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Journal of Organometallic Chemistry 672 (2003) 109–114

Journal of Organo metallic Chemistry

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Synthetic, spectroscopic, and structural studies of bis(2-methyl-4-phenylpentadienyl)ruthenium, Ru(2-CH_3-4-$C_6H_5C_5H_5$)$_2$: characterization of isomeric open ruthenocenes

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Received 27 January 2003; received in revised form 28 February 2003; accepted 3 March 2003

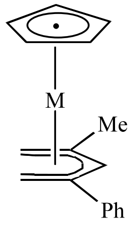
Abstract

Ru(2-methyl-4-phenylpentadienyl)$_2$ has been isolated from the reaction of ruthenium chloride complexes with the appropriate diene and zinc metal in ethanol. The complex exists as a pair of diastereomers, which could be readily separated due to their significantly different solubilities. Structural studies reveal, as expected, that one of the isomers exists in the C_1 point group, while the other possesses (noncrystallographic) C_2 symmetry.

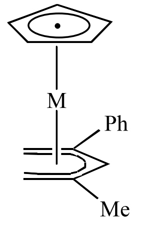
Keywords: Ruthenium complexes; Diastereomers; Structural studies; Pentadienyl complexes

1. Introduction

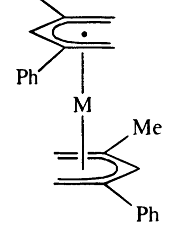
Although the existence of a series of metallocene complexes was recognized in the 1950s [1], it was not until the 1980s that a relatively comparable series of bis(pentadienyl)metal complexes (open metallocenes) was reported [2]. Despite a number of bonding and spectroscopic similarities between the two series, the differences between them appear far more profound, and may be traced back to differences between the two types of ligands themselves [3]. Thus, pentadienyl ligands are sterically much more demanding, lead to strong δ backbonding interactions, and can be simultaneously both more strongly bound and more reactive than their cyclic counterparts [4]. While most studies of open metallocenes have focussed on pentadienyl ligands with symmetric substitution patterns, there are a number of interesting aspects of the unsymmetrical ligands that can be exploited. In particular, half-open metallocenes such as **1** [5] would exist in two enantiomeric forms, while open metallocenes would exist in two diastereomeric forms, ideally represented as **2**. To date it does not appear that diastereomeric open metallocene isomers such as **2a** and **2b** have been separated, isolated, and fully characterized, although ^1H, ^{13}C and even ^{57}Fe



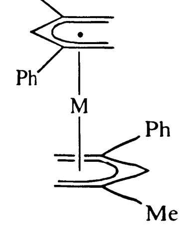
1a



1b



2a



2b

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doi:10.1016/S0022-328X(03)00149-9

NMR spectroscopic data have revealed their existence [6]. In at least some of these cases, the unsymmetrically methyl-substituted pentadienyl complexes did not yield crystals that diffracted well. As one would expect the presence of aromatic groups to lead to enhanced crystal packing forces, we have attempted the synthesis and characterization of an isomeric pair of open ruthenocenes using the 2-methyl-4-phenylpentadienyl ligand.

2. Experimental

All preparations, reactions, and manipulations of these compounds were carried out under a prepurified nitrogen atmosphere, using either Schlenk techniques or a glovebox. Hydrocarbon, ethereal and aromatic solvents were dried and deoxygenated by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. Spectroscopic data were obtained as previously described [7]. The ^{13}C-NMR spectra were not precisely integrated, but numbers of carbon atoms are reported in accord with their assignments. Elemental analyses were obtained from Desert Analytics. A mixture of 2-methyl-4-phenyl-(1,3 and 2,4)pentadienes was prepared by a modification [5] of previously reported procedures [8].

2.1. *Bis(2-methyl-4-phenylpentadienyl)ruthenium(II), Ru[2-CH$_3$-4-(C$_6$H$_5$)C$_5$H$_5$]$_2$*

To an ethanol solution (40 ml) of RuCl$_3$.xH$_2$O (2.0 g, 8 mmol) was added an excess of 2-methyl-4-phenyl-1,3-pentadiene and 2-methyl-4-phenyl-2,4-pentadiene (13 g, 82 mmol) and zinc dust (8 g, 122 mmol). The solution temperature increased with the addition of the zinc. The resulting dark brown solution was brought to reflux and stirring was continued for 3 h. The volatiles were removed in vacuo and the residue was extracted with hexanes, yielding a yellow–green oil which was chromatographed on a column of alumina, 2 cm × 10 cm (neutral, 80–200 mesh), and eluted with hexanes. After the yellow band was collected, the eluate was concentrated to approximately 5 ml and cooled to −90 °C, yielding yellow, moderately air-stable solids of both geometric isomers (2.2 g, 67%). The two isomers can be separated by fractional crystallization of less than saturated solutions. The *syn*-isomer (m.p. 148–149 °C), being the less soluble crystallized more readily, while the *anti*-isomer crystallized subsequently.

Anal. Calc. for C$_{24}$H$_{26}$Ru: C, 69.37; H, 6.31. Found: C, 69.20; H, 6.47%.

^{1}H-NMR (chloroform-d_1, ambient): *syn*-isomer δ 6.9–7.2 (m, 10H, Ph), 5.44 (s, 2H, H-3), 2.8 (br, 2H, H$_x$-5), 2.7 (v br, 2H, H$_x$-1), 2.07 (s, 6H, Me), 1.00 (br, 2H, H$_n$-5), 0.61 (br, 2H, H$_n$-1); *anti*-isomer 6.9–7.2 (m, 10H, Ph), 5.29 (s, 2H, H-3), 3.32 (d, $J = 3$ Hz, 2H, H$_x$-5), 2.55 (d, $J = 3$ Hz, 2H, H$_x$-1), 1.78 (s, 6H, Me), 1.41 (d, $J = 3$ Hz, 2H, H$_n$-5), 0.29 (d, $J = 3$ Hz, 2H, H_n-1).

^{13}C-NMR (chloroform-d_1, ambient): *syn*-isomer δ 143.1 (Ph), 129.4 (Ph), 127.9 (Ph), 127.5 (Ph), 101.5 (C-4), 100.3 (C-2), 99.4 (C-3), 48 (br, C-1), 42 (br, C-5), 26.7 (Me); *anti*-isomer 143.6 (Ph), 128.0 (Ph), 127.8 (Ph), 127.3 (Ph), 101.6 (C-4), 100.5 (C-2), 98.2 (C-3), 48.5 (C-1), 43.2 (C-5), 25.6 (Me).

Mass spectrum (EI, 70 eV) [*m/z* (relative intensity)]: 419 (10), 418 (43), 417 (43), 416 (84), 415 (100), 414 (67), 413 (69), 412 (39), 411 (26), 410 (25), 409 (15), 404 (11), 403 (45), 402 (24), 401 (96), 400 (54), 399 (58), 398 (43), 397 (19), 396 (13), 395 (17), 375 (16), 373 (10), 260 (10), 259 (10), 258 (15), 257 (19), 256 (22), 255 (23), 254 (25), 253 (20), 252 (17), 251 (10), 158 (15), 143 (35), 128 (15).

Barrier of rotation (*syn*-isomer): $\Delta G^{\ddagger} = 11.25(10)$ kcal mol^{-1}. H-3 ($T_c = -31.6$ °C, $\Delta\nu = 152.6$ Hz), Me ($T_c = -43.0$ °C, $\Delta\nu = 51.5$ Hz).

2.2. *Crystallographic structural determinations*

Crystallographic data are compiled in Table 1. For the *syn* isomer, related to **2a**, no symmetry higher than triclinic was observed. The centrosymmetric alternative was suggested by the distribution of *E*-statistics and

Table 1
Crystal data and refinement parameters for **2a** and **2b**

	2a	**2b′**
Formula	C$_{24}$H$_{26}$Ru	C$_{24}$H$_{26}$Ru
Formula weight	415.52	415.52
Temperature (K)	257(2)	243(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	*Cc*
Unit cell dimensions		
a (Å)	7.0333(7)	6.4551(13)
b (Å)	14.112(4)	21.207(5)
c (Å)	19.847(6)	13.598(3)
α (°)	101.30(3)	90
β (°)	92.28(2)	90.054(15)
γ (°)	94.48(2)	90
V (Å^3)	1922.7(9)	1861.4(7)
Z	4	4
D_{calc} (g cm^{-3})	1.435	1.483
Absorption coefficient (mm^{-1})	8.18	8.45
Theta range for data collection (°)	2.1–25.°	2.4–24.°
Index ranges	$-6 \le h \le 1$, $-14 \le k \le 14$, $-23 \le l \le 21$	$-6 \le h \le 1$, $-24 \le k \le 1$, $-15 \le l \le 15$
Reflections collected	6899	1852
Independent reflections	5074;2	1707;2
$R(F)$	0.0718	0.046
$R(wF^2)$	0.1561	0.111
Max/min difference Fourier peak (e Å^{-3})	0.86/−0.57	1.39/−0.77

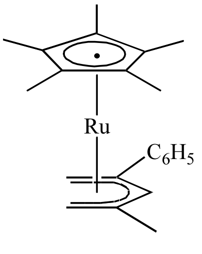
confirmed by the results of refinement. For the *anti* isomer, related to **2b**, the unit cell parameters suggested an orthorhombic crystal system, but a complete set of axial photographs revealed that there was a small number of symmetry violations in the *a* and *c* axis pictures. Hence, it was necessary to consider the possibility that the crystal belonged, instead, to the monoclinic system. Systematic absences and *E*-statistics suggested the two space groups $Cmc2_1$ or *Cc*. Our most satisfactory results were obtained in *Cc* treating the system as a merohedrally twinned monoclinic mimicking an orthorhombic setting. The use of the TWIN (1 0 0, 0 −1 0, 0 0 −1) command with BASF = 0.35 lowered the R factor from 9.56 to 4.57%. Four atoms, C(1), C(2), C(4) and C(14) were persistently non-positive-definite and were refined isotropically. All other non-hydrogen atoms were anisotropically refined and hydrogen atoms were treated as idealized contributions. All software is contained in the SHELXTL library (ver. 5.1, G. Sheldrick, Bruker AXS, Madison, WI).

3. Results and discussion

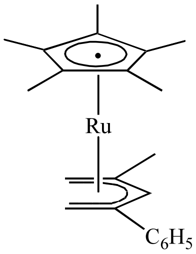
The reactions of 'ruthenium trichloride hydrate' with zinc and 2,4-methylated 1,3-pentadienes in ethanol readily led to the formation of the desired open ruthenocenes, such as $Ru(2,4\text{-}C_7H_{11})_2$ and $Ru(2,3,4\text{-}C_8H_{13})_2$ (C_7H_{11} = dimethylpentadienyl; C_8H_{13} = trimethylpentadienyl) [9]. However, similar reactions involving dienes without the 2,4-disubstitution pattern did not readily yield the desired open ruthenocenes, although an alternative but less direct approach developed by Cox and coworkers [10] has allowed us to isolate $Ru(2,3\text{-}C_7H_{11})_2$, and obtain structural data for at least one of the two spectroscopically observed isomers [11]. We, therefore, turned our attention to the syntheses of Ru(2-methyl-4-phenylpentadienyl)$_2$ isomers (**2**, M = Ru). As we had earlier found it straightforward to isolate the corresponding $Ru(C_5Me_5)$(2-methyl-4-phenylpentadienyl) complex (**3**) such was also expected to be the case for **2**. Indeed, the appropriate reaction (Eq. (1)) led to a yellow ether-soluble product, which

$$RuCl_3\cdot nH_2O \xrightarrow{a} Ru(2\text{-}CH_3\text{-}4\text{-}C_6H_5C_5H_5)_2 \quad (\mathbf{2})$$
$$\text{for a = Zn, EtOH, 2-methyl-4-phenyl-(1,3 and 2,4)-pentadienes} \qquad (1)$$

could be readily isolated in good yield following crystallization at −90 °C. As was observed for other open ruthenocenes, in the solid state the product was found to be air stable for prolonged periods [9]. Analytical and spectroscopic data clearly established the constitution of the product to be that of **2**, and more specifically the NMR data confirmed the expected presence of the two isomers, **2a** and **2b**. Notably, and initially surprisingly, the solubility properties of these isomers differed dramatically, **2a** being reasonably soluble in ether but less so in hydrocarbons, while **2b** was soluble in either.

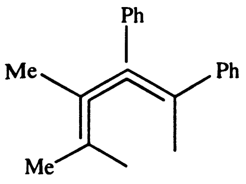


3a

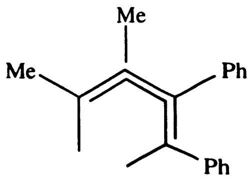


3b

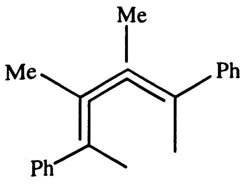
While the structures of **2a** and **2b** above have been presented in *anti*-eclipsed conformations for simplicity, in reality these species were expected to exist in nearly ideal *gauche*-eclipsed conformations, as had all previous open metallocenes of divalent iron [12], ruthenium [9,13], and osmium [14]. Thus, **2a** should actually exist as a pair of enantiomeric rotamers, **2a′** and **2a″**, each having C_1 symmetry, while **2b** should exist as a pair of diastereomeric rotamers, **2b′** and **2b″**, each having C_2 symmetry. Based on the expected magnitude of the barrier to ligand oscillation [9], the **2a′**⇌**2a″** process should be slow on the NMR timescale at room temperature, whereas at higher temperatures the equilibration should become rapid, ultimately yielding a more simplified spectral pattern in which the two ligands become equivalent [9]. Indeed, this behavior was observed, and from the coalescence temperatures a barrier of 11.25(10) kcal mol^{-1} could be estimated [15], which is slightly higher than the values of ca. 10 kcal mol^{-1} observed for $Ru(2,4\text{-}C_7H_{11})_2$ and $Ru(2,3,4\text{-}C_8H_{13})_2$ [9]. In the case of **2b**, however, due to



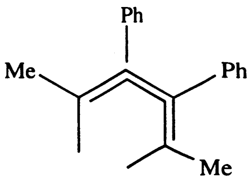
2a'



2a''



2b'



2b''

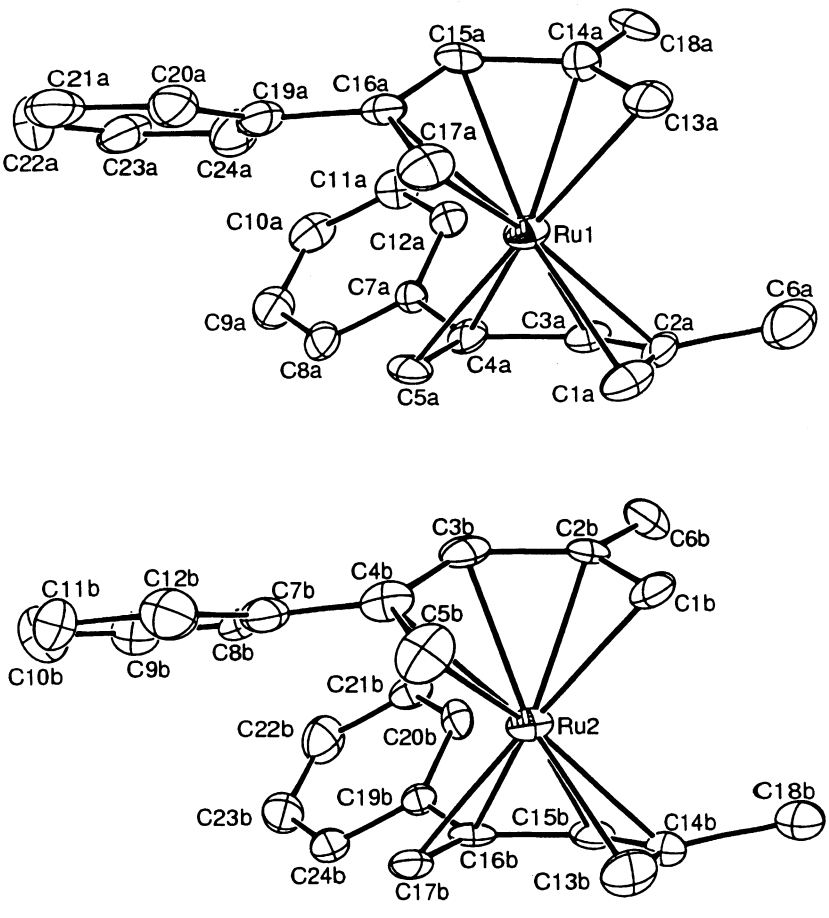


Fig. 1. Solid state structure of **2a**. Both crystallographically independent molecules are shown.

the nonequivalence of **2b**′ and **2b**″, one might observe either one or both of these isomers at room temperature. Should both be observed, they would also be expected to display dynamic behavior characterized by a similar barrier. That such behavior was not displayed provided a clear indication that one of these isomers is significantly more stable than the other, which therefore was not present in sufficient quantity to be observable.

The solid state structures of **2a** and **2b** have been determined, and are presented in Figs. 1 and 2. The less soluble **2a** isomer crystallized with two independent but essentially identical molecules in the asymmetric unit. Each adopted the conformation that had been presumed, although the structural parameters that were obtained suffered from apparent twinning of the crystal. While isomer **2a** belongs only to the C_1 point group, its Ru–C distances are fairly uniform (Tables 2 and 3), with average Ru–C[1,5], Ru–C[2,4], and Ru–C[3] distances of 2.179(5), 2.199(5), and 2.233(7) Å. The lengthening of the Ru–C[3] bonds and the overall average Ru–C distance of 2.198 Å are similar to observations for other open ruthenocenes [9,13].

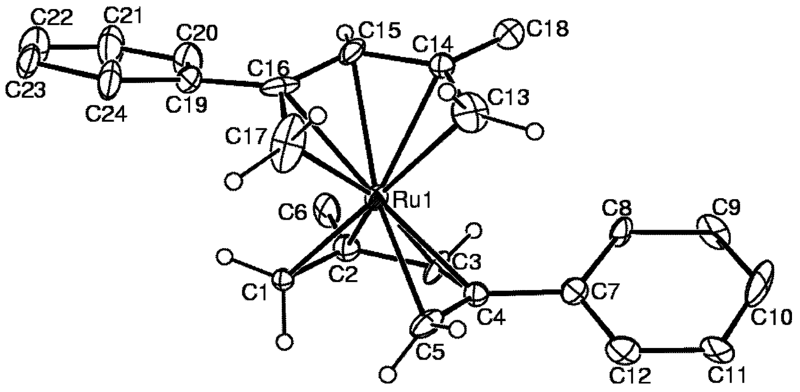


Fig. 2. Solid state structure of **2b**′.

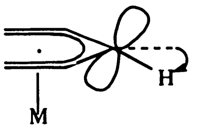
Table 2
Selected bond lengths (Å) and bond angles (°) for **2a**

Bond lengths			
Ru(1)–C(1A)	2.178(13)	Ru(2)–C(1B)	2.194(14)
Ru(1)–C(2A)	2.192(13)	Ru(2)–C(2B)	2.191(12)
Ru(1)–C(3A)	2.255(13)	Ru(2)–C(3B)	2.215(13)
Ru(1)–C(4A)	2.202(13)	Ru(2)–C(4B)	2.199(14)
Ru(1)–C(5A)	2.184(12)	Ru(2)–C(5B)	2.154(12)
Ru(1)–C(13A)	2.195(13)	Ru(2)–C(13B)	2.162(13)
Ru(1)–C(14A)	2.171(12)	Ru(2)–C(14B)	2.213(13)
Ru(1)–C(15A)	2.241(13)	Ru(2)–C(15B)	2.220(13)
Ru(1)–C(16A)	2.235(13)	Ru(2)–C(16B)	2.191(12)
Ru(1)–C(17A)	2.174(14)	Ru(2)–C(17B)	2.192(13)
C(1A)–C(2A)	1.415(18)	C(1B)–C(2B)	1.426(18)
C(2A)–C(3A)	1.426(17)	C(2B)–C(3B)	1.416(17)
C(2A)–C(6A)	1.503(18)	C(2B)–C(6B)	1.502(18)
C(3A)–C(4A)	1.452(16)	C(3B)–C(4B)	1.419(18)
C(4A)–C(5A)	1.410(17)	C(4B)–C(5B)	1.431(17)
C(4A)–C(7A)	1.505(16)	C(4B)–C(7B)	1.504(19)
C(13A)–C(14A)	1.415(17)	C(13B)–C(14B)	1.440(18)
C(14A)–C(15A)	1.420(16)	C(14B)–C(15B)	1.406(17)
C(14A)–C(18A)	1.512(18)	C(14B)–C(18B)	1.511(17)
C(15A)–C(16A)	1.431(16)	C(15B)–C(16B)	1.425(17)
C(16A)–C(17A)	1.441(17)	C(16B)–C(17B)	1.397(17)
C(16A)–C(19A)	1.502(17)	C(16B)–C(19B)	1.476(17)
Bond angles			
C(1A)–C(2A)–C(3A)	124.1(12)	C(1B)–C(2B)–C(3B)	121.4(13)
C(2A)–C(3A)–C(4A)	124.3(12)	C(2B)–C(3B)–C(4B)	126.7(12)
C(3A)–C(4A)–C(5A)	120.1(12)	C(3B)–C(4B)–C(5B)	121.2(13)

Table 3
Selected bond lengths (Å) and bond angles (°) for **2b′**

Bond length			
Ru(1)–C(1)	2.168(15)	Ru(1)–C(13)	2.265(20)
Ru(1)–C(2)	2.203(20)	Ru(1)–C(14)	2.229(20)
Ru(1)–C(3)	2.250(16)	Ru(1)–C(15)	2.254(17)
Ru(1)–C(4)	2.156(20)	Ru(1)–C(16)	2.237(15)
Ru(1)–C(5)	2.104(18)	Ru(1)–C(17)	2.131(20)
C(1)–C(2)	1.47(4)	C(13)–C(14)	1.36(5)
C(2)–C(3)	1.48(3)	C(14)–C(15)	1.42(3)
C(2)–C(6)	1.43(3)	C(14)–C(18)	1.57(3)
C(3)–C(4)	1.47(4)	C(15)–C(16)	1.31(3)
C(4)–C(5)	1.33(4)	C(16)–C(17)	1.43(4)
C(4)–C(7)	1.50(2)	C(16)–C(19)	1.55(2)
Bond angles			
C(1)–C(2)–C(3)	116.2(19)	C(13)–C(14)–C(15)	123.9(24)
C(2)–C(3)–C(4)	126.2(19)	C(14)–C(15)–C(16)	127.6(24)
C(3)–C(4)–C(5)	121.5(18)	C(15)–C(16)–C(17)	118.0(21)

The two metal-bound ligand planes in **2a** are tilted 20.4° from a parallel orientation, with the open edges being pointed toward each other. Perhaps as a result of this, there is a greater bend of the internal substituents, C6(A,B) and C19(A,B), toward the ruthenium center relative to the bends of the external substituents, C7(A,B) and C18(A,B) (10.1–12.0°, average 10.8°, vs. 6.8–8.7°, average 7.6°). These tilts reflect an attempt to bring about better overlap between the metal and ligand orbitals by pointing the π orbitals more toward the metal center [16], as in **4**.



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Although there is no crystallographic symmetry imposed on **2b′**, the structural parameters conform reasonably well to C_2 symmetry, with respective average Ru–C[1–5] distances of 2.216(13), 2.216(14), 2.252(12), 2.197(13), and 2.117(14) Å. The lengthened Ru–C[3] distance is again typical of open ruthenocenes. There is also a significant lengthening of the Ru–C[1] bond relative to Ru–C[5], perhaps a result of the proximity of the other ligand's phenyl substituent. The overall average Ru–C distance, 2.200 Å, is similar to **2a** and again to those in other open ruthenocenes. As observed for **2a**, there is a substantial tilt of the two ligands from a parallel orientation, ca. 19.2°. In this case, the tilt by the internal (methyl) groups is greater than that by the external (phenyl) groups, 9.6 versus 6.4°.

The structural data should be expected to provide some explanation for the differing solubilities of these isomers. In fact, C–H/π interactions have already been proposed to be important factors in determining crystal packing arrangements not only in phenyl-substituted half-open ruthenocenes [5] but also in phenyl-substituted complexes in general [17]. As can be seen in Fig. 1, the two phenyl substituents for isomer **2a′** associate together in a manner not unlike that of the gas phase benzene dimer [18]. The average separations of H24 from the C(7–12) plane, and from C7, C8, and C12 (2.68, 2.72, 2.96 and 2.92 Å, respectively) are consistent with such a (C–H)/π interaction. Due to the proximity of these substituents to one another, one would probably expect a reduction in their exposure to other molecules in the lattice, thereby reducing intermolecular interactions and leading to higher solubilities. That **2a** is actually less soluble than **2b**, however, indicates that the situation is more complex. Notably, for **2b**, the observed isomer, **2b′**, is the one which keeps the two phenyl substituents more separated, possibly an indication that an intramolecular interaction is less favorable in this case than an intermolecular one. It is therefore conceivable that in solution the favored isomer is **2b″**.

4. Conclusions

The present study indicates that open metallocenes incorporating unsymmetric pentadienyl ligands can exist as pairs of diastereomers having substantially different properties. A remaining question of interest is the possibility of interconversion of such isomers, as has been observed for related iron and titanium complexes [4,11]. While such an interconversion does not readily take place for **2**, there are indications that other open ruthenocenes can isomerize with photochemical initiation, and these processes are under continuing study.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 201712 and 201713 for compounds **2a** and **2b′**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.)

Acknowledgements

R.D.E. is grateful to the University of Utah and the National Science Foundation for partial support of this work.

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