trans-Bis-[(−)ephedrinate]-palladium[II] complex: synthesis, molecular modeling and use as catalyst

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Abstract

The reaction between palladium acetate, (−)-ephedrine and potassium acetate led to bis-chelate complex Pd[OCH(Ph)NH(Me)]₂ whose the *trans*-structure is obtained from calculations. The use of this complex to catalyze either the 1,4-hydrogenation of (*E*)-2-benzyliden-1-tetralone or Heck reaction of phenyl iodide with 3-methyl-3-buten-2-ol led to a low enantiomeric excess.
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1. Introduction

Over the last past years, we have been involved with the use of enantiopure amino alcohols (AH*s) in palladium-catalyzed enantioselective hydrogenation of α,β-unsaturated ketones [1,2] and asymmetric tautomerization of prochiral enols produced from Pd-induced domino reactions [3–5]. Although AH*s have been used with various metals to carry out enantioselective reactions,[2] it seemed that the synthesis and the structure of palladium complexes having these bidentate chiral species as ligands have never been reported.[3] Hence, we recently disclosed that reaction of palladium chloride (**1**) with two equivalents of (−)-ephedrine (**2**) can lead to complexes **3** and **4** (Eq. (1)) [15]. The structure of **4**, which was determined by X-ray crystallography [15], was surprising since it corresponds to the deprotonation of one AH* to form an anionic chelating ligand while the other AH* is *N*-coordinated and presents a free alcoholic arm. Our efforts to obtain the Pd-complex with two chelating ligands from **1** and **2** under various experimental conditions was unsuccessful.

Inspired by the study of van Koten and co-workers who has complexed achiral diethanolamines to palladium [16], we now report that we succeeded in this synthesis in using palladium acetate instead of **1**. To the best of our knowledge, a palladium complex with two homochiral anionic chelating ligands is disclosed for the first time.

2. Synthesis

The complexation proceeded by addition at room temperature of potassium carbonate to a 2/1 solution of **2** and palladium acetate in benzene (Eq. (2)). The
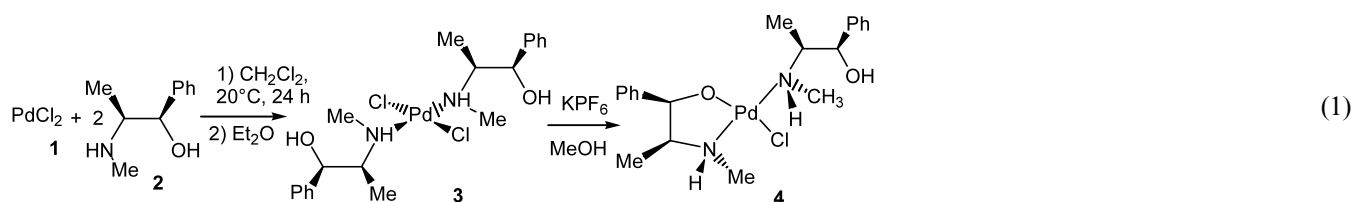
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(1)

elemental analysis of the homogeneous solid which was isolated was in agreement with **5** as formula. From comparison of NMR spectra of **2** and **5** (Tables 1 and 2), it appeared that, in contrast to **3**, all signals of the aminoalcohol were modified by di-coordination to palladium. Furthermore, the N–H streching vibration at 3297 cm^{-1} of **2** was shifted to 3230 cm^{-1} for **5**. These NMR and IR data are consistent with two *N,O*-chelate bonded amino alkoxide ligands. Thereby, the N atom becomes a stable tetrahedral array, i.e. an additional stereogenic center. A single set of signals being obtained from NMR spectroscopies of **5** (Tables 1 and 2), this implies the presence of a C_2 symmetry axis. Consequently, both N-atoms have the same configuration. Structures **5**-*cis* and **5**-*trans* have both a C_2 symmetry axis. IR spectrum of **5** in the area 200–800 cm^{-1} showed bands at 286, 497, 574 and 666 cm^{-1}. From comparison with IR data of *cis*- and *trans*-Pd(NH$_3$)$_2$Cl$_2$ [17,18], these values are rather in agreement with **5**-*trans* as structure of the isolated complex. Moreover, *trans*-geometry has been previously determined for bis-*N,O*-chelated Pd[II] complexes obtained from achiral aminoalcohols [16]. Unfortunately, we failed to prepare suitable crystals of **5** for X-ray analysis. Since IR and NMR spectra were not enough informative to determine the stereochemistry around the palladium center with confidence, theoretical calculations were performed.

(2)
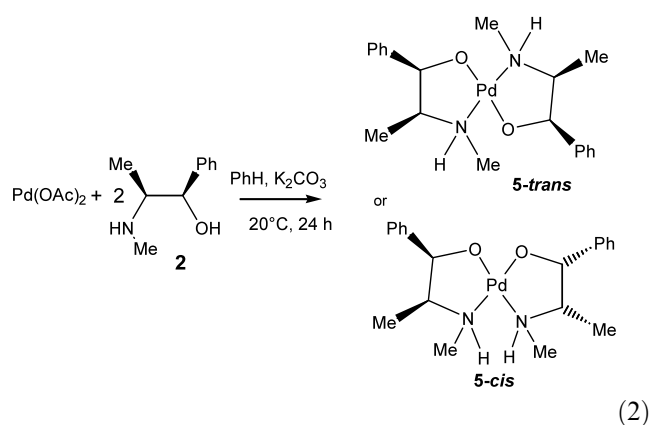
3. Computational studies

The computations reported in this work have been performed using the Gaussian 98 suite of program [19]. Both geometry and energy calculations were performed with the B3LYP hybrid functional [20,21]. The basis set we used was grounded on the LANL2DZ basis set [22–24]. This combines either a relativistic effective core potential (RECP) plus a double-ζ gaussian basis (for the palladium atom) after Hay and Wadt, or simply an all electron double-ζ gaussian basis (for hydrogen, carbon, nitrogen and oxygen) after Dunning: 'D95' [25]. For a better description of the metal ligand-interaction, the LANL2DZ basis set has been supplemented with

Table 1
^{1}H-NMR of (−)-ephedrine and the isolated complex [a]

	Me–C	*Me*–N	MeC–*H*	PhC–*H*	*Ph*
2	$\delta = 0.85$, d, $J = 6.2$	$\delta = 2.5$, ws	$\delta = 2.80$, m	$\delta = 4.75$, d, $J = 3.1$	$\delta = 7.30$, m
3	$\delta = 0.82$, d, $J = 6.2$	$\delta = 2.45$, ws	$\delta = 2.78$, m	$\delta = 4.75$, d, $J = 3.0$	$\delta = 7.25$, m
5	$\delta = 1.00$, d, $J = 6.2$	$\delta = 2.40$, d, $J = 5.0$	$\delta = 2.15$, m	$\delta = 5.20$, wd, $J = 2.5$	$\delta = 7.10$, m

[a] δ in ppm, J in Hz; ws: wide singlet.

Table 2
^{13}C-NMR of (−)-ephedrine and the isolated complex [a]

|	Me−C	Me−N	Me−C	Ph−C	Ph
2	$\delta = 14.3$	$\delta = 34.0$	$\delta = 60.8$	$\delta = 73.0$	$\delta = 126.1, 127.0, 128.1$
3	$\delta = 14.3$	$\delta = 34.0$	$\delta = 60.4$	$\delta = 73.0$	$\delta = 126.1, 127.0, 128.1$
5	$\delta = 10.2$	$\delta = 35.5$	$\delta = 65.3$	$\delta = 82.3$	$\delta = 125.7, 126.8, 128.1$

[a] δ in ppm.

diffuses and polarization functions taken from the D95 basis set. Diffuses (sp_v) and polarization (d_v) functions were added on N and O atoms with the exponent values $sp_N = 0.0639$, $d_N = 0.80$ and $sp_O = 0.0845$, $d_O = 0.85$, respectively. Following the usual notation, our basis set will be noted in the following lanl2dz+(d).[4] It has been shown that accurate geometries can be obtained via DFT computations although *reaction energies* require 'state of the art' level of calculation [26]. As we shall see in the following, conformational energy differences are much easier to obtain than *reaction energies*.

3.1. Model system

The reliability of our computations has been addressed on a model system with hydrogen atoms replacing methyl and phenyl groups Pd(NH$_2$CH$_2$CH$_2$O)$_2$ (**6**). With such a small system we have been able to perform the computations up to the MP4 level,[5] that is close to a 'state of the art' calculation, to check for the convergence of the perturbation serie (MP2, MP3, MP4DQ, ... MP4SDTQ) and compare to the B3LYP results.

Two isomers, **6**-*trans* and **6**-*cis* have been considered, with a square-planar coordination of the palladium atom.[6] For each of them we carried out the calculations
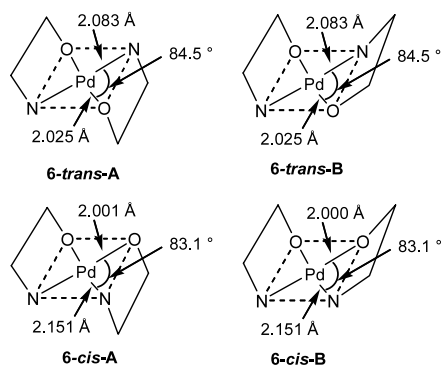
Scheme 1.

on the two extreme envelope conformations **A** or **B** (Scheme 1). The main geometrical parameters shown on Scheme 1 compare well with those established by X-ray diffraction for van Koten and co-workers achiral *N,O*-bis chelated Pd^{II} complex [16]. A *trans* structure was pointed out, with a Pd−N distance in the range 2.06–2.08 Å (depending on the substituents at the N atom) and a Pd−O distance close to 2.00 Å. These values differ from our results by less than 0.03 Å (Scheme 1, **6**-*trans*-**A** and -**B**: Pd−N 2.083 and Pd−O 2.025 Å). For *cis*/*trans* structural effects, one shall rely on Zeizinger et al. ab initio study of the elementary model (Pd(NH$_3$)$_2$(OH)$_2$) of our system [27]. Larger Pd−N distance in the *cis* (2.08 Å) than in the *trans* structure (2.02 Å, $\Delta_{PdN} = -0.06$ Å) were reported. The Pd−O distances are also larger for the *trans* (1.98 Å) than for the *cis* structure (1.95 Å, $\Delta_{PdO} = -0.03$ Å). The same trend is encountered in our bis-chelated systems ($\Delta_{PdN} = -0.07$ and $\Delta_{PdO} = -0.02$ Å).

The envelope conformation has almost no influence on the relative energies (Table 3). For instance, at the MP4SDTQ level, **6**-*trans*-**A** and **6**-*trans*-**B** differ by only 0.1 kcal mol^{-1}. In contrast, the difference between *cis* and *trans* arrangements is manifest: **6**-*cis*-**A** and -**B** are both 10.8 kcal mol^{-1} higher in energy than **6**-*trans*-**A** and -**B** (as obtained at our best MP4SDTQ level).

The test of the computational methods shows also that the energy difference between *cis* and *trans* arrangements is an easy task for current computational levels. The Møller–Plesset perturbation series (MP2, MP3, MP4DQ, ... MP4SDTQ) easily corrects the Hartree−Fock results, and tends to the B3LYP results. The agreement between these methods, that are fundamentally different, is a good sign for the accuracy of the B3LYP results. For the real system computations, we used the B3LYP approximation that is computationally manifold faster than the MP4 calculations.

As pointed out in Fig. 1 for the C_2 symmetric conformers, the optimized structures all hold axial and equatorial positions on the carbon atoms. For the real system, those positions are to be substituted by one phenyl and one methyl group according to the structure of (−)-ephedrine.

3.2. Real system

For the conformation of the real system, let us first examine the *trans*-isomer (Scheme 2). Since a C_2 symmetric structure is experimentally observed, only a *trans*-**B** type of structure could be adopted by the system. One shall then place the phenyl ephedrinate's substituents, either as axial (as in *trans*-**B**) or equatorial (*trans*-**B**′). Meanwhile, the methyl groups (syn to the phenyls) adopt an equatorial (*trans*-**B**) or axial (*trans*-**B**′) position. We expect larger steric repulsions arising from axial phenyls than from axial methyls. That would

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[4] However, neither diffuse nor d orbitals were added on carbon atoms.

[5] 4th order frozen core Møller−Plesset perturbation.

[6] Such a coordination is usual, see in particular Ref. [15,16] and references therein.

Table 3
Absolute and relative energies of the model system [a]

Level	6-*trans*-B [b]	6-*trans*-A [c]	6-*trans*-B [c]	6-*cis*-A [c]	6-*cis*-B [c]
HF	− 542.91519	0.0	0.0	14.3	14.3
MP2	− 544.12820	0.1	0.0	11.8	11.8
MP3	− 544.15588	0.0	0.0	12.8	12.9
MP4DQ	− 544.17509	0.0	0.0	12.7	12.7
MP4SDQ	− 544.19601	0.1	0.0	11.7	11.8
MP4SDTQ	− 544.23820	0.1	0.0	10.8	10.8
B3LYP	− 546.37631	0.0	0.0	10.6	10.5

[a] Computed with the lanl2dz+(*d*) basis set on B3LYP/lanl2dz+(*d*) optimized geometries.
[b] Absolute energies (Hartree) of the lowest structure, used as the reference energies.
[c] Energies in kcal mol^{-1}, relative to the lowest structure (6-*trans*-B).
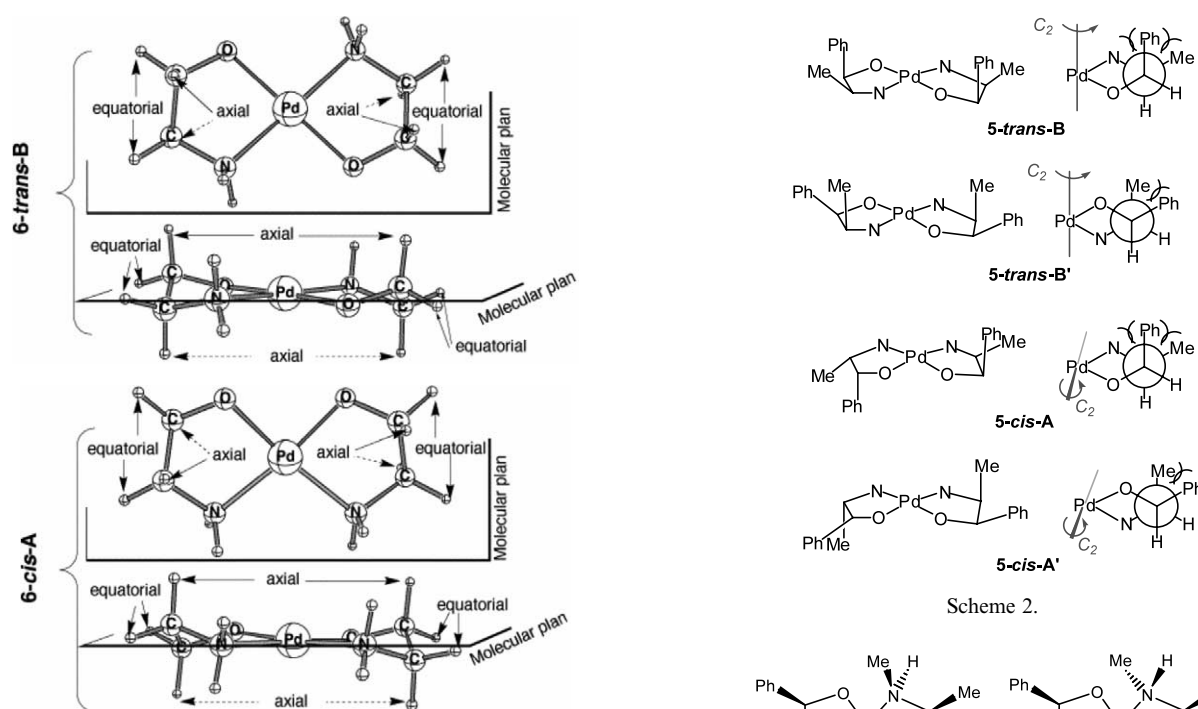

Fig. 1. Shape of the C_2 symmetric optimized structures (6-*trans*-B and 6-*cis*-A). The arrows point to axial (almost parallel to a vertical axis) and equatorial positions. Dash arrows are used for atoms that are not seeable in the top view.

favor *trans*-B′ over *trans*-B. A similar reasoning with the *cis*-isomer led us to retain 5-*cis*-A′ as the most likely C_2 symmetric *cis* conformer.

The above observations allowed us to limit our study to 5-*trans*-B′ (5-*trans*) and 5-*cis*-A′ (5-*cis*). However, one still has to consider the unknown stereogenic center introduced by the coordination of the N-atom. The corresponding methyl groups can be *syn* or *anti* to the other substituents of the ephedrinates. As 5 has a C_2 symmetry, these two methyl groups are either *syn* or *anti* together, no mixing being allowed. This led us to consider the structures shown in Scheme 3.

The optimized structures for the *cis* and the *trans* isomers with both configurations of the N-methyl
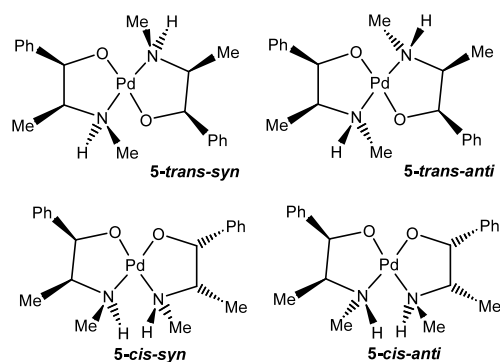
Scheme 2.

Scheme 3.

groups are given in Fig. 2. As encountered in the model system and in previous theoretical work on similar systems [27], the oxygen trans to a nitrogen atom induces a weaker coordination of the nitrogen: the Pd–N bond lengths are larger in the *cis* (ca. 2.15 Å) than in the *trans* (ca. 2.09 Å) structures. The configuration at the nitrogen atom does not induce any significant
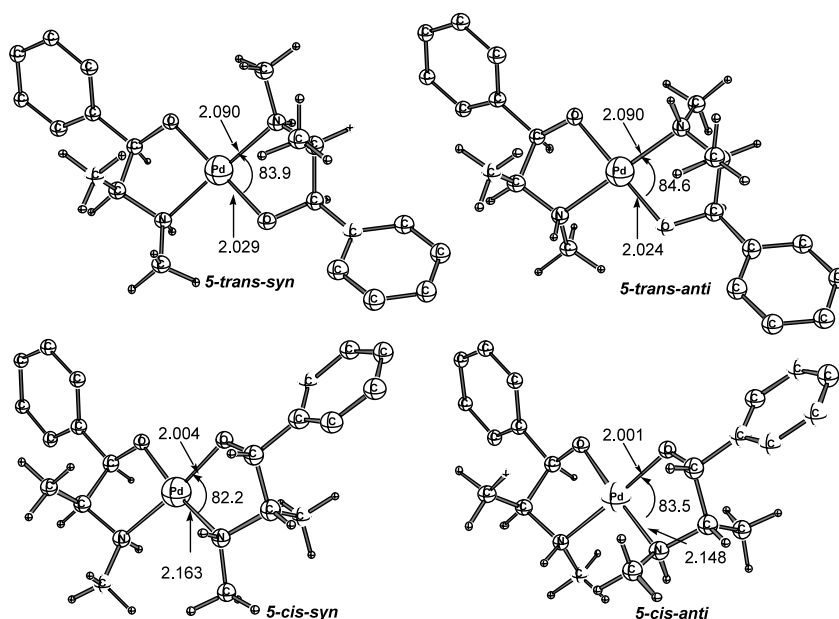
Fig. 2. Main geometrical parameters for **5** as optimized at the B3LYP/lanl2dz+(*d*) level (*C*$_2$ symmetry). For the sake of visibility the hydrogen atoms of the phenyls are omitted.

modifications of the geometrical parameters. For the relative energies, our calculations (Table 4) indicate a clear predilection for a *trans* isomer, about 11 kcal mol^{-1} more stable than the lowest *cis* isomer. The relative configuration of the nitrogen centers does not induce any significant effects, although *anti* isomers are found to be slightly lower in energy (-1.5 kcal mol^{-1}) than the *syn* counterparts.

One shall finally note that model and real systems have similar metal–ligand distances (within 0.01 Å) i.e. no significant effects are encountered from the methyl and phenyl substituents to differentiate *cis* and *trans* isomers. They also barely affect the *cis*/*trans* isomerization energy (ca. 11 kcal mol^{-1}). Zeizinger et al. ab initio study of the elementary model (Pd(NH$_3$)$_2$(OH)$_2$) of our system indicated a much smaller preference for the trans isomer (0.2 kcal mol^{-1}) [27]. The larger *cis*/*trans* isomerization energy we obtain may be attributed to the bis-chelated nature of these systems that forces the orientation of the ligands.

4. Use of the *trans*-bis-[(−)ephedrinate]-palladium^{II} complex

We have previously carried out the 1,4-hydrogenation of (*E*)-2-benzyliden-1-tetralone using **5**-*trans* as catalyst: 2-benzyl-1-tetralone was obtained with a fair chemical yield but with only 2% enantiomeric excess [2].

A considerable interest is presently devoted to the intermolecular [28] and intramolecular [29,30] asymmetric Heck reactions. In this context, Uemura and co-workers have reported the first enantioselective phenylation of *trans*- and *cis*-crotyl alcohols; this reaction which would involve an enol as intermediate, provided the corresponding β-phenylated aldehyde with ee up to 17% [31]. Our previous studies of Heck reactions of allylic alcohols [32] led us to envisage to carry out the enantioselective phenylation of α-substituted allylic alcohols to obtain the chirality in α-position (Eq. (3)).[7] A number of trials were carried out from phenyl iodide and 3-methyl-3-buten-2-ol under various conditions, the

Table 4

Absolute and relative energies of the real system at the B3LYP/lanl2dz+(*d*) level (within *C*$_2$ symmetry).

	E (Hartree)	ZPC (Hartree)	*S* (eu) [a]	Δ*E*	ΔZPC	*T*Δ*S*^{298}	Δ*G*^{298}
				kcal mol^{-1} [b]			
5-*cis*-*syn*	−1165.61301	0.45444	173.6	12.7	0.1	−0.2	**13.0**
5-*cis*-*anti*	−1165.61495	0.45398	173.9	11.5	−0.2	−0.2	**11.5**
5-*trans*-*syn*	−1165.63270	0.45486	171.6	0.4	0.3	−0.8	**1.5**
5-*trans*-*anti*	−1165.63331	0.45434	174.4	0.0	0.0	0.0	**0.0**

The corresponding structures are in Scheme 3 and Fig. 2.
[a] Entropic unit (eu = cal mol^{-1} K^{-1}).
[b] Relative to the lowest isomer **5**-*trans*-*anti*.

Table 5
Heck coupling of phenyl iodide with 3-methyl-3-buten-2-ol

Equivalents of PhI	Base (equivalents)	Time	Yield (%)	ee (%) [a]
1	NaHCO$_3$ (1)	2 h	91	3
1	NaOAc (1)	2 h	37	6
1	Ag$_2$CO$_3$ (1)	30 min	10	0
1	($-$)-ephedrine (2)	2 h	90	4
6	($-$)-ephedrine (2)	2 h	88	5

[a] The *R*-configuration of the main enantiomer was assigned by optical rotation comparison with literature data [34].

main results using **5**-*trans* as catalyst being reported in Table 5: the expected ketone was efficiently produced but with no more than 6% enantiomeric excess.

$$(3)$$
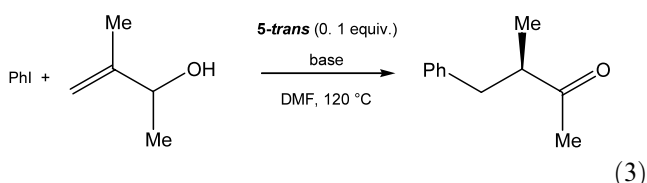
The above results led us to discard this catalyst for such asymmetric reactions. Since various Pd^{II} complexes with nitrogen and oxygen donors exhibit antitumour activity [35–37], the study of biological properties of **5**-*trans* has now to be considered.

5. Conclusion

The chelation of ($-$)-ephedrine to palladium acetate in a basic medium provides bis-chelate complex Pd[OCH(Ph)NH(Me)]$_2$ which the *trans*-structure is supported from ab-initio calculations. This complex catalyzes Heck reactions and the 1,4-hydrogenation of α,β-unsaturated ketones but does not induce an attractive enantioselectivity.

6. Experimental

Melting points have been determined on a Kofler bank. ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker AC 250 spectrometer with CDCl$_3$ as solvent. IR spectra (KBr pellets) were recorded on a Spectra file Plus Midac spectrometer and on a Nicolet magna 550 spectrometer for 600–4000 and 200–600 cm^{-1} (University of Caen) areas, respectively. Elemental analyses were performed by 'Service Central d'Analyses du CNRS' in Lyon.

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[7] A related reaction was previously reported using an optically active cationic rhodium complex [33].

6.1. Synthesis of **5**

To a solution of Pd(OAc)$_2$ (0.4 g, 1.77 mmol) and ($-$)-ephedrine (0.6 g, 3.55 mmol) in benzene (10 mL) under an argon atmosphere was added K$_2$CO$_3$ (0.5 g, 3.54 mmol). The mixture was stirred at room temperature (r.t.) for 24 h, then filtered over Celite. After evaporation of the solvent under reduced pressure, the resulting orange solid was triturated with Et$_2$O (5 mL × 2). Et$_2$O was eliminated with a double-tipped needle to deliver **5** as an orange hygroscopic powder (0.68 g, 88% yield). M.p.: 84 °C. [α]$_D^{21}$: $-$60 ($c = 0.6$, CHCl$_3$). ^{1}H- and ^{13}C-NMR: see Tables 1 and 2. IR, cm^{-1}: 3230, 3082, 2917, 2874, 1487, 1454, 1370, 1111, 1060, 993, 747, 703, 666, 574, 497, 286, 264. Elemental analysis: Anal. Calc. for C$_{20}$H$_{28}$N$_2$O$_2$Pd·0.5H$_2$O: C, 54.12; H, 6.59; N, 6.31; Pd, 23.97. Found: C, 54.33; H, 6.48; N, 6.15; Pd, 23.61%.

6.2. Heck reaction

A magnetically stirred mixture of **5**-*trans* (41 mg, 0.1 mmol), phenyl iodide (1 or 6 mmol), 3-methyl-3-buten-2-ol (86 mg, 1 mmol) and base (1 or 2 mmol) in DMF (2 mL) was heated at 120 °C for the time indicated in Table 5. After cooling to r.t., the mixture was filtered through a small pad of Celite. After conventional work up, a flash-chromatography led to 3-methyl-3-phenyl-2-butanone which was identified by comparison of its spectral properties with literature data [38].

7. Supplementary material

The xyz coordinates and energies for all the computed structures are available from S.H. on request.

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