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References

- Alsheri, S., Burgess, J., Fawcett, J. & Russell, D. R. (1999). *Polyhedron*. Submitted.
- Fait, J. (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Johnson, J. (1970). *Crystallographic Computing*, pp. 220–226. Copenhagen: Munksgaard.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1996). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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(Acetonitrile-*N*)(η^4 -2-methylbuta-1,3-diene)(η^5 -pentamethylcyclopentadienyl)-ruthenium(II) trifluoromethanesulfonate

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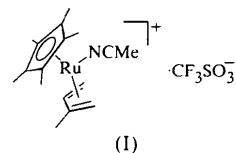
Abstract

The title compound, $[\text{Ru}\{\eta^5\text{-C}_5(\text{CH}_3)_5\}\{\eta^4\text{-CH}_2\text{C}(\text{CH}_3)\text{-CHCH}_2\}(\text{CH}_3\text{CN})](\text{CF}_3\text{SO}_3)$ or $[\text{Ru}(\text{C}_5\text{H}_8)(\text{C}_{10}\text{H}_{15})(\text{C}_2\text{H}_3\text{N})](\text{CF}_3\text{SO}_3)$, contains a half-sandwich ruthenium complex with an *exo*-oriented π -bonded diene moiety inclined at an angle of 16.0 (2)° to the cyclopentadienyl ring. The coordination geometry of ruthenium can be described as a three-legged piano stool.

Comment

Nucleophilic attack at metal-coordinated ligands is an important route in synthetic organic chemistry for obtaining new regio- and stereoselective functionalized molecules (Collman *et al.*, 1987). Such a process is particularly facile when the metal center is coordinatively saturated, substitutionally inert and sufficiently electron deficient, and when the ligand to be attacked is a conjugated or non-conjugated olefin (Davies *et al.*,

1978). Thus, cationic complexes of the type $[\text{Ru}(\eta^5\text{-Cp}^*)(\eta^4\text{-diene})(\text{CH}_3\text{CN})]^+$ (Cp* is pentamethylcyclopentadienyl) are expected to react readily with nucleophiles to give 3-allyl complexes and constitute a good model system for mechanistic studies. In this context and in the context of related work (Gemel *et al.*, 1996, 1997), the title compound, (acetonitrile-*N*)(η^4 -2-methylbuta-1,3-diene)(η^5 -pentamethylcyclopentadienyl)-ruthenium(II) trifluoromethanesulfonate, (I), was studied by X-ray diffraction.



A view of (I) is shown in Fig. 1. The Ru—C bond lengths exhibit a comparatively narrow spread of 2.180 (3)–2.241 (3) Å for the cyclopentadienyl moiety and 2.173 (3)–2.242 (3) Å for the 2-methylbutadiene moiety. A moderate asymmetry in the Ru—C bond lengths (Table 1) should stem from repulsive interactions between the methyl groups of Cp* and the 2-methylbutadiene moiety. The Cp* moiety shows mean values for cyclic and exocyclic C—C bonds of 1.426 (14) and 1.504 (4) Å, respectively. The 2-methylbutadiene moiety is *exo*-oriented and adopts a staggered configuration relative to the Cp* unit. The angle between the least-squares planes through the cyclopentadienyl ring and the 2-methylbutadiene C atoms is 16.0 (2)°. The diene exhibits the expected short–long–short pattern of bond lengths (Table 1). Its terminal CH₂ groups were refined with respect to H-atom positions and adopt orientations indicating that the Ru atom polarizes the diene π -electron system considerably and alters the hybridization of C11 and C14 from pure sp^2 in the free diene towards sp^3 in the π -bonded diene [note that the CH₂ groups in Fig. 1 are distinctly inclined to the diene least-squares plane by 34 (2)° for C11H₂ and 35 (2)° for C14H₂]. This corroborates earlier findings on two related neutral complexes, namely $[\text{Ru}(\eta^5\text{-Cp}^*)(\eta^4\text{-butadiene})(\eta^1\text{-OSO}_2\text{CF}_3)]$ and $[\text{Ru}(\eta^5\text{-Cp}^*)(\eta^4\text{-butadiene})(\eta^1\text{-OCOFCF}_3)]$ (Gemel *et al.*, 1997), which also show a staggered orientation of butadiene *versus* Cp*, but which display larger inclination angles between the Cp* and butadiene moieties of 20.2 and 19.7°, respectively. It should be mentioned that the *exo*-orientation of the butadiene in the title compound and these two complexes is controlled by the electron configuration at the divalent ruthenium center. In corresponding complexes of tetravalent ruthenium, *e.g.* $[\text{Ru}(\eta^5\text{-Cp}^*)(\eta^4\text{-2,3-dimethylbutadiene})\text{Br}_2]^+$ (Gemel *et al.*, 1996), the butadiene moiety is reverted relative to Fig. 1, *i.e.* with the terminal C atoms of the butadiene on the left side of the figure and the inner C atoms on the right side (*endo* orientation). In compounds of this type, the inclination

between the Cp* and butadiene moieties is distinctly greater than in the title compound (about 36°), and the difference between the Ru—C bonds to terminal and non-terminal C atoms (2.18 and 2.41 Å, respectively) is consistent with a metallacycle-like bonding character of the diene.

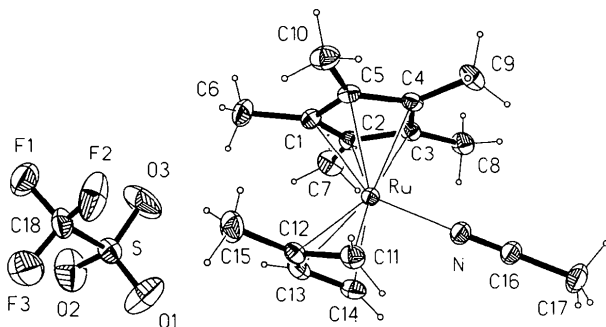


Fig. 1. The molecular diagram of (I). Displacement ellipsoids are drawn at the 20% probability level and H atoms are drawn as small circles of arbitrary radii. The disordered CF₃SO₃⁻ group is shown only in its dominant orientation.

Experimental

The title compound was prepared by treating [Ru{η⁵-C₅(CH₃)₅}{η²-CH₂C(CH₃)CHCH₂}]Cl (Fagan *et al.*, 1990) with one equivalent of AgCF₃SO₃ in CH₃CN. Crystals were obtained by slow diffusion of diethyl ether into the resulting solution.

Crystal data

[Ru(C ₅ H ₈)(C ₁₀ H ₁₅)- (C ₂ H ₃ N)](CF ₃ SO ₃)	Mo Kα radiation
<i>M_r</i> = 494.53	λ = 0.71073 Å
Triclinic	Cell parameters from 28 reflections
<i>P</i> 1̄	θ = 15–21°
<i>a</i> = 8.178 (2) Å	μ = 0.876 mm ⁻¹
<i>b</i> = 10.674 (3) Å	<i>T</i> = 297 (2) K
<i>c</i> = 12.992 (3) Å	Plate
α = 75.79 (1)°	0.44 × 0.30 × 0.10 mm
β = 75.94 (1)°	Yellow
γ = 88.62 (1)°	
<i>V</i> = 1065.7 (5) Å ³	
<i>Z</i> = 2	
<i>D_x</i> = 1.541 Mg m ⁻³	
<i>D_m</i> not measured	

Data collection

Philips PW1100 four-circle diffractometer	3413 reflections with <i>I</i> > 2σ(<i>I</i>)
ω–2θ scans	θ _{max} = 25.04°
Absorption correction: Gaussian (SHELX76; Sheldrick, 1976)	<i>h</i> = 0 → 9
<i>T</i> _{min} = 0.79, <i>T</i> _{max} = 0.92	<i>k</i> = –12 → 12
3759 measured reflections	<i>l</i> = –14 → 15
3759 independent reflections	3 standard reflections frequency: 120 min intensity decay: 0.6%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.030
wR(*F*²) = 0.077
S = 1.062
 3759 reflections
 280 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.5182P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.003
 Δρ_{max} = 0.534 e Å⁻³
 Δρ_{min} = –0.483 e Å⁻³
 Extinction correction: SHELX97
 Extinction coefficient: 0.0014 (7)
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ru—C1	2.224 (3)	C4—C5	1.414 (4)
Ru—C2	2.201 (3)	C4—C9	1.497 (4)
Ru—C3	2.180 (3)	C5—C10	1.508 (5)
Ru—C4	2.201 (3)	C11—C12	1.397 (5)
Ru—C5	2.241 (3)	C12—C13	1.433 (5)
Ru—C11	2.242 (3)	C12—C15	1.489 (5)
Ru—C12	2.234 (3)	C13—C14	1.390 (5)
Ru—C13	2.173 (3)	N—C16	1.134 (4)
Ru—C14	2.203 (3)	C16—C17	1.456 (5)
Ru—N	2.059 (3)	S—O1	1.390 (5)
C1—C2	1.427 (5)	S—O2	1.365 (5)
C1—C5	1.427 (5)	S—O3	1.365 (5)
C1—C6	1.506 (5)	S—C18	1.787 (6)
C2—C3	1.411 (4)	C18—F1	1.320 (7)
C2—C7	1.508 (4)	C18—F2	1.303 (6)
C3—C4	1.451 (4)	C18—F3	1.310 (7)
C3—C8	1.501 (4)		
C11—C12—C13	118.9 (3)	C12—C13—C14	121.6 (3)
C11—C12—C15	121.1 (3)	Ru—N—C16	175.4 (3)
C13—C12—C15	119.8 (3)	N—C16—C17	178.8 (4)

The CF₃SO₃⁻ anion was disordered over two positions rotated against each other about the C—S bond axis by approximately 180° and showing occupancy factors of 0.775 (3) and 0.225 (3). The anion was refined using hard *U_{ij}* restraints for corresponding atom pairs and soft distance-equality restraints for 1–2 (σ = 0.02 Å) and 1–3 distances (σ = 0.04 Å). H atoms were refined as parts of idealized and rigid CH₂ and CH₃ groups, and with a riding model for CH [*U*(H) = 1.2*U*_{eq}(C) for CH and CH₂ and *U*(H) = 1.5*U*_{eq}(C) for CH₃].

Data collection: SERVER4 (Mereiter & Völlenklee, 1990). Cell refinement: LLSQ6 (Mereiter & Völlenklee, 1990). Data reduction: PW115 (Mereiter & Völlenklee, 1990). Program(s) used to solve structure: SHELX97 (Sheldrick, 1997). Program(s) used to refine structure: SHELX97. Molecular graphics: SHELXTL (Siemens, 1994). Software used to prepare material for publication: SHELX97.

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References

- Collman, J. P., Hegedus, L. S., Norton, J. R. & Finke, R. G. (1987). In *Principles and Application of Organotransition Chemistry*, 2nd ed. Mill Valley, CA: University Science Books.

- Davies, S. G., Green, M. H. L. & Mingos, D. M. P. (1978). *Tetrahedron*, **34**, 3047–3077.
- Fagan, P. J., Mahoney, W. S., Calabrese, J. C. & Williams, I. D. (1990). *Organometallics*, **9**, 1843–1852.
- Gemel, C., Kalt, D., Mereiter, K., Sapunov, V. N., Schmid, R. & Kirchner, K. (1997). *Organometallics*, **16**, 427–433.
- Gemel, C., Mereiter, K., Schmid, R. & Kirchner, K. (1996). *Organometallics*, **15**, 532–542.
- Mereiter, K. & Völlenkne, H. (1990). *SERVER4, PW115 and LLSQ6. PC Programs for Controlling a PW1100 Four-Circle Diffractometer, for Data Reduction and for Unit-Cell Least-Squares Refinement*. Technical University of Vienna, Austria.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. University of Cambridge, England.
- Sheldrick, G. M. (1997). *SHELX97. Program System for the Determination and Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Ternary lanthanide complexes of hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate (Tp^{py}) and anionic O,O-bidentate chelates: [Tb(Tp^{py})(dbm)₂] and [Eu(Tp^{py})(trop)(NO₃)] (Hdbm is dibenzoylmethane and Htrop is tropolone)

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Abstract

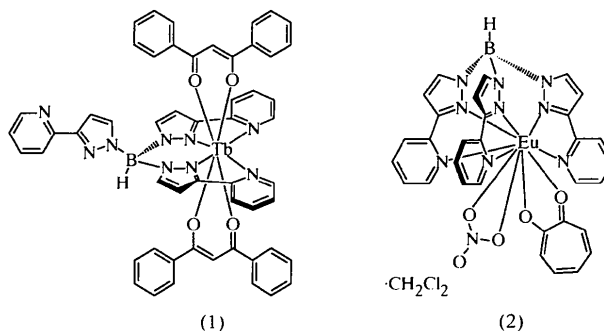
The reaction of lanthanide(III) salts with the potentially hexadentate podand ligand hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate (Tp^{py}) and either dibenzoylmethane (Hdbm) or tropolone (Htrop) afforded bis(1,3-diphenyl-1,3-propanedionato-*O,O'*){hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate}terbium(III), [Tb(C₂₄H₁₉BN₉)(C₁₅H₁₁O₂)₂], and {hydrotris[3-(2-pyridyl)pyrazol-1-yl]borate}(2-hydroxycyclohepta-2,4,6-trien-1-onato-*O,O'*)(nitrate-*O,O'*)europium(III) dichloromethane solvate, [Eu(C₂₄H₁₉BN₉)(C₇H₅O₂)(NO₃)]·CH₂Cl₂, respectively. The former complex is eight-coordinate involving two bidentate dbm ligands and one Tp^{py} ligand which is only tetradentate with one bidentate arm pendant. In contrast, the latter complex is ten-coordinate, with Tp^{py} coordinated in its usual hexadentate mode, with, in addition, one bidentate nitrate ion and one bidentate tropolonate anion.

Comment

We have been interested in the structures and luminescence properties of complexes of lanthanide(III) ions, especially Tb^{III} and Eu^{III}, with podand ligands based on poly(pyrazolyl)borates (Jones *et al.*, 1997; Bardwell *et al.*, 1997; Armaroli *et al.*, 1997; Harden *et al.*, 1998; Reeves *et al.*, 1999). Generally, the complexes contain two types of ligand: one or two of the poly(pyrazolyl)borate ligands (depending on its denticity) and additional nitrate ligands which complete the coordination sphere and render the complexes neutral.

We thought that a simple way to extend the chemistry of these complexes would be to replace the nitrate ions with other chelating anionic O-donor ligands; obvious possibilities are carboxylates, catecholates, acetylacetonates and related ligands. A particular appeal of this is that binucleating bridging ligands containing two separate bidentate chelating sites based on these donor types are well known, so if we could attach one such bidentate chelating ligand to the {Ln(Tp^{py})}²⁺ core then, in principle, use of an appropriate bridging ligand containing two such binding sites might lead to dinuclear complexes. Accordingly, we investigated the reactions of lanthanide(III) salts with Tp^{py} in the presence of either dibenzoylmethane (Hdbm) or tropolone (Htrop) to investigate the possible formation and structures of new ternary complexes.

The reaction of terbium(III) chloride hydrate, K[Tp^{py}] and Hdbm (1:1:2 molar ratio), and a few drops of triethylamine in aqueous MeOH afforded a pale yellow precipitate. The fast atom bombardment (FAB) mass spectrum showed a strong peak at *m/z* = 826, corresponding to loss of one dbm ligand from the molecule to give the fragment {Tb(Tp^{py})(dbm)}⁺. X-ray quality crystals were grown by recrystallization from a CH₂Cl₂/hexane mixture; the structure of the complex is shown in Fig. 1, confirming the formulation of the complex as [Tb(Tp^{py})(dbm)₂], (1).



The Tb^{III} centre is in an eight-coordinate N₄O₄ environment arising from two bidentate dbm ligands and one Tp^{py} ligand which is only tetradentate with one bidentate arm being pendant (this behaviour is called 'hypodentate'). In all of its previously structurally characterized complexes with lanthanides, Tp^{py} has