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Absolute configuration, coordination and stereochemical influence of 1,3,5,7-tetramethyl-2,6,9-trioxo-bicyclo[3,3,1]nona-3,7-diene in Rh(I) and cationic Pd(II) complexes

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Abstract

Relevant stereochemical and coordination features of 1,3,5,7-tetramethyl-2,6,9-trioxo-bicyclo[3,3,1]nona-3,7-diene (TOND), a chiral molecule of C_2 symmetry are described. The X-ray crystal structure of [RhCl{(S)-CHPhMeNH$_2$}{(+)-TOND}] has ascertained that the absolute configuration of (+)-TOND is R,R. Furthermore, the synthesis of stable cationic Pd(II) π-allyl complexes of general formula [Pd(η^3-allyl)(TOND)][BF$_4$] has allowed to probe the ability of this ligand to afford stereoselective coordination of prochiral fragments. The X-ray molecular structure of the representative compound [Pd(η^3-crotyl)(TOND)][BF$_4$] has been determined. Finally, the influence of TOND on the stereochemistry of prochiral nitrogen donors of diamine and phosphamine chelates has been explored in rhodium complexes of general formula [Rh(chelate)(TOND)][BF$_4$]. The configurations of the nitrogen donors have resulted as stereospecifically selected by the presence of TOND.

Keywords: Palladium; Rhodium; Diolefin; Crystal structure; Absolute configuration

1. Introduction

About 20 years ago the isolation of 1,3,5,7-tetramethyl-2,6,9-trioxo-bicyclo[3,3,1]nona-3,7-diene (TOND, Fig. 1), its resolution and some data concerning its coordination properties were reported in a study from our laboratory [1]. The attainment of TOND as a coordinated moiety by condensation of two acetylacetone molecules on Pt(II) had been previously described [2]. No further report concerning the coordination properties of 2,6,9-trioxo-bicyclo[3,3,1]nona-3,7-dienes has, meanwhile, appeared [3] in spite of two aspects that in principle could attract interest on TOND and related molecules. First, we recall that TOND is a chiral chelating molecule, with stereochemical features clearly distinct from those displayed by most chelating ligands of the same symmetry (C_2) such as the diamines or the diphosphines. In fact, in generating a chiral pocket, TOND protrudes two methyls towards the opposite ligands. Furthermore, according to previous results, TOND seemed to behave as a labile ligand. If so, its complexes could attract interest as possible useful precursors of other species. Of course, a significant lability of a chiral ligand is expected to forbid its main potential use, i.e., the one addressed to prompt stereoselective syntheses. However, it is to note: (i) TOND can exhibit a fair range of coordinating ability [1]; (ii) other trioxobicyclononadienes have meanwhile been prepared [4,5] potentially apt to give strong ligands; (iii) in case the stereochemical influence of a labile chiral ligand on adjacent ligands is substantial, some aspects of it could anyway be useful. For instance, it could induce asym-

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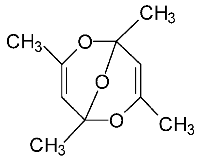


Fig. 1. Structure of TOND.

metry in a nearby coordinated moiety, and its easy removal could facilitate investigation of the stereochemical behaviour of that moiety. This could be the case of coordinated prochiral groups [6].

This work had, thus, three aims concerning the title molecule: (i) to assess the absolute configuration of enantiomeric TOND. This has been achieved by an X-ray diffraction study of the pure diastereomer [RhCl{(S)-α-methylbenzenemethanamine}{(+)-TOND}]; (ii) To provide further information on its coordinating properties; (iii) Look after its ability to afford chiral induction in the bonding of prochiral ligands. We report results concerning all the above aspects and, as for the second aim, we also describe the solid state molecular structure of [Pd(η^3-MeCHCHCH$_2$)(TOND)][BF$_4$].

Table 1
Selected bond lengths (Å) and angles (°) for [RhCl{(S)-CHPhMeNH$_2$}{(+)-(TOND)}]

Bond lengths			
Rh–C(1)	2.106(7)	C(1)–C(3)	1.39(1)
Rh–C(2)	2.145(6)	C(2)–C(4)	1.38(1)
Rh–C(3)	2.063(7)	C(1)–O(2)	1.383(8)
Rh–C(4)	2.092(6)	O(2)–C(8)	1.443(7)
Rh–N	2.126(5)	C(8)–C(4)	1.514(9)
Rh–Cl	2.409(2)	C(2)–O(1)	1.400(8)
N–C(11)	1.411(9)	C(2)–C(6)	1.514(9)
C(11)–C(12)	1.542(9)	O(1)–C(7)	1.412(8)
C(8)–C(10)	1.529(8)	C(7)–O(3)	1.414(7)
C(7)–C(9)	1.511(9)	C(8)–O(3)	1.411(7)
C(1)–C(5)	1.505(8)	C(7)–C(3)	1.52(1)
Bond angle			
N–Rh–Cl	89.0(1)	Rh–N–C(1)	114.1(4)

2. Results and discussion

2.1. Absolute configuration of TOND

Enantiomerically pure (+)-TOND has been isolated through the rhodium complex [RhCl{(S)-CHMePhNH$_2$}{(+)-TOND}] [1]. An X-ray diffraction experiment on this complex has disclosed that the absolute configuration of the dextrorotatory diene is *R*,*R*. The molecular geometry is illustrated in Fig. 2, while selected bond lengths and angles are reported in Table 1. The coordination is the expected square planar with the double bonds of the TOND ligand almost orthogonal to the coordination plane. Coordinated TOND retains its idealized C_2 symmetry but the bonding interactions of the two teeth with the rhodium atom are slightly but significantly not equivalent [Rh–C(1,3) 2.106(7), 2.063(7); Rh–C(2,4) 2.145(6), 2.092(6) Å], i.e., the double bond *trans* to Cl [C(1)=C(3)] is some 0.033 Å closer to the metal atom than that *trans* to N [C(2)=C(4)]. In addition some asymmetry is observed for each Rh–(C=C) interaction [0.043 for C(1,3) and 0.053 Å for C(2,4)]. It is probably significant that the asymmetry is more pronounced for the weaker Rh–C interactions. The asymmetric coordination of each C=C group is a consequence of the chemical non-equivalence of the olefin carbons. The longer distances, exhibited by the carbon atoms bearing the methyl substituents [C(1) and C(2)], can be primarily attributed to some rhodium–methyl repulsion [Rh···C(5) 3.078(6), Rh···C(6) 3.082(6) Å]. Another effect of the methyl groups protruding from the TOND ligand is to push the chloride and nitrogen atoms out of the ideal coordination plane defined by the metal atom and the midpoints of the C=C bonds (deviations, −0.87 for Cl and +0.52 Å for N). The bite angle of the TOND ligand, calculated from the midpoints of the C=C double bonds, is 84.3(3)°. The rhodium–diolefin interactions can be compared with those found in the rhodium(I) complex [Rh(η-1,5-cyclooctadiene)[1-3-η-(exo-4-methyl-1,2,3,4-tetraphenylcyclobutenyl)]] [7] (average Rh–(C=C) 2.16(1) Å, bite angle 87.0(5)°).

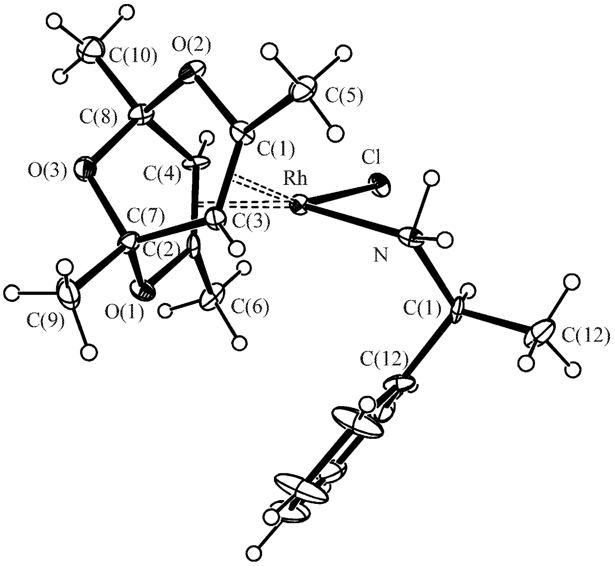


Fig. 2. ORTEP drawing (30% probability) of [RhCl{(S)-CHMePhNH$_2$}{(+)-TOND}].

2.2. Coordinating properties of TOND

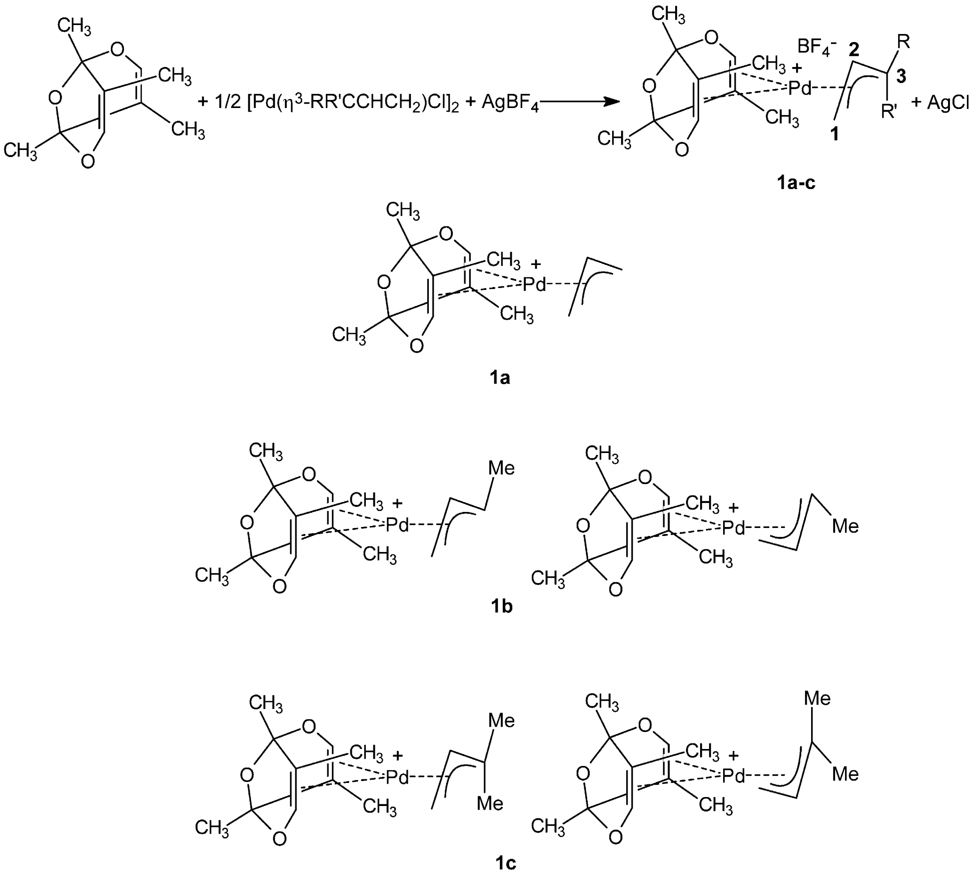
2.2.1. Palladium complexes

The results here reported, together with previous ones [1], give evidence that TOND has coordinating ability towards d^8 ions comparable to that of the cyclic diolefin most commonly used as labile chelate, i.e., 1,5-cyclooctadiene (1,5-COD). As in the case of that ligand, it is possible to obtain cationic complexes containing in the coordination environment, beside the diolefin, either another ligand moiety apt to undergo useful reactions, or a stronger ligand able to prompt chemoselective (and possibly stereoselective) reactions of substrates displacing TOND.

Synthetic procedures similar to those adopted [8] for the corresponding 1,5-COD complexes have led to obtain stable $[Pd(\eta^3\text{-}RR'CCHCH_2)(TOND)][BF_4]$ compounds **1a**–**c** (**1a**: $R = R' = H$; **1b**: $R = H$, $R' = Me$; **1c**: $R = R' = Me$; see Scheme 1). These π-allyl derivatives are yellow microcrystalline solids that can be kept in freezer for several weeks without appreciable decomposition. They are soluble in the common halogenated solvents. ^{1}H-NMR data give an insight into the reciprocal stereoselection of TOND and π-allyl ligands in the coordination sphere of Pd(II). As for the simple allyl derivative **1a** we only note broadening of TOND methyl signals, in keeping with fast η^3–η^1–η^3 rearrangement.

In the case of **1b** the following features are observed: (i) two diastereoisomers in ca. 1:1 ratio are present, and the attribution of the allylic protons to each species is made through homonuclear decoupling experiments. (ii) The methyl substituent is in *syn* position in both diastereoisomers as revealed by the values of the $^2J_{H-H}$ coupling constants within the allyl moiety. (iii) Broad and averaged signals are observed for the methyl groups of TOND, what can be ascribed to fast rearrangement. (iv) The anti-protons of the two diastereomers display a fairly large chemical shift difference, suggesting that they might experience different interactions with the TOND moiety. This prompted us to investigate the dimethylallyl derivative, in which the substitution of the anti-proton by a larger group would possibly result in a stability difference (in addition to the ‘chemical environment’ difference) between the two diastereomers. The increase of sterical hindrance affords a significant stereoselection, as the spectra reveal two diastereomers in ca. 2:1 ratio. These derivatives also display *syn* structure and dynamic behaviour.

Further insight in the structural features of the allyl derivatives has been obtained by an X-ray diffraction analysis of the cation $[Pd(\eta^3\text{-}MeCHCHCH_2)(TOND)]^+$



Scheme 1.

(**1b**) in its $[BF_4]^-$ salt (Fig. 3). Selected bond lengths and angles are reported in Table 2. The geometry of the cation is ideally square planar and the coordination plane is defined by the palladium atom and the midpoints of the double bonds in the TOND ligand, which are positioned almost orthogonal to this plane. The η^3-crotyl ligand ideally occupies two coordination sites and exhibits partial disorder generated by coordination through either enantioface. Fig. 3a shows the geometry of the main diastereoisomer present in the crystal (71%) while Fig. 3b focuses the positioning of the η^3-$MeCHCHCH_2$ ligand in its alternative coordination modes.

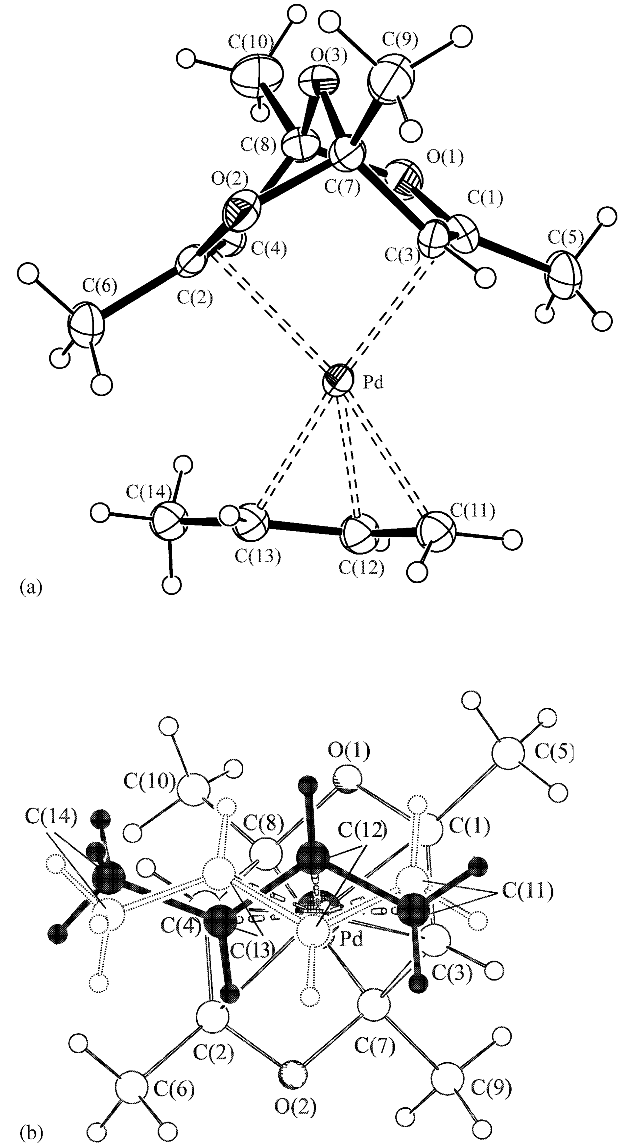


Fig. 3. ORTEP drawing (30% probability) of the dominant isomer (71%) of Pd(crotyl)(TOND) in its $[BF_4]^-$ salt. Fig. 3b: view of the molecule showing the two orientations of the $MeCHCHCH_2$ ligand found in the crystal (the major isomer is black and the minor one is drawn with dotted lines).

Table 2
Selected bond lengths (Å) for $[Pd(crotyl)(TOND)]^+$ (**1b**)

Pd–C(11)	2.187(5) [2.11(1)] [a]	C(1)–C(3)	1.370(5)
Pd–C(12)	2.123(4) [2.09(1)] [a]	C(2)–C(4)	1.372(4)
Pd–C(13)	2.135(3) [2.17(1)] [a]	C(1)–O(1)	1.350(4)
Pd–C(1)	2.394(3)	O(1)–C(8)	1.457(4)
Pd–C(2)	2.408(3)	C(8)–C(4)	1.515(4)
Pd–C(3)	2.247(3)	C(2)–O(2)	1.359(3)
Pd–C(4)	2.248(3)	C(2)–C(6)	1.487(4)
C(11)–C(12)	1.405 [b]	O(2)–C(7)	1.452(4)
C(12)–C(13)	1.410 [b]	C(7)–O(3)	1.399(4)
C(13)–C(14)	1.478 [b]	C(8)–O(3)	1.412(4)
C(8)–C(10)	1.503(5)	C(7)–C(3)	1.518(4)
C(7)–C(9)	1.516(4)	C(1)–C(5)	1.503(5)

[a] The values in parentheses refer to the second image of the crotyl ligand.

[b] Values taken from Ref. [12] (see Section 4).

The TOND ligand conforms to a C_2 idealized symmetry with the twofold axis defined by Pd and O(3). The coordinated π bonds exhibit a significant asymmetry of the palladium–carbon interactions (average values Pd–C(3,4) 2.25, Pd–C(1,2) 2.40 Å). The fact cannot be ascribed to external factors, such as interactions with the crotyl ligand or the counterion because it was observed also in the more symmetrical and neutral $[PtCl_2(TOND)]$, the only other structural report of the ligand [9]. In that case, the bond asymmetry was attributed to electronic factors, but we incline towards a simpler explanation in terms of non bonded contacts, in accordance with what just discussed for $[RhCl(CHMePhNH_2)(TOND)]$ (vide supra). A space filling model of the molecule reveals that the methyl groups attached to the stretched Pd–C bonds [C(1) and C(2)] are positioned in the vicinity of palladium atom and are in contact with it (average distance 3.26 Å). Therefore, the 0.15 Å stretching of the involved Pd–C(1,2) bonds seems dictated by the necessity to avoid shorter contacts. The higher asymmetry of these bonds with respect to those in $[RhCl(CHMePhNH_2)(TOND)]$ should be attributed to weaker Pd–(C=C) interactions (average 2.32 Å) with respect to the Rh–(C=C) ones (average 2.10 Å). Very probably the longer Pd–C(TOND) distances are evidence of the allyl ligand *trans* influence. Also the bite angle (C=C)–Pd–(C=C) (81.1(3)°) is more acute than that in the rhodium derivative (84.3(3)°), in accord with the shorter rhodium–olefin interactions. The similarity of the Pd(II)–(TOND) and Pd(II)–(COD) interactions can be appreciated by comparison with the recent structural report of the cation $[Pd(Me)(R_2phen)(COD)]^+$ (average distance Pd–C(olefin) 2.27 Å, bite angle 84.1°) [10]. For the sake of completeness, we wish to cite that the behaviour of the similar diene ligand, norbornadiene, is not strictly comparable, and exhibits more acute bite angles, in the range 67°–72° [11]. Concerning the coordination of the crotyl ligand we note that even though the region of space accessible to it is neatly shaped by the methyl groups protruding from the TOND ligand, its coordination is only partially selective because it is able to place its terminal methyl in the allowed pocket whichever is the coordinated face. The isomers ratio in the solid state (71–29%) shows that one isomer is dominant at a difference with what found in solution (1:1 ratio). The main isomer is presumably favoured by a better solid state packing efficiency.

The allyl planes in the two geometries are tilted with reference to the coordination plane by +71.5° and −67.3°, respectively. These angles do not describe all the difference because displacements affect all the crotyl atoms and the alternative positions of C(14) are separated by only 0.48 Å (Fig. 3b and Section 4) in order for the terminal methyl [C(14)] to occupy the allowed pocket in both isomers. The uneven population of the two coordination modes is explained by a shorter contact methyl(TOND)–methyl(crotyl) in the less favoured isomer [C(14)···C(6) 3.78, C(14A)···C(6) 3.59 Å].

2.2.2. *Rhodium complexes*

Stable [Rh(chelate)(TOND)][BF_4] (chelate = diamine or phosphamine) complexes analogous of the COD derivatives used as precursors [12] of catalytic species have been prepared. The synthetic procedures were suggested from those used for the 1,5-COD compounds. As for chemical properties, a preliminary test has assessed that [Rh(*o*-$Ph_2PC_6H_4$-NHMe)(TOND)][BF_4] catalyzes hydroboration of styrene with an efficiency at least comparable to that displayed by analogous 1,5-COD derivatives, in the same conditions reported for the latter catalysts [13].

2.3. *Asymmetric induction by coordinated TOND*

The first result concerning the ability of TOND in the chiral recognition of other ligands bonded to the same molecule dealt with the dimeric complex [{RhCl(TOND)}$_2$] [1]. It was found [1] that coordination of two TOND moieties of the same configuration was significantly favoured (7:3) with respect to the coordination of different enantiomers, i.e. the *meso* compound, although the two diene moieties were placed at a distance, with reference to opposite double bond centers, exceeding 6 Å.

Further assessment of the stereoselective ability of TOND has been achieved by studying its influence on the stereochemistry of the prochiral nitrogens in one *N*,*N*- and one *N*,*P*-chelate ligand in the above rhodium cations. We have chosen the *N*,*N*-chelate assuming that in one configuration it could well match the chiral pocket of TOND. In the case of the *P*,*N* ligand this is still true for the amine function. The ^{1}H-NMR spectrum of [Rh(MeNHCH$_2$CH$_2$NHMe)(TOND)]BF_4 shows that the secondary nitrogen atoms of the diamine are coordinated in only one configuration. In fact, only one couple of antipodic diastereoisomers with C_2 symmetry is detected by inspection of well-resolved signals. The diastereotopic protons on each CH_2 appear as doublets at 3.04 and 2.56 ppm, while the equivalent olefin protons of TOND resonate at 3.19 ppm. Also the configuration of *o*-Ph_2P-C_6H_4-NHMe in complex [Rh(*o*-Ph_2P-C_6H_4-NHMe)(TOND)]BF_4 is stereospecifically selected due to the mutual chiral recognition with TOND. In particular, also in this case, the NMR spectrum discloses the presence of a single isomer, whose non-equivalent olefin protons resonate at 4.60 and 2.62 ppm. On the ground of the type of metal center, which is not ‘inert’, and the fact that NMR spectra of the complexes do not appreciably change neither after standing of the solution for several hours at room temperature, nor by lowering the temperature at 203 K, nor by addition of a small amount of TFA, we are inclined to consider the observed stereoselection as thermodynamically driven.

3. Conclusions

Our studies have established that the absolute configuration of TOND is *R*,*R* for the dextrorotatory antipode. Moreover, within the chemistry of the investigated d^8 ions Rh(I), Pt(II) and Pd(II), it can be concluded that the behaviour of TOND is very similar to that of 1,5-COD. As for stereochemical features, taking for granted that the chirality of TOND cannot be easily exploited in direct promotion of asymmetric syntheses, yet some aspects appear to deserve interest. The mutual recognition between TOND and prochiral chelates of the same general or local symmetry resulted to be complete within the accuracy of results.

On the whole, our results suggest that TOND itself is a potentially useful tool in stereochemical studies, and that stronger ligands derived from 2,6,9-trioxo-bicyclo[3,3,1]nona-3,7-diene could be quite useful in asymmetric synthesis.

4. Experimental

^{1}H-NMR spectra were recorded on a Varian Gemini 200 spectrometer. $CDCl_3$ and CD_3NO_2 were used as solvents, and $CHCl_3$ ($\delta = 7.26$) and CHD_2NO_2 ($\delta = 4.33$) as internal standards. The following abbreviations were used for describing NMR multiplicities relative to proton–proton couplings: no attribute, singlet; d, doublet; dd double doublet; h, heptet; m, multiplet; dt, double triplet; dq, double quartet; app, apparent; br, broad signal. Within the description of the spectra of the π-allyl complexes, the subscripts refer to the carbon atom to which the protons are attached (1, 2 or 3, see Scheme 1), and the letters *s* and *a* specify *syn* and *anti* position, respectively. *N*,*N*′-dimethyl-ethylenediamine was purchased from Aldrich and used as received. Solvents of commercial reagent grade were dried by standard methods. 2-(*N*-methyl)aminophenyldiphenylphosphine was obtained according to a procedure previously reported [14] and recrystallized from the minimum amount of methanol, by cooling the solution at 253 K. *N*,*N*′-1,2-ethanediylidene-bis[α-methyl-benzenemethanamine] and *N*-(2-pyridinylmethylene)-α-methyl-benzenemethanamine were obtained according to literature methods [15]. The synthesis of racemic and enantiomeric TOND was accomplished as previously described [1]. The η^3-allyl complexes [{PdCl(η^3-RR′CCHCH$_2$)}$_2$] were obtained according to literature methods [16]. The preparation of the pure diastereoisomer [RhCl{(S)-CHPhMeNH$_2$}{(+)-TOND}] was the same previously reported [1] for the racemic mixture, but for the use of (+)-[{RhCl(TOND)}$_2$] as starting material. All operations in the preparation and handling of TOND complexes were made in nitrogen atmosphere by use of Schlenk techniques. Elemental analysis of the new compounds are reported in Table 3.

4.1. Synthesis of [{RhCl(TOND)}$_2$]

In order to avoid the use of excess TOND as previously reported [1], the synthesis was effected in a methylene chloride, by using the minimum amount of solvent sufficient to dissolve [{RhCl(C$_2$H$_4$)$_2$}$_2$]. A slight excess of TOND (2.05:1) was added and the solution was stirred 1.5 h at room temperature (r.t.) while ethylene evolved. The solution was filtered on a small Celite pad, concentrated until crystallization began, and finally a volume of hexane was added dropwise to increase the precipitate. The yield was ca. 95%.

4.2. Synthesis of [Pd(η^3-RR′CCHCH$_2$)(TOND)][BF$_4$] (**1a**: $R = H_{3s}$, $R' = H_{3a}$; **1b**: $R = Me$, $R' = H_{3a}$; **1c**: $R = R' = Me$)

To a stirred solution of [{PdCl(η^3-RR′CCHCH$_2$)}$_2$] (0.20 mmol) in 5 ml of dry methylene chloride was added silver tetrafluoroborate (0.078 g, 0.40 mmol). After 5 min the resulting suspension was poured in a flask containing the racemic TOND (0.073 g, 0.40 mmol). After 15 min stirring the suspension was filtered on a small Celite pad and the volume of the filtrate was reduced to ca. 1 ml. Addition of diethylether and cooling at 253 K afforded crystals of the product in ca. 70% yield. ^{1}H-NMR (δ): **1a** 6.03 (app h, 1H, H$_2$, $J_{1a2} = 13$ Hz, $J_{1s2} = 7$ Hz, $J_{23s} = 7$ Hz, $J_{23a} = 13$ Hz) 5.04 (d, 1H, H$_{1s}$ or H$_{3s}$), 4.63 (s, 2H, =CH TOND), 4.49 (d, 1 H, H$_{3s}$ or H$_{3a}$), 4.15 (d, 1H, H$_{1a}$ or H$_{1s}$), 3.37 (d, 1H, H$_{3a}$ or H$_{1a}$), 2.40 (br, 3H, Me), 1.75 (br, 6H, Me), 1.55 (br, 3H, Me) ppm. **1b** (diastereomer): 5.91 (dt, 1H, H$_2$, $J_{23a} = J_{1a2} = 13$ Hz, $J_{1s2} = 7$ Hz), 5.16 (s, 2H, =CH TOND), 4.34 (d, 1H, H$_{1s}$), 4.28 (m, 1H, H$_{3a}$, $J_{3aMe} = 5$ Hz), 4.10 (d, 1H, H$_{1a}$), 2.43 (br, 3H, Me), 2.30 (br, 3H, Me), 1.81 (br, 6H, Me), 1.74 (d, 3H, Me$_3$) ppm. **1b** (diastereomer): 5.71 (dt, 1H, H$_2$, $J_{23a} = J_{1a2} = 14$ Hz, $J_{1s2} = 7$ Hz), 5.16 (s, 2H, =CH TOND), 4.98 (m, 1H, H$_{3a}$, $J_{3aMe} = 5$ Hz), 4.74 (d, 1H, H$_{1s}$), 3.08 (d, 1H, H$_{1a}$), 2.43 (br, 3H), 2.30 (br, 3H), 1.81 (br, 6H), 1.66 (d, 3H, Me$_3$) ppm. **1c** (minor diastereomer, selected signals): 5.74 (dd, 1H, H$_2$, $J_{1s2} = 8$ Hz, $J_{1a2} = 13$ Hz), 5.07 (s, 2H, =CH TOND), 4.22 (m, 2H, H$_{1s}$, H$_{1a}$) ppm. **1c** (major diastereomer, selected signals): 5.47 (dd, 1H, H$_2$, $J_{1s2} = 7$ Hz, $J_{1a2} = 12$ Hz), 5.07 (s, 2H, =CH TOND), 4.66 (d, 1H, H$_{1s}$), 3.16 (d, 1H, H$_{1a}$) ppm.

4.3. Synthesis of [Rh(chelate)(TOND)][BF$_4$] (**2a**, chelate = MeNHCH$_2$CH$_2$NHMe; **2b**, chelate = *o*-Ph$_2$P-C$_6$H$_4$-NHMe)

[{RhCl(TOND)}$_2$] (0.032 g, 0.050 mmol) was dissolved in 0.5 ml of methylene chloride, and the solution was cooled at 273 K. A solution of silver tetrafluoroborate (0.019 g, 0.100 mmol) in a minimum amount of methylene chloride was added dropwise and stirring was continued for 10 min. The suspension was filtered on a small Celite pad and the ligand (0.10 mmol) dissolved in 0.2 ml of methylene chloride was added to the stirred solution at 273 K. Removal of the solvent in vacuo after 15 min afforded the product, which according to its ^{1}H-NMR spectrum was fairly pure. ^{1}H-NMR (δ): **2a** 3.19 (2H, =CH TOND, $J_{Rh-H} = 4$ Hz), 3.04 (d, 2H, NC*H*HC*H*HN), 2.66 (3H, NMe), 2.56 (d, 2H, NCH*H*CH*H*N), 1.94 (6H, Me), 1.56 (6H, Me) ppm.

Table 3
Elemental analyses for the new compounds

Compound	Molecular formula	%C Found (calc.)	%H Found (calc.)	%N Found (calc.)
1a	$C_{13}H_{19}BF_4O_3Pd$	37.16 (37.49)	4.88 (4.60)	
1b	$C_{14}H_{21}BF_4O_3Pd$	39.25 (39.06)	5.07 (4.92)	
1c	$C_{15}H_{23}BF_4O_3Pd$	40.20 (40.53)	5.42 (5.21)	
2a	$C_{14}H_{26}BF_4N_2O_3Rh$	36.67 (36.55)	5.65 (5.70)	6.31 (6.09)
2b	$C_{29}H_{32}BF_4NO_3PRh$	52.21 (52.52)	4.96 (4.86)	2.03 (2.11)

2b 7.9–7.2 (m, 14H, aromatics), 5.75 (br, 1H, NH), 4.60 (1H, =CH TOND), 3.21 (d, 3H, NMe), 2.62 (1H, =CH TOND), 2.19 (3H, Me), 1.78 (3H, Me), 1.56 (3H, Me), 1.50 (3H, Me) ppm.

4.4. X-ray structure determination of [RhCl{(S)-CHPhMeNH$_2$}{(+)-TOND}] and [Pd(η^3-MeCHCHCH$_2$)(TOND)][BF$_4$] (**1b**)

Crystals of the title species suitable for X-ray diffraction experiments were grown from methylene chloride–diethylether mixtures at r.t. The rhodium complex, in spite of repeated crystallizations, gave extremely tiny but fortunately good quality crystals. Crystal data and experimental details are reported in Table 4. The diffraction experiments were carried out at low temperature on a Bruker AXS SMART 2000 CCD diffractometer using Mo–K$_\alpha$ radiation. Intensity data were measured over full diffraction spheres using 0.3° wide ω scans, crystal-to-detector distance 5.0 cm. The software SMART [17a] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by software SAINT [17a] and an empirical absorption correction was applied with SADABS [17b]. The structures were solved by direct methods (SIR-97) [17c] and subsequent Fourier syntheses, and refined by full-matrix least-squares calculations on F^2 (SHELXTL) [18] attributing anisotropic thermal parameters to the non-hydrogen atoms.

Table 4
Crystal data and experimental details for [RhCl{(S)-CHMePhNH$_2$}{(+)-TOND}] and [Pd(crotyl)(TOND)][BF$_4$] (**1b**)

	[RhCl(CHMePhNH$_2$)(TOND)]	[Pd(crotyl)(TOND)]BF$_4$
Formula	$C_{18}H_{25}ClNO_3Rh$	$C_{14}H_{20}BF_4O_3Pd$
Formula weight	441.75	429.51
T (K)	193(2)	240(2)
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)
a (Å)	6.759(2)	8.149(2)
b (Å)	15.142(4)	18.091(6)
c (Å)	17.909(4)	11.830(4)
α (°)	90	90
β (°)	90	103.552(7)
γ (°)	90	90
V (Å^3)	1832.9(8)	1695.5(9)
Z	4	4
D_{calc} (Mg m^{-3})	1.601	1.683
μ(Mo–K$_\alpha$) (mm^{-1})	1.093	1.143
$F(0\,0\,0)$	904	860
Crystal size (mm)	0.02 × 0.02 × 0.1	0.35 × 0.24 × 0.20
Theta range for data collection (°)	2–27	2–30
Reflections collected	18 265($\pm h$, $\pm k$, $\pm l$)	21807($\pm h$, $\pm k$, $\pm l$)
Unique observed reflections [$I > 2\sigma(I)$]	4017	4981
Goodness of fit on F^2	0.924	1.056
$R_1(F)$ [a], $wR_2(F^2)$ [b] [$I > 2\sigma(I)$]	0.040, 0.0538	0.0477, 0.0979
Absolute structure parameter	0.04(5)	–
Weighting scheme	$a = 0.0048$, $b = 0.0000$ [b]	$a = 0.0503$, $b = 1.0552$ [b]
Largest difference peak and hole (e Å^{-3})	0.95 and −0.86	1.14 and −1.82

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

The rationalization of the molecular geometry was straightforward for the rhodium complex and its absolute configuration was unambiguously determined (Flack parameter 0.04(5)) for C(1) R, C(2) R, C(11) S (Fig. 2). The latter value was obviously in accord with the configuration of the enantiomerically pure amine used for the synthesis.

The palladium cation showed disorder for the crotyl ligand (η^3-MeCHCHCH$_2$)$^-$. This ligand exhibited the expected coordination mode but the central CH group (C(12) in Fig. 3) was found unevenly split over two sites (approximate separation 0.9 Å, occupation ca. 0.72 and 0.28, respectively). This situation indicated coordination of the ligand through either enantioface forming a mutual angle of about 138°. This fact was not unusual for the allyl anion but seemed unexplainable for the crotyl because a corresponding splitting of the terminal methyl group (C(14) in Fig. 3), equivalent both in separation and occupation, was not observed. Also the thermal motions of the involved atoms were not markedly anomalous. At first, we hypothesized the presence of some non-methylated allyl but the chemical evidence ruled out this possibility. Then we decided to refine two rigid models of the crotyl ligand (taken from an ordered structure [19]) oriented as indicated by the only split atom. The method worked well, produced a reasonable model of the crystal structure and explained the reason why two images of the terminal methyl were not observed in the electron density map. The coordination of the η^3-crotyl in its alternative modes did not result hinged around the terminal carbons of the allyl unit [C(11) and C(13)], as one could expect, because the chiral pocket produced by the facing TOND ligand forced the terminal methyl [C(14)] in the same region of space, irrespective of the coordinated face. In order to fulfil this constraint mismatch of the two images of the ligand affected all the carbon atoms (Fig. 3b) but their separation was not sufficient to show distinct electron density peaks of all the atoms. The apparent distances between corresponding atoms of the crotyl ligands were found as follows: C(11)···C(11A) 0.36, C(12)···C(12A) 0.91, C(13)···C(13A) 0.59, C(14)···C(14A) 0.48 Å. In conclusion, the actual crystal consists of a solid solution of the racemic mixture of two diastereoisomers with molar ratio 71:29. In the final refinement of the structure model by least-squares calculations on F^2 isotropic thermal factors were assigned to the two crotyl models. The hydrogen atoms were placed in calculated positions and refined with idealized geometry (C(sp^3)–H = 0.98, C(sp^2)–H = 0.93 Å).

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 207559 for [RhCl{(S)-CHMePhNH$_2$}{(+)-TOND}] and no. 207560 for [Pd(crotyl)(TOND)][BF$_4$] (**1b**). Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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