [5] was filtered off. The ^{1}H 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-CH=NR (R = C$_6$H$_4$OMe-4, Me, CMe$_3$), bipy; ol = fumaronitrile, dimethylfumarate, 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 ($CDCl_2$, $CDCl_3$, $(CD_3)_2CO$). After 1 h (py-2-CH=NR) or 12 h (bipy) the sparingly soluble complex [Pd(η^2-ol)(N–N′)] was filtered out, and the solution was examined by ^{1}H 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 [Pd(η^2-nq)(py-2-CH=NC$_6$H$_4$OMe-4)]

The cationic complex [Pd(η^3-1,1-Me$_2$C$_3$H$_3$)(py-2-CH=NC$_6$H$_4$OMe-4)]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. $C_{23}H_{18}N_2O_2Pd$ calcd.: C, 57.93; H, 3.80; N, 5.88%), and IR spectra [ν(C=O) at 1625 and 1573 cm^{-1}; *cf.* the ν(C=O) band of uncoordinated 1,4-naphthoquinone at 1650 cm^{-1}].

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