[(η⁶-Cyclooctatetraene){η⁵-(+)-neomenthylcyclopentadienyl}ruthenium(II)] Hexafluorophosphate: Synthesis and Characterization of a Chiral Mixed Sandwich Complex

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Dedicated to Prof. Dr. Rüdiger Mews on the occasion of his 60th birthday

Keywords: Chirality / Cyclopentadienyl ligands / Sandwich complexes / Ruthenium

Three different {η⁵-(+)-neomenthylcyclopentadienyl}ruthenium complexes have been synthesized from (–)-menthol: [(η⁶-benzene){η⁵-(+)-neomenthylcyclopentadienyl}ruthenium(II)] hexafluorophosphate (**1**), [tris(acetonitrile){η⁵-(+)-neomenthylcyclopentadienyl}ruthenium(II)] hexafluorophosphate (**2**) and [(η⁶-cyclooctatetraene){η⁵-(+)-neomenthylcyclopentadienyl}ruthenium(II)] hexafluorophosphate (**3**). X-ray structural determination (space group $P2_12_12_1$) and NMR spectroscopic studies of **3** show it exists as a single stereoisomer in both the solid and solution phase, with $[\alpha]_D^{20} = +92.5$. The chiral modification of the Cp ligand induces anisochrony for all of the magnetically active nuclei of the unsubstituted COT ligand.

Introduction

Iterative nucleophilic and electrophilic addition to a coordinated cyclooctatetraene (COT) in $[(\eta^6\text{-COT})(\eta^5\text{-Cp})M]^+$ (Cp = cyclopentadienyl; M = Fe, Ru) has been shown to be a powerful tool for the formation of stereo- and regioselectively substituted cycloocta-1,3-dienes.[1,2] Since the first nucleophilic addition creates a stereogenic carbon atom in the *cyclo*-C_8 ligand (Figure 1), we attempted to synthesize a starting COT complex containing a chiral modified Cp ligand, which would be expected to influence the stereochemical selectivity of the initial nucleophilic addition. We chose the (+)-neomenthyl substituent as a chiral auxiliary on the cyclopentadienyl ring [(+)-NMCp];[3] this has widely been used in the synthesis of Cp complexes active in enantioselective transformations.[4]

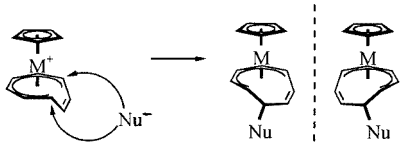

Figure 1. Nucleophilic attack on the two enantiotopic sites in $[(\eta^6\text{-COT})(\eta^5\text{-Cp})M]^+$ (M = Fe, Ru)

Results and Discussion

Synthesis

(+)-Neomenthylcyclopentadiene [(+)-NMCpH] was prepared according to a known procedure[3] and subsequently transformed into the thallium salt by addition of TlOEt (Scheme 1).

The thallium salt [(+)-NMCp]Tl reacts with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ [5] in acetonitrile, yielding $[(\eta^6\text{-}C_6H_6)\{\eta^5\text{-}(+)\text{-NMCp}\}Ru]X$ [X = Cl, Scheme 1, b; X = PF_6 (**1**), Scheme 1, c]. Irradiation of complex **1** in acetonitrile with a high-pressure mercury lamp gives the {η⁵-(+)-NMCp}Ru half-sandwich complex **2**. Addition of COT to a solution of **2** in acetonitrile affords product **3** as a light yellow powder in very good yields. Crystals of **3** are air-stable and soluble in dichloromethane but almost insoluble in diethyl ether.

X-ray Structure Analysis

Crystals of **3** suitable for X-ray structural analysis were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **3** at room temperature. Data collection parameters and selected bond lengths and angles are listed in Table 1 and Table 2, respectively. Complex **3** crystallizes in the chiral orthorhombic space group $P2_12_12_1$. The cation (Fig-

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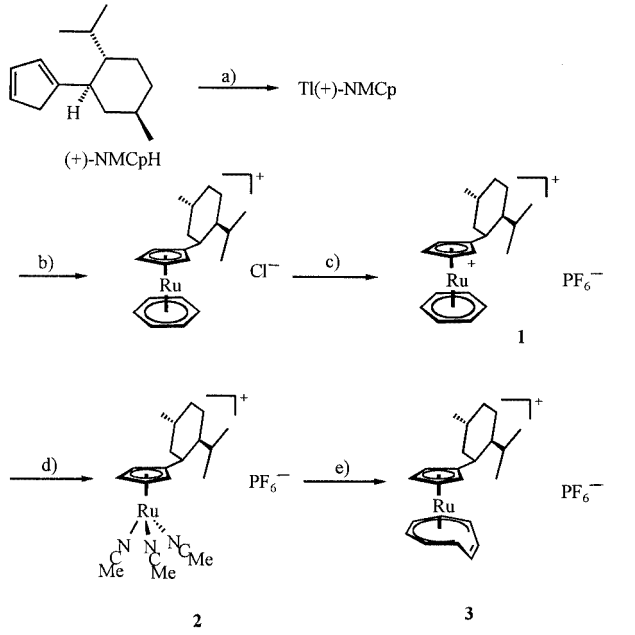

Scheme 1. Synthesis of [(η⁶-cyclooctatetraene){η⁵-(+)-neomenthylcyclopentadienyl}ruthenium(II)] hexafluorophosphate (**3**): a) TlOEt, THF, room temperature; b) MeCN, $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, room temperature; c) MeOH, NH_4PF_6; d) MeCN, hν; e) COT, MeCN

ure 2) adopts a typical sandwich-like structure with the Cp ligand and the η⁶-coordinated part of the COT ligand almost parallel. The uncoordinated double bond of the COT ligand, C7−C8, protrudes from the plane of the metal-bound carbon atoms *exo* with respect to the metal center. The dihedral angle between the "best" planes of the coordinated carbon atoms C1−C2−C5−C6 and of the carbon atoms C1−C6−C7−C8 is 120°, very similar to the corresponding structural feature in $[(\eta^6\text{-COT})(\eta^5\text{-Cp})Fe]^+$.[6] The COT ring exhibits slight rotational disorder by a torsion around the axis connecting the Ru atom and the six coordinated carbon atoms. This results in large anisotropic temperature factors for the atoms in the COT ring and a very short C7−C8 bond length of 128.9(3) pm (typical C=C double bond length of 134 pm).

Attempts to resolve this disorder did not improve the model; the *R*1 value rises about 0.5% and standard deviations increase as well. Most notably, the C7−C8 bond lengths in the disordered model were not chemically sensible; a nondisordered model was thus used and refined anisotropically. The Ru−C(COT) bond lengths of 214.1−222.6 pm are in the typical range of cationic $(\eta^6\text{-}cyclo\text{-}C_8)Ru$ complexes.[1b] The distances between the Ru center and the carbon atoms of the Cp ligand of 218.1(2)−222.98(19) pm correspond to Ru−C(Cp) bond lengths of other cationic CpRu complexes[7] except for the bond to C9 [226.14(16) pm], the atom which bears the (+)-neomenthyl substituent. This slight elongation of the Ru−C9 bond may be due to packing effects within the crystal.

Table 1. Crystal data and structure refinement for [(η⁶-cyclooctatetraene){η⁵-(+)-neomenthylcyclopentadienyl}ruthenium(II)] hexafluorophosphate (**3**)

	3
Empirical formula	$C_{23}H_{31}F_6PRu$
Formula mass	553.52
T [K]	153(2)
λ [pm]	71.073
Crystal system	orthorhombic *P*
Space group	$P2_12_12_1$
a [pm]	1062.36(6)
b [pm]	1211.68(7)
c [pm]	1769.78(11)
V [10^6 pm^3]	2278.1(2)
Z	4
$\rho_{calcd.}$ [Mg/m^3]	1.614
μ [mm^{-1}]	0.815
F(000)	1128
Crystal size [mm]	0.3 × 0.3 × 0.1
Scan range [°]	2.30−27.99
Index range	$-14 \le h \le 14$ $-16 \le k \le 15$ $-22 \le l \le 23$
Reflections measured	27406
Reflections unique	5218
R_{int}	0.0397
Parameters	308
Reflections [$I > 4\,\sigma(I)$]	5218
GoF[a]	1.052
$R1/wR^2$ [$I > 2\sigma(I)$][b]	0.0227/0.0581
$R1/wR^2$ (all data)[b]	0.0233/0.0584
Residual min./max. [e/Å^3]	0.452/−0.342

[a] GoF (goodness of fit) = $[\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = numbers of reflections, p = numbers of parameters). [b] Weight = $1/[\sigma^2(F_o^2) + 0.0351 \times P)^2 + 0.440P]$, $P = [\max(F_o^2,0) + 2\,F_c^2]/3$.

Table 2. Selected bond lengths [pm] and angles [°] for [(η⁶-cyclooctatetraene){η⁵-(+)-neomenthylcyclopentadienyl}ruthenium(II)] hexafluorophosphate (**3**)

Ru1−C1	222.62	C2−C3	141.9(5)
Ru1−C2	214.1(2)	C3−C4	142.8(5)
Ru1−C3	220.2(2)	C4−C5	140.3(6)
Ru1−C4	220.9(3)	C5−C6	139.5(4)
Ru1−C5	215.7(2)	C6−C7	148.5(3)
Ru1−C6	222.0(2)	C7−C8	128.9(3)
Ru1−C9	226.14(16)	C9−C13	142.2(3)
Ru1−C10	218.57(19)	C9−C10	144.2(3)
Ru1−C11	218.1(2)	C9−C14	152.7(2)
Ru1−C12	220.0(2)	C10−C11	143.0(3)
Ru1−C13	222.98(19)	C11−C12	142.0(3)
C1−C2	139.0(4)	C12−C13	143.0(3)
C1−C8	148.6(3)		
Xa−Ru1−Xb[a]	166.7		
P1[b]−P2[c]	120.0		
P2−P3[d]	156.7		

[a] Xa, Xb = pivots of the Cp ligand and coordinated part of the COT ligand, respectively. [b] P1: Best plane of C1, C2, C5, C6. [c] P2: Best plane of C1, C6, C7, C8. [d] P3: Best plane of C2, C3, C4, C5.

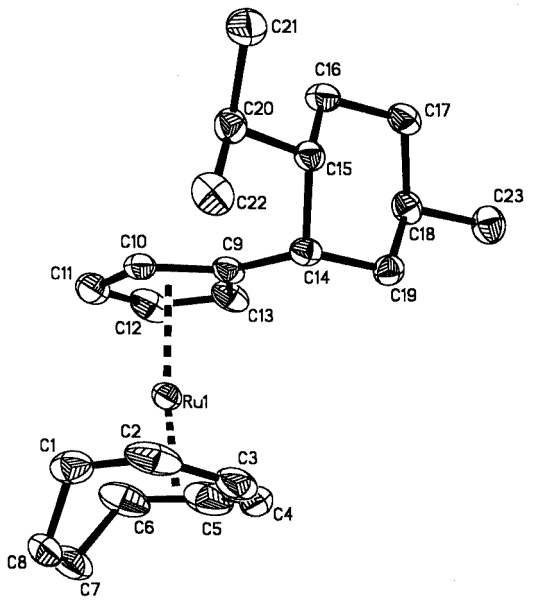

Figure 2. Molecular structure of [(η^6-cyclooctatetraene){η^5-(+)-neomenthylcyclopentadienyl}ruthenium(II)] hexafluorophosphate (**3**); thermal ellipsoids are drawn at the 50% probability level and the hydrogen atoms and the PF_6^- counterion are omitted for clarity

The most important result of this structural analysis is the unambiguous identification of the presence of only one stereoisomer, the (+)-neomenthyl derivative; this is also confirmed by ^1H and ^{13}C NMR spectra of **3** (vide infra). The (+)-neomenthyl substituent adopts a conformation which places it at the most remote position with respect to the sandwich moiety.

NMR Spectroscopy

Complex **3** displays ^1H and ^{13}C NMR signals due to the (+)-neomenthyl substituent (^1H: δ = 0.7−2.9 ppm; ^{13}C: δ = 20−50 ppm), and the Cp and COT ligands (^1H: δ = 5.0−6.3 ppm; ^{13}C: δ = 82−138 ppm). The ^1H and ^{13}C chemical shifts of the metal-bound hydrocarbon units clearly testify to the cationic nature of **3**,[1b] and the number of signals confirms the formation of a single stereoisomer. Due to the chiral (+)-neomenthyl substituent all of the Cp protons are inequivalent and give rise to four multiplets in the range δ = 5.3−5.6 ppm, consistent with the chemical shifts observed in other monocationic CpRu sandwich complexes.[1,8]

Remarkably, the chiral (+)-neomenthyl substituent also induces anisochrony in all of the nuclei of the COT ligand. In Figure 3, both experimental (bottom) and calculated (top) ^1H NMR spectra of the COT region display signals due to eight chemically inequivalent hydrogen atoms. Even the uncoordinated C=C double bond, which is most distant from the chiral neomenthyl group, displays two different resonance signals in the ^1H and ^{13}C NMR spectra (δ = 5.0840 and 5.0934 ppm for 7-H and 8-H, δ =134.99 and 135.07 ppm for C-7 and C-8). The largest shift difference of the resonance signals of nuclei which are equivalent in the COT ligand of a corresponding complex without a chiral induction, for example [(η^5-Cp)Ru(η^6-COT)]$^+$, is found for 1-H and 6-H (δ = 5.6937 and 5.7903 ppm), and C-3 and C-4 (δ = 104.1 and 103.2 ppm).

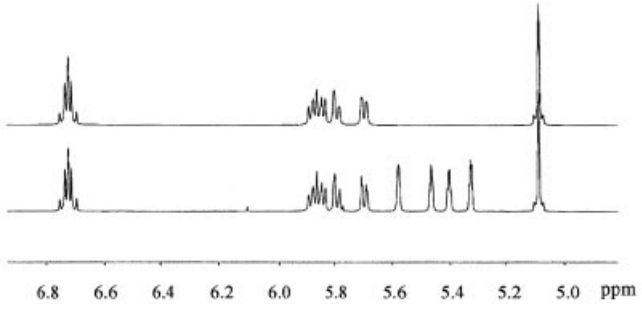

Figure 3. Experimental (bottom) and calculated (top) ^1H NMR spectra of [(η^6-cyclooctatetraene){η^5-(+)-neomenthylcyclopentadienyl}ruthenium(II)] hexafluorophosphate (**3**); signals due to theCp ligand are omitted from the calculated spectrum for simplicity [parameters used for the calculation: δ = 5.0840, 5.0934 (7-H, 8-H), 5.6937, 5.7903 (1-H, 6-H), 5.8419, 5.8717 (2-H, 5-H), 6.7085, 6.7294 ppm (3-H, 4-H); $^3J_{1\text{-}2}$ = 8.474, $^3J_{1\text{-}8}$ = 2.644, $^3J_{2\text{-}3}$ = 6.940, $^3J_{3\text{-}4}$ = 8.963, $^3J_{4\text{-}5}$ = 6.968, $^3J_{5\text{-}6}$ = 8.764, $^3J_{6\text{-}7}$ = 2.514, $^3J_{7\text{-}8}$ = 6.558 Hz; significant changes in the calculated spectra are observed on changing the shifts by 0.001 ppm and the coupling constants by 0.001 Hz]

Optical Activity

A specific optical rotation of $[\alpha]_D^{20}$= +92.5 was determined for **3**. The optical activity of complex **3** is consistent with a Cotton effect observed in CD spectra of **3**, which is negative for the electronic absorption at higher energy (λ = 267 nm: [θ] = −6760 °·L·mol^{-1}·cm^{-1}) and positive at lower energy (λ = 325 nm: [θ] = +3500 °·L·mol^{-1}·cm^{-1}). Since the molar extinction coefficient of these absorption bands is very low [ε (267 nm) = 1726 L·mol^{-1}·cm^{-1}; ε (325 nm) = 673 L·mol^{-1}·cm^{-1}], we assign these Cotton effects to d-d transitions.

Conclusions

The introduction of the chiral (+)-neomenthyl substituent on the cyclopentadienyl ligand allows the synthesis of the [(η^6-cyclooctatetraene){η^5-(+)-neomenthylcyclopentadienyl}ruthenium(II)] cation, which is the first structurally characterized chiral cyclooctatetraene complex. The chiral Cp ligand even induces inequivalence at all positions of the COT ligand as demonstrated by NMR experiments. This inequivalence suggests that chiral induction in nucleophilic additions to the COT ligand may be possible, and this is currently under investigation.

Experimental Section

General: All reactions were carried out under nitrogen. Solvents were saturated with nitrogen and freshly distilled from an appropriate drying agent. NMR: Bruker WM 500, AM 360 and Varian

Gemini 200. IR (KBr disks): FT-IR 1720 X (Perkin−Elmer). UV/Vis (MeCN solution): Perkin−Elmer, Model 554. CD (MeCN solution): Jasco, Model J 500-C. Elemental analysis: Heraeus-CHN-O-Rapid (Zentrale Elementanalytik, Fachbereich Chemie, Universität Hamburg). (+)-Neomenthylcyclopentadiene[3] and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ [5] were synthesized according to literature procedures. $RuCl_3{\cdot}xH_2O$ was a gift from Degussa AG. Cyclohexadiene and TlOEt were purchased from Aldrich and Merck, respectively.

[(+)-Neomenthylcyclopentadienyl]thallium: A solution of TlOEt (4.0 mL, 56.1 mmol) in THF (10 mL) was added to a solution of (+)-NMCpH (11.27 g, 55.1 mmol) in THF (120 mL) at room temperature. After stirring for 17 h, about 100 mL of the solvent was evaporated in vacuo. The resulting off-white precipitate was collected on a filter and washed with small amounts of toluene. The solid material was dried in vacuo. Yield: 6.98 g (31.1%) of [(+)-NMCp]Tl. The product is air-sensitive and was used without further purification.

[(η^6-Benzene){η^5-(+)-neomenthylcyclopentadienyl}ruthenium(II)] Hexafluorophosphate (1): Solid [(+)-NMCp]Tl (5.9 g, 14.47 mmol) was added to a suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (3.14 g, 6.28 mmol) in acetonitrile (300 mL). After stirring at room temperature for 20 h, the reaction mixture was filtered through Celite and the filter was washed four times with 10 mL of acetonitrile. The acetonitrile solution was concentrated to dryness, and the residue was dissolved in absolute methanol (40 mL). Solid NH_4PF_6 (2.21 g, 13.56 mmol) was added to the methanol solution, whereupon the product precipitated. After 3.5 h of stirring, the reaction mixture was filtered, and the solid material was washed three times with methanol and once with diethyl ether. The light yellow solid material was dried in vacuo yielding 4.30 g (64.9%) of **1**. IR: $\tilde{\nu}$ = 3094 (m), 2943 (s), 2871 (m), 2845 (m), 1443 (s), 1410 (m), 1391 (m), 1382 (w), 1367 (w), 840 (broad vs), 558 (vs), 443 (m), 423 (m) cm^{-1}. ^1H NMR (360 MHz, CD_3CN): δ = 0.727 (d, ^3J = 6.5 Hz, 3 H, Me), 0.882 (d, ^3J = 6.4 Hz, 3 H, Me), 0.930 (d, ^3J = 6.3 Hz, 3 H, Me), 0.84−1.17 [m, 3 H, (+)-neomenthyl], 1.22 [m, 1 H, (+)-neomenthyl], 1.60−1.82 [m, 4 H, (+)-neomenthyl], 2.80 [m, 1 H, (+)-neomenthyl], 5.21 (m, 1 H, Cp), 5.25 (m, 1 H, Cp), 5.32 (m, 1 H, Cp), 5.44 (m, 1 H, Cp), 6.10 (s, 6 H, C_6H_6) ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 20.76, 22.05, 23.02, 24.87, 28.42, 30.26, 35.78, 36.26, 44.25, 48.46 [(+)-neomenthyl], 79.05 (Cp), 80.46 (Cp), 82.37 (Cp), 83.48 (Cp), 87.13 (C_6H_6), 118.25 (C_qCp) ppm. $C_{21}H_{29}F_6PRu$ (527.50): calcd. C 47.82, H 5.54; found C 48.18, H 5.74.

[Tris(acetonitrile){η^5-(+)-neomenthylcyclopentadienyl}-ruthenium(II)] Hexafluorophosphate by Photolysis of 1: A solution of **1** (3.62 g, 6.86 mmol) in acetonitrile (300 mL) was irradiated with a high-pressure Hg lamp for 26 h. The solution was then concentrated to dryness and the residue identified as $[(MeCN)_3(\eta^5\text{-}NMCp)Ru]PF_6$ (**2**) by means of ^1H NMR spectroscopy. This was used for the reaction with COT (vide infra) without further purification. ^1H NMR (200 MHz, CD_2Cl_2): δ = 0.84 (d, ^3J = 6.2 Hz, Me), 0.95 (d, ^3J = 6.2 Hz, Me), 0.97 (d, ^3J = 6.2 Hz, Me), 0.9−1.7 [m, 9 H, (+)-neomenthyl], 2.44 (s, 9 H, MeCN), 2.7 [m, 1 H, (+)-neomenthyl], 4.13 (m, 1 H, Cp), 4.21 (m, 1 H, Cp), 4.30 (m, 1 H, Cp), 4.51 (m, 1 H, Cp) ppm.

[(η^6-Cyclooctatetraene){η^5-(+)-neomenthylcyclopentadienyl}-ruthenium(II)] Hexafluorophosphate (3): COT (3.1 mL, 27.6 mmol) was added to a solution of **2** (3.9 g, 6.8 mmol) in acetonitrile (180 mL). The solution was stirred overnight at room temperature and then concentrated to dryness. The residue was suspended in a mixture of diethyl ether (10 mL) and CH_2Cl_2 (4 mL). The light yellow solid material was filtered and dried in vacuo. Yield: 3.5 g (93%) of **3** as a light yellow powder. IR (KBr): $\tilde{\nu}$ = 3130 (m), 2974 (s), 2952 (s), 2924 (s), 2868 (s), 2853 (s), 2844 (m), 1690 (m), 1460 (s), 1447 (m), 1401 (m), 1386 (s), 1370 (m), 1332 (m), 1148 (m), 831 (vs), 798 (s), 742 (m), 640 (w), 558 (vs), 519 (w), 427 (m), 421 (m) cm^{-1}. ^1H NMR (500 MHz, CD_3CN): δ = 0.709 (d, ^3J = 6.4 Hz, 3 H, Me), 0.874 (d, ^3J = 6.1 Hz, 3 H, Me), 0.929 (d, ^3J = 6.1, 3 H, Me), 0.9−1.5 [m, 3 H, (+)-neomenthyl], 1.28 [m, 1 H, (+)-neomenthyl], 1.44 [m, 1 H, (+)-neomenthyl], 1.65 [m, 2 H, (+)-neomenthyl], 1.82 [m, 1 H, (+)-neomenthyl], 1.97 [m, 1 H, (+)-neomenthyl], 2.87 [m, 1 H, (+)-neomenthyl], 5.084 (m, 1 H, 7-H or 8-H), 5.093 (m, 1 H, 8-H or 7-H), 5.33 (m, 1 H, Cp), 5.40 (m, 1 H, Cp), 5.46 (m, 1 H, Cp), 5.57 (m, 1 H, Cp), 5.694 (dm, 1 H, 1H or 6-H), 5.790 (dm, 1 H, 6-H or 1-H), 5.842 (m, 1 H, 2-H or 5-H), 5.872 (m, 1 H, 5H or 2H), 6.709 (m, 1 H, 3-H or 4-H), 6.729 (m, 1 H, 4-H or 5-H) ppm (the chemical shifts for the COT protons were taken from the calculated spectra, see Figure 3). ^{13}C NMR (50 MHz, CD_3CN): δ = 20.6, 22.0, 22.9, 24.8, 28.7, 30.2, 35.7, 36.3, 43.8, 48.5, [(+)-neomenthyl], 83.0, 84.3, 84.9, 86.9 (Cp), 88.7, 88.9, 94.1, 94.5, 103.2, 104.1 (COT), 114.3 (C_qCp), 134.99, 135.07 (COT) ppm. $[\alpha]_D^{20}$ = +92.5 (*c* = 0.6, CH_2Cl_2). CD (MeCN): λ_{max} (ε, [θ]) = 267 (1726, −6760), 325 (673, +3500) nm ($L{\cdot}mol^{-1}{\cdot}cm^{-1}$, $°{\cdot}L{\cdot}mol^{-1}{\cdot}cm^{-1}$). $C_{23}H_{31}F_6PRu$ (553.52): calcd. C 49.91, H 5.64; found C 49.14, H 5.71.

X-ray Structural Analysis of 3: Suitable crystals were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **3**. Determination of cell parameters and collection of reflection intensities were carried out using a Bruker−Apex three-circle diffractometer with a CCD detector at −120 °C. An absorption correction was applied using the SADABS Program (see Table 1). The structure was solved by direct methods using SHELXS-97[9] and refined using SHELXL-97.[10] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions using a riding model approach. For more details see Table 1. CCDC-188541 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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