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Studies of dirhodium(II) tetrakis(trifluoroacetate). Part 8. One-dimensional polymers of $Rh_2(O_2CCF_3)_4$ with aromatic ligands: benzene, *p*-xylene and naphthalene

F. Albert Cotton *, Evgeny V. Dikarev, Marina A. Petrukhina, Salah-Eddine Stiriba

Laboratory for Molecular Structure and Bonding, Department of Chemistry, PO Box 30012, Texas A&M University, College Station, TX 77842-3012, USA

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Abstract

The interaction of benzene, *p*-xylene, and naphthalene with a strong two-ended Lewis acid, $Rh_2(O_2CCF_3)_4$, led to one-dimensional linear polymers of 1:1 composition, $[Rh_2(O_2CCF_3)_4:L]_{\infty}$, where $L = C_6H_6$ (1), *p*-(CH₃)₂C₆H₄ (2), and $C_{10}H_8$ (3). Compounds 1–3 have been characterized by elemental analysis and IR spectroscopy and their structures have been determined by X-ray diffraction. In the crystal structures of the compounds the alternating arrangement of the dirhodium(II) tetrakis(trifluoroacetate) units with the aromatic ligands coordinated to their axial positions forms infinite chains extended along one direction of the unit cell. The rare bridging off-centered, $\eta^2:\eta^2$ coordination of arene groups by the Rh(II) centers was found to be preferred in all three cases with the two closest Rh–C_{arene} distances averaged to 2.662(6) Å in the benzene complex (1), to 2.684(7) Å in the *p*-xylene analogue (2), and to 2.588(9) Å in the naphthalene product (3). © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Dirhodium(II) tetrakis(trifluoroacetate) exhibits an extensive axial coordination chemistry with a variety of strong N, O, P-containing bases [1]. Our research interest has been recently focused on studies of weak axial interactions by the powerful two-ended Lewis acid, $Rh_2(O_2CCF_3)_4$ [2]. We introduced a solid state deposition technique ('solventless' synthesis) [2] as an efficient way to study these interactions and to avoid competitive coordination of solvents in solutions. Our recent results have included the first structurally characterized π -complex with an aromatic ligand (hexamethylbenzene), $[Rh_2(O_2CCF_3)_4 \cdot (C_6Me_6)]_{\infty}$ [2a] and a compound $[Rh_2(O_2CCF_3)_4 \cdot (C_2Ph_2)]_{\infty}$ [2e] with both a triple carbon–carbon bond and an arene system from the bifunctional diphenylacetylene ligand involved in coordin-

ation (Scheme 1). A rare off-centered orientation of the aromatic ligands at the Rh(II) centers has been found in both dirhodium trifluoroacetate chain compounds, with the C_6Me_6 and the Ph_2C_2 ligands. We believe systematic research is needed in order to get more insight into complexation of arenes by the electron-deficient dirhodium(II) carboxylate molecules, as these interactions have an important role in some catalytic and aromatic substitution reactions [3]. Therefore, we have extended the number of arene ligands to benzene, p-xylene and naphthalene and report here on their interactions with $Rh_2(O_2CCF_3)_4$. The first two ligands are commonly used as non-coordinating solvents for studying weak interactions in the Lewis acid-Lewis base systems. Naphthalene is the first conjugated arene molecule used for such reactions with the dirhodium moiety. With all three ligands the products are analogous one-dimensional linear polymers of 1:1 composition, namely $[Rh_2(O_2CCF_3)_4 \cdot C_6H_6]_{\infty}$ (1), $[Rh_2$ - $(O_2CCF_3)_4 \cdot (p - (CH_3)_2C_6H_4)]_{\infty}$ (2) and $[Rh_2(O_2CCF_3)_4 \cdot (P - (CH_3)_2C_6H_4)]_{\infty}$ $C_{10}H_8]_{\infty}$ (3). They have been crystallographically characterized and their structures have been compared.

^{*} Corresponding author. Tel.: +1-979-845-4432; fax: +1-979-845-9351.

E-mail address: cotton@tamu.edu (F.A. Cotton).



Scheme 1.

2. Experimental

2.1. General

All manipulations were carried out under an atmosphere of dry, oxygen-free dinitrogen by employing Schlenk techniques. Solvents were dried and deoxygenated by refluxing over appropriate agents before use. The anhydrous form of $Rh_2(O_2CCF_3)_4$ was prepared using a literature procedure [4]. Naphthalene $(C_{10}H_8)$ was purchased from Aldrich and sublimed before use. The IR spectra were recorded on a Perkin– Elmer 16PC FTIR spectrophotometer using KBr pellets. Elemental analysis was done by Canadian Microanalytical Services, Ltd.

2.2. Synthesis of $Rh_2(O_2CCF_3)_4 \cdot C_6H_6$ (1)

A few drops of distilled benzene were added to the solid unligated $Rh_2(O_2CCF_3)_4$ (0.10 g, 0.15 mmol) in a Pyrex tube. The excess of benzene was removed under vacuum. The tube was then sealed and left in a furnace at 90°C for 24 h. Green crystals of **1** were deposited on the walls after slow cooling of the tube over 48 h to r.t. Yield: 0.030 g, 27%.

2.3. Synthesis of $Rh_2(O_2CCF_3)_4 \cdot (p - (CH_3)_2C_6H_4)$ (2)

2.3.1. $Rh_2(O_2CCF_3)_4$ in benzene containing p-xylene

The solution containing $Rh_2(O_2CCF_3)_4$ (0.10 g, 0.15 mmol) in 5 ml of benzene containing *p*-xylene (the ratio of p-(CH₃)₂C₆H₄ to C₆H₆ was found by NMR to be about 1:100) was layered with 10 ml of hexanes at r.t. This resulted in deposition of a few crystals of **2** in a week.

2.3.2. $Rh_2(O_2CCF_3)_4$ in p-xylene

The vial containing solution of $Rh_2(O_2CCF_3)_4$ (0.10 g, 0.15 mmol) in 5 ml of *p*-xylene was placed in the Ar

glovebox. After keeping the solution for one week at 0°C light-green plates of **2** had appeared. Yield: 0.089 g, 77%.

2.3.3. p-Xylene added to unligated $Rh_2(O_2CCF_3)_4$

A few drops of anhydrous *p*-xylene were added to the solid unligated $Rh_2(O_2CCF_3)_4$ (0.10 g, 0.15 mmol) in a Pyrex tube. The excess of solvent was removed under vacuum. The tube was then sealed and left in a furnace at 95°C for 2 days. Green crystals of **2** were deposited on the walls after slow cooling of the tube over 24 h to r.t. Yield: 0.046 g, 40%.

Anal. Calc. for $C_{16}H_{10}F_{12}O_8Rh_2$: C, 25.25; H, 1.32. Found: C, 24.98; H, 1.32%. IR (KBr, cm⁻¹): 1665.6 (s), 1191.4 (s), 868.4 (s), 840.9 (m), 794.9 (m), 739.4 (s), 540.8 (s).

2.4. Synthesis of $Rh_2(O_2CCF_3)_4 \cdot C_{10}H_8$ (3)

Unligated Rh₂(O₂CCF₃)₄ (0.066 g, 0.10 mmol) was mixed with freshly sublimed naphthalene (0.012 g, 0.10 mmol) under an inert atmosphere. The mixture was sealed in an evacuated Pyrex tube and the tube was placed in a furnace at 90°C. Green block-shaped crystals of **3** were deposited over two days in the 'cold' zone of the tube, where the temperature was about 5°C lower. Yield: 0.027 g, 35%. *Anal.* Calcd. for C₁₈H₈F₁₂O₈Rh₂: C, 27.50; H, 1.03. Found: C, 27.47; H, 1.03%. IR (KBr, cm⁻¹): 1683.9 (m), 1669.6 (s), 1653.0 (m), 1558.3 (s), 1540.0 (m), 1506.4 (m), 1456.7 (m), 1192.2 (s), 1167.5 (s), 861.0 (m), 784.8 (m), 739.8 (s), 525.9 (m), 457.8 (m), 418.0 (m).

2.5. X-ray structure determinations

Single crystals of compounds 1-3 were obtained as described above. X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo K α radiation. Details concern-

ing data collection have been fully described elsewhere [4]. Each crystal was mounted on the tip of a quartz fibre with silicone grease, and the set-up was quickly placed in the cold N₂ stream (-60° C) of a low-temperature controller. Fifty reflections were used in the cell indexing and about 200 reflections in the cell refinement.

All calculations were done on a DEC Alpha running VMS. The coordinates of rhodium and oxygen atoms for the structures were found in direct method Emaps using the structure solution program SHELXTL [5]. The positions of the remaining atoms were located after an alternating series of least-squares cycles and difference Fourier maps using the SHELXL-93 package [6]. The fluorine atoms of all CF₃ groups were found to be disordered over two or three different rotational orientations. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered fluorine atoms. Hydrogen atoms of aromatic ligands were included in the structure factor calculations at idealized positions. Relevant crystallographic data for compounds 1-3 are summarized in Table 1.

3. Results and discussion

3.1. Synthesis

Our experimental procedure included both the solid state deposition approach (1-3) and solution synthesis (2). Preparations of 1 and 2 are good examples of using a solid deposition technique for studying interactions of $Rh_2(O_2CCF_3)_4$ with liquid ligands, benzene and p-xylene in this case. The key factor in this synthesis is the use of extremely small amounts of suitable solvent, almost close to the equimolar ratio of the arene to the dirhodium molecules. This solid state approach was recently shown to be an effective route for obtaining unusual structures and compositions unattainable in solutions for the systems containing solvents, for example, $Rh_2(O_2CCF_3)_4$ -THF [2b] and $Rh_2(O_2CCF_3)_4$ -DMSO [2d]. The fact that dirhodium trifluoroacetate was forming an adduct with benzene became obvious a few years ago [4], but at that time suitable crystals had not been obtained from solution. The solid state approach (Section 2.2) applied here for benzene produced crystals of $Rh_2(O_2CCF_3)_4 \cdot C_6H_6$ (1) in moderate yield and of quality suitable for X-ray diffraction study.

Table 1

Crystal data and details on data collection and refinement for $Rh_2(O_2CCF_3)_4$ · C_6H_6 (1), $Rh_2(O_2CCF_3)_4$ · $(p-(CH_3)_2C_6H_4)$ (2) and $Rh_2(O_2CCF_3)_4$ · $C_{10}H_8$ (3)

	1	2	3
Formula	$C_{14}H_6F_{12}O_8Rh_2$	$C_{16}H_{10}F_{12}O_8Rh_2$	$C_{18}H_8F_{12}O_8Rh_2$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	<i>P</i> 1 (No. 2)
a (Å)	8.2818(5)	8.3121(9)	8.573(2)
b (Å)	15.624(2)	15.896(6)	9.069(9)
<i>c</i> (Å)	8.574(2)	8.6884(9)	9.332(6)
α (°)			69.71(2)
β (°)	103.81(1)	91.59(1)	63.50(2)
γ (°)			77.62(3)
V (Å ³)	1077.4(3)	1147.5(5)	607.5(7)
Ζ	2	2	1
Crystal size (mm)	$0.25 \times 0.15 \times 0.05$	$0.23 \times 0.20 \times 0.03$	$0.25 \times 0.12 \times 0.10$
Radiation Mo Kα (λ, Å)	(0.71073)	(0.71073)	(0.71073)
Temperature (°C)	-60	-60	-60
Data collection range, 2θ (°)	5.22-45.00	5.12-45.48	4.80-45.10
Reflections collected/unique	$4830/1382 \ (R_{\rm int} = 0.0515)$	$4750/1512 \ (R_{\rm int} = 0.0391)$	$3303/1524 \ (R_{\rm int} = 0.0672)$
Data/observ/restraints/params	1382/1272/30/157	1512/1410/54/191	1524/1409/12/175
$R_1^{a}, wR_2^{b} [I \ge 2\sigma(I)]$	0.0381, 0.0891	0.0403, 0.0957	0.0546, 0.1382
R_1^{a} , wR_2^{b} (all data)	0.0420, 0.0933	0.0436, 0.1004	0.0603, 0.1517
Goodnes-of-fit [°]	1.116	1.119	1.107
Largest difference peak and hole (e $Å^{-3}$)	1.004 and -0.574	0.735 and -0.589	1.201 and -0.813

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|$.

^b $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}.$

^c Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$, based on all data.



Fig. 1. Fragment showing the alternating arrangement of $Rh_2(O_2CCF_3)_4$ and C_6H_6 in the chain structure of 1. Rhodium and oxygen atoms are represented by thermal ellipsoids at the 40% probability level. Carbon, fluorine and hydrogen atoms are shown as spheres of arbitrary radii. Axial contacts to Rh atoms are drawn by dashed lines. Only rhodium atoms are labeled for clarity.



Fig. 2. Crystal packing of 1D chains of **2** viewed along the [100] direction of the unit cell.

The formation of complex 2, $Rh_2(O_2CCF_3)_4$ ·(p- $(CH_3)_2C_6H_4$), was first observed accidentally in the benzene-hexane solution system (Section 2.3.1). The presence of *p*-xylene was explained by the fact that it is added to both benzene and hexanes stills at the stage of the preparation the Na-K amalgam. Later the yield of 2 was increased by using neat p-xylene as a solvent (Section 2.3.2); in addition, product 2 was also obtained by the solid state approach (Section 2.3.3). The first synthesis of 2 (Section 2.3.1) is an interesting example of a competition in solution of weak π -donor ligands for coordination by the strong Lewis acid, $Rh_2(O_2CCF_3)_4$. The *p*-xylene, being a stronger donor than benzene (even though present in solutions as a minor component), binds preferentially to axial positions of dirhodium trifluoroacetate units to form 2. This fact should be taken into account when studying

weak interactions in so-called 'noncoordinating' solvents such as benzene, toluene or xylenes, which can be considered as weak Lewis bases themselves, as we clearly observed for the systems containing Rh_2 -(O_2CCF_3)₄. Similar observations were made when studying weakly coordinating anions, which have about the same nucleophilicity toward various cations as toluene [7]. Interestingly, in the case of *p*-xylene ligand, both solution and solid state techniques yielded the same product, the chain polymer of 1:1 composition in which the aromatic ring is acting as a bidentate ligand, while for THF and DMSO [2b,d], solution reactions always resulted only in the formation of the discrete bis-adduct molecules with monodentate coordination of ligands.

The solid state deposition approach ('solventless' technique, indeed, in this case) has been used (Section 2.4) for studying complexation of $Rh_2(O_2CCF_3)_4$ with the solid sublimable ligand, naphthalene, to give crystals of $Rh_2(O_2CCF_3)_4 \cdot C_{10}H_8$ (3). In contrast to the single ring aromatic ligands, benzene and p-xylene, naphthalene, the simplest compound having fused arene rings, was used for coordination with Rh2-(O₂CCF₃)₄. From previous reports on transition-metalnaphthalene complexes, (η^6 -naphthalene) sandwiches containing a metal in the zero-valent state (Cr, Mo, etc) have been traditionally prepared by metal vapor synthesis technique [8]. Recently, the naphthalene radical anion reductions of a variety of transition metal precursors have been introduced as a convenient method for the synthesis of anionic bis or tris(naphthalene) metal complexes [9], with examples such as $[(\eta^6-C_{10}H_8)_2Ti]^{2-1}$ [9b], or structurally characterized $[(\eta^4-C_{10}H_8)_3Zr]^2$ [9c]. Some mixed ligand naphthalene complexes have been also obtained using this technique, as for example $[\operatorname{Ru}(\eta^6-\operatorname{C}_{10}H_8)(1,5-\operatorname{cyclooctadiene})]$ [10] and $[\operatorname{Fe}(\eta^6-$ C₁₀H₈)(Cy₂PC₂H₄PCy₂)] [11].

3.2. Crystal structures

Three new complexes 1-3 have been obtained as green crystals, which were extremely unstable for 1 (loss of benzene), relatively stable for 3, with 2 being an intermediate case; any exposure to solvent media led to the solvolytic cleavage of 1-3. All products have been examined by X-ray crystallography and the 1:1 composition was confirmed by elemental analysis. All three structures consisted of the dirhodium(II) tetrakis(trifluoroacetate) molecules alternating with aromatic ligands, C_6H_6 (1), p-(CH₃)₂ C_6H_4 (2), and $C_{10}H_8$ (3), which are bound at axial positions of the Rh₂ units thus forming linear one-dimensional chains (Fig. 1). These chains lying parallel in the crystal are extended in the structure along the [100] direction ([001] in the case of 3) of the unit cell (Fig. 2). Selected distances and angles for 1-3 are given in Table 2. The coordination of arene

Table 2 Selected distances (Å) and angles (°) for $[Rh_2(O_2CCF_3)_4 \cdot arene]$ coordination polymers

Arene	Rh–Rh	Rh–C _{arene}	Rh-arene _{center}	C–C _{aver}	Rh-Rh-C _{arene}	Ref.
C ₆ H ₆	2.4115(9)	2.646(6), 2.678(6)	2.98	1.39(1)	164.2(2), 164.1(2)	this work
$(CH_{3})_{2}C_{6}H_{4}$	2.417(1)	2.598(7), 2.770(7)	2.99	1.39(1)	167.6(2), 161.1(2)	this work
$C_{10}H_{8}$	2.422(2)	2.609(9), 2.567(9)	2.97	1.39(1)	164.1(2), 166.1(2)	this work
$(CH_3)_6C_6$	2.422(1)	2.770(6), 2.787(6)	2.98	1.40(1)	165.4(1), 164.1(1)	[2a]
$(C_6H_5)_2C_2$	2.4256(6)	2.696(5), 2.750(6)	3.06	1.369(9)	165.1(1), 164.7(1)	[2e]

ligands in 1-3 was found to be off-center (Fig. 3) as in the cases of the C₆Me₆ and the Ph₂C₂ dirhodium complexes reported earlier [2a,e]. For benzene and p-xylene ligands (1 and 2) two opposite edges of the arene ring approach the axial sites of the neighboring dirhodium dimers in the $\eta^2(1,2):\eta^2(4,5)$ bridging fashion. For the single-ring aromatic ligands, in addition to the common η^6 -binding mode, there are only a few examples with benzene and *p*-xylene ligands bonding two metal centers in the off-centered way, for example, $[(^{t}Bu_{3}SiO)_{3}Ta]_{2}[\mu-\eta^{2}(1,2):\eta^{2}(4,5)-C_{6}H_{6}]$ [12] and $[(Cy_2PC_2H_4PCy_2)Co]_2[\mu-\eta^3:\eta^3-C_6H_4(CH_3)_2]$ [13]. There was also a systematic study of the Ag(I)-aromatic interactions, including benzene, xylenes and naphthalene ligands [14], which were all examples of an η^2 off-centered donation of π -electrons to Ag⁺, including one unusual η^1 -benzene compound [15].

In complex **3** both arene rings of the naphthalene molecule are engaged in coordination to the different Rh(II) centers in the $\eta^2(1,2):\eta^2(5,6)$ mode (see numbering in Scheme 2, Fig. 4). This is a rare unsymmetrical mode for the μ^2 -naphthalene in transition metal complexes [16–18]. The two coordination modes of naph-



Fig. 3. The view almost down the Rh–Rh axis of the $Rh_2(O_2CCF_3)_4$ (*p*-(CH₃)₂C₆H₄) unit in the chain structure of **2**. Rhodium and oxygen atoms are represented by thermal ellipsoids at the 40% probability level. Carbon, fluorine and hydrogen atoms are shown as spheres of arbitrary radii. Two closest axial contacts to Rh atoms are drawn by dashed lines.





thalene mentioned above, the most common for the discrete transition metal complexes obtained so far, were η^4 and η^6 . Several different bridging, μ^2 modes of naphthalene have been found [16–18] in a number of the multidecker compounds with different d- and f-block transition metals: $CpV(\mu^2-\eta^6:\eta^6-C_{10}H_8)VCp$ [16a], $[CpV(\mu^2-\eta^6:\eta^2-C_{10}H_8)Yb(THF)Cp]_n$ ($Cp = \eta^5-C_5H_5$) [16b], $(C_6H_6)Ru(\mu^2-\eta^4:\eta^6-C_{10}H_8)Cr(CO)_3$ [17].

The two closest Rh–C_{arene} distances average to 2.662(6) in (1), 2.684(7) in (2) and to 2.588(9) Å in (3) indicating the tightest metal–arene interaction in the naphthalene compound. At first glance, this contrasts to the general assumption that naphthalene binds less strongly to a metal than benzene [19], and to the data on bond-dissociation energies via calorimetric methods revealing that the naphthalene–Cr bond in the Cr(CO)₃ complex is 6 kcal mol⁻¹ weaker than the benzene–Cr bond [8c]. However, it is worth emphasizing that those data were valid for the discrete η^6 -compounds, while in the chain polymers 1 and 2 each arene ring coordinates two metal centers, and in 3 different rings of naphthalene are involved in coordination. This means that axial



Fig. 4. Fragment showing the alternating arrangement of $Rh_2(O_2CCF_3)_4$ and $C_{10}H_8$ in the chain structure of 3. Rhodium and oxygen atoms are represented by thermal ellipsoids at the 40% probability level. Carbon, fluorine and hydrogen atoms are shown as spheres of arbitrary radii. The shortest $Rh-C_{arene}$ contacts are drawn by dashed lines. Only rhodium atoms are labeled for clarity.



Scheme 3.

contacts to arene are expected to be shorter in 3 than in 1 and 2. Actually the Rh–arene center distances are very close, being in the range of 2.97–2.99 Å, for all dirhodium polymers mentioned in Table 2, except in the diphenylacetylene compound where the distance is 3.06 Å. All of the arene complexes, 1–3, demonstrate asymmetry in the two nearest metal–carbon distances. The difference in these two Rh–C_{arene} contacts is the most significant (0.172 Å) in complex 2 with *p*-xylene compared to the benzene (0.032 Å) and to the naphthalene (0.042 Å) polymers. It was 0.017 Å in the [Rh₂(O₂CCF₃)₄·C₆Me₆]_∞ compound [2a].

The unsymmetrical $\eta^2:\eta^2$ complexation of arene groups (Scheme 3a) seems to be preferred for the dirhodium(II) trifluoroacetate one-dimensional polymers based on the several examples obtained so far. This contrasts to the dichromium carboxylates with coordinated aromatic ligands of the 1:1 composition, including benzene and p-xylene analogues, in which arene rings were lying centrically on the line between two dimetal units and thus having a η^6 (Scheme 3b) symmetrical coordination [20]. In $[Bi_2(O_2CCF_3)_4]$ · $C_6Me_6]_{\infty}$, the only arene adduct of a main group element tetracarboxylate, the C_6Me_6 molecules are also acting in an η^6 coordination mode [21].

The unsymmetrical complexation of aromatics in 1-3 causes no detectable distortion of the arene rings. The mean C-C distances are the same, averaged to 1.39(1) in 1-3.

There was an attempt to compare the inductive effect of different substituents of arene ligands on the Cr–Cr and the Cr–ring center distances [20]. One might expect that the stronger the nucleophile substituent is, the stronger is the interaction of an axial ligand with the dimetal moiety (which, in turn, would result in the elongation of the metal–metal distance). However, there was no simple relationship found for a number of relative compounds between the ionization potentials of arenes and the Cr–Cr distances [20]. The latter was shown to be influenced by other variables, packing forces being the most important one. This is also the case for a number of dirhodium tetrakis(trifluoroacetate) chain polymers with coordinated arenes studied here. The present results show that the electronic properties of aromatic ligands in donor-acceptor complexes with $Rh_2(O_2CCF_3)_4$ are not simply correlated with their coordination strength. For example, the relatively strong donor, hexamethylbenzene, has the longest Rh-C_{arene} contacts (averaged to 2.779(6) Å [2a]) among the arenes studied (Table 2). The difference, 0.19 Å, shortest Rh-Carene contacts in in these two $[Rh_2(O_2CCF_3)_4 \cdot (C_6Me_6)]_{\infty}$ compared to the naphthalene analogue (2.588(9) Å) is significant, while the Rh-Rh distances are exactly the same for two compounds. Obviously, packing forces and other stereochemical factors are very important in these arene-metal interactions, capable of overriding electronic factors.

In 3 the naphthalene molecule approaches the rhodium atoms via the 1,2 and 5,6 C–C bonds. This could well be an electronic effect since it is these bonds that have the highest π -bond order, 0.73, compared to 0.61 for the 2,3 and 6,7 bonds (Scheme 2), according to Hückel calculations [22].

3.3. Conclusions

In summary, complexation of π -arene ligands, benzene, *p*-xylene and naphthalene, with the dirhodium unit has been examined by preparing a number of 1:1 coordination polymers with Rh₂(O₂CCF₃)₄. It is found that dirhodium tetrakis (trifluoroacetate) exhibits a selective coordination toward weak donor bases, such as benzene and p-xylene, in solutions. The crystalline complexes 1-3 have a one-dimensional framework constructed by the dirhodium units and arene ligands bound to its axial positions through two carbon atoms at each end. The geometry of coordinated arene bridges is unsymmetrical, an $\eta^2:\eta^2$ type, in all cases. Complex 3, $[Rh_2(O_2CCF_3)_4 \cdot (C_{10}H_8)]_{\infty}$ constitutes the first example of such products with a dicyclic arene system. We think that related and novel compounds with polycyclic aromatic ligands having an extended delocalized π -system will generally be accessible by the technique introduced, and studies on arene ligands with multicoordination-site possibilities are under way.

4. Supplementary Material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 140762, 140763 and 140764 for compounds **1**, **2** and **3**, respectively. Copies of the data can 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).

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