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Stability of the silicon–ruthenium bond in the presence of a strong nucleophile. Phase sensitive ^{1}H NMR COSY and crystal structure of $Ru(CO)_2(NH_2CH_2C_6H_5)_2(Si(C_6H_5)(CH_3)_2)I$ [†]

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Abstract

The ruthenium(II) complex $Ru(CO)_2(NH_2(NH_2CH_2C_6H_5)_2(Si(C_6H_5)(CH_3)_2)I$ has been prepared by the reaction of $Ru(CO)_4(Si(C_6H_5)(CH_3)_2)I$ with benzylamine. Two-dimensional homonuclear ^{1}H NMR experiments examine the scalar coupling of the enantiotopic amino and methylene protons of the benzylamine ligand. X-ray analysis of $Ru(CO)_2(NH_2CH_2C_6H_5)_2(Si(C_6H_5)(CH_3)_2)I \cdot 1/3C_5H_{12}$ (triclinic; $P\bar{1}$; $a = 14.266(4)$, $b = 15.748(5)$, $c = 20.082(6)$ Å; $\alpha = 94.38(3)$, $\beta = 96.30(2)$, $\gamma = 101.52(2)°$) indicates three crystallographically unique complexes form a clathrate with a pentane guest.

1. Introduction

Silicon–transition metal compounds typically form simple adducts with Lewis bases [1]. The tendency to form an adduct decreases as the Lewis basicity decreases [2]. In reactions involving primary or secondary amines, intermediate adducts may be observed; however, the reaction ultimately leads to the cleavage of the silicon–metal bond [1d, 3]. In this paper we report the reaction of $Ru(CO)_4(Si(C_6H_5)(CH_3)_2)I$ with benzylamine ($BzNH_2$) which results in the formation of $Ru(CO)_2(NH_2CH_2C_6H_5)_2(Si(C_6H_5)(CH_3)_2)I$ (eqn. (1) rather than the elimination of a silanamine (eqn. (2)).

$$Ru(CO)_4(SiR_3)I + 2BzNH_2 \rightarrow Ru(CO)_2(BzNH_2)_2(SiR_3)I + 2\,CO \quad (1)$$

$$Ru(CO)_4(SiR_3)I + BzNH_2 \rightarrow HRu(CO)_4I + BzNHSiR_3 \quad (2)$$

X-ray crystallographic and NMR spectroscopic analysis of $Ru(CO)_2(NH_2CH_2C_6H_5)_2(Si(C_6H_5)(CH_3)_2)I$ will address the inequivalence of the two methylene and the inequivalence of the two amino protons of the benzylamine ligands which, in the ^{1}H NMR spectra, result in a four spin system with six coupling constants.

2. Experimental section

All manipulations were carried out under an atmosphere of purified argon, with the use of standard Schlenk techniques, or in a helium-filled drybox. All chemicals were reagent grade or better. Solvents were distilled from appropriate drying agents under an argon atmosphere. Dimethylphenylsilane (Petrarch), benzylamine (Aldrich), and benzene-d_6 (Aldrich) were vacuum distilled from CaH_2. $Ru_3(CO)_{12}$ (Strem) was recrystallized from acetone and dried under vacuum.

All NMR experiments were carried out on a Bruker Model MSL-300 (300.1 MHz) spectrometer. IR spectra were recorded on a Perkin-Elmer 1800 spectrometer. Elemental analyses were performed by Galbraith Laboratories. The compounds $[Ru(CO)_4(SiPhMe_2)]_2$ and $Ru(CO)_4(SiPhMe_2)I$ were prepared by adapting procedures described for analogous compounds [4].

2.1. *Synthesis of* $[Ru(CO)_4(SiPhMe_2)]_2$ *(1)*

A medium-walled glass tube, equipped with a high vacuum stopcock, was charged with 1.00 g (1.56 mmole)

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[†] This paper is dedicated to the memory of Dr. John C. Cooper.

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of Ru$_3$(CO)$_{12}$, 2.50 ml (16.3 mmole) of HSiMe$_2$Ph and 5.0 ml of heptane. The suspension was degassed and then placed in an 90°C oil bath. After 30 min the tube was removed from the bath, and upon cooling, a yellow solid formed. The yellow solid was dissolved in cyclohexane and filtered through a fine glass frit. Solvent volume was reduced to 10 ml under reduced pressure. A fine crystalline sample of [Ru(CO)$_4$(SiPhMe$_2$)]$_2$ was collected by vacuum filtration and washed with pentane. Yield: 1.31 g (80%). IR (cyclohexane): ν(CO) 2047w, 2018s, 2007wsh cm^{-1}. ^{1}H NMR (C$_6$D$_6$): 0.83 (s), 7.5–7.0 (m) ppm. Anal. Found: C, 41.28; H, 3.11; Si, 8.03 C$_{24}$H$_{22}$O$_8$Ru$_2$Si$_2$ calcd.: C, 41.37; H, 3.18; Si, 8.06%.

2.2. Synthesis of Ru(CO)$_4$(SiPhMe$_2$)I (2)

A suspension of 0.354 g (0.508 mmole) of [Ru(CO)$_4$(SiPhMe$_2$)]$_2$ in 20 ml of cyclopentane was cooled to −10°C using an EtOH/ice bath. Iodine (0.129 g, 0.508 mmole) was added to the suspension and the reaction mixture was stirred at −10°C for 1 h. The solution was filtered and then cooled to −78°C. The fine yellow precipitate of Ru(CO)$_4$(SiPhMe$_2$)I was collected by vacuum filtration and dried under vacuum. Yield: 0.197 g (41%). IR (cyclopentane) ν(CO) 2058 s, 2019w cm^{-1}. ^{1}NMR (C$_6$D$_6$): 0.69 (s), 7.0–7.5 (m) ppm.

2.3. Synthesis of Ru(CO)$_2$(NH$_2$CH$_2$C$_6$H$_5$)$_2$(Si(C$_6$-H$_5$)(CH$_3$)$_2$)I (3)

Benzylamine (0.50 ml, 4.6 mmole) was added to 0.384 g (0.808 mmole) of Ru(CO)$_4$(SiPhMe$_2$)I dissolved in 75 ml of pentane. The bright yellow solution immediately changed to a cloudy white solution from which colorless crystals slowly separated. The crystalline solid, Ru(CO)$_2$-(NH$_2$CH$_2$C$_6$H$_5$)$_2$(SiPhMe$_2$)I, was collected by vacuum filtration, washed with pentane and dried under vacuum. Yield: 0.545 g (98%). Crystallographic grade crystals were grown by the slow diffusion of pentane into a saturated toluene solution of the complex. IR (cyclohexane): ν(CO) 2022s, 1959s cm^{-1}. ^{1}NMR (C$_6$D$_6$): 0.62 (5, 6H), 1.66 (tbr, 2H), 2.05 (tbr, 2H), 3.15 (td, 2H), 4.13 (td, 2H), 6.8–7.4(m) ppm. ^{13}C NMR (C$_6$D$_6$): 2.47(q), 52.34(t), 127–134(m) 142.02(s) 144.50(s), 201.05(s)ppm. Anal. Found: C, 46.73; H, 4.87; N, 4.25. C$_{24}$H$_{29}$IN$_2$O$_2$RuSi · 1/3C$_5$H$_{12}$ calcd.: C, 46.88; H, 5.06; N, 4.26%.

3. X-Ray crystallographic study of Ru(CO)$_2$(NH$_2$CH$_2$C$_6$H$_5$)$_2$(Si(C$_6$H$_5$)(CH$_3$)$_2$)I · 1/3C$_5$H$_{12}$

A single crystal of dimensions 0.15 × 0.16 × 0.43 mm was used for data collection on a Siemens R3m/V automated diffractometer using incident beam graphite-monochromated Mo Kα radiation. The triclinic unit cell parameters were determined from a least-squares treatment of 25 centered reflections where $24 \leq 2\theta \leq 28°$. The structure solution and E value statistics determine the space group as $P\bar{1}$. Data were collected by the θ-2θ scan method to a $2\theta_{max} = 45°$ covering the range, $-15 \leq h \leq 15$, $0 \leq k \leq 16$, $-21 \leq l \leq 21$. Standards were monitored every 100 relfections and a 2.9% random variation was observed over data collection. The scan width was [2θ(K$_{\alpha1}$) − 1.0] to [2θ(K$_{\alpha2}$) + 1.0]° and the θ scan rate was fixed at 10.0° per minute. There were 11498 reflections measured of which there were 11478 unique ($R_{int} = 4.5\%$) and 8565 observed with $F_o > 3\sigma(F_o)$. The data were corrected for Lorentz, polarization, and absorption effects.

The structure was solved with direct methods, and all remaining atoms were located in Fourier difference maps. The block diagonal matrix least-squares refinement [5] minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$ and $g = 0.00023$. There was a total of 894 parameters refined. These include atomic coordinates and anisotropic thermal parameters for all but the hydrogen atoms. The hydrogen atoms were placed in idealized positions and then allowed to ride on the carbons to which they are bonded. The coordinate shift of the carbon atoms was applied to the bonded hydrogen with C–H = 0.96 Å. Amine hydrogen positions were refined with fixed isotropic thermal parameters. Maximum and minimum difference Fourier peaks were 0.86 and −1.21 eÅ^{-3} near iodine, $R(F) = 0.049$, $wR(F) = 0.045$, and the error in an observation of unit weight, S, was 1.45. Atomic scattering factors are from the *International Tables for X-ray Crystallography* (1974) [6].

4. Results and discussion

The reactivity of Ru(CO)$_4$(Si(C$_6$H$_5$)(CH$_3$)$_2$I (**2**) in the presence of benzylamine is in marked contrast to that of [Ru(CO)$_4$(Si(C$_6$H$_5$)(CH$_3$)$_2$)]$_2$ (**1**). While benzylamine readily reacts with **1** to produce PhMe$_2$SiNHCH$_2$C$_6$H$_5$ [3c,4b], **2** undergoes a rapid ligand substitution reaction which yields the disubstituted complex. Even in the presence of a large excess of benzylamine, the sole reaction product is Ru(CO)$_2$(NH$_2$CH$_2$C$_6$H$_5$)$_2$(Si(C$_6$H$_5$)(CH$_3$)$_2$)I which can be isolated in near quantitative yields.

The difference in the reactivity of **1** and **2** may, in part, be attributed to two factors. First, the change in oxidation state and the replacement of the metal–metal bond, in **1**, with the electronegative iodo ligand, in **2**, weakens the ruthenium–carbon bond, as evidenced by the energy change of the carbon–oxygen stretch. Second, the low cohesive energy density of the solvent favors the ligand substitution reaction [7].

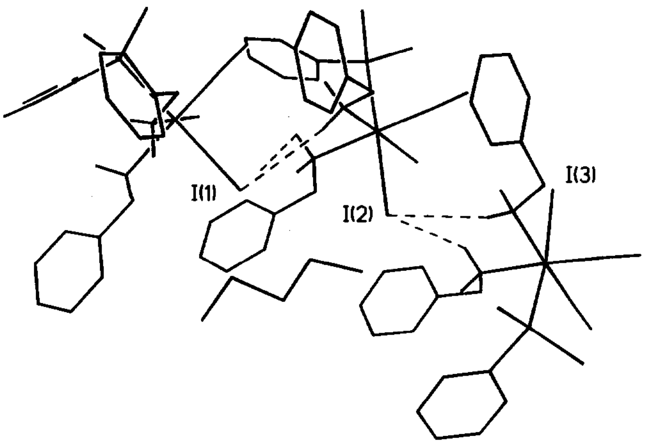

Fig. 1. Line drawing of asymmetric unit with all but amine hydrogens omitted for clarity. Dotted lines indicate hydrogen bonding.

4.1. X-Ray structure analysis of $Ru(CO)_2(NH_2CH_2C_6H_5)(Si(C_6H_5)(CH_3)_2)I \cdot 1/3C_5H_{12}$

Compound **3** crystallizes in the triclinic $P\bar{1}$ space group with three crystallographically unique molecules of **3** and a pentane solvent molecule in the asymmetric unit (Fig. 1). One of the molecules of **3** is shown in Fig. 2 and Table 1 contains a selected set of bond distances and angles. The six-coordinate Ru^{II} geometry in each of the complexes is octahedral with the carbonyl and benzylamine groups arranged trans with respect to one another. The carbons of the carbonyls and the nitrogens of the benzylamine ligands form the vertices in the equatorial plane (the $Ru(i)C_2N_2$ least-squares planes have a maximum deviation from the plane of 0.02, 0.004, and 0.03 Å for each of the three complexes $i = 1$, 2, and 3 respectively), and the Si(i) and I(i) atoms form the remaining vertices of the octahedron.

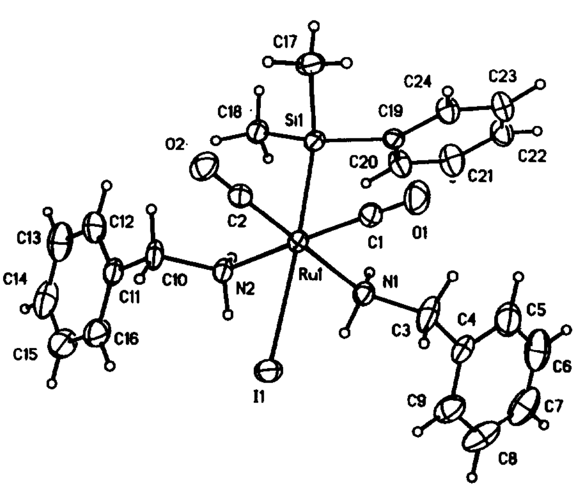

Fig. 2. Thermal ellipsoid plot of **3** drawn at the 20% probability level. Numbering for complexes not shown is similar.

TABLE 1. Summary of crsytallographic data for **3**

a	14.266(4) Å	Space group	$P\bar{1}$
b	15.748(5) Å	T	233 K
c	20.082(6) Å	λ	0.71073 Å
α	94.38(3)	Z	6 [a]
β	96.30(2)	ρ_{calc}	1.499 g/cm
γ	101.52(2)	FW	657.6
V	4371(2) Å^3	μ	16.4 cm^{-1}
$F(000)$	1968	$R(F)$	4.87%
Formula	$C_{24}H_{29}N_2O_2SiRuI$ $\cdot 1/3C_5H_{12}$	$wR(F)$	4.47%

[a] 3 complexes per asymmetric unit.

The conformations of the complexes are similar; the most significant differences among the three complexes are the relative arrangements of the benzylamine phenyl groups with respect to the associated $Ru(i)C_2N_2$ plane. The dihedral angles between the phenyl and $Ru(i)C_2N_2$ planes are: 57.6, 72.6 and 102.6° for the phenyl group *trans* to the Si phenyl, and 109.3, 69.1 and 98.5°, respectively, for the remaining benzylamine phenyl planes (for $i = 1$, 2, and 3). The three **3** molecules also have unique packing environments in which there are two weak intermolecular hydrogen bonds for each I atom with each nitrogen acting as a donor. The three dimensional network of hydrogen bonds links the complexes forming a clathrate with a pentane guest.

All of the complexes have a common Ru geometry with average bond distances of Ru–C = 1.850(7) Å, Ru–N = 2.195(5) Å, Ru–Si = 2.402(8) Å, and Ru–I = 2.861 Å. The Ru–Si distance is shorter than the distances observed in analogous compounds: $Ru_2(PPh_2CH_2SiMe_2)_2(CO)_6$, 2.465(1) Å [8]; $[Ru(SiMe_3)(CO)_2(C_8H_8(SiMe_3))]$, 2.414(2) Å [9]; $[Ru(SiMe_3)(CO)_2(C_7H_7(C_6F_5)(SiMe_3))]$, 2.43 Å [10]. The opposing Ru–I distance is longer than normal. Ru–I = 2.72 Å [11] in $Ru(CO)_4I_2$ and Ru–I = 2.771 and 2.780 Å [12] in $[Ph_3PMe]_2[Ru_2(CO)_4I_6]$. The Ru–C bonds are somewhat shorter than expected. Compounds with similar Ru bonding environments have Ru–C = 1.88(1) Å [13] in $RuCl_2(CO)_2(C_6H_5CN)$, and 1.882(5) to 1.897(3) Å [14] in $RuCl_2(CO)_2(C_{14}H_{10}N_4)$. In the previously cited compounds [10–14], Ru–C distances range from 1.83 to 2.02 Å. The Ru–N bonds are longer than expected. In the previously cited benzonitrile compound [14], the Ru–N distance is 2.12(1) Å and in $[(C_5H_8N_2)Ru(NH_3)_4(CO)]^{2+}$ Ru–N = 2.135 to 2.137 Å [15]. Other bond distances and angles in the complexes and pentane solvate are normal. Tables of atomic coordinates, bond lengths, bond angles, anisotropic coefficients and hydrogen atom coordinates are available from the authors on request.

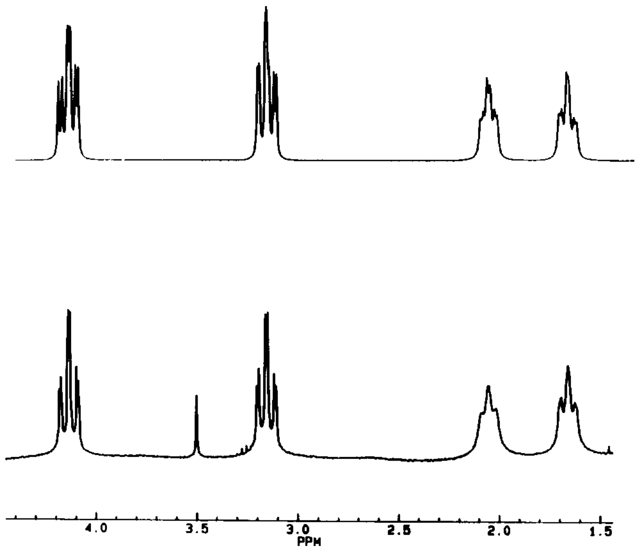

Fig. 3. (a) Simulated ^1H spectrum of 3 based upon scalar (J) couplings from two-dimensional phase sensitive COSY experiment. (b) One dimensional ^1H spectrum of 3 (resonance at 3.50 ppm due to excess $BzNH_2$).

4.2. Spectroscopy

Figure 3 shows a portion of the ^1H NMR spectrum of compound 3. The peaks between 1.5 and 4.3 ppm correspond to the aliphatic protons on the two benzylamine ligands. The two upfield multiplets at 1.66 and 2.05 ppm are assigned to the four amino protons, based on their chemical shifts and broadened linewidth due to bonding to quadrupolar nitrogen. The two downfield multiplets at 3.15 and 4.13 ppm, therefore, correspond to the four methylene protons on the benzylamine ligands. In accordance with the known structure, each of the four multiplets integrates for a total of two protons which is consistent with the total of eight aliphatic protons on the two benzylamine ligands.

Using the data from the one-dimensional NMR experiment, one is unable to determine whether each multiplet represents two protons bonded to the same atom, which suggests inequivalence of the benzylamine ligands, or whether each multiplet represents two equivalent protons on different ligands, which suggests inequivalence of protons bonded to the same atom.

The COSY spectrum over the the chemical shift range of 1.5 to 4.3 ppm was recorded. Of particular interest is that each of the four multiplets in the region of 1.5 to 4.3 ppm contains crosspeaks to all of the other multiplets in this region but to no other multiplets outside the region. This result can only occur if each of the four protons on each benzylamine ligand exhibits a

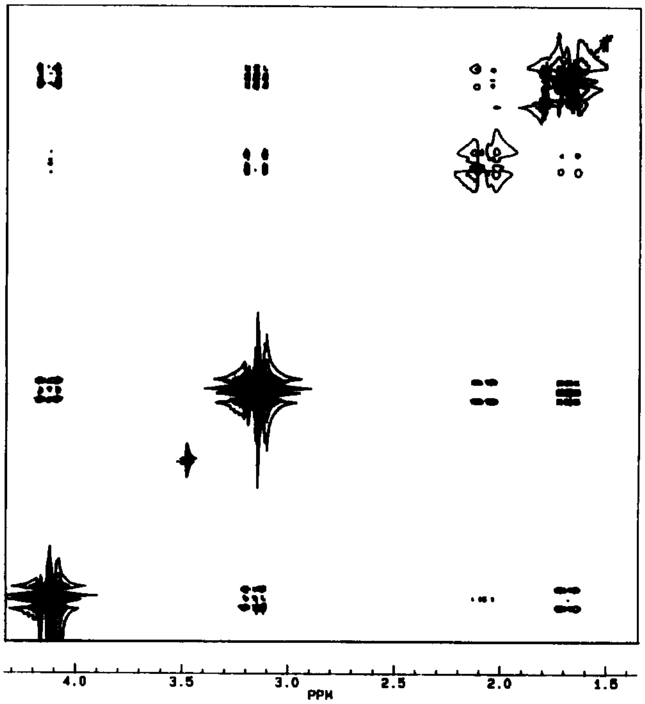

Fig. 4. Phase sensitive ^1H COSY spectrum of 3 between 1.4 and 4.4 ppm.

TABLE 2. Selected bond distances and angles

Molecule	1	2	3
Bonds			
Ru–I	2.848(1)	2.878(1)	2.857(1)
Ru–Si	2.412(2)	2.399(3)	3.397(3)
Ru–C(1)	1.860(8)	1.852(10)	1.840(10)
Ru–C(2)	1.851(8)	1.856(10)	1.844(10)
Ru–N(1)	2.189(7)	2.194(7)	2.185(8)
Ru–N(2)	2.188(7)	2.195(6)	2.198(6)
Bond angles			
I–Ru–Si	175.5(1)	176.0(1)	172.7(1)
C(1)–Ru–C(2)	87.4(4)	86.9(4)	86.5(4)
N(1)–Ru–N(2)	86.4(4)	86.4(3)	88.4(2)
C(1)–Ru–N(1)	91.3(3)	92.4(4)	92.5(4)
C(2)–Ru–N(2)	94.9(3)	94.3(3)	92.6(3)
Torsion angles			
N(1)–Ru–N(2)–C(10)	174.8(5)	165.3 (6)	176.0(6)
N(2)–Ru–N(1)–C(3)	−160.2(6)	−162.0(6)	−157.6(6)
Ru–Si–C(19)–C(20)	87.5(7)	100.2(8)	107.2(8)
Hydrogen bond parameters			
	I---H	I---N	∠N–H---I
I(1)---H(1ab)–N(1a)	2.92(5)	3.182(8)	165(5)
I(1)---H(2aa)–N(2a)	2.95(6)	3.838(8)	165(5)
I(2)---H(2bb)–N(1b) [a]	2.96(5)	3.604(7)	130(6)
I(2)---H(2bb)–N(2b) [a]	3.20(6)	3.738(8)	119(7)
I(3)---H(1a)–N(1) [b]	3.02(5)	3.566(8)	120(6)
I(3)---H(2b)–N(2) [b]	2.96(6)	3.668(8)	135(5)

[a] Related by symmetry $(1.0-x, 3.0-y, 1.0-z)$.

[b] Related by symmetry $(1.0-x, 2.0-y, 1.0-z)$.

Atoms in the three complexes are numbered $i=1, 2, 3$ for Si(i), Ru(i), and I(i), and numbered similarly with suffix A or B for C, N, and O in complexes $i=2$ and 3, respectively.

TABLE 3. Experimental scalar (J) couplings (Hz) determined from the two-dimensional ^{1}H phase sensitive COSY experiment of **3**. Each of the four spins in the region $d = 4.1$ to 1.7 ppm are numbered 1 through 4 starting from the left.

$J_{12} = 13.0$	$J_{13} = 4.7$
$J_{14} = 11.8$	$J_{23} = 11.2$
$J_{24} = 3.6$	$J_{34} = 10.6$

different chemical shift. We therefore conclude that the four aliphatic protons on each benzylamine ligand are chemical-shift inequivalent and that each is scalar coupled to the remaining three protons.

To investigate the magnitude of the scalar couplings among the four protons on the benzylamine ligands, we made use of phase sensitive COSY. Figure 4 shows the two-dimensional phase-sensitive COSY plot of compound **3**. The six scalar couplings were measured (see Table 3) and then entered into an NMR spectrum simulation routine [16]. The results were found to correspond well with the experimental spectrum (see Fig. 3). The large coupling differences exhibited by the four protons on the benzylamine ligands attest to the rigid nature of the ligand structure and further confirm the inequivalence of each of the four aliphatic protons on each ligand. The magnitude of the vicinal couplings suggests a staggered conformation about the C–N bond in which the phenyl group and the ruthenium are *anti*.

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