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Synthesis, molecular structure, and ^1H NMR analysis of bis(tetraphenylcyclopentadienyl)ruthenium(II)

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Abstract

Reaction of $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ with $\text{K}(\eta^5\text{-C}_5\text{HPh}_4)$ in refluxing diglyme yields $(\eta^5\text{-C}_5\text{HPh}_4)_2\text{Ru}$ in ca 50% yield. The complex was not susceptible to oxidation or reduction. $(\text{C}_5\text{HPh}_4)_2\text{Ru}$ crystallizes in the triclinic $P\bar{1}$ space group with $a = 8.549(4)$, $b = 10.793(4)$, $c = 12.842(5)$ Å, $\alpha = 65.98(3)$, $\beta = 73.10(3)$, $\gamma = 83.49(3)^\circ$ and $Z = 1$. The least-squares data refined to $R(F) = 3.53\%$ and $R(wF) = 3.82\%$ for the 3952 independent observed reflections with $F_o \geq 5\sigma(F_o)$. The metal-centroid distance is 1.832(2) Å and all other bond lengths and angles are similar to other octaphenylmetallocenes. ^1H NMR analysis employing 2D J -resolved, COSY and low temperature techniques allowed assignment of all protons in the molecule. The motional processes of the phenyl groups are discussed.

Introduction

Polyphenylated cyclopentadienyl ligands have received increasing attention because of their electronic and steric properties [1]. The steric bulk of these ligands markedly reduces the reactivity of complexes incorporating them. While few second- and third-row metallocenes have been isolated because of their high reactivity [2], use of the tetraphenylcyclopentadienyl ligand $(\eta^5\text{-C}_5\text{HPh}_4)$ offers the possibility for their syntheses. However, many of the preparations known to generate unsubstituted metallocenes do not work with this ligand because of its large size and low solubility. The direct reaction of metal dichlorides with the C_5HPh_4 anion that was applied to many of the first-row metals [3,4] is not applicable here because the corresponding simple metal halides do not exist. Thus, routes employing metal complexes are required and the conditions for reaction need to be established.

While known almost as long as ferrocene [5], relatively few substituted derivatives of ruthenocene have been prepared [6]. The development of ruthenocenes is probably limited because of their chemical similarity [7] to ferrocenes coupled to the higher costs and generally lower yields [8] associated with their syntheses. Recently, a convenient, high yield synthetic method for the preparation of ruthenocenes was developed [9,10] that appeared applicable to bulky or poorly soluble cyclopenta-

dienyl derivatives. Herein, we describe the synthesis and physical properties of octaphenylruthenocene.

Experimental

General data

All reactions of air- and moisture-sensitive materials were performed under an argon atmosphere employing standard Schlenk techniques. Solids were manipulated under argon in a Vacuum Atmospheres glovebox equipped with a HE-493 dri-train.

Table 1

Crystallographic data for octaphenylruthenocene

<i>(a) Crystal parameters</i>	
Formula	C ₅₈ H ₄₂ Ru
Formula weight	840.04
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> , Å	8.549(4)
<i>b</i> , Å	10.793(4)
<i>c</i> , Å	12.842(5)
α , deg	65.98(3)
β , deg	73.10(3)
γ , deg	83.49(3)
<i>V</i> , Å ³	1035.6(7)
<i>Z</i>	1
Crystal dimensions, mm	0.32 × 0.38 × 0.51
Crystal color	yellow
<i>D</i> (calc), g cm ⁻³	1.347
μ (Mo- <i>K</i> _α), cm ⁻¹	4.08
Temp., K	296
<i>T</i> _{max} / <i>T</i> _{min}	1.012
<i>(b) Data collection</i>	
Diffractometer	Nicolet R3m
Monochromator	graphite
Radiation	Mo- <i>K</i> _α ($\lambda = 0.71073$ Å)
2 θ scan range, deg	4–52
Data collected (<i>h</i> , <i>k</i> , <i>l</i>)	±11, ±14, +16
Reflections collected	4258
Independent reflections	4065
<i>R</i> (merg), %	2.18
Independent observed reflections	3952 ($F_o \geq 5\sigma(F_o)$)
Standard reflections	3 standard/197 reflections
Variation in standards	<1%
<i>(c) Refinement</i>	
<i>R</i> (<i>F</i>), %	3.53
<i>R</i> (<i>wF</i>), %	3.82
Δ/σ (max)	0.008
$\Delta(\rho)$, eÅ ⁻³	0.418
<i>N</i> _o / <i>N</i> _v	17.5
GOF	1.233

Diglyme was distilled from sodium/benzophenone ketyl under argon. Tetrahydrofuran (THF) was distilled from potassium/benzophenone ketyl under argon. $K(C_5HPh_4) \cdot \frac{1}{2}THF$ [4], $Tl(C_5HPh_4)$ [11], $\{Ru(COD)Cl_2\}_x$ (COD = 1,5-cyclooctadiene) [12], $\{Os(COD)Cl_2\}_x$ [13], and $[Os(C_6H_6)Cl_2]_2$ [14] were prepared by literature procedures. $[Ru(p\text{-cymene})Cl_2]_2$, cobaltocene, $AgPF_6$, potassium, THF- d_8 (Aldrich), I_2 , and all other solvents (Fisher) were used as received. The elemental analysis was performed by Schwartzkopf Microanalytical Laboratory, Woodside, NY.

NMR spectroscopy

1H NMR spectra were recorded on a Varian XL-200 spectrometer with an upgrade to a Motorola data system at 200.06 MHz. A 1H 2D J -resolved spectrum was obtained using a 4-step phase cycle to suppress axial peaks and artifacts from quadrature imbalance and to provide phase modulation in t_2 . The spectral window of ± 34 Hz was centered at 6.89 ppm. Resonances outside this window (from traces of water, undeuterated solvent, and other minor impurities) were suppressed by a

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for $(C_5HPh_4)_2Ru$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Ru	0	0	0	29.8(1)
C(1)	2149(3)	1189(2)	-387(2)	38(1)
C(2)	2248(3)	917(2)	-1402(2)	36(1)
C(3)	2319(3)	-540(2)	-1036(2)	36(1)
C(4)	2274(3)	-1131(2)	196(2)	36(1)
C(5)	2193(3)	-64(2)	607(2)	37(1)
C(21)	3111(2)	3196(2)	-2940(2)	54(1)
C(22)	3148	4233	-4042	74(2)
C(23)	2414	4040	-4803	77(2)
C(24)	1643	2810	-4463	63(1)
C(25)	1605	1774	-3362	46(1)
C(26)	2339	1967	-2601	39(1)
C(31)	1791(2)	-2486(2)	-1487(2)	53(1)
C(32)	2199	-3223	-2203	73(2)
C(33)	3474	-2781	-3240	84(2)
C(34)	4341	-1602	-3561	76(2)
C(35)	3932	-866	-2845	56(1)
C(36)	2658	-1307	-1808	41(1)
C(41)	1355(2)	-3524(2)	1628(2)	55(1)
C(42)	1725	-4890	2171	70(2)
C(43)	3330	-5337	1899	72(2)
C(44)	4566	-4417	1085	71(2)
C(45)	4196	-3050	543	54(1)
C(46)	2591	-2604	814	40(1)
C(51)	1672(3)	942(2)	2106(2)	51(1)
C(52)	1577	847	3239	61(1)
C(53)	2025	-351	4062	63(1)
C(54)	2568	-1455	3752	68(2)
C(55)	2662	-1360	2619	59(1)
C(56)	2215	-162	1796	41(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

100 Hz four-pole Butterworth filter. A ± 15 Hz window was employed for F_1 and a 90° pulse ($10.5 \mu\text{s}$) was used for F_2 . Four 128 point FID's (acquisition time 0.934 s) were accumulated at each of 128 t_1 values (15 ms increment). The resulting symmetrical data matrix was magnitude calculated after the second F.T.; it was symmetrized. The data matrix was tilted 45° .

A ^1H COSY (correlated spectroscopy) spectrum was obtained using a 16-step phase cycle. The spectral window of ± 50 Hz was centered at 6.93 ppm. Resonances outside this window were suppressed by a 100 Hz four-pole Butterworth filter. A 90° pulse ($10.5 \mu\text{s}$) was used for both F_1 and F_2 . Sixteen 512 point FID's (acquisition time 2.56 s) were accumulated at each of 256 t_1 values (10 ms increment). The resulting symmetrical data matrix was treated by multiplying by a pseudo-echo and zero-filling before Fourier transformation in each dimension. The data were magnitude calculated after the second F.T.; they were not symmetrized.

X-Ray data collection for $(\text{C}_5\text{HPh}_4)_2\text{Ru}$

Crystal, data collection, and refinement parameters are collected in Table 1. A yellow crystal of octaphenylruthenocene was mounted on a fine glass fiber with epoxy cement. The unit cell parameters were obtained from the least squares fit of 25 reflections ($20 \leq 2\theta \leq 25^\circ$). Preliminary photographic characterization showed $\bar{1}$ Laue symmetry. The centrosymmetric alternative, $P\bar{1}$, was suggested by E -statistics and was confirmed by the chemically sensible results of refinement. There was no absorption correction applied to the data set (regular shaped crystal; $T_{\text{max}}/T_{\text{min}} = 1.012$; $\mu = 4.08 \text{ cm}^{-1}$).

Structure solution and refinement

The structure was solved by taking the coordinates from the previously determined octaphenylferrocene, replacing Ru for Fe, and allowing the structure to

Table 3

Selected bond distances (\AA) and angles ($^\circ$) for $(\text{C}_5\text{HPh}_4)_2\text{Ru}$

<i>Bond distances</i>			
Ru-CNT ^a	1.832(2)	C(4)-C(46)	1.494(3)
C(1)-C(2)	1.426(4)	C(5)-C(56)	1.493(4)
C(2)-C(3)	1.446(3)	Ru-C(1A)	2.181(3)
C(3)-C(4)	1.435(4)	Ru-C(2)	2.209(2)
C(4)-C(5)	1.437(4)	Ru-C(3A)	2.209(2)
C(5)-C(1)	1.439(3)	Ru-C(4)	2.197(2)
C(2)-C(26)	1.480(3)	Ru-C(5A)	2.214(3)
C(3)-C(36)	1.482(3)		
<i>Bond angles</i>			
CNT-Ru-CNT(A)	180.0(1)	C(1)-C(5)-C(56)	124.5(2)
C(1)-C(2)-C(3)	107.1(1)	C(2)-C(3)-C(36)	127.2(2)
C(2)-C(3)-C(4)	107.8(3)	C(3)-C(2)-C(26)	128.1(3)
C(3)-C(4)-C(5)	109.0(2)	C(3)-C(4)-C(46)	121.9(2)
C(1)-C(5)-C(4)	106.4(2)	C(4)-C(3)-C(36)	124.3(2)
C(2)-C(1)-C(5)	109.8(2)	C(4)-C(5)-C(56)	124.5(2)
C(1)-C(2)-C(26)	124.8(2)	C(5)-C(4)-C(46)	128.1(2)

^a CNT = the centroid of atoms C(1) to C(5)

refine. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were included as idealized isotropic contributions ($d(\text{CH}) = 0.960 \text{ \AA}$, $U = 1.2 U$ for attached C), and all phenyl rings were constrained as rigid planar hexagons ($d(\text{CC}) = 1.396 \text{ \AA}$). Table 2 contains position parameters and Table 3 contains selected bond distances and angles for the structure.

All computer programs and the sources of the scattering factors are contained in the SHELXTL program library (5.1) (G.M. Sheldrick; Nicolet Corp.; Madison, WI).

Synthesis of bis(tetraphenylcyclopentadienyl)ruthenium(II) (I)

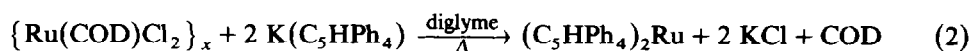
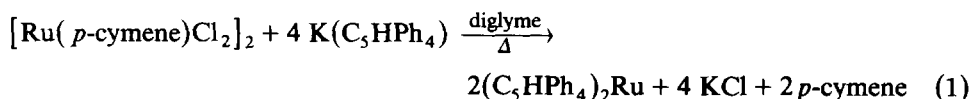
Method 1. Dry diglyme (30 mL) was added to a mixture of $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (1.00 g, 1.63 mmol) and $\text{K}(\text{C}_5\text{HPh}_4) \cdot \frac{1}{2}\text{THF}$ (3.04 g, 6.84 mmol). After refluxing for 48 h, the reaction mixture was cooled to room temperature, filtered in the air, washed with pentane (20 mL), and suction dried. The beige residue was extracted with boiling toluene and the solution concentrated to saturation at its boiling point (ca 75 mL). It was cooled to -20°C overnight, filtered, washed with pentane, and oven dried yielding 1.36 g (1.63 mmol, 50%) of beige microcrystals of I. Recrystallization of I from slow diffusion of pentane into a solution of I in CH_2Cl_2 yields large yellow crystals of I, m.p. 336°C . Anal. Found: C, 82.77 H, 5.05. $\text{C}_{58}\text{H}_{42}\text{Ru}$ calcd.: C, 82.93; H, 5.04%.

Method 2. Procedure is the same as method 1 except that $\{\text{Ru}(\text{COD})\text{Cl}_2\}_x$ was used in place of $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ in the same molar ratio. Yield: 35%.

Results and discussion

Synthesis and reactivity

Reaction of $\text{K}(\text{C}_5\text{HPh}_4)$ and either $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (eq. 1) or $\{\text{Ru}(\text{COD})\text{Cl}_2\}_x$ (eq. 2) in refluxing diglyme gives $(\text{C}_5\text{HPh}_4)_2\text{Ru}$ in moderate yields



after crystallization from hot toluene. When refluxing tetrahydrofuran was employed as the reaction solvent no $(\text{C}_5\text{HPh}_4)_2\text{Ru}$ was produced. Octaphenylruthenocene forms bright yellow crystals after recrystallization from CH_2Cl_2 /pentane.

Like the octaphenylmetallocenes of the first-row transition metals [4], the reactivity of $(\text{C}_5\text{HPh}_4)_2\text{Ru}$ is reduced compared to $(\text{C}_5\text{H}_5)_2\text{Ru}$ and $(\text{C}_5\text{Me}_5)_2\text{Ru}$. Octaphenylruthenocene is not oxidized by I_2 [15], even in refluxing toluene, or by AgPF_6 [16]. Likewise, cobaltocene does not reduce I.

Interestingly, similar reactions between $\{\text{Os}(\text{COD})\text{Cl}_2\}_x$ or $[\text{Os}(\text{C}_6\text{H}_6)\text{Cl}_2]_2$ and $\text{K}(\text{C}_5\text{HPh}_4)$ in refluxing diglyme did not yield any $(\text{C}_5\text{HPh}_4)_2\text{Os}$, nor did the reaction between $\{\text{Os}(\text{COD})\text{Cl}_2\}_x$ and $\text{Ti}(\text{C}_5\text{HPh}_4)$. This behavior contrasts that observed by Albers and co-workers [9] for the $(\text{C}_5\text{Me}_5)_2\text{M}$ ($\text{M} = \text{Ru}, \text{Os}$) systems. Both of these compounds formed much more rapidly (ca 2 h), at lower temperature (refluxing ethanol), and in higher yields (70 and 82%, respectively) than the complexes described here. The much higher temperature required here (160°C) was surprising in light of the conditions used to produce analogous first-row compounds

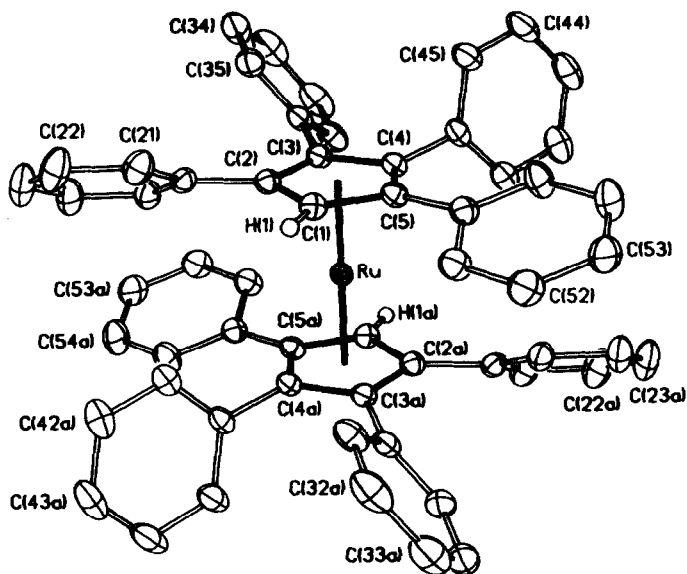


Fig. 1. Molecular structure and labeling scheme for $(C_5HPh_4)_2Ru$. Thermal ellipsoids at 35% probability.

[3,4]. Those systems proceeded for both the $C_5Me_5^-$ [17] and $C_5HPh_4^-$ ligands at the same temperatures, although longer reaction times were occasionally required for the $C_5HPh_4^-$ ligand. The poor reactivity observed for these and other [18] second- and third-row complexes may result from a need to displace a bound olefin or arene from the starting complexes. Stronger metal–ligand bonding for the lower transition metals [19] may make this more difficult.

Molecular structure

The crystal structure of $(C_5HPh_4)_2Ru$ is isomorphous to that of $(C_5HPh_4)_2Fe$ [3]. It crystallizes into discrete, well-separated molecules with a staggered C_5 ring configuration and the Ru atom on a crystallographic center of symmetry (Figs. 1 and 2). The M–CNT distance increases from 1.695 Å in $(C_5HPh_4)_2Fe$ to 1.832 Å in $(C_5HPh_4)_2Ru$. This value is close to that expected from the increase in covalent radius on going from iron to ruthenium (0.08 Å) [20].

The increased separation of the C_5 rings caused only small changes in the phenyl ring torsion angles (Table 4). It is interesting that while the M–CNT distance for

Table 4

Phenyl ring torsion angles ($^\circ$)

Cp carbon	Ru	Fe ^a	Cr ^b
2	33.9	33.0	31.9
3	49.8	47.5	46.9
4	77.7	77.1	69.9
5	17.3	15.3	19.7

^a See ref. 4. ^b See ref. 5.

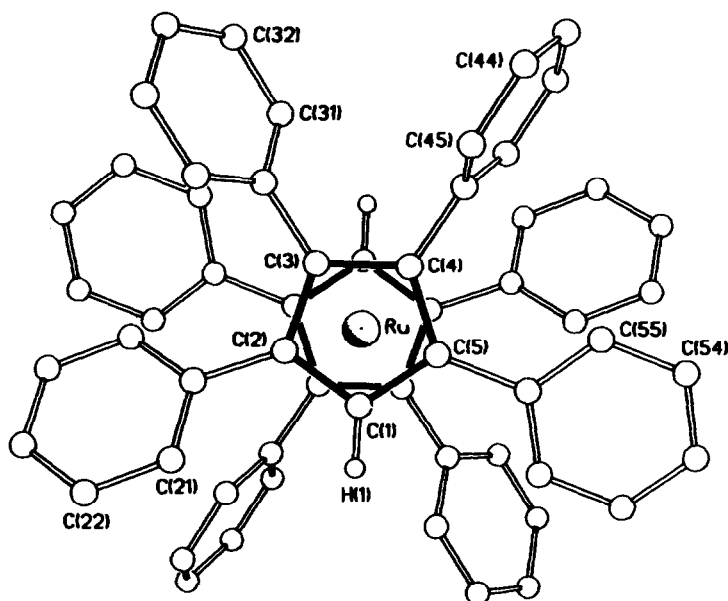


Fig. 2. $(C_5HPh_4)_2Ru$ viewed down CNT–Ru–CNT(A) showing the staggered C_5 ring configuration.

$(C_5HPh_4)_2Cr$ [4] is the same as that for $(C_5HPh_4)_2Ru$, at least one torsion angle differs significantly (phenyl ring 4). A possible explanation of this lies in the positioning of the C_5 rings relative to the metal centers. In $(C_5HPh_4)_2Ru$, the variation in Ru–C bond lengths is very small (2.180–2.214 Å, $\Delta_{(Ru-C)} = 0.034$ Å). In contrast, the variation in bond distances for $(C_5HPh_4)_2Cr$ is nearly three times larger (2.141–2.234 Å, $\Delta_{(Cr-C)} = 0.093$ Å). This suggests that the ruthenium atom is located nearer to directly beneath the center of the C_5 ring than is chromium. This shift of the C_5 rings away from each other in $(C_5HPh_4)_2Cr$ vs $(C_5HPh_4)_2Ru$ could explain the differences in the torsion angles of the phenyl groups. In the chromium compound, interactions would decrease as the phenyl rings moved away from each other.

1H NMR spectroscopy

The aromatic region of the 1H NMR (Fig. 3) displays three groups of resonances (A, B, and C) that integrate to 6, 10, and 4 protons respectively, relative to the cyclopentadienyl resonance (1 proton) at 6.20 ppm. Phenyl groups in similar compounds have been shown to rotate rapidly on the NMR time scale and are assumed to do so here [3,8]. By symmetry, phenyl rings at the 1 and 4 positions are identical as are those at the 2 and 3 positions, thus 6 groups of resonances (3 from each ring) are expected. The 2D J -resolved spectrum (Fig. 3) shows that multiplet A consists of an apparent doublet and triplet, multiplet B an apparent doublet and two apparent triplets, and multiplet C an apparent triplet. These are the expected number and types of resonances for this system. The COSY spectrum (Fig. 4) shows that multiplets A and B and multiplets B and C are coupled to each other, but not multiplets A and C.

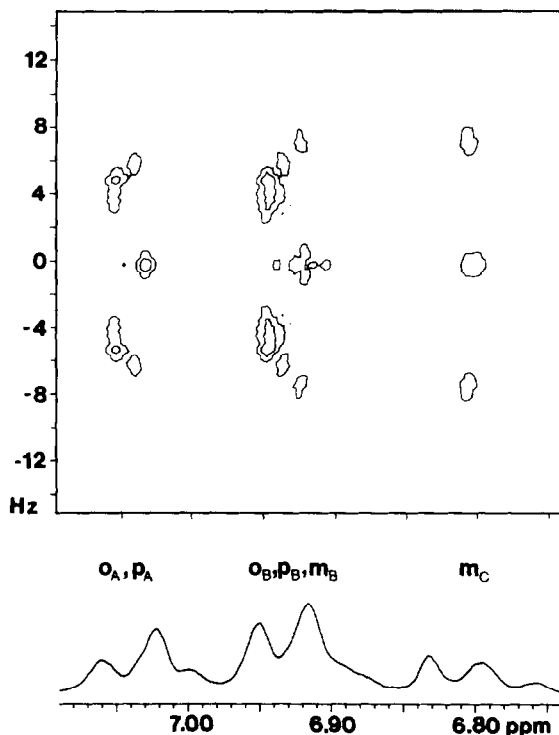


Fig. 3. ^1H 2D J -resolved NMR spectrum of $(\text{C}_5\text{HPh}_4)_2\text{Ru}$ in $\text{THF-}d_8$ solvent.

In general, *ortho* protons have the largest coupling constant and *para* protons the smallest. The *meta* protons, which couple to both the *ortho* and *para* protons, are expected to yield a complex pattern. Because of line broadening they may produce an apparent triplet with a "coupling constant" intermediate between the *ortho* and *para* values. The *ortho* protons ($J_{(\text{C}-\text{H})} = 10.2$ Hz) are expected to be doublets and are assigned to the doublets in multiplets A and B (o_A and o_B , respectively) from the 2D J spectrum. The integration requires the *para* protons also be located in multiplets A and B. The A triplet and the downfield B triplet have the same small coupling constant (6.1 Hz) and therefore arise from the *para* protons (p_A and p_B). The *meta* protons must then be assigned to the multiplets B and C (m_B and m_C). Consistent with this are the identical coupling constants (7.2 Hz) for the upfield triplet in multiplet B and multiplet C which are between the *ortho* and *para* values. Because multiplets A and C are not coupled, p_A must be coupled to m_B , not m_C . Likewise, m_C must be coupled to o_B , not o_A . Thus o_A , m_B , and p_A are coupled to each other as are o_B , m_C , and p_B .

Cooling the sample (Fig. 5) causes substantial changes in multiplet B well before significant changes in multiplets A or C occur. At very low temperature (-80°C) both multiplets A and C also appear to begin to collapse. Slowed rotation should occur first for the more crowded phenyl rings in positions 2 and 3, with the *ortho* protons collapsing first [3]. The low temperature results are consistent with slowed rotation and thus the *ortho* resonance associated with phenyl rings 2 and 3 is assigned as the *ortho* doublet in B. Thus resonances o_B , m_C , and p_B arise from

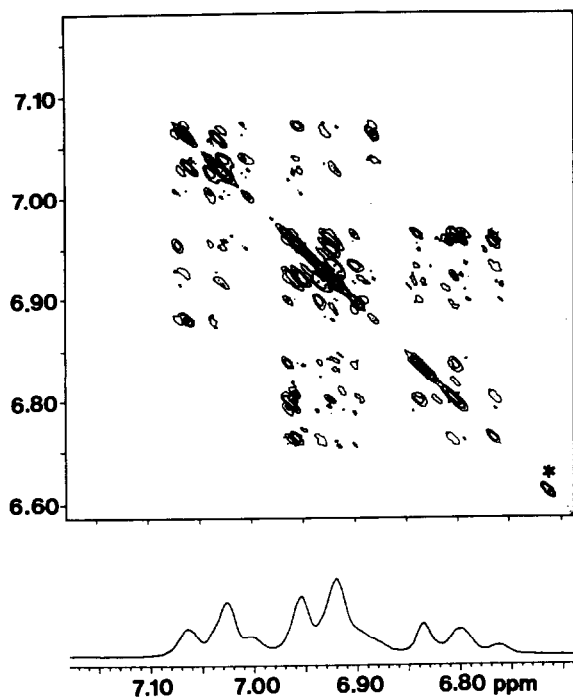


Fig. 4. ^1H COSY NMR spectrum of $(\text{C}_5\text{HPh}_4)_2\text{Ru}$ in $\text{THF-}d_8$ solvent. The asterisk denotes a peak from fold-over of the methine proton.

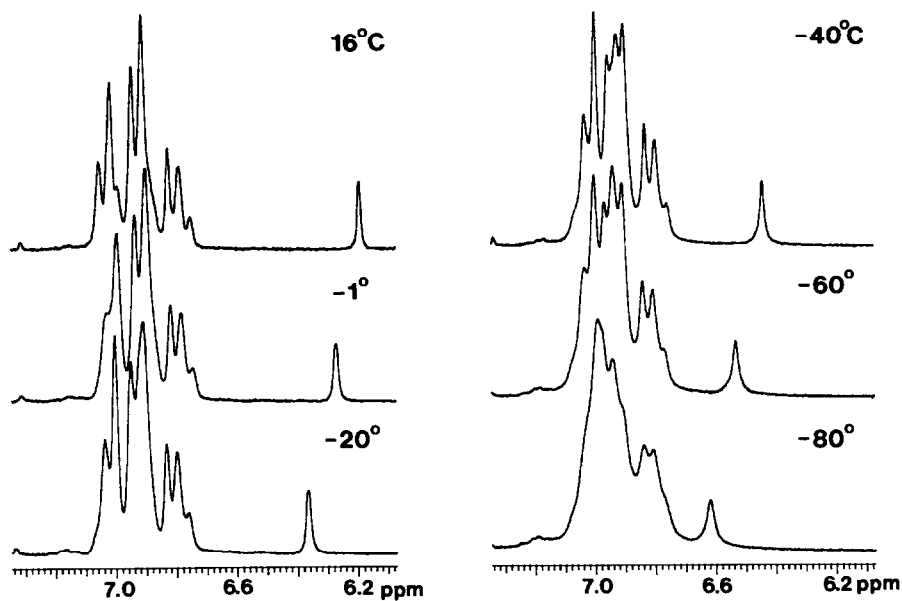


Fig. 5. Temperature dependence of the ^1H NMR spectrum of $(\text{C}_5\text{HPh}_4)_2\text{Ru}$. Temperatures are in degrees Celcius.

phenyl rings 2 and 3. The other resonances o_A , m_B , and p_A are assigned to the phenyl rings in positions 1 and 4.

No low temperature limiting spectrum was obtained before the solvent freezing point, therefore the barrier to phenyl ring rotation could not be measured. The comparable barriers to phenyl ring rotation for $(C_5HPh_4)_2Fe$ and the more crowded $(C_5HPh_4)_2TiCl_2$ (9 vs 9.6 kcal [3,8]) suggest that $(C_5HPh_4)_2Ru$, which has a very similar structure to $(C_5HPh_4)_2Fe$, should have barrier of approximately 9 kcal/mol. Consistent with this is the observation that the Cp methine protons move downfield at a nearly identical rate (vs temperature) as the analogous proton in $(C_5HPh_4)_2Fe$. The downfield shift arises from the methine proton spending more time in the deshielding region of the phenyl rings 1 and 4 as ring rotation slows and those rings become coplanar with the C_5 ring [3].

Acknowledgments

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Supplementary material available. Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen-atom coordinates (4 pages) and structure factors (12 pages) are available from one of the authors (ALR).

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