Diastereoselective Synthesis of Chiral (Triazolinylidene)rhodium Complexes Containing an Axis of Chirality

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Deprotonation of chiral triazolium salts **1** and reaction of the resulting nucleophilic carbenes with $[(COD)RhCl]_2$ or $[(NBD)RhCl]_2$ afforded square-planar complexes **2–6** in yields of 65–95%. The complexes contain an axis of chirality and a diastereomeric excess of up to 97% was achieved. The relative and absolute configurations of these complexes were determined by NMR spectroscopic investigations and X-ray structure analysis. The application of the rhodium(COD) complexes as catalysts in an asymmetric hydrosilylation reaction has been examined, resulting in enantiomeric excesses of up to 44%. Similar results were achieved for aromatic and aliphatic ketones and a nonlinear temperature effect (principle of isoinversion) was observed.

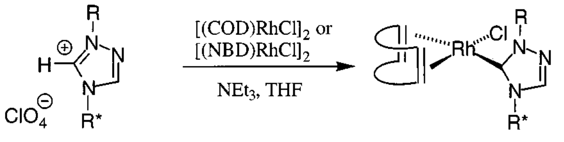
Introduction

Metal complexes of nucleophilic carbenes have already been investigated[1][2]. Recent investigations have included chiral modifications and the application of these complexes as catalysts in asymmetric synthesis. The first chiral carbene complexes bearing imidazolidinylidene ligands were introduced by Lappert et al. in 1983[3], followed by chiral imidazolinylidene complexes by Herrmann et al.[4] and by complexes containing chiral imidazolinylidenes and triazolinylidenes by our group[5][6]. Using the C_1-symmetrical triazolinylidenes as ligands, different rotamers were obtained as a result of hindered rotation about the carbene carbon−metal bond[5]. To prevent the formation of these various rotamers, one possibility is to employ chelating carbene ligands. These ligands have previously been used to prepare ruthenium and rhodium complexes bearing a stereogenic center at the metal atom[6]. Another possibility is to use nonchelating carbene ligands with hindered rotation about the carbene carbon−metal bond, causing an axis of chirality when in a perpendicular orientation to the square-plane of the metal complex. We now report the diastereoselective synthesis of rhodium(I) complexes containing this kind of chirality and the application of these complexes in a hydrosilylation reaction.

Results and Discussion

Following our work on palladium(II) complexes containing two carbene ligands and therefore two axes of chirality in the *cis* form (resulting in two diastereomers and one *meso* form according to our nomenclature[5]), we prepared square-planar rhodium complexes containing one carbene ligand perpendicular to the square-plane of the complex[3][7].

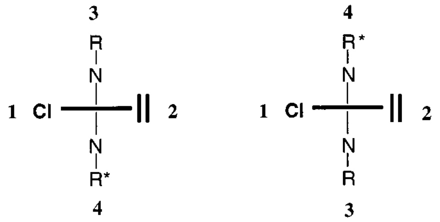
Scheme 1. Preparation of rhodium(COD) and -NBD complexes



1 **2-6**

The axis of chirality is represented by the carbene carbon−rhodium bond. The two substituents of the first plane are the chlorine atom and the olefin *trans* to the chlorine, whereas the substituents of the second plane are the nitrogen atoms neighboring the carbene carbon atom (see Figure 1).

Figure 1. Axis of chirality



(S_a) (R_a)

Rhodium(COD) Complexes: The rhodium(COD) complexes **2−4** were prepared by reaction of a triazolium salt **1** with$[(COD)RhCl]_2$ in THF with NEt_3 in yields of 65−95%, the yield depending on the substituent R at *N*1. With a

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phenyl group as the substituent at *N*1, the yield was higher than with an alkyl group (see Table 1).

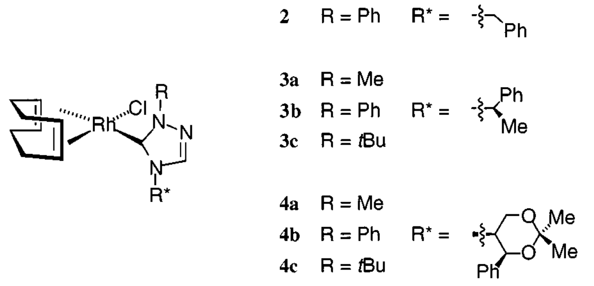


Table 1. Yields and diastereomeric excesses (*de*) of rhodium(COD) complexes **2–4**

	Yield [%]	*de* [%][a]
2	90	–
3a	70	41
3b	95	40
3c	78	36
4a	79	93
4b	95	91
4c	65	97

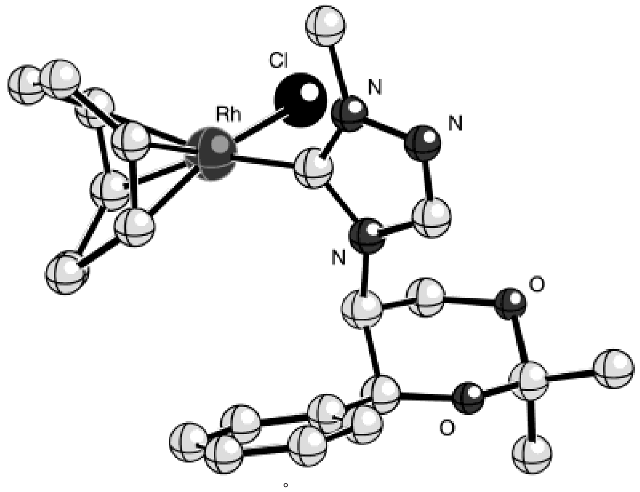
[a] Determined by ^{1}H-NMR spectroscopy.

The benzyl group in complex **2** (two doublets of $^2J = 14$ Hz for the two benzylic protons in the ^{1}H-NMR spectrum) indicates the existence of the axis of chirality within the complex, the two protons becoming diastereotopic because of the hindered rotation about the carbene carbon–rhodium bond. Calculation of the barrier for rotation of the carbene–carbon rhodium bond at the MP2/TZVP//RI-DFT/SV(P) level of theory yielded an energy of 93 kJ/mol, which is consistent with the experimentally found hindered rotation[8]. The diastereomeric excess of the complexes with chiral substituents R*, **3** and **4**, was determined by ^{1}H-NMR spectroscopy to be 36–41% for **3a–c** [R* = (*R*)-1-phenylethyl]. Using the 2,2-dimethyl-4-phenyl-1,3-dioxanyl residue as chiral substituent R* **4a–c**, diastereomeric excesses of up to 97% could be achieved, the best obtained being with the bulky *t*-butyl group (**4c**). Despite the mixture of diastereomers in solution, the major diastereomer of **4a** could be crystallized and its structure in the solid state was determined by X-ray structure analysis (Figure 2).[9][10]

The X-ray structure shows the rhodium atom with a square-planar arrangement of the ligands and a bond angle Cl–Rh–C(carbene) of 88.3(2)°. The interatomic distances within the triazolinylidene heterocycle are similar to those obtained for other (triazolinylidene)metal complexes[5][6]. The carbene carbon bond length amounts to 2.004(7) A, identical to the value obtained by Lappert et al. for an (imidazolidinylidene)rhodium(COD) complex [2.004(4) A][3]. The configuration of the axis of chirality was assigned as (S_a) for this complex **4a**.

Rhodium(NBD) Complexes: The rhodium(NBD) complexes **5–6** were prepared in the same way as the rhodium(COD) complexes.

Figure 2. Molecular structure of (S_a)-**4a**[a]



[a] Selected bond lengths (A) and angles (°): Rh–C(carbene) 2.004(7), Rh–Cl 2.366(2), Cl–Rh–C(carbene) 88.3(2).

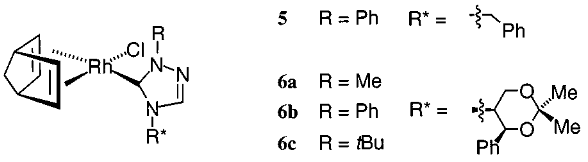


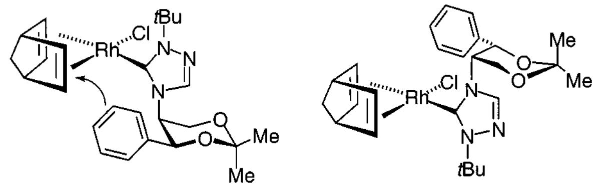
Table 2. Yields and diastereomeric excesses (*de*) of rhodium(NBD) complexes **5** and **6**

	Yield [%]	*de* [%][a]
5	95	–[b]
6a	93	[b]
6b	95	[b]
6c	75	87

[a] Determined by ^{1}H-NMR spectroscopy. – [b] Due to broad signals (rotation of the ligand), a diastereomeric excess could not be determined.

They did not show the same hindrance of rotation about the carbene carbon–rhodium bond as the rhodium(COD) complexes. For the achiral benzyl group, at room temperature no splitting of the benzylic protons was observed in the ^{1}H-NMR spectrum. These findings were again supported by MP2/TZVP//RI-DFT/SV(P) calculations, which gave a rotational barrier of 58 kJ/mol for the rotation about the carbene carbon–rhodium bond in complex **5**, much lower than that of complex **2**[8]. This is probably due to the significantly smaller size of the NBD ligand compared to the COD ligand, which leads to a considerably decreased steric interaction in the course of the rotation. By analogy, no evidence for the existence of two diastereomers was observed in the NMR spectra of complexes **6a** and **6b** with a chiral ligand, and only very broad signals were observed for the triazolinylidene ligand. Nevertheless, complex **6c** with a bulky *t*-butyl substituent showed a hindered rotation. A diastereomeric excess of 87% was determined, lower than that for the rhodium(COD) complex **4c** (97%). NMR spectroscopic investigations (NOE′s and ring-current effects) revealed the relative and therefore the absolute configuration of complex **6c**.

Figure 3. NMR spectroscopic investigations of complex **6c**



6c major diastereomer   **6c** minor diastereomer

In both diastereomers, the dioxane ring in the chair conformation points away from the rhodium atom. For the major diastereomer (S_a), the phenyl substituent of the dioxanyl group points at the olefinic protons of the double bond *trans* to the chlorine atom, causing a ring-current effect and a NOE. The former leads to a significant highfield shift of these protons. For the minor diastereomer (R_a) with the phenyl group pointing at the chlorine atom, neither this ring-current effect nor the NOE was observed. This conformation and configuration of **6c** in solution is identical to the structure obtained for **4a** in the solid state. The lower diastereomeric excess of the rhodium(NBD) complex **6c** compared to rhodium(COD) complex **4c** and the rotation of the ligand in case of complexes **5**, **6a−b** may be caused by a lower steric hindrance of the NBD ligand compared to the COD ligand. Upon cooling to −40°C, the broad signal of the benzylic protons of complex **5** in the ^{1}H-NMR spectrum sharpened due to a more hindered rotation, now appearing as two doublets. NMR spectroscopic investigations of Rh, Cr, Mo, and W complexes with hindered carbene ligand rotation at lower temperatures have already been reported[11].

Substitution Reactions: The chlorine atom of the complexes **2−6** was exchanged with iodine using NaI in MeOH and the resulting complexes were purified by column chromatography. Some examples for this substitution reaction are summarized in Table 3.

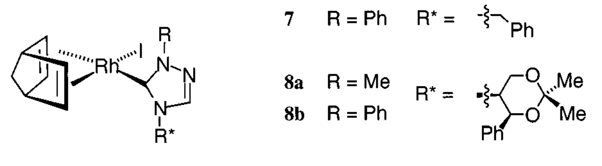


Table 3. Yields and diastereomeric excesses (*de*) of rhodium(NBD) complexes **7** and **8**

	Yield [%]	*de* [%][a]
7	90	–
8a	70	87
8b	83	87

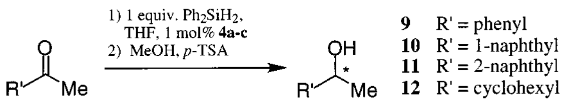
[a] Determined by ^{1}H-NMR spectroscopy.

The (iodo)rhodium(NBD) complexes **7** and **8** showed a hindered rotation at room temperature, in contrast to the chloro complexes **5**, **6a−b**. The diastereomeric excess of the complexes **8a−b** was determined to be 87%, identical to the result obtained for the chloro complex **6c**. For complex **7**, the barrier for the rotation about the carbene carbon−rhodium bond was again calculated at the MP2/TZVP//RI-DFT/SV(P) level of theory, yielding a barrier height of 73 kJ/mol[8]. The energy obtained is somewhat higher than for the corresponding chloro complex **5**, suggesting that the steric interaction of the iodine ligand is more significant. This is in agreement with experiment, since we did not observe rotation about the carbene carbon−rhodium bond in the NMR spectra.

Asymmetric Hydrosilylation: The hydrosilylation reaction with achiral (imidazolidinylidene)rhodium(COD) complexes, by Lappert et al.[12] was further developed by Herrmann et al. using chiral imidazolinylidene ligands, which gave enantiomeric excesses of up to 32%[4].

The potential of the (triazolinylidene)rhodium(COD) and -(NBD) complexes as catalysts was examined in a hydrosilylation reaction. The best enantioselectivities were achieved with complexes **4a−c**. In typical hydrosilylations, the methyl ketones **9−12** were reduced to the corresponding alcohols with diphenylsilane and 1 mol% of the catalyst in THF[13].

Scheme 2. Asymmetric hydrosilylation of methyl ketones **9−12**



Enantiomeric excesses of up to 44% were achieved with similar results being observed for aromatic and aliphatic ketones. The configuration of the resulting alcohol depends upon the achiral group R at *N*1 of the triazolinylidene ligand. For example, the enantiomeric excess changes from 44% (*S*) (catalyst **4a**) to 43% (*R*) (catalyst **4c**) with acetylcyclohexane **12** as the starting material and no change of the chirality information within the catalyst.

Table 4. Reaction conditions, yields and enantiomeric excesses for the hydrosilylation reaction

Catalyst	Ketone	Temperature [°C]	Time	Yield [%]	*ee* [%]
4a	**9**	22	4h	90	20 (*S*)
4c	**9**	11	6d	60	40 (*R*)
4a	**10**	42	4h	80	37 (*R*)
4b	**10**	2	10d	40	32 (*R*)
4a	**11**	2	5d	90	19 (*S*)
4c	**11**	22	16h	40	24 (*R*)
4a	**12**	−10	6d	75	44 (*S*)
4b	**12**	2	4d	80	43 (*S*)
4c	**12**	22	3d	70	43 (*R*)

The optimum reaction temperature in order to achieve the highest enantioselectivities varies from +42°C to −10°C for the different systems. We found a decreasing enantioselectivity with increasing or decreasing temperature with respect to the optimum conditions (principle of isoinversion[14]). This nonlinear temperature effect has also been observed by Scharf et al.[15] for a hydrosilylation reaction with rhodium(NBD) complexes and chiral cyclic monophosphonite ligands.

Conclusion

Axially chiral (triazolinylidene)rhodium(COD) and -(NBD) complexes have been prepared with diastereomeric excesses of up to 97%. The NMR spectroscopic and theoretical investigations show the steric requirements needed for hindered rotation about the carbene carbon−rhodium bond. This new type of chiral complex was examined in asymmetric hydrosilylation reactions with enantiomeric excesses of up to 44% for aromatic and aliphatic ketones. This represents a good result for a nonchelating ligand, probably caused in part by the axis of chirality.

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Experimental Section

General: All solvents were dried and distilled before use. The triazolium perchlorates[16], $[(COD)RhCl]_2$ and $[(NBD)RhCl]_2$[17] were prepared according to literature procedures. − Column chromatography: Merck silica gel 60, 0.040−0.063 mm (230−400 mesh) (flash). − Optical rotation values: Perkin-Elmer P 241, solvent UVASOL-quality. − Melting points (uncorrected): Büchi 510. − IR: Perkin-Elmer FT 1750. − NMR: Varian VXR 300 and Gemini 300 (300 and 75 MHz for ^1H and ^{13}C, respectively), Varian Unity 500 (500 and 125 MHz for ^1H and ^{13}C, respectively), $CDCl_3$ as solvent, TMS as internal standard, room temperature if not otherwise noticed. − MS: Finnigan MAT (70 eV) and Finnigan SSQ 7000 (70 eV).

1. General Procedure for the Preparation of (Chloro)rhodium(COD) Complexes **2−4**: $(COD)RhCl]_2$ (50 mg, 0.10 mmol), NEt_3 (0.2 ml, 1.4 mmol) and 1.1 equiv. of the corresponding triazolium perchlorate **1** (0.22 mmol) were dissolved in 40 ml of THF and the solution was stirred at room temperature for 14 h. The solution was evaporated to dryness in vacuo and the products were purified by column chromatography (silica gel, Et_2O/pentane, 2:1).

Chloro(η^4-1,5-cyclooctadiene)(1-phenyl-4-benzyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)rhodium(I) (**2**): Yield 86 mg (90%), m.p. 184°C. − IR (KBr): ν = 3110 cm^{-1} (m), 3047 (m), 3005 (m), 2931 (s), 2880 (s), 2833 (m), 1595 (s), 1545 (m), 1497 (s), 1476 (m), 1457 (m), 1435 (m), 1396 (s), 1355 (s), 1333 (s), 1222 (s), 766 (s), 723 (s), 706 (s), 650 (s). − ^1H NMR (300 MHz): δ = 1.66 (m, 1 H, CH_2CH_2), 1,84 (m, 4 H, CH_2CH_2), 2.12 (m, 1 H, CH_2CH_2), 2.30 (m, 2 H, CH_2CH_2), 2.74 (m, 1 H, CHCH), 3.08 (m, 1 H, CHCH), 5.12 (m, 1 H, CHCH), 5.22 (m, 1 H, CHCH), 5.86 (d, J = 14.83 Hz, 1 H, $PhCH_2$), 6.06 (d, J = 14.83 Hz, 1 H, $PhCH_2$), 7.50 (m, 8 H, C_6H_5), 7.90 (s, 1 H, N_2CH), 8.56 (m, 2 H, C_6H_5). − ^{13}C NMR (75 MHz): δ = 28.64, 28.87, 32.23, 32.60 (CH_2CH_2), 53.37 ($PhCH_2$), 69.07 (d, J = 14.3 Hz, CHCH), 70.35 (d, J = 14.3 Hz, CHCH), 98.83 (d, J = 7.4 Hz, CHCH), 99.53 (d, J = 7.4 Hz, CHCH), 123.75, 128.48, 128.73, 128.82, 128.90, 129.31 (C_5H_5CR), 134.70, 139.74 (C_5H_5CR), 142.42 (CHN), 186.94 (d, J = 51.0 Hz, NCRh). − MS (70 eV); m/z (%): 481.1 (38.2) $[M^+]$, 445.0 (12.1) $[M^+ - HCl]$, 372.9 (43.6) $[M^+ - COD]$, 336.9 (100) $[M^+ - COD - Cl]$. − HR-MS; m/z: $C_{23}H_{25}ClN_3Rh$ $[M^+]$: calcd. 481.0785; found 481.0785.

(R)-Chloro(η^4-1,5-cyclooctadiene)(1-methyl-4-(1-phenylethyl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)rhodium(I) (**3a**): Yield 60 mg (70%), diasteromeric excess (*de*) 41%, m.p. 78−80°C − $[\alpha]_D^{25}$ = +63 (c = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3029 cm^{-1} (m), 2978 (s), 2933 (s), 2875 (s), 2829 (s), 1531 (s), 1495 (s), 1474 (s), 1404 (s), 1383 (s), 1335 (s), 794 (s), 732 (s), 701 (s). − ^1H NMR (300 MHz): δ = 1.74 (m, 1 H, CH_2CH_2), 1.92 (d, J = 7.14 Hz, 3 H, $CHCH_3$), 2.00 (m, 3 H, CH_2CH_2), 2.40 (m, 4 H, CH_2CH_2), 2.93 (m, 1 H, CHCH), 3.36 (m, 2 H, CHCH), 4.27 (s, 3 H, NCH_3), 5.12 (m, 2 H, CHCH), 6.73 (q, J = 7.41 Hz, 1 H, $CHCH_3$), 7.33 (m, 2 H, C_6H_5), 7.40 (m, 2 H, C_6H_5), 7.60 (s, 1 H minor diastereomer, N_2CH), 7.64 (m, 1 H, C_6H_5), 7.92 (s, 1 H, N_2CH). − ^{13}C NMR (75 MHz): δ = 22.93 (CH_3), 28.35, 29.18, 32.20, 33.36 (CH_2CH_2), 39.98 (NCH_3), 58.48 ($CHCH_3$), 68.40 (d, J = 14.3 Hz, CHCH), 69.61 (d, J = 15.0 Hz, CHCH), 99.46 (d, J = 7.4 Hz, CHCH), 99.85 (d, J = 6.9 Hz, CHCH), 126.36, 128.36, 129.20 (C_5H_5CR), 138.80 (C_5H_5CR), 140.24 (N_2CH), 186.02 (d, J = 50.3 Hz, NCRh). − MS (70 eV); m/z (%): 433.0 (11.0) $[M^+]$, 324.9 (100) $[M^+ - COD]$, 288.8 (17.5) $[M^+ - COD - Cl]$, 260.9 (45.5), 105.0 (42.8). − HR-MS; m/z: $C_{19}H_{25}ClN_3Rh$ $[M^+]$: calcd. 433.0785; found 433.0784.

(R)-Chloro(η^4-1,5-cyclooctadiene)(1-phenyl-4-(1-phenylethyl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)rhodium(I) (**3b**): Yield 94 mg (95%), *de* 40%, m.p. 207°C. − $[\alpha]_D^{25}$ = +142 (c = 0.1, $CHCl_3$). − IR (KBr): ν = 3031 cm^{-1} (m), 2995 (m), 2969 (m), 2935 (s), 2914 (s), 2874 (s), 2829 (s), 1597 (s), 1531 (s), 1500 (s), 1476 (m), 1452 (m), 1409 (s), 1387 (m), 1345 (s), 762 (s), 718 (s), 691 (s), 663 (s). − ^1H NMR (300 MHz): δ = 1.65 (m, 1 H, CH_2CH_2), 1.76 (m, 2 H, CH_2CH_2), 1.90 (m, 2 H, CH_2CH_2), 2.00 (d, J = 7.15 Hz, 3 H, $CHCH_3$), 2.15 (m, 1 H, CH_2CH_2), 2.35 (m, 2 H, CH_2CH_2), 2.68 (m, 1 H, CHCH), 2.81 (m, 2 H, CHCH), 5.15 (m, 2 H, CHCH), 7.02 (q, J = 7.14 Hz, 1 H, $CHCH_3$), 7.39 (m, 2 H, C_6H_5), 7.46 (m, 4 H, C_6H_5), 7.56 (m, 2 H, C_6H_5), 7.72 (s, 1 H minor diastereomer, N_2CH), 8.18 (s, 1 H, N_2CH), 8.55 (m, 2 H, C_6H_5). − ^{13}C NMR (75 MHz): δ = 22.79 (CH_3), 28.20, 29.17, 32.18, 32.76 (CH_2CH_2), 59.49 ($CHCH_3$), 68.76 (d, J = 14.3 Hz, CHCH), 71.02 (d, J = 13.8 Hz, CHCH), 98.50 (d, J = 7.5 Hz, CHCH), 99.42 (d, J = 7.4 Hz, CHCH), 123.95, 125.55, 128.41, 128.47, 128.84, 129.25 (C_5H_5CR), 138.28, 139.89 (C_5H_5CR), 140.67 (N_2CH), 186.85 (d, J = 51.0 Hz, NCRh). − MS (70 eV); m/z (%): 495.0 (36.3) $[M^+]$, 386.9 (66.5) $[M^+ -COD]$, 350.9 (64.3) $[M^+ - COD - HCl]$, 246.9 (44.9), 105.0 (77.7). − HR-MS, m/z: $C_{24}H_{27}ClN_3Rh$ $[M^+]$: calcd. 495.0942; found 495.0942.

(R)-(1-tButyl-4-(1-phenylethyl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)(chloro)(η^4-1,5-cyclooctadiene)rhodium(I) (**3c**): Yield 74 mg (78%), *de* 36%, m.p. 81°C. − $[\alpha]_D^{25}$ = +38 (c = 0.1, $CHCl_3$). − IR (KBr): ν = 3047 cm^{-1} (m), 2976 (s), 2933 (s), 2876 (s), 2831 (s), 1545 (s), 1496 (m), 1475 (s), 1454 (s), 1406 (s), 1383 (s), 1365 (s), 762 (m), 703 (s), 673 (m). − ^1H NMR (300 MHz): δ = 1.87 (m, 4 H, CH_2CH_2), 1.97 (d, J = 7.69 Hz, 3 H, $CHCH_3$), 2.01 (s, 9 H, $C(CH_3)_3$), 2.36 (m, 1 H, CH_2CH_2), 3.20 (m, 1 H, CHCH), 3.35 (m, 1 H, CHCH), 5.04 (m, 2 H, CHCH), 7.36 (m, 5 H, C_6H_5, $CHCH_3$), 7.70 (m, 1 H, C_6H_5), 7.72 (s, 1 H minor diastereomer, N_2CH), 7.88 (s, 1 H, N_2CH). − ^{13}C NMR (75 MHz): δ = 23.37 (CH_3), 28.79, 28.86 (CH_2CH_2), 31.25 $[C(CH_3)_3]$, 32.17, 32.70 (CH_2CH_2), 59.76 ($CHCH_3$), 61.95 $[C(CH_3)_3]$, 68.51 (d, J = 14.3 Hz, CHCH), 69.74 (d, J = 14.9 Hz, CHCH), 95.63 (d, J = 7.5 Hz, CHCH), 97.63 (d, J = 7.4 Hz, CHCH), 126.08, 127.51, 129.19 (C_5H_5CR), 139.64 (C_5H_5CR), 140.67 (N_2CH), 184.10 (d, J = 56.7 Hz, NCRh). − MS (70 eV); m/z (%): 475.0 (37.1) $[M^+]$, 440.1 (10.8) $[M^+ - Cl]$, 402.8 (14.2), 366.9 (50.5) $[M^+ - COD]$, 331.0 (24.3) $[M^+ - COD - HCl]$, 310.9 (100.0) $[M^+ - COD - C_4H_8]$, 105.1 (18.6). − HR-MS, m/z: $C_{22}H_{31}ClN_3Rh$ $[M^+]$: calcd. 475.1255; found 475.1255.

(S_a,4S,5S)-Chloro(η^4-1,5-cyclooctadiene)(1-methyl-4-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5-dihydro-1H-1,2,4-triazol-5-

ylidene)rhodium(I) (**4a**): Yield 84 mg (79%), *de* 93%, m.p. >230°C − $[\alpha]_D{}^{25}$ = +80 (c = 0.1, $CHCl_3$). − IR (KBr): ν = 3174 cm^{-1} (w), 2990 (m), 2939 (s), 2914 (m), 2875 (s), 2833 (m), 1533 (m), 1499 (m), 1478 (m), 1448 (m), 1376 (s), 1204 (s), 1188 (s), 1165 (s), 1121 (s), 1078 (s), 1017 (m), 732 (s), 701 (s). − ^1H NMR (300 MHz): δ = 1.65 (s, 3 H, CCH_3), 1.69 (s, 3 H, CCH_3), 1.88 (m, 5 H, CH_2CH_2), 2.14 (m, 1 H, CH_2CH_2), 2.30 (m, 4 H, CH_2CH_2, CHCH), 2.96 (m, 1 H, CHCH), 4.19 (s, 3 H, NCH_3), 4.27 (br. d, J = 12.91 Hz, 1 H, OCH_2), 4.52 (d/d, J = 12.92/2.20 Hz, 1 H, OCH_2), 4.91 (m, 1 H, CHCH), 5.01 (m, 1 H, CHCH), 5.50 (d, J = 2.48 Hz, 1 H, OCH), 5.72 (d/d/d, J = 1.65/1.65/1.65 Hz, 1 H, OCHCH), 7.24 (m, 5 H, C_6H_5), 8.35 (s, 1 H minor diastereomer, N_2CH), 8.73 (s, 1 H, N_2CH). − ^{13}C NMR (75 MHz): δ = 18.44 (CCH_3), 28.48 (CH_2CH_2), 29.04 (CH_2CH_2), 29.73 (CCH_3), 32.28 (CH_2CH_2), 33.26 (CH_2CH_2), 39.76 (NCH_3), 57.25 (OCHCH), 64.89 (OCH_2), 68.26 (d, J = 13.8 Hz, CHCH), 69.13 (d, J = 14.3 Hz, CHCH), 73.09 (OCH), 99.31 (d, J = 6.8 Hz, CHCH), 99.64 (d, J = 7.4 Hz, CHCH), 100.47 $[OC(CH_3)_2]$, 126.13, 128.52, 128.64 (C_5H_5CR), 137.35 (C_5H_5CR), 143.17 (N_2CH), 187.33 (d, J = 52.3 Hz, NCRh). − MS (70 eV); m/z (%): 519.0 (24.7) [M^+], 411.0 (100.0) [M^+ − COD], 376.9 (6.7) [M^+ −COD − Cl]. − HR-MS, m/z: $C_{23}H_{31}ClN_3O_2Rh$ [M^+]: calcd. 519.1153; found 519.1153.

(S_a,4S,5S)-Chloro(η⁴-1,5-cyclooctadiene)(1-phenyl-4-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)rhodium(I) (**4b**): Yield 110 mg (95%), *de* 91%, m.p. >230°C − $[\alpha]_D{}^{25}$ = +8 (c = 0.1, $CHCl_3$). − IR (KBr): ν = 3161 cm^{-1} (m), 2991 (m), 2935 (s), 2910 (m), 2877 (s), 2831 (m), 1597 (m), 1538 (m), 1499 (s), 1464 (m), 1452 (m), 1430 (m), 1402 (s), 1382 (s), 1366 (s), 1187 (s), 1160 (s), 1112 (s), 1078 (s), 1010 (s), 763 (s), 736 (s), 719 (s), 699 (s). − ^1H NMR (300 MHz): δ = 1.43 (m, 1 H, CH_2CH_2), 1.61 (m, 2 H, CH_2CH_2), 1.68 (s, 3 H, CCH_3), 1.72 (s, 3 H, CCH_3), 1.75 (m, 3 H, CH_2CH_2), 2.06 (m, 1 H, CH_2CH_2), 2.19 (m, 1 H, CH_2CH_2), 2.27 (m, 2 H, CHCH), 4.42 (d/d, J = 12.91/1.37 Hz, 1 H, OCH_2), 4.60 (d/d, J = 12.91/2.20 Hz, 1 H, OCH_2), 4.90 (m, 1 H, CHCH), 5.11 (m, 1 H, CHCH), 5.58 (d, J = 2.47 Hz, 1 H, OCH), 6.00 (d/d/d, J = 1.64/1.64/1.64 Hz, 1 H, OCHCH), 7.23 (m, 1 H, C_6H_5), 7.30 (m, 4 H, C_6H_5), 7.42 (m, 1 H, C_6H_5), 7.51 (m, 2 H, C_6H_5), 8.43 (m, 2 H, C_6H_5), 8.45 (s, 1 H minor diastereomer, N_2CH), 8.95 (s, 1 H, N_2CH). − ^{13}C NMR (75 MHz): δ = 18.47 (CCH_3), 28.67 (CH_2CH_2), 28.78 (CH_2CH_2), 29.77 (CCH_3), 31.70 (CH_2CH_2), 33.09 (CH_2CH_2), 58.14 (OCHCH), 64.99 (OCH_2), 68.39 (d, J = 14.4 Hz, CHCH), 70.79 (d, J = 13.7 Hz, CHCH), 73.12 (OCH), 98.63 (d, J = 6.9 Hz, CHCH), 98.87 (d, J = 7.4 Hz, CHCH), 100.53 ($OC(CH_3)_2$), 124.13, 126.13, 128.41, 128.53, 128.66 (C_5H_5CR), 137.40, 139.73 (C_5H_5CR), 143.56 (N_2CH), 186.75 (d, J = 51.6 Hz, NCRh). − MS (70 eV); m/z (%): 581.2 (11.7) [M^+], 546.2 (16.8) [M^+ −Cl], 473.0 (14.9) [M^+ − COD], 437.0 (63.7) [M^+ − COD − Cl]. − HR-MS, m/z: $C_{28}H_{33}ClN_3O_2Rh$ [M^+]: calcd. 581.1309; found 581.1306.

(S_a,4S,5S)-(1-tButyl-4-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)(chloro)(η⁴-1,5-cyclooctadiene)rhodium(I) (**4c**): Yield 72 mg (65%), *de* 97%, m.p. 228°C. − $[\alpha]_D{}^{25}$ = +39 (c = 0.1, $CHCl_3$). − IR (KBr): ν = 3031 cm^{-1} (w), 2990 (m), 2939 (m), 2914 (m), 2876 (s), 2833 (m), 1534 (m), 1478 (m), 1448 (m), 1376 (s), 1188 (s), 1121 (s), 1078 (s), 1016 (s), 732 (s), 701 (s). − ^1H NMR (300 MHz): δ = 1.65 (s, 3 H, CCH_3), 1.70 (s, 3 H, CCH_3), 1.77 (m, 2 H, CH_2CH_2), 1.88 (m, 2 H, CH_2CH_2), 1.92 [s, 9 H, $C(CH_3)_3$], 2.02 (m, 1 H, CHCH), 2.16 (m, 1 H, CH_2CH_2), 2.24 (m, 2 H, CH_2CH_2), 2.36 (m, 1 H, CH_2CH_2), 2.90 (m, 1 H, CHCH), 4.41 (d/d, J = 12.64/1.37 Hz, 1 H, OCH_2), 4.56 (d/d, J = 12.91/2.20 Hz, 1 H, OCH_2), 4.86 (m, 1 H, CHCH), 4.97 (m, 1 H, CHCH), 5.52 (d, J = 2.47 Hz, 1 H, OCH), 6.20 (d/d/d, J = 1.65/1.65/1.65 Hz, 1 H, OCHCH), 7.26 (m, 5 H, C_6H_5), 8.49 (s, 1 H minor diastereomer, N_2CH), 8.87 (s, 1 H, N_2CH). − ^{13}C NMR (75 MHz): δ = 18.50 (CCH_3), 28.19 (CH_2CH_2), 29.37 (CH_2CH_2), 29.68 (CCH_3), 30.88 (CH_2CH_2), 31.23 [$C(CH_3)_3$], 31.34 (CH_2CH_2), 58.53 (OCHCH), 61.70 [$C(CH_3)_3$], 65.09 (OCH_2), 68.01 (d, J = 14.3 Hz, CHCH), 68.99 (d, J = 14.99 Hz, CHCH), 73.69 (OCH), 95.90 (d, J = 7.5 Hz, CHCH), 97.70 (d, J = 8.0 Hz, CHCH), 100.51 [$OC(CH_3)_2$], 126.55, 128.53, 128.73 (C_5H_5CR), 137.25 (C_5H_5CR), 142.45 (N_2CH), 183.93 (d, J = 51.0 Hz, NCRh). − MS (70 eV); m/z (%): 561.2 (88.7) [M^+], 453.0 (100) [M^+ − COD], 417.0 (58.2) [M^+ − COD − Cl], 396.9 (81.4). − HR-MS, m/z: $C_{26}H_{37}ClN_3O_2Rh$ [M^+]: calcd. 561.1622; found 561.1620.

2. General Procedure for the Preparation of (Chloro)rhodium(NBD) Complexes **5** *and* **6**: $[(NBD)RhCl]_2$ (46 mg, 0.1 mmol), NEt_3 (0.2 ml, 1.4 mmol) and 1.1 equiv. of the corresponding triazolium perchlorate **1** (0.22 mmol) were dissolved in 40 ml of THF and the solution was stirred at room temperature for 14 h. The solution was evaporated to dryness in vacuo and the products were purified by column chromatography (silica gel, Et_2O/pentane, 2:1).

Chloro(η⁴-1,5-norbornadiene)(1-phenyl-4-benzyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)rhodium(I) (**5**): Yield 88 mg (95%), m.p. 192°C. − IR (KBr): ν = 3118 cm^{-1} (m), 3047 (m), 3002 (m), 2958 (m), 2919 (m), 2841 (m), 1596 (s), 1541 (m), 1497 (s), 1456 (m), 1397 (s), 1338 (s), 1306 (s), 1222 (s), 763 (s), 726 (s), 705 (s). − ^1H NMR (500 MHz): δ = 1.10 (d/d/d, J = 8.51/1.38/1.38 Hz, 1 H, $CHCH_2$), 1.18 (d/d/d, J = 8.51/1.65/1.65 Hz, 1 H, $CHCH_2$), 2.69 (m, 2 H, $CHCHCHCH_2$), 3.47 (m, 2 H, CH_2CH), 4.87 (m, 2 H, $CHCHCHCH_2$), 5.80 (br. s, 2 H, $PhCH_2$), 7.48 (m, 4 H, C_6H_5), 7.61 (m, 4 H, C_6H_5), 8.01 (s, 1 H, N_2CH), 8.54 (m, 2 H, C_6H_5). − ^1H NMR (500 MHz, −40°C): δ = 1.09 (br. d, J = 8.55 Hz, 1 H, $CHCH_2$), 1.17 (br. d, J = 8.24 Hz, 1 H, $CHCH_2$), 2.59 (m, 2 H, $CHCHCHCH_2$), 3.46 (m, 2 H, CH_2CH), 4.85 (m, 1 H, $CHCHCHCH_2$), 4.91 (m, 1 H, $CHCHCHCH_2$), 5.50 (d, J = 14.65 Hz, 1 H, $PhCH_2$), 6.08 (d, J = 14.65 Hz, 1 H, $PhCH_2$), 7.48 (m, 2 H, C_6H_5), 7.54 (m, 2 H, C_6H_5), 7.62 (m, 2 H, C_6H_5), 7.69 (m, 2 H, C_6H_5), 8.31 (s, 1 H, N_2CH), 8.53 (m, 2 H, C_6H_5). − ^{13}C NMR (75 MHz): δ = 49.36 (m, $CH_2CHCHCH$), 50.67 (d, J = 2.9 Hz, CH_2CH), 52.97 ($PhCH_2$), 63.00 (d, J = 5.1 Hz, CH_2CHCH), 78.34 (d, J = 6.0 Hz, $CH_2CHCHCH$), 123.50, 128.56, 128.72, 128.78, 129.17 (C_5H_5CR), 135.32, 139.84 (C_5H_5CR), 142.63 (CHN), 189.00 (d, J = 57.5 Hz, NCRh). − MS (70 eV); m/z (%): 465.1 (3.6) [M^+], 429.0 (3.3) [M^+ −HCl], 372.9 (3.0) [M^+ − NBD], 336.9 (16.0) [M^+ − NBD − HCl], 91.0 (100.0). − HR-MS, m/z: $C_{22}H_{21}ClN_3Rh$ [M^+]: calcd. 465.0472; found 465.0477.

(4S,5S)-Chloro(1-methyl-4-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)(η⁴-1,5-norbornadiene)rhodium(I) (**6a**): Yield 94 mg (93%), m.p. 199°C. − $[\alpha]_D{}^{25}$ = +128 (c = 0.1, $CHCl_3$). − IR (KBr): ν = 2994 cm^{-1} (s), 2953 (m), 2922 (m), 2882 (m), 2837 (m), 1533 (m), 1483 (m), 1451 (m), 1441 (m), 1407 (m), 1383 (s), 1305 (m), 1237 (s), 1204 (s), 1187 (s), 1162 (s), 1115 (s), 1079 (s), 762 (m), 734 (s), 705 (s). − ^1H NMR (300 MHz): δ = 1.29 (d/d, J = 1.37/1.37 Hz, 2 H, $CHCH_2$), 1.64 (s, 3 H, CCH_3), 1.68 (s, 3 H, CCH_3), 2.34 (m, 1 H, $CH_2CHCHCH$), 3.33 (m, 1 H, $CH_2CHCHCH$), 3.63 (m, 1 H, CH_2CH), 3.73 (m, 1 H, CH_2CH), 4.05 (s, 3 H, NCH_3), 4.14 (d/d, J = 12.91/1.37 Hz, 1 H, OCH_2), 4.54 (d/d, J = 12.91/2.20 Hz, 1 H, OCH_2), 4.78 (m, 1 H, $CH_2CHCHCH$), 4.85 (m, 1 H, $CH_2CHCHCH$), 5.55 (d, J = 2.47 Hz, OCH), 5.90 (d/d/d, J = 1.37/1.37/1.37 Hz, 1 H, OCH_2CH), 7.24 (m, 1 H, C_6H_5), 7.34 (m, 4 H, C_6H_5), 8.63 (s, 1 H, N_2CH). − ^{13}C NMR (75 MHz): δ = 19.04 (CCH_3), 30.27 (CCH_3), 40.05 (NCH_3), 49.60 (d, J = 11.9 Hz, $CH_2CHCHCH$), 50.03 (d, J = 12.5 Hz, $CH_2CHCHCH$), 51.52 (d, J = 5.7 Hz, CH_2CH), 57.21 (OCH_2), 64.29 ($CH_2CHCHCH$),

65.58 (OCH$_2$*C*H), 73.15 (OCH), 79.53 (d, *J* = 5.7 Hz, CH$_2$CH*C*HCH), 81.07 (d, *J* = 5.7 Hz, CH$_2$CH*C*HCH), 100.94 [*C*(CH$_3$)$_2$], 126.64, 128.86, 129.21 (*C*$_5$H$_5$CR), 137.89 (C$_5$H$_5$*C*R), 143.52 (N$_2$CH), 186.64 (d, *J* = 58.1 Hz, NCRh). − MS (70 eV); *m/z* (%): 503.1 (4.7) [M$^+$], 468.2 (54.6) [M$^+$ − Cl], 411.0 (71.3) [M$^+$ − NBD], 376.2 (17.7) [M$^+$ − NBD − HCl], 323.1 (41.1), 287.1 (36.6), 211.1 (60.8), 272.1 (9.0), 184.1 (80.6), 91.2 (100.0). − HR-MS, *m/z*: C$_{22}$H$_{27}$N$_3$O$_2$Rh [M$^+$ − Cl]: calcd. 468.1151; found 468.1154.

(4S,5S)-Chloro(η^4-1,5-norbornadiene)(1-phenyl-4-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)rhodium(I) (**6b**): Yield 108 mg (95%), m.p. 226°C. − [α]$_D^{25}$ = +13 (*c* = 0.1, CHCl$_3$) − IR (KBr): ν = 3049 cm^{-1} (w), 2985 (s), 2922 (m), 2956 (s), 2937 (m), 2912 (m), 2837 (w), 1597 (m), 1533 (m), 1501 (s), 1453 (m), 1410 (m), 1383 (s), 1326 (m), 1234 (s), 1201 (s), 1161 (s), 1115 (s), 1074 (s), 1014 (s), 762 (s), 734 (s), 704 (s). − ^{1}H NMR (300 MHz): δ = 1.05 (d/d/d, *J* = 8.24/1.50/1.50 Hz, 1 H, CHC*H*$_2$), 1.16 (d/d/d, *J* = 8.52/1.38/1.38 Hz, 1 H, CHC*H*$_2$), 1.67 (s, 3 H, CCH$_3$), 1.71 (s, 3 H, CCH$_3$), 2.00 (m, 1 H, CH$_2$CHC*H*CH), 2.40 (m, 1 H, CH$_2$CHC*H*CH), 3.37 (m, 1 H, CH$_2$C*H*), 3.50 (m, 1 H, CH$_2$C*H*), 4.29 (br. d, *J* = 12.37 Hz, 1 H, OCH$_2$), 4.62 (d/d, *J* = 12.91/1.92 Hz, 1 H, OCH$_2$), 4.80 (m, 2 H, CH$_2$CHC*H*CH), 5.63 (d, *J* = 2.47 Hz, OCH), 6.11 (d/d/d, *J* = 1.65/1.65/1.65 Hz, OCH$_2$C*H*), 7.22 (m, 1 H, C$_6$H$_5$), 7.34 (m, 2 H, C$_6$H$_5$), 7.46 (m, 3 H, C$_6$H$_5$), 7.55 (m, 2 H, C$_6$H$_5$), 8.34 (m, 2 H, C$_6$H$_5$), 8.82 (s, 1 H, N$_2$CH). − ^{13}C NMR (75 MHz): δ = 18.51 (*C*CH$_3$), 29.74 (*C*CH$_3$), 48.71 (br. CH$_2$*C*H), 50.51 (CH$_2$CH*C*HCH), 50.80 (br. CH$_2$*C*H), 57.37 (OCH$_2$), 63.26 (d, *J* = 5.2 Hz, *C*H$_2$CHCHCH), 65.06 (OCH$_2$*C*H), 72.51 (OCH), 77.46 (d, *J* = 5.2 Hz, CH$_2$CH*C*HCH), 77.82 (d, *J* = 6.2 Hz, CH$_2$CH*C*HCH), 100.45 [*C*(CH$_3$)$_2$], 123.86, 126.05, 128.31, 128.53, 128.60, 128.62 (*C*$_5$H$_5$CR), 137.32, 139.55 (C$_5$H$_5$*C*R), 143.32 (N$_2$CH), 187.54 (d, *J* = 58.1 Hz, NCRh). − MS (70 eV); *m/z* (%): 565.2 (19.0) [M$^+$], 473.1 (19.9) [M$^+$ −NBD], 437.1 (100.0) [M$^+$ − NBD − HCl], 349.0 (12.8), 273.0 (16.6), 247.0 (15.1). − HR-MS, *m/z*: C$_{27}$H$_{29}$ClN$_3$O$_2$Rh [M$^+$]: calcd. 565.0996; found 565.1001.

(S$_a$,4S,5S)-(1-tButyl-4-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)(chloro)(η^4-1,5-norbornadiene)rhodium(I) (**6c**): Yield 82 mg (75%), *de* 87%, m.p. 113°C. − [α]$_D^{25}$= +36 (*c* = 0.1, CHCl$_3$). − IR (KBr): ν = 3060 cm^{-1} (w), 2988 (s), 2939 (m), 2878 (m), 1543 (m), 1498 (m), 1475 (m), 1454 (m), 1400 (s), 1384 (s), 1306 (m), 1267 (s), 1234 (s), 1206 (s), 1192 (s), 1166 (s), 1112 (s), 1078 (s), 1010 (m), 754 (m), 704 (s). − ^{1}H NMR (500 MHz, major diastereomer): δ = 1.19 (d/d/d, *J* = 8.54/1.53/1.53 Hz, 1 H, CHC*H*$_2$), 1.22 (d/d/d, *J* = 8.54/1.53/1.53 Hz, 1 H, CHC*H*$_2$), 1.64 (s, 3 H, CCH$_3$), 1.71 (s, 3 H, CCH$_3$), 1.88 (s, 9 H, C(CH$_3$)$_3$), 2.26 (m, 1 H, CH$_2$CHC*H*CH), 3.13 (m, 1 H, CH$_2$CHC*H*CH), 3.63 (m, 2 H, CH$_2$C*H*), 4.26 (d/d, *J* = 12.82/1.53 Hz, 1 H, OCH$_2$), 4.55 (m, 1 H, CH$_2$CHC*H*CH), 4.59 (d/d, *J* = 12.82/1.53 Hz, 1 H, OCH$_2$), 4.70 (m, 1 H, CH$_2$CHC*H*CH), 5.59 (d, *J* = 2.44 Hz, OCH), 6.45 (d/d/d, *J* = 1.53/1.53/1.53 Hz, OCH$_2$C*H*), 7.25 (m, 1 H, C$_6$H$_5$), 7.28 (m, 2 H, C$_6$H$_5$), 7.30 (m, 2 H, C$_6$H$_5$), 8.78 (s, 1 H, N$_2$CH). − ^{1}H NMR (500 MHz, minor diastereomer): δ = 1.32 (d/d/d, *J* = 8.54/1.67/1.67 Hz, 1 H, CHC*H*$_2$), 1.35 (d/d/d, *J* = 8.54/1.60/1.60 Hz, 1 H, CHC*H*$_2$), 1.64 (s, 3 H, CCH$_3$), 1.73 (s, 3 H, CCH$_3$), 1.85 (s, 9 H, C(CH$_3$)$_3$), 2.23 (m, 1 H, CH$_2$CHC*H*CH), 3.39 (m, 1 H, CH$_2$CHC*H*CH), 3.76 (m, 2 H, CH$_2$C*H*), 4.29 (d/d, *J* = 11.52/1.83 Hz, 1 H, OCH$_2$), 4.75 (m, 2 H, CH$_2$CHC*H*CH), 4.82 (d/d, *J* = 12.51/2.90 Hz, 1 H, OCH$_2$), 5.61 (d, *J* = 2.83 Hz, OCH), 6.27 (d/d/d, *J* = 1.76/2.60/2.60 Hz, OCH$_2$C*H*), 7.12 (m, 1 H, C$_6$H$_5$), 7.22 (m, 2 H, C$_6$H$_5$), 7.44 (m, 2 H, C$_6$H$_5$), 8.40 (s, 1 H, N$_2$CH). − ^{13}C NMR (75 MHz): δ = 18.53 (*C*CH$_3$), 29.66 (*C*CH$_3$), 31.14 [C(*C*H$_3$)$_3$], 47.40 (d, *J* = 12.5 Hz, CH$_2$CH*C*HCH), 48.65 (d, *J* = 12.0 Hz, CH$_2$CH*C*HCH), 50.22 (d, *J* = 2.4 Hz, CH$_2$*C*H), 50.32 (d, *J* = 2.9 Hz, CH$_2$*C*H), 58.50 (OCH$_2$*C*H), 60.95 [C(*C*H$_3$)$_3$], 63.04 (d, J = 4.9 Hz, *C*H$_2$CHCHCH), 65.11 (O*C*H$_2$), 72.19 (d, *J* = 6.0 Hz, CH$_2$CH*C*HCH), 73.41 (OCH), 75.64 (d, *J* = 6.5 Hz, CH$_2$CHC*H*CH), 100.46 [*C*(CH$_3$)$_2$], 126.59, 128.51, 128.55 (*C*$_5$H$_5$CR), 137.35 (C$_5$H$_5$*C*R), 142.11 (N$_2$CH), 185.46 (d, *J* = 56.7 Hz, NCRh). − MS (70 eV); *m/z* (%): 545.2 (39.0) [M$^+$], 453.0 (100.0) [M$^+$ − NBD], 417.0 (98.7) [M$^+$ − NBD − HCl], 396.9 (95.7), 361.0 (49.0), 308.9 (47.7), 272.9 (55.4), 196.9 (41.1), 105.0 (63.1), 91.1 (69.9). − HR-MS, *m/z*: C$_{25}$H$_{33}$ClN$_3$O$_2$Rh [M$^+$]: calcd. 545.1309; found 545.1308.

3. General Procedure for the Preparation of (Iodo)rhodium(NBD) Complexes **7** *and* **8**: Chloro)rhodium(NBD) complexes **5**, **6a−b** (0.1 mmol) and NaI (40 mg, 0.26 mmol) were dissolved in 10 ml of MeOH. The solution was stirred at room temperature for 6 h, evaporated to dryness in vacuo and the products were purified by column chromatography (silica gel, Et$_2$O/pentane, 1:1).

*Iodo(η^4-*1,5-norbornadiene)(1-phenyl-4-benzyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)rhodium(I) (**7**): Yield 50 mg (90%), m.p. 172°C. − IR (KBr): ν = 3120 cm^{-1} (m), 3052 (m), 3006 (m), 2949 (m), 2912 (m), 2863 (m), 2840 (m), 1595 (m), 1534 (m), 1498 (s), 1458 (m), 1384 (m), 1343 (m), 1303 (s), 761 (s), 732 (s), 697 (s). − ^{1}H NMR (500 MHz): δ = 1.09 (d/d/d, *J* = 8.51/1.65/1.65 Hz, 1 H, CHC*H*$_2$), 1.24 (d/d/d, *J* = 8.52/1.65/1.65 Hz, 1 H, CHC*H*$_2$), 2.91 (m, 2 H, CH$_2$CHC*H*CH), 3.47 (m, 2 H, CH$_2$C*H*), 5.06 (m, 1 H, CH$_2$CHC*H*CH), 5.10 (m, 1 H, CH$_2$CHC*H*CH), 5.56 (d, *J* = 14.55 Hz, 1 H, PhCH$_2$), 6.03 (d, *J* = 14.56 Hz, 1 H, PhCH$_2$), 7.48 (m, 4 H, C$_6$H$_5$), 7.58 (m, 4 H, C$_6$H$_5$), 7.98 (s, 1 H, N$_2$CH), 8.56 (m, 2 H, C$_6$H$_5$). − ^{13}C NMR (75 MHz): δ = 51.18 (d, *J* = 2.33 Hz, CH$_2$*C*H), 51.83 (d, *J* = 11.9 Hz, CH$_2$CH*C*HCH), 52.92 (d, *J* = 12.0 Hz, CH$_2$CH*C*HCH), 53.47 (PhCH$_2$), 64.39 (d, *J* = 5.1 Hz, *C*H$_2$CHCH), 75.48 (d, *J* = 8.0 Hz, CH$_2$CH*C*HCH), 75.58 (d, *J* = 5.7 Hz, CH$_2$CH*C*HCH), 123.02, 128.43, 128.66, 128.83, 129.14, 129.19 (*C*$_5$H$_5$CR), 135.01, 139.93 (C$_5$H$_5$*C*R), 142.70 (CHN), 190.80 (d, *J* = 55.2 Hz, NCRh). − MS (70 eV); *m/z* (%): 557.0 (0.3) [M$^+$], 430.0 (2.6) [M$^+$ − I], 337.2 (10.4) [M$^+$ − NBD − I], 126.0 (27.8), 72.1 (100.0). − HR-MS, *m/z*: C$_{22}$H$_{21}$N$_3$Rh [M$^+$ − I]: calcd. 430.0783; found 430.0783.

(S$_a$,4S,5S)-Iodo(1-methyl-4-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)(η^4-1,5-norbornadiene)rhodium(I) (**8a**): Yield 42 mg (70%), *de* 87%, m.p. 122−124°C. − [α]$_D^{25}$ = +97 (*c* = 0.1, CHCl$_3$). − IR (KBr): ν = 2989 cm^{-1} (s), 2922 (m), 2873 (m), 1563 (m), 1532 (m), 1498 (m), 1451 (m), 1403 (m), 1383 (s), 1307 (m), 1203 (s), 1188 (s), 1163 (s), 1117 (s), 1078 (s), 761 (m), 732 (s), 701 (s). − ^{1}H NMR (300 MHz): δ = 1.24 (d, *J* = 8.12 Hz, 1 H, CHC*H*$_2$), 1.32 (d, *J* = 8.18 Hz, 1 H, CHC*H*$_2$), 1.64 (s, 3 H, CCH$_3$), 1.68 (s, 3 H, CCH$_3$), 2.23 (m, 1 H, CH$_2$CHC*H*CH), 3.47 (m, 1 H, CH$_2$CHC*H*CH), 3.57 (m, 1 H, CH$_2$C*H*), 3.71 (m, 1 H, CH$_2$C*H*), 4.04 (s, 3 H, NCH$_3$), 4.26 (br. d, *J* = 12.63 Hz, 1 H, OCH$_2$), 4.57 (d/d, *J* = 12.91/2.20 Hz, 1 H, OCH$_2$), 5.01 (m, 2 H, CH$_2$CHC*H*CH), 5.55 (d, *J* = 2.20 Hz, OCH), 5.73 (m, 1 H, OCH$_2$C*H*), 7.29 (m, 5 H, C$_6$H$_5$), 8.35 (s, 1 H minor diastereomer, N$_2$CH), 8.70 (s, 1 H, N$_2$CH). − ^{13}C NMR (75 MHz): δ = 18.44 (*C*CH$_3$), 29.70 (*C*CH$_3$), 39.32 (NCH$_3$), 51.43 (m, CH$_2$CH*C*HCH, CH$_2$*C*H), 53.14 (d, *J* = 12.0 Hz, CH$_2$CH*C*HCH), 56.48 (OCH$_2$), 64.55 (OCH$_2$*C*H), 65.08 (d, *J* = 5.2 Hz, *C*H$_2$CHCHCH), 73.00 (OCH), 77.34 (d, *J* = 6.0 Hz, CH$_2$CHC*H*CH), 100.51 [*C*(CH$_3$)$_2$], 126.41, 128.54, 128.72 (*C*$_5$H$_5$CR), 137.39 (C$_5$H$_5$*C*R), 143.16 (N$_2$CH), 188.20 (d, *J* = 55.9 Hz, NCRh). − MS (70 eV); *m/z* (%): 595.0 (1.6) [M$^+$], 502.9 (4.88) [M$^+$ − NBD], 468.0 (100.0) [M$^+$ − I], 376.0 (21.2) [M$^+$ − NBD

− I], 287.9 (16.2), 184.0 (23.1). − HR-MS, *m/z*: $C_{22}H_{27}N_3O_2Rh$ [M^+ − I]: calcd. 468.1151; found 468.1153.

(S_a,4S,5S)-Iodo(η^4-1,5-norbornadiene)(1-phenyl-4-(2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)rhodium(I) (**8b**): Yield 54 mg (83%), *de* 87%, m.p. > 230°C. $-[\alpha]_D^{25} = +79$ ($c = 0.1$, $CHCl_3$). − IR (KBr): $\nu = 2990$ cm^{-1} (s), 2958 (m), 2922 (m), 2876 (m), 2838 (m), 1596 (m), 1536 (m), 1500 (s), 1460 (m), 1450 (m), 1427 (m), 1383 (s), 1368 (s), 1354 (s), 1199 (s), 1163 (s), 1117 (s), 1073 (s), 1017 (s), 831 (s), 708 (s), 698 (s). − ^1H NMR (300 MHz): $\delta = 0.98$ (d/d/d, $J = 8.52/1.50/1.50$ Hz, 1 H, $\mathrm{CHC}H_2$), 1.17 (d/d/d, $J = 8.50/1.38/1.38$ Hz, 1 H, $\mathrm{CHC}H_2$), 1.68 (s, 3 H, CCH_3), 1.70 (s, 3 H, CCH_3), 1.85 (m, 1 H, $\mathrm{CH_2CHC}H\mathrm{CH}$), 2.51 (m, 1 H, $\mathrm{CH_2CHC}H\mathrm{CH}$), 3.29 (m, 1 H, $\mathrm{CH_2C}H$), 3.44 (m, 1 H, $\mathrm{CH_2C}H$), 4.35 (d/d, $J = 13.18/1.10$ Hz, 1 H, OCH_2), 4.53 (d/d, $J = 12.91/2.47$ Hz, 1 H, OCH_2), 4.95 (m, 2 H, $\mathrm{CH_2CHC}H\mathrm{CH}$), 5.58 (d, $J = 2.19$ Hz, OCH), 6.02 (d/d/d, $J = 1.37/1.37/1.37$ Hz, $\mathrm{OCH_2C}H$), 7.23 (m, 1 H, C_6H_5), 7.36 (m, 4 H, C_6H_5), 7.45 (m, 1 H, C_6H_5), 7.54 (m, 2 H, C_6H_5), 8.36 (m, 2 H, C_6H_5), 8.54 (s, 1 H minor diastereomer, N_2CH), 8.92 (s, 1 H, N_2CH). − ^{13}C NMR (75 MHz): $\delta = 19.04$ ($C\mathrm{CH_3}$), 30.31 ($C\mathrm{CH_3}$), 51.50 (m, $\mathrm{CH_2}C\mathrm{H}$, $\mathrm{CH_2CH}C\mathrm{HCH}$), 54.93 (d, $J = 12.0$ Hz, $\mathrm{CH_2CH_2CH}C\mathrm{HCH}$), 58.10 ($OCH_2$), 65.11 (d, $J = 5.1$ Hz, $C\mathrm{H_2CHCHCH}$), 65.24 ($\mathrm{OCH_2}C\mathrm{H}$), 73.60 (OCH), 75.09 (d, $J = 5.7$ Hz, $\mathrm{CH_2CH}C\mathrm{HCH}$), 76.31 (d, $J = 6.2$ Hz, $\mathrm{CH_2CH}C\mathrm{HCH}$), 101.15 [$C(\mathrm{CH_3})_2$], 123.93, 127.00, 128.99, 129.14, 129.27 ($C_5\mathrm{H_5CR}$), 138.06, 140.23 ($\mathrm{C_5H_5}C\mathrm{R}$), 144.07 ($N_2CH$), 189.87 (d, $J = 56.3$ Hz, NCRh). − MS (70 eV); *m/z* (%): 657.0 (1.8) [M^+], 530.1 (97.7) [M^+ − I], 437.9 (100.0) [M^+ − NBD − I], 349.9 (12.3), 246.9 (11.1). − HR-MS, *m/z*: $C_{27}H_{29}N_3O_2Rh$ [M^+ − I]: calcd. 530.1308; found 530.1309.

4. General Procedure for a Catalytic Hydrosilylation Reaction: Under a nitrogen atmosphere, the ketones **9−12** (1 mmol) and Ph_2SiH_2 (184 mg, 1 mmol) were added to a solution of the (triazolinylidene)rhodium(COD) complex **4a−c** (1 mol%) in 2 ml of THF stirred at reaction temperature. The reaction was quenched by addition of methanol (0.5 ml) containing 1% of *p*-toluenesulfonic acid (*p*-TSA). After evaporation of the solvent in vacuo and purification of the product by column chromatography (silica gel, pentane/Et_2O, 2:1), the enantiomeric excess of the product alcohol was determined by gas chromatography (LIPODEX E, CP-CHIRASIL-DEX CB, 7-CD PERME).

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Geometries have been calculated at the RI-DFT (K. Eichkorn, O. Treutler, H. Ihm, M. Häser, R. Ahlrichs, *Chem. Phys. Letters* **1995**, *242*, 652) level with the Becke−Perdew functional using TURBOMOLE's SV(P) basis sets (K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119). Energies were calculated at the MP2 level with TZVP basis sets by optimization for different rotation angles.

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[10] Suitable crystals were obtained from CH_2Cl_2/pentane mixtures at room temp. The compound crystallizes in the orthorhombic space group $P2_12_12_1$; $a = 10.601(5)$, $b = 11.441(3)$, $c = 19.178(6)$ A. At a cell volume of 2326.1 A^3, $Z = 4$ and $M_{\mathrm{ber.}} = 519.87$, the calculated density and the absorption coefficient are $\rho = 1.484$ mg m^{-3} and $\mu = 7.180$ mm^{-1}, respectively. The total number of electrons per unit cell amounts to $F(000) = 1072$. The data collection was performed at 203 K on a Siemens P4 diffractometer, Cu-K_α radiation (graphite monochromator, $\lambda = 1.54178$ A), 1735 reflections measured ($+h$, $+k$, $+l$), 1735 independent reflections, $4.50° < \theta < 55.85°$. Structure solved by direct methods [SHELXTL (G. M. Sheldrick, Univ. Göttingen, Germany), refinement on F^2]. The hydrogen atoms were located and refined isotropically. 1733 observed reflections [$I > 2\sigma(I)$] were used in the final refinement of 295 parameters terminating at $R = 0.0327$ ($R_W = 0.0738$). Maximal residual electron density −0.314/+ 0.339 e A^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101134. Copies of the data can be obtained free of charge on application to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, [Fax: (internat.) +44 (0)1223 336033, e-mail: deposit@chemcrys.cam.ac.uk].

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