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Crystallographic report

Crystal structures of organometallic aqua complexes $[Cp^*Rh^{III}(bpy)(OH_2)]^{2+}$ and $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)]^{2+}$ used as key catalysts in regioselective reduction of NAD^+ analogues

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Crystal structures of organometallic aqua complexes $[Cp^*Rh^{III}(bpy)(OH_2)]^{2+}$ (1, Cp* = η^5-C_5Me_5, bpy = 2,2′-bipyridine) and $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)]^{2+}$ (2, 6,6′-Me_2bpy = 6,6′-dimethyl-2,2′-bipyridine) used as key catalysts in regioselective reduction of NAD^+ analogues were determined definitely by X-ray analysis. The yellow crystals of $1(PF_6)_2$ and orange crystals of $2(CF_3SO_3)_2$ used in the X-ray analysis were obtained from aqueous solutions of $1(PF_6)_2$ and $2(CF_3SO_3)_2$. The Rh–O_{aqua} length of 2.194(4) Å obtained for $1(PF_6)_2$ is significantly different from that of 2.157(3) Å obtained for the previously reported disorder model $[Cp^*Rh^{III}(bpy)(0.7H_2O/0.3CH_3OH)](CF_3SO_3)_2{\cdot}0.7H_2O$ in which the coordinated water is replaced by a coordinated methanol. The five-membered ring involving the Rh atom and the 6,6′-Me_2bpy chelating unit in $2(CF_3SO_3)_2$ is not flat, whereas the five-membered chelate ring in $1(PF_6)_2$ is nearly flat. Such a non-planar structure in $2(CF_3SO_3)_2$ is ascribed to the steric repulsion between the 6,6′-Me_2bpy ligand and the Cp* ligand. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: crystal structures; rhodium; aqua complexes; substituted bipyridine ligand

INTRODUCTION

Development of water-soluble organometallic catalysts is a worthy endeavour because of the many potential advantages, such as alleviation of environmental problems associated with the use of organic solvents and reaction-specific pH selectivity.[1–12] Pioneering studies on regioselective reduction of nicotinamide adenine dinucleotide (NAD^+) to NADH catalysed by water-soluble organometallic complexes have been made by Steckhan *et al.* and Fish *et al.*[13–23] They have demonstrated that a series of organorhodium aqua complexes such as $[Cp^*Rh^{III}(bpy)(OH_2)]^{2+}$ (**1**, Cp* = η^5-C_5Me_5, bpy = 2,2′-bipyridine) and $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)]^{2+}$ (**2**, 6,6′-Me_2bpy = 6,6′-dimethyl-2,2′-bipyridine) act as water-stable starting compounds to generate the corresponding hydride species $[Cp^*Rh^{III}(bpy)(H)]^+$ and $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(H)]^+$ in the catalytic cycle in water. In these studies, the structures of the aqua complexes **1** and **2** were determined by ^{1}H NMR.[16]

Fish *et al.* have succeeded in X-ray crystal structure analysis of **1** as a disorder model $[Cp^*Rh^{III}(bpy)(0.7H_2O/0.3CH_3OH)](CF_3SO_3)_2{\cdot}0.7H_2O$, in which the coordinated water is replaced by a coordinated methanol.[20] The relative occupancies were refined, then fixed,

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at $0.7H_2O/0.3CH_3OH$. There is also a water of solvation that is required to be absent when methanol is present; consequently, it is included at 0.7 occupancy. However, the definitive structures of **1** and **2** have yet to be disclosed by X-ray analysis.

We report herein the X-ray crystal structures of **1**$(PF_6)_2$ and **2**$(CF_3SO_3)_2$ used as the key catalysts in the regioselective reduction of NAD^+ analogues. The yellow crystals of **1**$(PF_6)_2$ and orange crystals of **2**$(CF_3SO_3)_2$ used in the X-ray analysis were obtained from aqueous solutions of **1**$(PF_6)_2$ and **2**$(CF_3SO_3)_2$. The structurally large difference between **1**$(PF_6)_2$ and the previously reported disorder model $[Cp^*Rh^{III}(bpy)(0.7H_2O/0.3CH_3OH)](CF_3SO_3)_2\cdot 0.7H_2O$ is described. Intriguingly, the five-membered ring formed by the Rh atom and the 6, 6′-Me$_2$bpy chelating unit in **2**$(CF_3SO_3)_2$ is not flat, whereas the five-membered chelate ring in **1**$(PF_6)_2$ is nearly flat. The difference in the coordination geometry between **1**$(PF_6)_2$ and **2**$(CF_3SO_3)_2$ is discussed on the basis of the steric repulsion between the Cp* ligand and the bpy or 6, 6′-Me$_2$bpy ligand.

EXPERIMENTAL

Materials and methods

D_2O (99.9% D) was purchased from Cambridge Isotope Laboratories. Purification of water (18.2 MΩ·cm) was performed with a Milli-Q system (Millipore; Milli-RO 5 plus and -Q plus). The ^1H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer at 20 °C. The ^1H NMR experiments in D_2O were performed by dissolving the samples in D_2O in an NMR tube (diameter = 5.0 mm) with a sealed capillary tube (diameter = 1.5 mm) containing 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP, as reference with the methyl proton resonance set at 0.00 ppm) dissolved in D_2O (10 mM). Complex $[Cp^*Rh^{III}(OH_2)_2(SO_4)]$ was prepared according to the literature.[24,25]

$[Cp^*Rh^{III}(bpy)(OH_2)](X)_n$ (i.e. $1(X)_n$, where X = SO_4 ($n = 1$) or PF_6 ($n = 2$))

A solution of $[Cp^*Rh^{III}(OH_2)_2(SO_4)]$ (100 mg, 0.270 mmol) and bpy (42.2 mg, 0.270 mmol) in H_2O (25 ml) was stirred at ambient temperature for 4 h under an Ar atmosphere. The solvent was evaporated under reduced pressure to yield an orange powder of **1**(SO_4), which was dried *in vacuo* (yield 95% based on $[Cp^*Rh^{III}(OH_2)_2(SO_4)]$).

^1H NMR (300 MHz, in D_2O, reference to TSP in D_2O): $\delta = 1.71$ (s, 15H, CH_3 of Cp*), 7.93 (t, $J = 6.6$ Hz, 2H, CH of bpy), 8.34 (t, $J = 7.9$ Hz, 2H, CH of bpy), 8.48 (d, $J = 8.1$ Hz, 2H, CH of bpy), 9.14 (d, $J = 5.3$ Hz, 2H, CH of bpy) ppm. Addition of NH_4PF_6 into an aqueous solution of **1**(SO_4) gave a powder of **1**$(PF_6)_2$. Anal. (calc.) for $C_{20}H_{25}N_2OF_{12}P_2Rh$: C, 34.21; H, 3.59; N, 3.99%. Found: C, 34.06; H, 3.54; N, 3.99%.

$[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)](X)_n$ (i.e. $2(X)_n$, where X = SO_4 ($n = 1$) or CF_3SO_3 ($n = 2$))

An orange powder of **2**(SO_4) was obtained by the same method as for **1**(SO_4) (yield 94% based on $[Cp^*Rh^{III}(OH_2)_2(SO_4)]$).

^1H NMR (300 MHz, in D_2O, reference to TSP in D_2O): $\delta = 1.34$ (s, 15H, CH_3 of Cp*), 2.88 (s, 6H, CH_3 of 6, 6′-Me$_2$bpy), 7.66 (d, $J = 7.9$ Hz, 2H, CH of 6, 6′-Me$_2$bpy), 8.03 (t, $J = 7.9$ Hz, 2H, CH of 6, 6′-Me$_2$bpy), 8.15 (d, $J = 7.9$ Hz, 2H, CH of 6, 6′-Me$_2$bpy) ppm. Addition of CF_3SO_3Na into an aqueous solution of **2**(SO_4) gave a powder of **2**$(CF_3SO_3)_2$. Anal. (calc.) for $C_{24}H_{29}N_2F_6O_7RhS_2$: C, 39.03; H, 3.96; N, 3.79%. Found: C, 38.86; H, 3.85; N, 3.80%.

X-ray crystallographic analysis

X-ray quality crystals of **1**$(PF_6)_2$ and **2**$(CF_3SO_3)_2$ were prepared by recrystallization from their aqueous solutions. Measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$). Data were collected and processed using the CrystalClear program (Rigaku). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Crystal data, data collection parameters, structure solution and refinement for all complexes were summarized in Table 1. More detailed information such as atomic coordinates, anisotropic displacement parameters and full bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-246087 and CCDC-246088, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data for $[Cp^*Rh^{III}(bpy)(OH_2)](PF_6)_2$ (i.e. **1**$(PF_6)_2$) and $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)](CF_3SO_3)_2$ (i.e. **2**$(CF_3SO_3)_2$)

	1$(PF_6)_2$	**2**$(CF_3SO_3)_2$
Empirical formula	$C_{20}H_{25}N_2OP_2F_{12}Rh$	$C_{24}H_{29}N_2O_7F_6S_2Rh$
Formula weight	702.26	738.52
Crystal dimensions (mm)	0.44 × 0.07 × 0.04	0.44 × 0.19 × 0.10
Temperature (°C)	−100.0	−100.0
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	11.123(4)	10.083(1)
b (Å)	15.743(6)	31.785(2)
c (Å)	14.956(5)	10.514(1)
β (deg)	88.656(5)	116.639(4)
V (Å^3)	2618(1)	3012.0(5)
Z	4	4
D_{calc} (g cm^{-3})	1.782	1.628
F_{000}	1400	1496
μ (Mo Kα) (cm^{-1})	8.76	7.85
No. of reflections observed (all, $2\theta < 54.97$)	5959	6827
No. of parameters	349	385
R^a	0.089	0.073
$R_w{}^b$	0.174	0.130
$R1^c$	0.059	0.046
Goodness-of-fit indicator	1.12	1.01
Max. peak in final difference map (e Å^{-3})	1.30	1.13
Min. peak in final difference map (e Å^{-3})	−1.01	−0.70

[a] $R = \Sigma(F_o{}^2 - F_c{}^2)/\Sigma F_o{}^2$.

[b] $R_w = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

[c] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2.0\sigma(I)$ data.

RESULTS AND DISCUSSION

Water-soluble rhodium(III) aqua complexes $[Cp^*Rh^{III}(bpy)(OH_2)]SO_4$ (i.e. **1**(SO_4)) and $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)]SO_4$ (i.e. **2**(SO_4)) were prepared by reactions of $[Cp^*Rh^{III}(OH_2)_2(SO_4)]$ with equimolar amount of bpy or 6, 6′-Me_2bpy, respectively.[9,11,18–23,26–28] Anion exchanges of **1**(SO_4) and **2**(SO_4) with NH_4PF_6 and CF_3SO_3Na in water gave the less-soluble complexes $[Cp^*Rh^{III}(bpy)(OH_2)](PF_6)_2$ (i.e. **1**$(PF_6)_2$) and $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)](CF_3SO_3)_2$ (i.e. **2**$(CF_3SO_3)_2$), respectively.

Yellow crystals of **1**$(PF_6)_2$ for the X-ray analysis were obtained from an aqueous solution of **1**$(PF_6)_2$. The crystal structure of **1**$(PF_6)_2$ is shown in Fig. 1. Selected bond lengths and angles are summarized in Table 2. Complex **1** adopts a distorted octahedral geometry that is surrounded by one Cp*, one bpy and one H_2O ligand. Fish *et al.* have reported previously the crystal structure of $[Cp^*Rh^{III}(bpy)(0.7H_2O/0.3CH_3OH)](CF_3SO_3)_2{\cdot}0.7H_2O$ as a disorder model for **1** in which the coordinated water is replaced by a coordinated methanol. The relative occupancies were refined and then fixed at $0.7H_2O/0.3CH_3OH$.[20] It is important to note that the bond lengths and angles in **1**(SO_4) are very different from those in the disorder model $[Cp^*Rh^{III}(bpy)(0.7H_2O/0.3CH_3OH)](CF_3SO_3)_2{\cdot}0.7H_2O$. In particular, the $Rh{-}O_{aqua}$ length of 2.194(4) Å in **1**$(PF_6)_2$ is significantly longer than that of 2.157(3) Å in the disorder model for **1**.

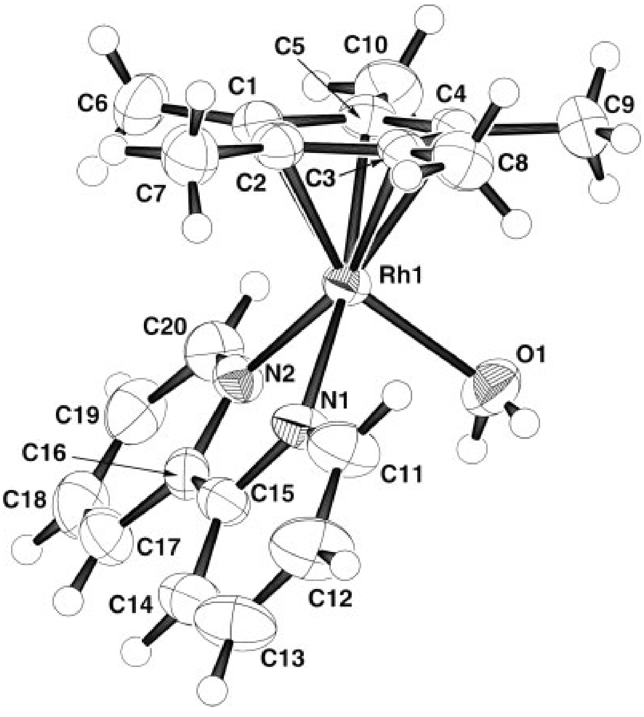

Figure 1. An ORTEP drawing of $[Cp^*Rh^{III}(bpy)(OH_2)](PF_6)_2$, i.e. **1**$(PF_6)_2$. The counter-ions (PF_6) are omitted for clarity.

Table 2. Selected bond lengths λ (Å) and angles ϕ (deg) of $[Cp^*Rh^{III}(bpy)(OH_2)](PF_6)_2$ (i.e. **1**$(PF_6)_2$) and $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)](CF_3SO_3)_2$ (i.e. **2**$(CF_3SO_3)_2$)

1$(PF_6)_2$			
Rh1–O1	2.194(4)	Rh1–N1	2.114(4)
Rh1–N2	2.114(4)	Rh1–C1	2.138(5)
Rh1–C2	2.146(5)	Rh1–C3	2.170(4)
Rh1–C4	2.182(5)	Rh1–C5	2.140(5)
O1–Rh1–N1	86.8(2)	O1–Rh1–N2	86.9(2)
O1–Rh1–C1	144.4(2)	O1–Rh1–C2	152.3(2)
O1–Rh1–C3	113.0(2)	O1–Rh1–C4	91.8(2)
O1–Rh1–C5	105.9(2)	N1–Rh1–N2	77.1(2)
N1–Rh1–C1	128.6(2)	N1–Rh1–C2	100.9(2)
N1–Rh1–C3	106.3(2)	N1–Rh1–C4	139.2(2)
N1–Rh1–C5	166.6(2)	N2–Rh1–C1	96.8(2)
N2–Rh1–C2	120.7(2)	N2–Rh1–C3	159.8(2)
N2–Rh1–C4	143.6(2)	N2–Rh1–C5	107.2(2)
C1–Rh1–C2	39.1(2)	C1–Rh1–C3	65.3(2)
C1–Rh1–C4	64.6(2)	C1–Rh1–C5	39.2(2)
C2–Rh1–C3	39.3(2)	C2–Rh1–C4	64.9(2)
C2–Rh1–C5	65.8(2)	C3–Rh1–C4	38.2(2)
C3–Rh1–C5	65.3(2)	C4–Rh1–C5	38.7(2)
2$(CF_3SO_3)_2$			
Rh1–O1	2.113(4)	Rh1–N1	2.121(3)
Rh1–N2	2.122(3)	Rh1–C1	2.123(4)
Rh1–C2	2.165(4)	Rh1–C3	2.153(4)
Rh1–C4	2.167(4)	Rh1–C5	2.173(4)
O1–Rh1–N1	86.7(2)	O1–Rh1–N2	88.6(2)
O1–Rh1–C1	165.9(1)	O1–Rh1–C2	134.3(2)
O1–Rh1–C3	102.3(2)	O1–Rh1–C4	101.2(2)
O1–Rh1–C5	130.5(2)	N1–Rh1–N2	75.6(1)
N1–Rh1–C1	105.4(1)	N1–Rh1–C2	95.8(1)
N1–Rh1–C3	120.1(2)	N1–Rh1–C4	158.5(2)
N1–Rh1–C5	142.3(1)	N2–Rh1–C1	101.2(1)
N2–Rh1–C2	136.3(1)	N2–Rh1–C3	160.9(1)
N2–Rh1–C4	124.1(2)	N2–Rh1–C5	96.7(1)
C1–Rh1–C2	39.0(1)	C1–Rh1–C3	65.6(1)
C1–Rh1–C4	64.9(1)	C1–Rh1–C5	38.9(1)
C2–Rh1–C3	38.6(2)	C2–Rh1–C4	64.3(2)
C2–Rh1–C5	64.1(2)	C3–Rh1–C4	38.9(2)
C3–Rh1–C5	64.3(2)	C4–Rh1–C5	37.7(2)

Orange crystals of **2**$(CF_3SO_3)_2$ used in X-ray analysis were obtained from an aqueous solution of **2**$(CF_3SO_3)_2$. An ORTEP drawing of **2**$(CF_3SO_3)_2$ is shown in Fig. 2 and selected bond lengths and angles are shown in Table 2. The coordination geometry of **2**$(CF_3SO_3)_2$ with the 6, 6′-Me_2bpy ligand is significantly different from **1**$(PF_6)_2$ with the bpy ligand. As shown in Fig. 3, the Rh1, N1, C15, C16 and N2 atoms in the five-membered chelate ring in **2**$(CF_3SO_3)_2$ does not lie in the plane, although the five atoms in **1**$(PF_6)_2$ do nearly lie in the plane. The dihedral angle of $\phi_1 = 151.6(2)^\circ$ between the N1, C15, C16 and N2 least-squares plane and the Rh1,

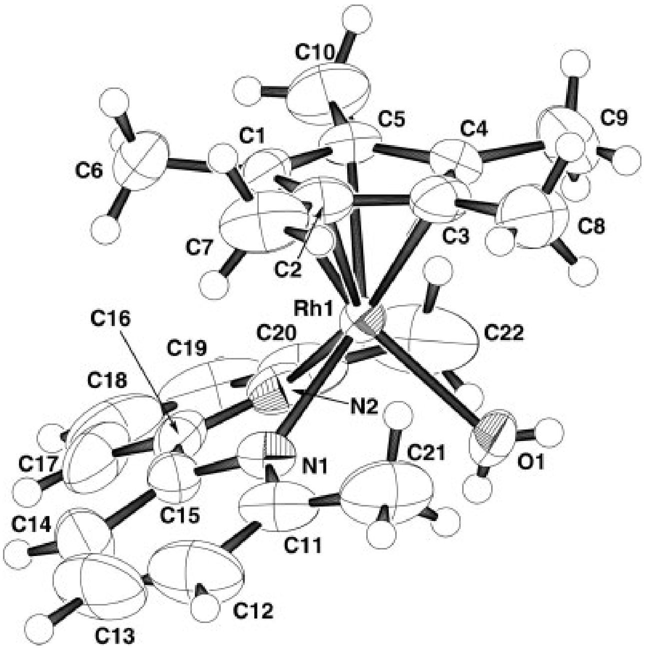

Figure 2. An ORTEP drawing of $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)(OH_2)](CF_3SO_3)_2$, i.e. $\mathbf{2}(CF_3SO_3)_2$. The counter-ions (CF_3SO_3) are omitted for clarity.

Table 3. Dihedral angles ϕ_1, ϕ_2 and ϕ_3 (deg) for **1** and **2**

	R = H (**1**)	R = Me (**2**)
ϕ_1	175.2(2)	151.6(2)
ϕ_2	57.5(2)	51.0(1)
ϕ_3	52.7(3)	22.6(2)

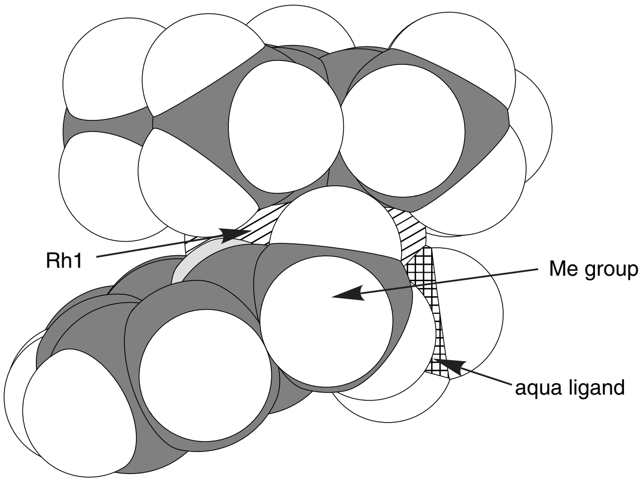

Figure 4. Space-filling model of $[Cp^*Rh(6,6'\text{-}Me_2bpy)(OH_2)]^{2+}$ (**2**).

N1 and N2 plane in $\mathbf{2}(CF_3SO_3)_2$ is considerably smaller than that of $\phi_1 = 175.2(2)°$ in $\mathbf{1}(PF_6)_2$ (Table 3). As depicted by a space-filling model for **2**, the unusual coordination of the 6, 6′-Me_2bpy ligand in $\mathbf{2}(CF_3SO_3)_2$ is attributable to the steric repulsion between the Cp* ligand and the two methyl groups of the 6, 6′-Me_2bpy ligand (Fig. 4).

Although there is no significant difference in the Rh–C and Rh–N bond lengths between $\mathbf{1}(PF_6)_2$ and $\mathbf{2}(CF_3SO_3)_2$, the $Rh\text{–}O_{aqua}$ bond length of $\mathbf{2}(CF_3SO_3)_2$ (2.113(4) Å) is considerably shorter than that of $\mathbf{1}(PF_6)_2$ (2.194(4) Å). This indicates that the Lewis acidity of the rhodium centre of **2** is higher than that of **1**. Steckhan *et al.* have reported previously that the hydride complex $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)H]^+$ is relatively stable in water, although the bpy analogue $[Cp^*Rh^{III}(bpy)H]^+$ cannot be observed in water.[16] The higher Lewis acidity of the rhodium centre of $[Cp^*Rh^{III}(6,6'\text{-}Me_2bpy)H]^+$ should stabilize the Rh–H bond to give the robust hydride complex in water.

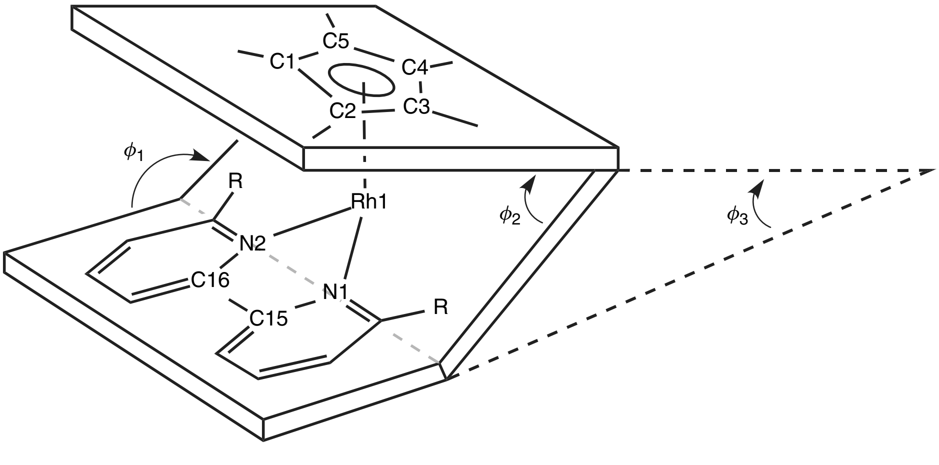

Figure 3. Dihedral angles between planes N1–C15–C16–N2 and Rh1–N1–N2 (ϕ_1), Rh1–N1–N2 and η^6-C_6Me_6 (ϕ_2) and N1–C15–C16–N2 and η^6-C_6Me_6 (ϕ_3). R = H (for **1**) or Me (for **2**).

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