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Ruthenium Tripyrazolylborate Complexes. 8. *trans*-Diene Coordination in Ruthenium Tripyrazolylborate Complexes

Christian Gemel,[†] Kurt Mereiter,[‡] Roland Schmid,[†] and Karl Kirchner*,[†]

Institute of Inorganic Chemistry and Institute of Mineralogy, Crystallography, and Structural Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

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A method of preparing RuTp(η⁴-diene)Cl complexes (diene = 1,3-butadiene, 2-methyl-1,3-butadiene, 2,4-hexadiene) is described, proceeding from RuTp(COD)Cl (COD = cycloocta-1,5-diene) through the intermediacy of Ru(III). The acyclic diene ligands are attached to the metal center in an *s-trans* manner, both in the solid state and in solution. So strong is the preference for *trans*-diene coordination that when a cyclic diene (1,3-cyclohexadiene) is used, elimination of HCl occurs yielding the η^5-cyclohexadienyl complex RuTp(η^5-C_6H_7).

Introduction

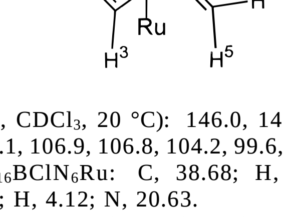
In our continuing studies on ruthenium tripyrazolylborate (Tp) complexes,[1,2] we have been utilizing, among other compounds, RuTp(COD)Cl (**1**) (COD = cycloocta-1,5-diene) as a convenient precursor. In this complex, COD can be replaced with a variety of ligands affording complexes of the types RuTp(L_2)Cl, RuTp$(L)_2$Cl, and RuTp(L)(L′)Cl where L_2, L, and L′ = N, O, and P donor mono- and bidentate ligands.[1,2] However, this straightforward synthetic route is restricted to robust ligands since in the presence of Tp as the coligand, COD is rather substitutionally inert, in sharp contrast to its lability in the neighborhood of Cp.[3] Thus, the displacement of COD in **1** needs boiling DMF solutions. Under such an aggravated condition, ligands such as 1,3-dienes (acyclic and cyclic) turned out to be impossible to coordinate. An alternative method, therefore, of obtaining diene complexes is deemed desirable.

Such a method is described in the present work proceeding through the intermediate oxidation of **1** whereupon COD is sufficiently labilized so as to give way to diene coordination. The RuTp(η^4-diene)Cl complexes so obtained may be compared with the known isolectronic RuCp(η^4-diene)Cl (Cp = cyclopentadienyl) and RuCp*(η^4-diene)Cl (Cp* = pentamethylcyclopentadienyl) analogs displaying a vast reaction chemistry.[4−7]

Experimental Section

General Information. All reactions were performed under an inert atmosphere of purified argon by using Schlenk techniques unless otherwise stated. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. RuTp(COD)Cl was prepared according to the literature.[2a] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Microanalyses were done by Microanalytical Laboratories, University of Vienna.

Syntheses. RuTp(η^4-CH_2=CHCH=CH_2)Cl (2). A solution of **1** (100 mg, 0.218 mmol) in xylene (5 mL) was heated at reflux for 3 h in the presence of air. The volatiles were removed in vacuo, and the residue was dissolved in MeOH under argon. After the solution was purged with 1,3-butadiene for 5 min, Zn (200 mg, 0.306 mmol) was added, and the mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2. Insoluble materials were removed by filtration. Removal of the solvent afforded **2** as a white solid. Purification was by recrystallization from acetone and Et_2O. Yield: 88 mg (73%). ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.08 (d, 1H, J = 2.2 Hz), 7.81 (d, 1H, J = 2.5 Hz), 7.76 (d, 1H, J = 2.9 Hz), 7.72 (d, 1H, J = 2.9 Hz), 7.68 (d, 1H, J = 2.9 Hz), 7.01 (d, 1H, J = 2.5 Hz), 6.34 (m, 1H), 6.29 (m, 1H), 6.13 (m, 1H), 5.03 (d, 1H, H^5, $^3J_{45}$ = 12.3 Hz), 4.80 (ddd, 1H, H^3, $^3J_{23}$ = 12.8 Hz, $^3J_{34}$ = 7.0 Hz, $^3J_{13}$ = 7.0 Hz), 4.40 (ddd, 1H, H^4, $^3J_{45}$ = 12.3 Hz, $^3J_{34}$ = 7.0 Hz, $^3J_{46}$ = 7.0 Hz), 4.30 (d, 1H, H^6, $^3J_{46}$ = 7.0 Hz), 4.21 (d, 1H, H^2, $^3J_{13}$ = 7.0 Hz), 3.93 (d, 1H, H^2, $^3J_{23}$ = 12.8 Hz).



^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 146.0, 145.2, 142.1, 137.9, 135.8, 135.0, 107.1, 106.9, 106.8, 104.2, 99.6, 74.9, 74.3. Anal. Calcd for $C_{13}H_{16}BClN_6Ru$: C, 38.68; H, 4.00; N, 20.82. Found: C, 38.46; H, 4.12; N, 20.63.

RuTp(η^4-CH_2=CHC(Me)=CH_2)Cl (3). A solution of **1** (100 mg, 0.218 mmol) in xylene (5 mL) was heated at reflux for 3 h in the presence of air. The volatiles were removed in vacuo, and the residue was dissolved in MeOH under argon. Zn (200

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* Author to whom correspondence should be addressed: e-mail kkirch@fbch.tuwien.ac.at.

[†] Institute of Inorganic Chemistry.

[‡] Institute of Mineralogy, Crystallography, and Structural Chemistry.

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mg, 0.306 mmol) was added, and the mixture was stirred for 3 h at room temperature. The solvent was then removed in vacuo, and the residue was dissolved in CH_2Cl_2. Isoprene (0.110 mL, 1.09 mmol) was added, and the solution was again stirred for 12 h. Insoluble materials were removed by filtration. Removal of the solvent afforded **3** as a pale yellow solid. Purification was by recrystallization from acetone and diethyl ether. Yield: 53 mg (58%). ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.08 (d, 1H, J = 1.9 Hz), 7.76 (d, 1H, J = 1.9 Hz), 7.74 (d, 1H, J = 2.2 Hz), 7.71 (d, 1H, J = 2.8 Hz), 7.70 (d, 1H, J = 2.8 Hz), 7.09 (d, 1H, J = 2.5 Hz), 6.33 (m, 1H), 6.28 (m, 1H), 6.15 (m, 1H), 5.04 (d, 1H, J = 12.4 Hz), 4.26 (dd, J = 12.4 Hz, J = 7.1 Hz), 4.0 (d, 1H, J = 7.1), 3.87 (s, 1H), 3.85 (s, 1H), 1.91 (s, 3H). Anal. Calcd for $C_{14}H_{18}BClN_6Ru$: C, 40.26; H, 4.34; N, 20.12. Found: C, 40.12; H, 4.07; N, 20.40.

RuTp(η^4-MeCH=CHCH=CHMe)Cl (4). This complex was prepared in analogous manner as decribed for **2** substituting 1,3-butadiene by 2,4-hexadiene. Yield: 76%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.05 (s, 1H), 7.78 (s, 1H), 7.76 (s, 2H), 7.71 (s, 1H), 7.04 (s, 1H), 6.35 (s, 1H), 6.29 (s, 1H), 6.14 (s, 1H), 5.57 (dq, 1H, J_q = 6.3 Hz, J_d = 11.8 Hz), 4.53 (dd, 1H, J = 8.0 Hz, J = 12.3 Hz), 4.36 (dq, 1H, J_q = 6.0 Hz, J_d = 12.3 Hz), 4.01 (dd, 1H, J = 11.8 Hz, J = 8.0 Hz), 1.68 (d, 3H, J = 6.0 Hz), 1.33 (d, 3H, J = 6.3 Hz). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 145.1, 144.1, 142.1, 137.9, 135.9, 135.5, 107.2, 106.7, 106.6, 101.4, 97.9, 89.3, 88.7, 18.1, 18.0. Anal. Calcd for $C_{15}H_{20}BClN_6Ru$: C, 41.73; H, 4.67; N, 19.47. Found: C, 41.58; H, 4.83; N, 19.68.

RuTp(η^5-C_6H_7) (5). This complex was prepared in analogous manner as decribed for **2** substituting 1,3-butadiene by 1,3-cyclohexadiene. Yield: 73%. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 7.59 (bs, 6H), 6.16 (bs, 3H), 5.69 (t, 1H, J = 4.4 Hz), 4.57 (dd, 2H, J = 6.9 Hz, J = 4.4 Hz), 2.76 (dt, 1H, J_t = 6.0 Hz, J_d = 13.0 Hz), 2.15 (t, 2H, J = 6.0 Hz), 2.13 (d, 1H, J = 13.0 Hz). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 143.0 (bs, CH), 134.9 (CH), 105.7 (CH), 89.7 (CH), 68.5 (CH), 28.7 (CH_2), 27.3 (CH). Anal. Calcd for $C_{15}H_{17}BN_6Ru$: C, 45.82; H, 4.36; N, 21.37. Found: C, 45.63; H, 4.48; N, 21.12.

X-ray Structure Determination for 2 and 4. Crystal data and experimental details are given in Table 1. X-ray data for **2** were collected on a Siemens Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, a nominal crystal-to-detector distance of 3.85 cm, 0.3° ω-scan frames) and for **4** on a Philips PW1100 four-circle diffractometer (Mo Kα radiation, ($\theta - 2\theta$)-scans). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption (**2**) were applied.

The structure of **2** was solved by Patterson methods using program SHELXS86.[8] Structure refinement on F^2 was carried out with program SHELXL93.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. The butadiene molecule was found to show disorder. Its two inner carbon atoms displayed unusually large anisotropic temperature factors with the thermal ellipsoid main axis approximately parallel to the Ru−Cl bond. This feature was interpreted as the result of two half-occupied superimposed and approximately mirror-related *trans*-*trans*-configured butadiene molecules. It was modeled by introducing two half-occupied molecules with identical terminal C atoms, split inner C atoms, SADI[9] distance restraints for equivalent bonds (Ru−C, C−C), and EADP[9] restraints for U_{ij}.

Table 1. Crystallographic Data for RuTp(η^4-CH_2=CHCH=CH_2)Cl (2) and RuTp(η^4-MeCH=CHCH=CHMe)Cl (4)

compound	**2**	**4**
formula	$C_{13}H_{16}BClN_6Ru$	$C_{15}H_{20}BClN_6Ru$
fw	403.65	431.70
crystal size, mm	0.30 × 0.15 × 0.10	0.45 × 0.30 × 0.20
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	8.731(2)	8.986(2)
b, Å	8.855(2)	13.043(5)
c, Å	11.257(2)	15.357(6)
α, deg	89.62(2)	
β, deg	72.68(2)	105.23(1)
γ, deg	75.69(2)	
V, Å^3	803.0(3)	1736.7(10)
F(000)	404	872
Z	2	4
ρ_{calcd}, g cm^{-3}	1.670	1.651
T, K	297(2)	297(2)
μ, mm^{-1} (Mo Kα)	1.146	1.066
abs corr	empirical	none
transmission factor min/max	0.93/0.62	
θ_{max}, deg	30.0	25
index ranges	$-11 \le h \le 12$ $-12 \le k \le 12$ $0 \le l \le 15$	$0 \le h \le 10$ $0 \le k \le 15$ $-18 \le l \le 17$
no. of rflns measd	8419	3262
no. of unique rflns	4549	3062
no. of rflns $F > 4\sigma(F)$	4020	2560
no. of params	205	264
$R(F)$ ($F > 4\sigma(F)$)[a]	0.0405	0.0284
$R(F)$ (all data)[a]	0.0491	0.0381
wR(F^2) (all data)[b]	0.1039	0.0702
diff Fourier peaks min/max, e Å^{-3}	−0.66/1.54	-0.51/0.44

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

The structure of **4** was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Thermal displacement parameters and the geometry of the 2,4-hexadiene indicated the presence of disorder in the form of two superimposed and approximately mirror-related *trans*-*trans*-configured molecules (A- and B-molecule). After various test calculations, the following refinement model was selected: mirror-related atoms (e.g., C10A and C10B) were assigned identical U_{ij} (EADP restraint of SHELXL93) and chemically equivalent bond lengths were restrained to have the same lengths (SADI 0.001 restraint of SHELXL93). A single population parameter refined to 0.649(5) for the A-molecule and to 0.351(5) for the B-molecule. The hydrogen atoms of the two hexadiene molecules were refined in x, y, and z either with distance restraints for CH groups or as rigid idealized groups for CH_3. Hydrogen atoms of the Tp moiety were inserted in idealized positions and were refined riding with the atoms to which they were bonded.

Results and Discussion

Refluxing **1** in xylene in the presence of air for 3 h gives, after removal of the solvent, a dark-green paramagnetic (i.e., trivalent) complex, tentatively formulated as $[RuTp(Cl)]_x$, which, however, has not been further characterized. Redissolving this complex in MeOH and adding Zn in the presence of the diene afforded the neutral complexes RuTp(η^4-diene)Cl in 58−76% isolated yields (Scheme 1), where diene = 1,3-butadiene (**2**), isoprene (**3**), or 2,4-hexadiene (**4**). All of these complexes are white to pale-yellow air-stable solids. Characterization was by elemental analysis and ^{1}H and $^{13}C\{^1H\}$

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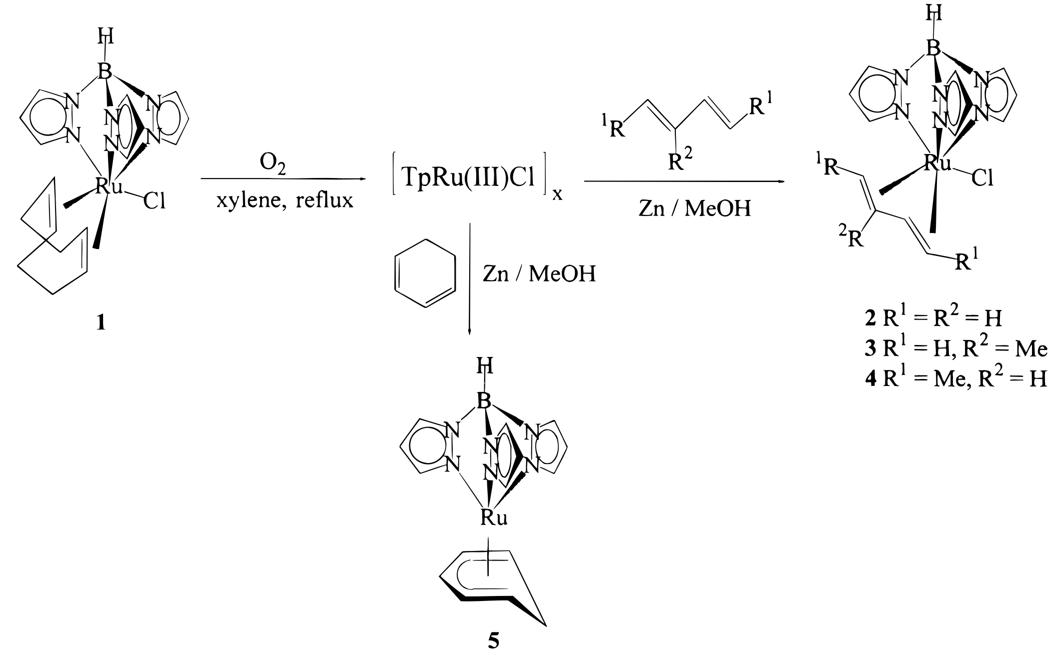
Scheme 1



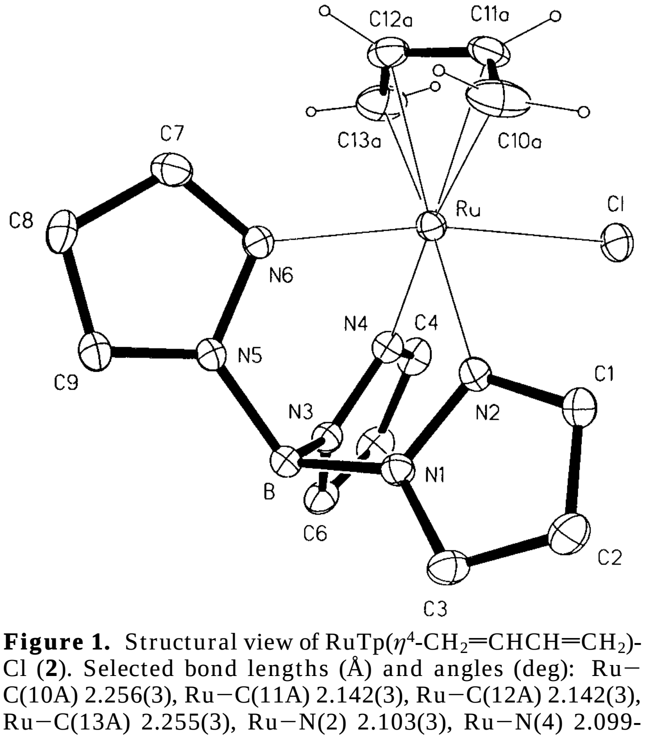


Figure 1. Structural view of RuTp(η^4-CH_2=CHCH=CH_2)Cl (**2**). Selected bond lengths (Å) and angles (deg): Ru−C(10A) 2.256(3), Ru−C(11A) 2.142(3), Ru−C(12A) 2.142(3), Ru−C(13A) 2.255(3), Ru−N(2) 2.103(3), Ru−N(4) 2.099(3), Ru−N(6) 2.109(3), Ru−Cl 2.409(1), C(10A)−C(11A) 1.297(5), C(11A)−C(12A) 1.450(8), C(12A)−C(13A) 1.297(5), C(13A)−Ru−N(2) 171.1(1), C(10A)−Ru−N(4) 171.8(2), N(2)−Ru−N(4) 83.3(1), N(2)−Ru−N(6) 86.6(1), N(4)−Ru−N(6) 86.4(1), N(2)−Ru−Cl 86.3(1), C(10A)−C(11A)−C(12A) 126.2(4), C(11A)−C(12A)−C(13A) 126.1(4).

NMR spectroscopies. Compounds **2** and **4** have also been characterized by X-ray crystallography.

A structural view of **2** is shown in Figure 1 with important bond distances and angles reported in the caption. The overall coordination geometry is approximately octahedral with η^4-*s-trans* coordination of the diene ligand. The three Ru−N(Tp) bond lengths show only minor variations and are within the range of other ruthenium Tp complexes.[1,2,10] The Ru−Cl bond distance is 2.409(1) Å. The diene ligand is nonplanar with a C(10A)−C(11A)−C(12A)−C(13A) torsion angle of 114.2(6)°. The C(10A)−C(11A)−C(12A) and C(11A)−C(12A)−C(13A) angles are 126.2(4) and 126.1(4)°, respectively. The Ru−C bond distances for the terminal carbon atoms (2.256(3) and 2.255(3) Å) are considerably longer than the Ru−C(internal) bonds (2.142(3) Å). Furthermore, the diene ligand exhibits a short−long−short pattern of C−C distances (1.297(5) vs 1.450(8) Å). A similar pattern is found in other examples of *s-trans*-diene coordination.[11−14] There are, however, also *trans*-1,3-diene complexes which show almost equal C−C bond lengths.[15] The structure of **4**, depicted in Figure 2, is very similar to that of **2**. Again, the diene adopts a *transoidal*, nonplanar arrangement with a torsion angle of 125.4(7)°. Further, the central atoms are closer to the metal center (2.153(3) Å) than are the terminal carbons (2.306(3) Å).

The ^1H and ^{13}C NMR spectroscopic properties of all three complexes **2**−**4** indicate that they retain the twisted η^4-*trans*-diene Ru configuration in solution. There is no evidence of isomerization to the *s-cis* form in contrast to the $Cp_2Zr(\eta^4$-diene) complexes.[16] The ^1H NMR spectrum of **2** displays the characteristic resonances of the diene ligand. The terminal protons give rise to four doublets centered at 5.03 (1H, H^5, $^3J_{45}$ =

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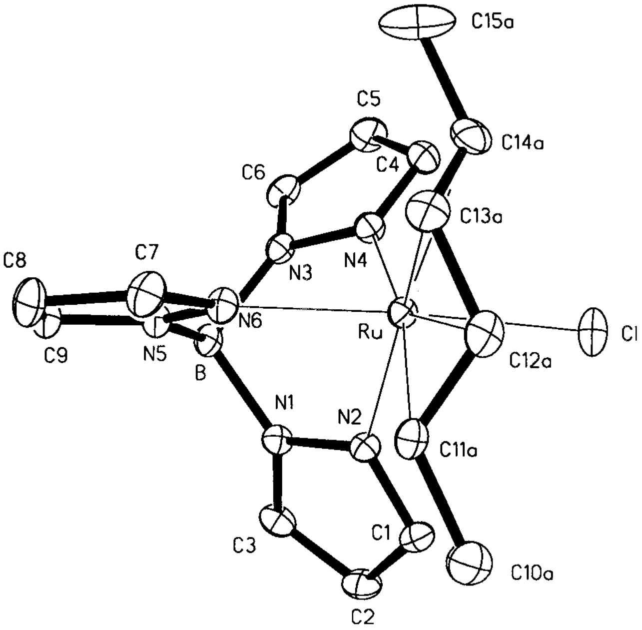

Figure 2. Structural view of RuTp(η^4-MeCH=CH-CH=CHMe)Cl (**4**). Selected bond lengths (Å) and angles (deg): Ru–C(11A) 2.306(3), Ru–C(12A) 2.153(3), Ru–C(13A) 2.153(3), Ru–C(14A) 2.306(3), Ru–N(2) 2.106(3), Ru–N(4) 2.091(3), Ru–N(6) 2.111(3), Ru–Cl 2.410(1), C(11A)–C(12A) 1.372(5), C(12A)–C(13A) 1.447(7), C(13A)–C(14A) 1372(5), C(14A)–Ru–N(2) 166.8(2), C(11A)–Ru–N(4) 169.8(1), N(2)–Ru–N(4) 82.1(1), N(2)–Ru–N(6) 86.4(1), N(4)–Ru–N(6) 87.9(1), N(2)–Ru–Cl 86.5(1), C(11A)–C(12A)–C(13A) 120.7(6), C(12A)–C(13A)–C(14A) 119.8(6).

12.3 Hz), 4.30 (1H, H^6, $^3J_{46} = 7.0$ Hz), 4.21 (1H, H^2, $^3J_{13} = 7.0$ Hz), and 3.93 (1H, H^2, $^3J_{23} = 12.8$ Hz) ppm, while the signal of the internal protons exhibt two doublets of doublets of doublets centered at 4.80 (1H, H^3, $^3J_{23} = 12.8$ Hz, $^3J_{34} = 7.0$ Hz, $^3J_{13} = 7.0$ Hz) and 4.40 (1H, H^4, $^3J_{45} = 12.3$ Hz, $^3J_{34} = 7.0$ Hz, $^3J_{46} = 7.0$ Hz) ppm. The twisted diene coordination pattern is also obvious from the small value of the vicinal *trans* coupling constant $^3J_{34} = 7.0$ Hz (and 8.0 Hz in **4**), approaching typical vicinal *cis* coupling constants. Further, the vicinal *trans* coupling constants are $^3J_{23} = 12.8$ Hz and $^3J_{46} = 12.3$ Hz. In the $^{13}C\{^1H\}$ NMR spectrum of **2**, the carbon resonances of the diene ligand are observed at 104.2, 99.6, 74.9, and 74.3 ppm. The assignment of the proton resonances of the butadiene ligand was afforded by NOE enhancement experiments. Irradiation of the Tp resonances at 8.08 and 7.81 ppm (hydrogen atoms pointing toward the metal center) showed a strong interaction between these protons and the H^2 and H^6 protons of the diene moiety (8 and 14%). The resonances of the Tp ligand are unremarkable. The NMR spectra of **3** and **4** are very similar to those obtained for **2**, with the expected modifications due to the presence of the methyl substituents.

Thus, the preference of the RuTpCl fragment to bind 1,3-dienes in the *trans* conformation is obvious. In view of this, it was of interest to exchange the acyclic for a cyclic conjugated diene, preventing *s-trans* coordination. Interestingly, following the above procedure with 1,3-cyclohexadiene creates a η^5-cyclohexadienyl ligand giving RuTp(η^5-C_6H_7) (**5**) in 73% yield (Scheme 1). This complex is already known in recent literature, arrived at, however, by another, very different, route of nucleophilic hydride attack to η^6-benzene in RuTp(η^6-C_6H_6)$^+$. The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data of **5** are in full conformity with the reported values.[17] In the present way of preparing **5**, one may wonder, however, why the reduction of cyclohexadiene stops at the cyclohexadienyl stage instead of going to benzene.[18]

The strong preference of the RuTpCl fragment to attach 1,3-dienes in a *s-trans* fashion is thus emphasized. The reason for this may be rather electronic than steric in origin. It would appear that this coordination mode is characteristic of octahedral or pseudo-octahedral ruthenium complexes bearing hard donor ligands. Recent examples include the Ru(acac)$_2$ and Ru(NH$_3$)$_4^{2+}$ fragments.[11−14] However, also in some complexes of the types RuCp*(η^4-diene)Cl and RuCp(η^4-diene)(CO) *s-trans* coordination has been reported.[7,19]

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Supporting Information Available: Listings of atomic coordinates, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **2** and **4** (17 pages). Ordering information is given on any current masthead page.

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