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Rhodium complexes of 3,4-di(β-naphthyl)-2,5-diarylcyclopentadienone: indirect detection of slowed naphthyl rotation

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Abstract

In the solid state, [(acetylacetonate)-3,4-di(β-naphthyl)-2,5-diarylcyclopentadienone]rhodium(I) (**4a**, aryl = phenyl, **4b**, aryl = *m*-xylyl) exist as head-to-tail dimers in which each rhodium is bonded to the γ-carbon of the acetylacetonate ligand in the other half of the molecule. These dimers are also favoured in solution at low temperature, and restricted naphthyl rotation results in the formation of numerous conformers whereby the naphthyls can adopt either proximal or distal orientations. These rotamers can be detected by observation of the ^{1}H- and ^{13}C-NMR methyl resonances in the acetylacetonate moiety. Triphenylphosphine cleaves the dimers (**4a** and **4b**) to give the corresponding monomers, $(C_4Ar_2(naphthyl)_2C{=}O)Rh(acac)PPh_3$ (**5a** and **5b**), and the crystal structure of **5a** exhibits a proximal/distal disorder of one naphthyl substituent. The rotamers of **5a** and **5b** are also present in solution, and the variable-temperature ^{31}P-NMR spectra yield activation enthalpies of 8.2 ± 0.5 kcal mol^{-1} for naphthyl rotation in each compound.

Keywords: Rhodium–acetylacetonate dimers; Hindered naphthyl rotation; Variable-temperature NMR; X-ray crystallography

1. Introduction

Recent reports from this laboratory have described the syntheses, structures and molecular dynamics of a number of propeller systems of the type $(C_nAr_n)^{z\pm}$ or $(C_nAr_n)ML_x$, where $n = 5$, 6, 7 and Ar is phenyl or ferrocenyl [1–6]. The goal is to build molecules in which rotations of the peripheral aryl groups and of the ML_x moiety are correlated in a fashion analogous to a bevel gear [7]. As explicated by Mislow [8], molecules that resemble a larger object in form only may be described as iconic models, whereas an analogic model 'may resemble its object in behavior as well as form'.

In earlier work, we and others have shown that in $(C_6Et_6)ML_3$ systems, such as $[(C_6Et_6)Cr(CO)(CS)(NO)]^+$, the barriers to ethyl rotation (11.5 kcal mol^{-1}) and to tripodal rotation (9.5 kcal mol^{-1}) are clearly different, indicating that these fluxional processes are not correlated [9,10]. It has also been demonstrated that, in the series $(C_5Ph_5)Fe(CO)(CHO)PR_3$ [1], $(C_6Ph_6)Cr(CO)_3$ [2], C_6Ph_5Fc [3], $[C_7Ph_7]^+$ [5] and C_7Ph_6FcH [3], enlarging the central ring (which, of course, decreases the angle between the substituents) leads to an increase in the dihedral angle between the peripheral and central ring planes: C_5Ph_5 ~ 50° [11], C_6Ph_6 ~ 65° [12], C_7Ph_7 ~ 80° [5]. However, in the heptaphenyltropylium cation, it also results in a loss of planarity such that the seven-membered ring adopts a shallow boat-like structure so as to minimize unfavorable steric interactions between *ipso* carbons [5].

Returning to the $(C_5Ph_5)ML_3$ series, it is relatively straightforward to derive a barrier for tripodal rotation

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since, when this process becomes slow on the NMR time-scale, the degeneracy of the ring carbons is broken, and gives rise to five individual ^{13}C resonances [1]. It is, however, more challenging to measure the barrier to peripheral ring rotation since, even on a high-field spectrometer, there is considerable peak overlap that renders spectral simulation a non-trivial task.

The greatly enhanced chemical shift range exhibited by ^{19}F nuclei, relative to that normally encountered in ^{1}H-NMR, prompted us to consider incorporation of a pentafluorophenyl ring that might provide a suitable label with which to monitor peripheral ring rotation. Consequently, we chose to synthesize $C_5(C_6H_5)_4(C_6F_5)OH$—a potential precursor to $C_5(C_6H_5)_4(C_6F_5)Br$, and thence to $[\eta^5\text{-}C_5(C_6H_5)_4(C_6F_5)]Fe(CO)_2Br$. Although 1,2,3,4-tetraphenyl-5-pentafluorophenylcyclopentadienol has now been prepared and characterized by X-ray crystallography, the yield is unacceptably low, and the major product arises from 1,6-addition of C_6F_5Li to tetraphenylcyclopentadienone (tetracyclone) [13]. In related work, Deck [14,15] has demonstrated the viability of using a C_6F_5 group to probe the barrier to peripheral ring rotation in complexes of the type $[C_5(C_6F_5)_nH_{5-n}]ML_x$, where $n = 2$, 3 or 4, and a corresponding penta-aryl derivative has recently appeared in a patent [16]. Very recently, Thépot and Lapinte have reported a convenient route to penta-arylcyclopentadienols containing either *ortho*- or *meta*-difluorophenyl rings [17]; these ligands hold promise of providing useful probes for the dynamics of $(C_5Ar_5)ML_n$ systems.

In an attempt to increase the steric demand of the peripheral rings, we chose to incorporate naphthyl substituents, which effectively serve as phenyl groups with a 'labeled edge', allowing for the distinction between *syn* and *anti* isomers. A few studies have been aimed towards the development of naphthyl substituents for use as controls over structure and reactivity, as well as peripheral substituents in propeller structures [18–28]. In addition, several α- and β-naphthyl substituted benzenes have been synthesized, and, in some cases, barriers to naphthyl rotation have been reported [24–27]. A notable application of the steric hindrance offered by a naphthyl group is the chiral cyclopentadienyl ligand proposed by Baker et al. [28] in which the constrained motion of an α-naphthyl substituent would restrict the site of metal coordination and generate a chiral cyclopentadienyl metal complex with the potential for use in asymmetric synthesis.

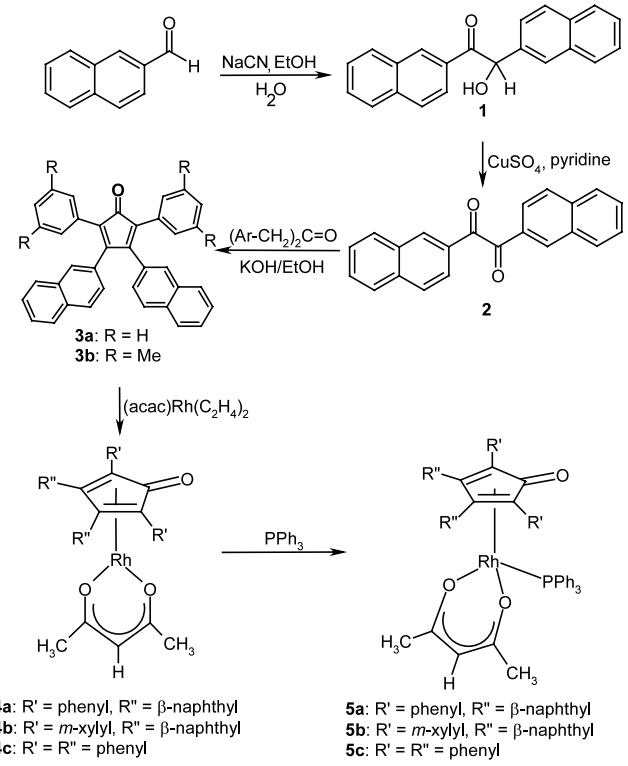
While numerous metal complexes of tetracyclone have been described [29], we are aware of only one naphthyl analogue, even though the syntheses of several potential ligands are known from cursory early reports [30]. A number of years ago, Rausch et al. reported the synthesis of a series of $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_4Ph_2R_2)$ and $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5Ph_2R_2C{=}O)$ complexes produced in good to low yields (81 and 8%, respectively), where R is an α- or β-naphthyl substituent; one complex was structurally characterized, but no dynamic studies were performed [23]. We now describe the syntheses, structures and fluxional behaviour of rhodium-acetylacetonate derivatives of 3,4-di(β-naphthyl)-2,5-diarylcyclopentadienone (aryl = phenyl, *m*-xylyl).

2. Results and discussion

As depicted in Scheme 1, the cyanide-catalyzed dimerization of β-naphthaldehyde to the corresponding naphthoin (**1**), subsequent oxidation with $CuSO_4$ in pyridine to yield β-naphthil (**2**), and reaction with 1,3-diphenylpropanone or 1,3-bis(*m*-xylyl)propanone [17] gives the required 3,4-di-(β-naphthyl)-2,5-diarylcyclopentadienones (**3a** and **3b**).

2.1. X-ray crystallographic results

Treatment of **3a** and **3b** with (acetylacetonato)bis(ethylene)rhodium(I) gave the desired complexes (**4a** and **4b**), whose structures are shown in Fig. 1. Both molecules adopt a head-to-tail dimeric arrangement in which the rhodium is bonded to the γ-carbon of the acetylacetonate ligand, as previously found for the analogous $(C_4Ph_4C{=}O)Rh(acac)$ complex (**5**) and simi-



Scheme 1. Synthesis of aryl-substituted cyclopentadienone complexes of $Rh(acac)(PPh_3)$, where aryl is phenyl, *m*-xylyl or β-naphthyl.

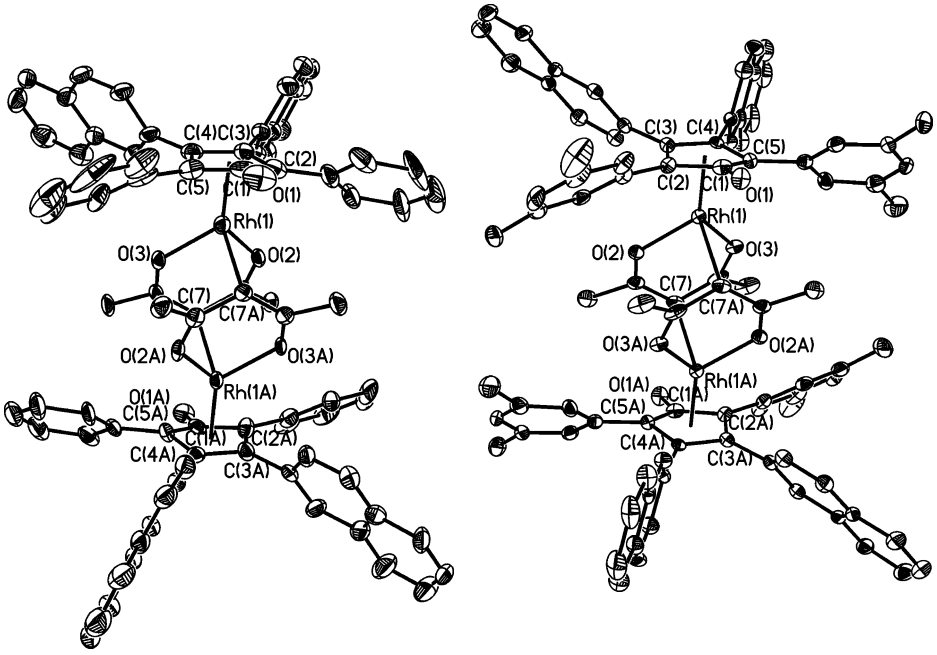


Fig. 1. Molecular structures of the dimers $[(C_4Ar_2(\beta\text{-naphthyl})_2C=O)\ Rh(acac)]_2$, Ar = phenyl, *m*-xylyl, (**4a**, **4b**; 30% thermal ellipsoids), with hydrogen atoms omitted for clarity.

lar compounds [29a,31–36]. The bond distance from the rhodium in one monomer to the γ-carbon of the acetylacetonate ligand of the other monomer is 2.353(9) in **4a** and 2.389(6) Å in **4b**, values comparable to the 2.39(1) Å found in the tetracyclone analogue, **4c** [29a]. These may also be compared with the increased bond length of 2.408 Å displayed in the [Cp*Ru(acac)] dimer [31,32], and the decreased 2.287(6) Å found in the dication $[\{Cp^*Rh(acac)\}_2]^{2+}$ synthesized by Maitlis and coworkers [35]. The aryl substituents in the α-positions of the cyclopentadienone rings of **4a** and **4b** are arranged in a 'cup-shaped' geometry around the metal, the latter being in a square pyramidal environment in which the centers of the two cyclopentadienone double bonds and the acetylacetonate oxygens form a square plane capped by the γ-carbon of the other monomer.

The Rh–C bond distances to the cyclopentadienone carbons C(2)–C(5) range from 2.116(10) to 2.155(6) Å in the dimers; however, the Rh(1)–C(1) distance is much longer, 2.412(12) [2.412(7) Å] for **4a** (**4b**), in agreement with previous studies [29a]. The carbonyl carbon is bent away from the plane of the cyclopentadienone ring by 19.5(1) [16.0(3)°], similar to that found for the tetracyclone analogue (17°). The Rh–acac ring forms an angle of 68.9(4) [69.8(3)°] with the plane of the cyclopentadienone ring carbons, closely approximating the 65° found in the tetracyclone derivative, but significantly deviating from the near orthogonal arrangement found in the 3-ferrocenyl-2,4,5-triphenylcyclopentadienone analogue (88°) [29a]. The latter complex is monomeric, presumably as a response to the steric requirements of the ferrocenyl substituent. The corresponding interplanar angle between the plane of the pentamethylcyclopentadienyl ring and that containing O(1)–Ru–O(2) in the $[Cp^*Ru(acac)]_2$ system is 58° [31,32].

Interestingly, in **4a**, the two naphthyl ligands on the cyclopentadienone ring of one monomeric moiety are arranged distal with respect to dimeric core, whereas the naphthyl rings in the other half of the molecule adopt proximal orientations, which precludes the presence of a C_2 axis in the dimer. In addition, **4a** contains open channels between the dimeric units, which are partially occupied by dichloromethane solvent molecules. The solvent is structurally essential, as the crystals rapidly collapse to powder if the solvent is allowed to evaporate. In **4b**, there is one naphthyl group distal and one proximal in each monomer, and the molecule possesses an inversion center. Crystals of **4b** do not have the same structural dependence on the presence of solvent; however, disordered, partially occupied solvent molecules are present in the structure.

In continuation of our investigation of the chemistry of these electrophilic species, **4a** and **4b** were allowed to react with two equivalents of triphenylphosphine at room temperature to give **5a** and **5b**, respectively, in which the dimers have been cleaved upon addition of the phosphine ligand. The crystal structures of these monomers appear as Fig. 2, and as before, the aryl groups in the α-positions of the cyclopentadienone rings exhibit a 'cup-shaped' orientation.

As before, the rhodium is in a square-based pyramidal environment, and the distances from rhodium to C(2) through C(5) in the cyclopentadienone ring range from

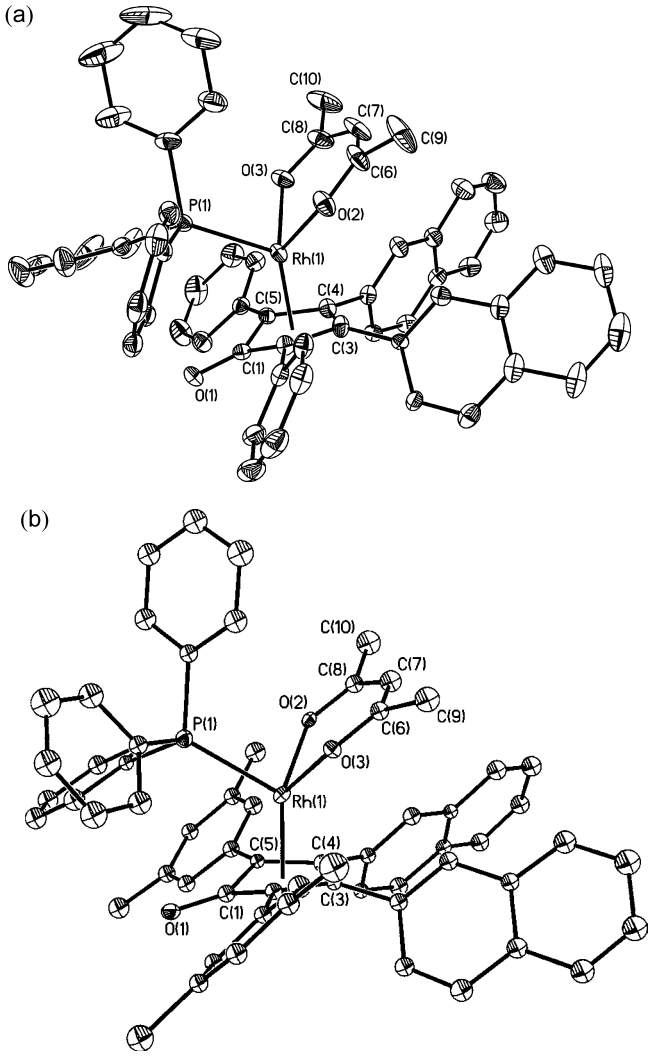


Fig. 2. Molecular structures of $(C_4Ar_2(\beta\text{-naphthyl})_2C{=}O)$ Rh(acac)(PPh_3), (a) Ar = phenyl, (b) Ar = *m*-xylyl, (**5a**, **5b**; 30% thermal ellipsoids), with hydrogen atoms omitted for clarity.

2.141(11) to 2.177(3) Å; the Rh–C(1) distance is 2.450(3) [2.448(13) Å] in **5a** (**5b**). The carbonyl group is bent away from the rest of the molecule by 21.0(3) [22(1)°], slightly greater than in the dimer. The Rh–P distance is 2.3861(10) [2.402(4) Å], somewhat longer than the conventional range of literature values (2.201–2.303 Å) [37], and significantly longer than the Ru–P distance (2.245 Å) found in Koelle's Cp*Ru(acac)($P(OMe)_3$) system [31]. In contrast to **4a**, **4b** and other dimeric structures, the plane of the acac ring in **5a** (**5b**) makes a much smaller angle of 37.3(2) [37.8(6)°] with the C(2)–C(5) plane of the cyclopentadienone ring, presumably as a result of the steric bulk of the added phosphine. This observation parallels the behaviour of Cp*Ru(acac)($P(OMe)_3$) which also forms a corresponding interplanar angle of 37° [31].

A particularly interesting feature of the crystal structure of **5a** (Fig. 3) is that one of the naphthyl rings

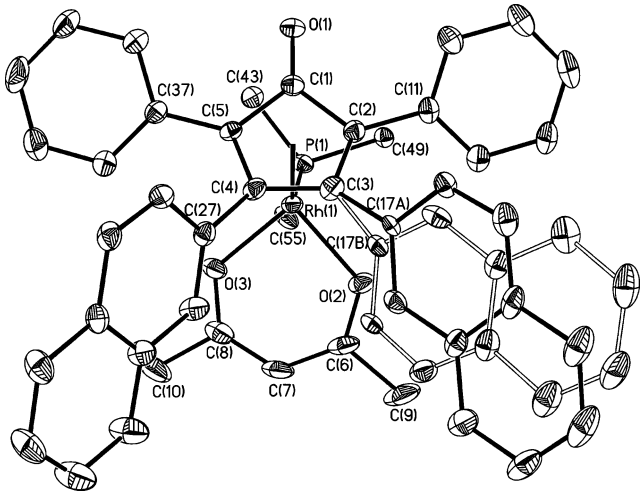
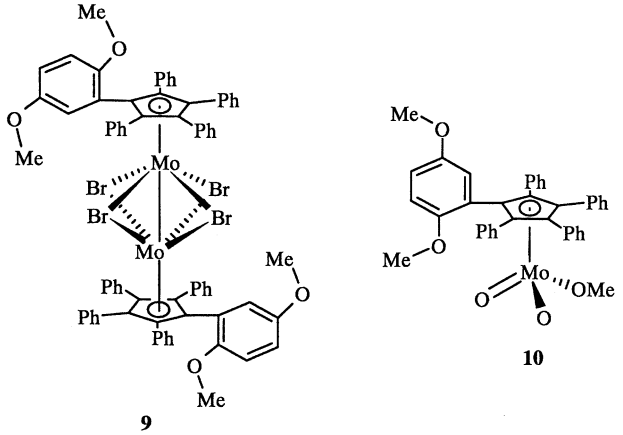


Fig. 3. Bird's eye view of **5a**, showing one disordered β-naphthyl substituent.

is disordered and exhibits both distal and proximal orientations in a 55:45 ratio, respectively. Similar behaviour has been reported in a molybdenum complex containing the 1-(2,5-dimethoxyphenyl)-2,3,4,5-tetraphenylcyclopentadienyl ligand, (**8**) [38,39]. In the dimeric species **9**, the dimethoxyphenyl groups are apparently rigid, and no barrier to rotation was determined, while in complex **10**, this aryl rotation barrier was reported to be 16.3 kcal mol^{-1}. The solid state structure of **10** revealed a disorder in which one of the dimethoxyphenyl groups was found in two conformations with occupancies of 0.24 and 0.76 (Scheme 2). In **5b**, both naphthyl groups are oriented distal to the metal.

It is interesting to note the presence of several combinations of naphthyl orientations in the four crystal structures: in **4a**, one monomer has both naphthyls distal, the other monomer has both proximal; in **4b**, both monomers contain one distal and one proximal naphthyl. In the monomer **5a**, one naphthyl



Scheme 2. Molecules **9** and **10**.

is distal and one is disordered proximal/distal, while **5b** contains two distal naphthyl groups. The various naphthyl conformations observed in the solid state illustrate the ability of these complexes to accommodate the bulk of the naphthyl groups, and support the contention that many of these rotamers are present in solution at low temperature, at the limits of restricted naphthyl rotation, in the absence of crystal packing forces.

2.2. Variable temperature NMR results

The ^{1}H- and ^{13}C-NMR spectra of **4a** and **4b** at room temperature each showed a single methyl signal for the acac ligand, and the expected, well-resolved resonances readily assignable to the β-naphthyl and phenyl, or *m*-xylyl, substituents. However, in both systems, cooling the sample from 303 to 263 K resulted in the broadening and dispersion of the ^{1}H and ^{13}C aromatic resonances.

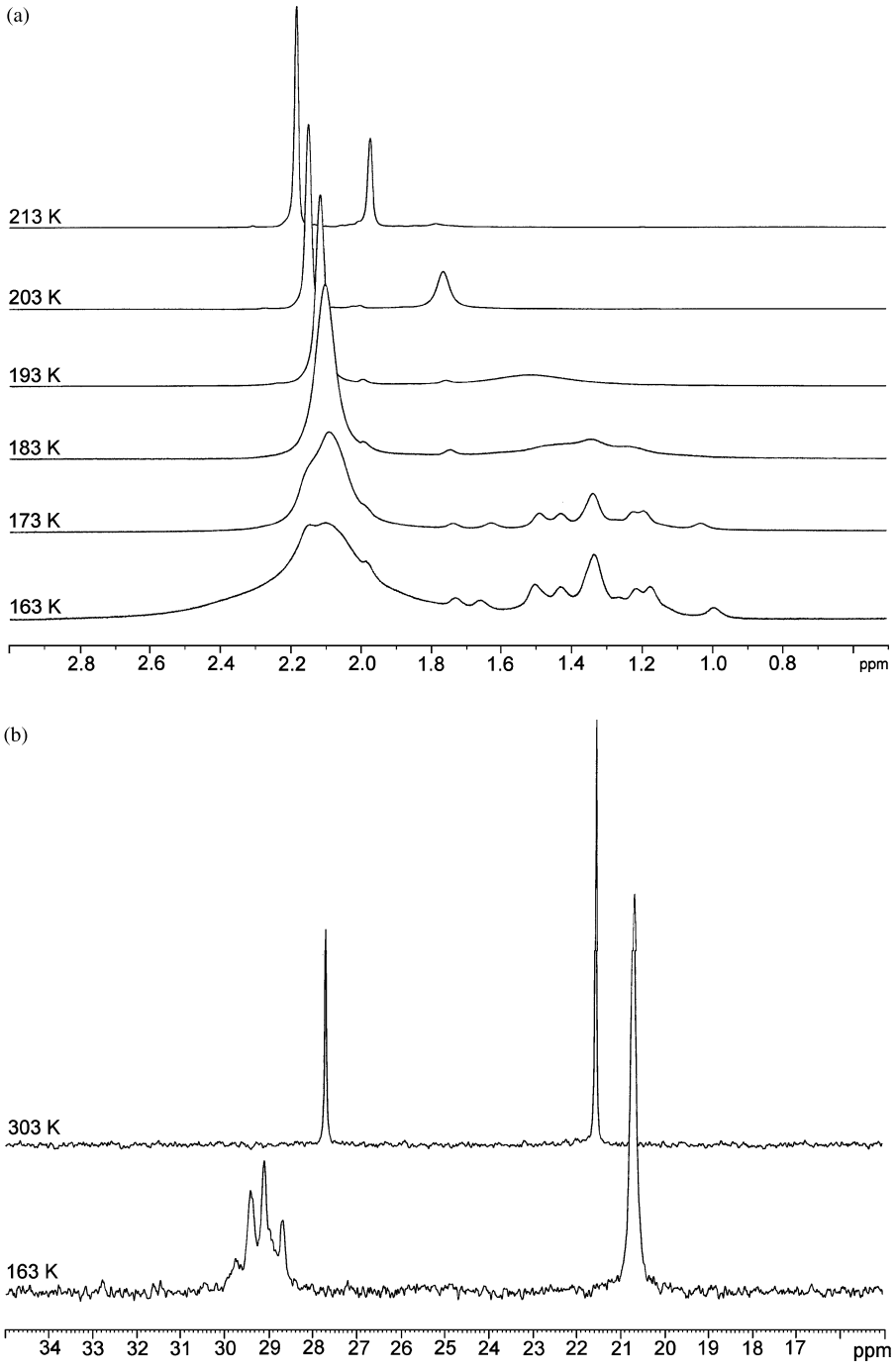


Fig. 4. Variable-temperature 500 MHz ^{1}H-NMR spectrum of **4b** in the region of the *m*-xylyl-methyl and acac-methyl protons. (b): Variable-temperature 125 MHz ^{13}C-NMR spectrum of **4b** in the region of the *m*-xylyl-methyl and acac-methyl carbons.

Moreover, as the temperature was reduced, the initially sharp ^{1}H peaks at 2.13 and 2.16 ppm for the acac–methyl protons in **4a** and **4b** respectively, broadened and gradually moved to markedly lower frequency. Furthermore, in both molecules, as shown in Fig. 4a for **4b**, further cooling induced the splitting of the broad peak for the acac methyl protons and, at 173 K, several peaks centered around 1.35 ppm began to emerge.

Similar splitting behaviour is also observed in the ^{13}C regime, whereby the resonance of the acac methyl carbon at 27.7 ppm (for **4b**) clearly splits into several peaks (Fig. 4(b)). The anticipated observation of a Rh–C coupling for the dimer is prevented by the monomer–dimer exchange process. Thus, a J_{Rh-C} of ca. 10 Hz, as seen in Rh–Cp* systems [35], would not be discernible, even at slow monomer–dimer exchange rates.

It is apparent that the methyl groups of the acetylacetonate ligand serve as a probe for the observation of the fluxional behaviour of the naphthyl groups. In order for the protons and carbons of the acac methyl groups to split, they must be in different magnetic environments at low temperature. Thus, assuming that **4a** and **4b** exhibit rapid monomer–dimer equilibria at room temperature (analogous to the behavior of Koelle's Cp*Ru(acac) system) [36], then time-averaged NMR spectra would be expected in which there is only one peak for the acac–methyl protons and carbons, and all the naphthyl environments should also be equivalent. However, at lower temperatures, as the dimer concentration increases, restricted rotation of the naphthyl groups becomes evident. One obvious effect on the ^{1}H-NMR spectra is the gradual shift to lower frequency of the acac–methyl resonances as the temperature is reduced; this phenomenon is readily explained in terms of the increasing fraction of dimer in the sample, whereby the methyl protons lie in the aromatic shielding region of the aryl substituents in the other half of the molecule.

Although a barrier to Rh(acac) rotation relative to a tetra-substituted cyclopentadienone ring has been reported [29a], this involved the replacement of a peripheral phenyl group in tetracyclone by a bulky ferrocenyl substituent. This not only prevents dimer formation but also provides the asymmetrical substitution required for the examination of the fluxional behaviour of the acetylacetonate group. In that case, two methyl signals were observed at low temperature in the ^{1}H- and ^{13}C-NMR, yielding a barrier to acac rotation of 12.5 kcal mol^{-1}. We note, however, that the fluxional process merely interconverts isoenergetic rotamers. In both **4a** and **4b**, and for the tetracyclone analogue, **4c**, the solid state structures are such that the ketonic unit eclipses the Rh(1)–C(7A) bond. EHMO calculations reveal that this rotamer is favoured because of better overlap between the frontier orbitals of the Rh(acac) and the π system of the cyclopentadienone. As a result of this, one would not anticipate the presence of detectable quantities of other rotamers, since the 'pseudo-tripod' cannot adopt conformers of comparable energy. This leaves restricted naphthyl rotation as the only viable explanation for the plethora of acac–methyl resonances.

If the dimer of **4b** shown in Fig. 1 were the only isomer present in solution, then two methyl signals would be anticipated, as the molecule would have effective C_i symmetry. The observation of multiple methyl resonances indicates not only that rotation of the naphthyls is hindered, but also that several conformations can co-exist at low temperature. Table 1 and Plate 1 list the seven possible isomers of the dimers (each of which bears four acac–methyl groups) that may be present as a result of restricted naphthyl rotation. If all rotamers were equally probable, thus giving rise to a statistical distribution, there would be sixteen equally intense methyl singlets. At 173 K, the ^{1}H- and ^{13}C-NMR spectra of **4a** and **4b** exhibit several acac–methyl environments, and we suggest that the numerous peaks originate from the presence of the more energetically favourable rotamers, with intensities governed by the relative fraction of each isomer present. This interpretation is supported by the variable-temperature ^{1}H-NMR behaviour of (tetracyclone)Rh(acac), **4c**, whose acac–methyl signal likewise exhibits a gradual shielding upon cooling (δ 2.09 ppm at 303 K and 1.12 at 163 K) which never loses its singlet character. The complexity of the spectra of **4a** and **4b** preclude the determination of activation parameters, since the assignment of each line to its respective rotamer and the determination of the relative population of the isomers is not viable [40].

With the goal of determining a barrier for naphthyl rotation, variable-temperature NMR data were also acquired for **5a** and **5b**. In the spectra of both complexes, the peaks for the acac–methyl protons and carbons do not split, even at 163 K. However, as illustrated in Fig. 5, the ^{31}P-NMR spectrum of **5a** (**5b**) yields a doublet with J_{Rh-P} of 165.6 (167.3 Hz) at room temperature, which decoalesces into two doublets at 163 K.

There are several possible explanations for the origin of the ^{31}P splitting at low temperature, (a consequence of the use of an indirect method of observation): (i) hindered rotation of the metal tripod, (ii) restricted rotation about the P–C_{ipso} bonds of the triphenylphosphine propeller, and (iii) restricted naphthyl rotation. Molecular modeling studies suggest that there is no significant steric barrier to tripodal rotation attributable to the presence of the naphthyl groups, which might have been expected to interfere with the bulky triphenylphosphine ligand during rotation. Moreover, a variable-temperature study of the (tetracyclone)Rh(acac)(PPh_3) analogue, **5c**, shows no splitting in either the proton or phosphorus NMR spectra at low tem-

Table 1
Possible isomers of **4a** and **4b**

Isomer	Point group	Naphthyl orientation	Number of identical isomers, or enantiomers	Number of methyl resonances	Predicted intensities of methyl peaks
A	C_{2h}	All distal	1	1	4
B	C_{2h}	All proximal	1	1	4
C	C_s	Upper half, both distal; lower half, both proximal; or vice versa	2	2	4,4
D	C_1	3 distal, 1 proximal	4	4	4,4,4,4
E	C_1	3 proximal, 1 distal	4	4	4,4,4,4
F	C_2	1 distal, 1 proximal on each ring	2	2	4,4
G	C_i	1 distal, 1 proximal on each ring, with an inversion center	2	2	4,4

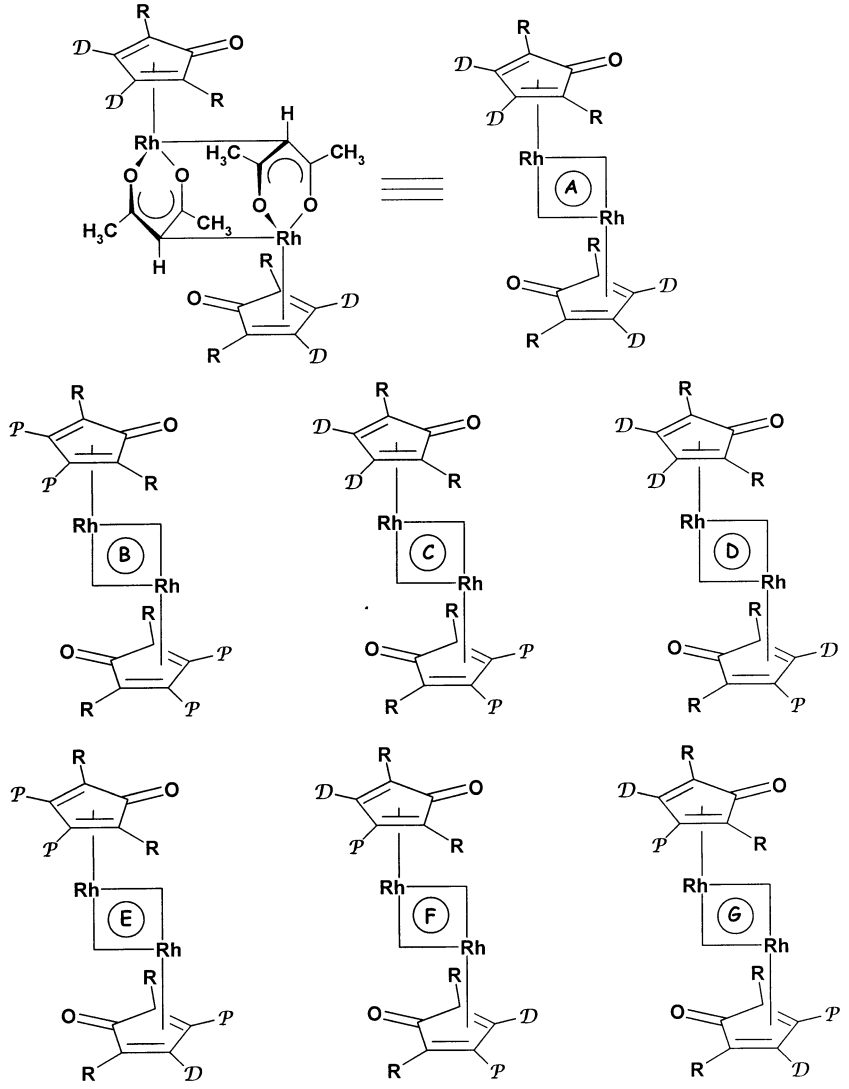


Plate 1. Possible isomers of **4**; P and D represent Proximal and Distal β-naphthyl substituents, respectively, R is a phenyl or *m*-xylyl substituent. Only one enantiomer of the chiral compounds is shown.

perature. This observation supports the view that the fluxional behavior is attributable to restricted rotation of the naphthyl groups, rather than slowed rotation of the Rh(acac)(PPh_3) unit with respect to the cyclopentadienone ring. The substitution of two phenyl groups by two naphthyl substituents (which effectively act as *meta*-substituted phenyl rings) is not likely to create enough steric strain to drastically increase the barrier to tripodal

Table 2
Crystallographic collection and refinement parameters for **4a**, **4b**, **5a** and **5b**

	4a	**4b**	**5a**	**5b**
Empirical formula	$C_{84}H_{62}O_6Rh_2\cdot(CH_2Cl_2)_{2.54}$	$C_{46}H_{39}O_3Rh\cdot(CH_2Cl_2)_{0.70}$	$C_{60}H_{46}O_3PRh\cdot CH_2Cl_2$	$C_{64}H_{54}O_3PRh\cdot C_6H_{14}$
Molecular weight	1589.13	802.13	1033.77	1005.01
Description	red needle	red plate	yellow needle	orange plate
Size (mm^3)	$0.1 \times 0.22 \times 0.5$	$0.10 \times 0.10 \times 0.08$	$0.20 \times 0.06 \times 0.03$	$0.21 \times 0.09 \times 0.03$
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	tetragonal	monoclinic	Monoclinic	Monoclinic
Space group	$I4_1/a$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	26.633(7)	15.698(7)	10.084(3)	12.300(5)
b (Å)	26.633(7)	21.468(12)	21.330(6)	20.625(8)
c (Å)	43.698(16)	12.646(7)	23.082(6)	22.487(9)
α (°)	90	90	90	90
β (°)	90	108.228(15)	96.795(4)	102.156(6)
γ (°)	90	90	90	90
V ($Å^3$)	30 995(16)	4047(4)	4930(2)	5577(4)
Z	16	4	4	4
Calculated density ($g\ cm^{-3}$)	1.362	1.316	1.393	1.300
Scan mode	ϕ- and ω-scans	ϕ- and ω-scans	ϕ- and ω-scans	ϕ- and ω-scans
$F(000)$	12 973	1654	2128	2288
Absorption coefficient (mm^{-1})	0.654	0.553	0.534	0.383
θ range (°)	1.43–25.00	1.37–27.64	1.30–27.50	1.35–20.80
Index ranges	$-33 \le h \le 34$, $-32 \le k \le 34$, $-56 \le l \le 56$	$-20 \le h \le 20$, $-27 \le k \le 25$, $-15 \le l \le 16$	$-13 \le h \le 13$, $-24 \le k \le 27$, $-29 \le l \le 27$	$-13 \le h \le 13$, $-22 \le k \le 22$, $-24 \le l \le 24$
Reflections collected	11 4275	35 434	46 593	27 351
Independent reflections	13 652	9296	11 274	5818
Data/restraints/params	12 531/0/930	9294/0/484	11 274/28/817	5643/0/327
Goodness of fit on F^2 (all)	1.385	1.060	1.011	0.940
Final R ($I > 2\sigma(I)$)	$R_1 = 0.0969$, $wR_2 = 0.2646$	$R_1 = 0.0782$, $wR_2 = 0.1969$	$R_1 = 0.0423$, $wR_2 = 0.0930$	$R_1 = 0.0711$, $wR_2 = 0.1571$
R indices (all data)	$R_1 = 0.1808$, $wR_2 = 0.3897$	$R_1 = 0.1685$, $wR_2 = 0.2339$	$R_1 = 0.0788$, $wR_2 = 0.1044$	$R_1 = 0.1916$, $wR_2 = 0.2400$
Transmission (ratio of max to min)	0.871372	0.764648	0.529629	0.876043
Largest difference peak and hole ($e\ Å^{-3}$)	4.223 and −1.215	1.190 and −0.831	0.456 and −0.484	0.678 and −0.551

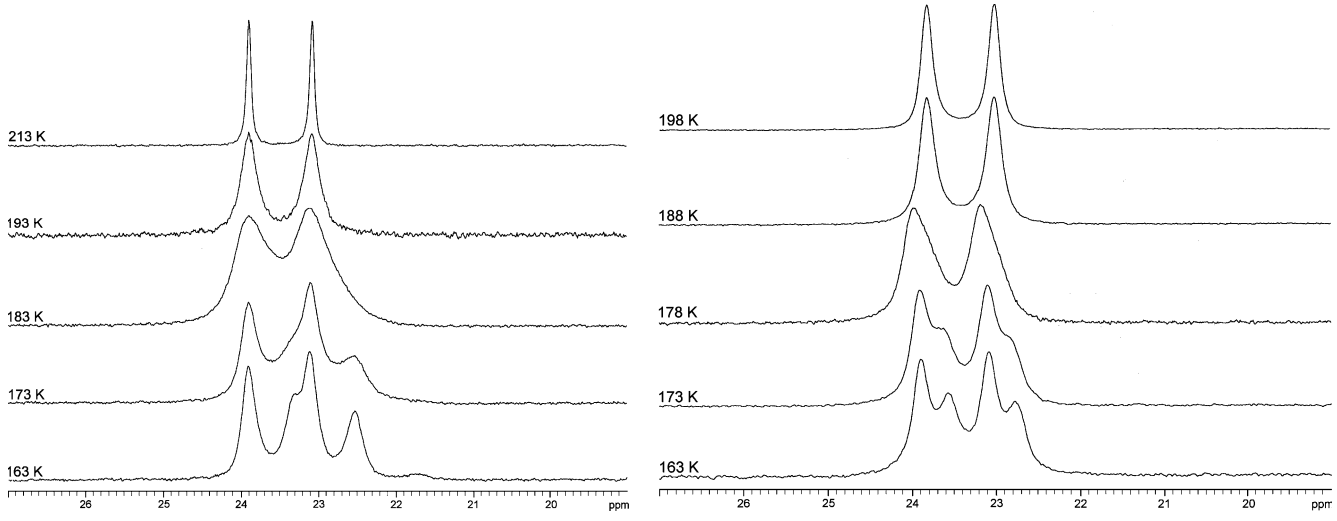


Fig. 5. Variable-temperature 202 MHz ^{31}P-NMR spectra of **5a** and **5b**, respectively.

rotation, especially if the naphthyl groups can rotate and move to accommodate the bulk of the triphenylphosphine. However, EHMO calculations suggest that there is a significant electronic barrier to tripodal rotation in the PPh_3 systems ($\sim$12 kcal mol^{-1}). This is a consequence of the less favourable overlap of the frontier orbitals on the cyclopentadienone ring with those of the Rh(acac)(PPh_3) unit when the tripod is rotated through 180° from that observed crystallographically. Slowed tripodal rotation would merely result in the formation of a single rotamer, with essentially no detectable concentration of any other, and only one peak would be expected in the ^{31}P-NMR spectrum. Thus, restricted tripodal rotation is not the origin of the fluxional behaviour in these systems.

There is precedence in the literature for the observation of restricted rotation about the P–C_{ipso} bonds of the triphenylphosphine ligand [41–54]. In the solid state [41] and in solution [42], PPh_3 adopts a chiral, propeller conformation in which the helix can be oriented in a clockwise or anti-clockwise orientation, resulting in a pair of enantiomers. Conformational analyses of the dynamic behaviour of triphenylphosphine have been performed by Mislow [43] and Kurland [44], and the interconversion of enantiomers or full rotation about P–C_{ipso} bonds have been determined to involve cooperative motion of the phenyl substituents [41,45]. The use of PR_3 as a probe to monitor dynamic behaviour in other regions of a molecule has also been established [1,47–54], and we have previously suggested that the ligand may not serve as an innocent probe, but may also give rise to different conformers at low-temperature [1]. Barriers to rotation of tri-substituted phosphines in many organometallic derivatives have been established [45–48], and several studies have shown that steric, rather than electronic, factors are dominant in determining their magnitude [49]. Examples include an upper barrier of 7.6 kcal mol^{-1} for P–C_{ipso} rotation in (C_5H_5)Fe(CO)(CN)(PPh_3) estimated by Faller, et al. [48] and 10.3 kcal mol^{-1} determined by Davies, et al. [45] for (C_5H_5)Fe(CO)($COCH_3$)(PPh_3).

In **5a** and **5b**, cessation of P–C_{ipso} rotation would result in the formation of enantiomers, as expected, however, these would not be differentiable by NMR without the presence of another source of chirality in the molecule, that is, the creation of diastereomers. As described by Willem [40], the 'fundamental inability of NMR spectroscopy to distinguish enantiomers or enantiotopic sites in an achiral environment' prevents the observation of this behaviour without another chiral center in the molecule. This necessarily involves the restricted rotation of the naphthyl substituents, which would result in the formation of diastereomers and allow for the differentiation of phosphorus environments by NMR. Thus, even if P–C_{ipso} rotation is slowed, the naphthyl groups must also exhibit restricted rotation in order for the different environments of the phosphorus atoms to be distinguishable. Similarly, restricted Rh–P rotation alone would not result in decoalescence of the phosphorus spectrum.

Consequently, we assert that the observation of the second ^{31}P-NMR doublet is consistent only with the slowed interconversion of the naphthyl groups between their two favoured conformations (distal/distal and distal/proximal). The presence of the two rotamers would place the phosphorus nuclei in different environments, thus influencing the appearance of the ^{31}P-NMR spectrum. Activation enthalpies for the naphthyl rotation processes in **5a** and **5b** were derived from Eyring plots prepared by lineshape analysis of the ^{31}P spectra, yielding barriers of 8.2$\pm$0.5 kcal mol^{-1} (Fig. 6).

This may be compared with the reported barriers of 8–10 kcal mol^{-1} for pentafluorophenyl rotation in [1,2,4-(C_6F_5)$_3$$C_5H_2$]$_2$Fe and [1,2,4-($C_6F_5$)$_3$$C_5H_2$]Re(CO)$_3$ [14] and 9$\pm$1 kcal mol^{-1} for hindered phenyl rotation in [C_5(C_6H_5)$_4$H]$_2$Fe [55]. Restricted aryl rotation in other substituted cyclopentadienones has been reported; for instance, ^{1}H- and ^{13}C-NMR at 233 K were used to determine barriers of $\sim$15 and $\sim$20 kcal mol^{-1} for the rotation of the α- and β-substituents, respectively, in tetra-*o*-tolylcyclopentadienone [40]. Haywood–Farmer and Battiste observed two signals in the methyl region of the room temperature ^{1}H-NMR of 2,4-diphenyl-3,5-bis(*o*-tolyl)cyclopentadienone, and determined a barrier of 21.8$\pm$0.4 kcal mol^{-1} for *o*-tolyl rotation [56]. In 1979, Rausch et al. observed six methyl peaks in the ^{1}H-NMR of cyclopentadienyl cobalt 3,5-diphenyl-2,4-bis(mesityl)cyclopentadienone, however, no variable-temperature studies were performed to determine a barrier to mesityl rotation [57]. It has been established that substitution in the *ortho* position of the peripheral groups in these sterically encumbered molecules dramatically increases barriers to rotation, and that *meta*-substitution merely reflects the buttressing effects of the *ortho*-protons [6,58]. A β-naphthyl group acts effectively as a *meta*-substituted phenyl group, thus the barrier to rotation would be expected to be much lower than in these *ortho*-substituted cyclopentadienones. However, α-naphthyl substituents would be expected to offer significantly greater steric hindrance and rigidity, and studies of the extension of this chemistry to these bulky groups are ongoing.

Finally, there is another interesting feature of the ^{31}P-NMR spectra of **5a**–**c** that merits comment; the spectral lineshapes exhibited a significant temperature and magnetic field dependence (Fig. 7). At room temperature, the 202 MHz ^{31}P spectra exhibited low intensity, broad, asymmetrical peaks, however, as the temperature was decreased, the peaks became sharper and more symmetrical. The ^{31}P spectra were also run on a lower field instrument (81 MHz), and the peaks were noticeably sharper.

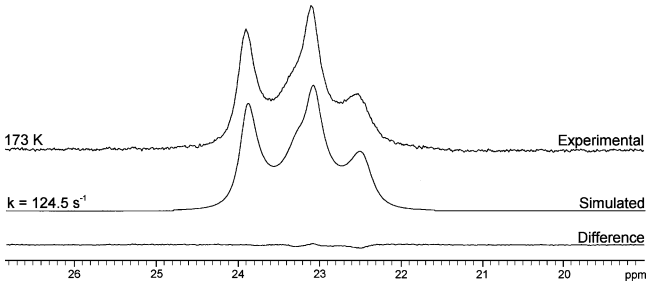


Fig. 6. Example of simulated lineshape spectra using the MEXICO program for **5a**.

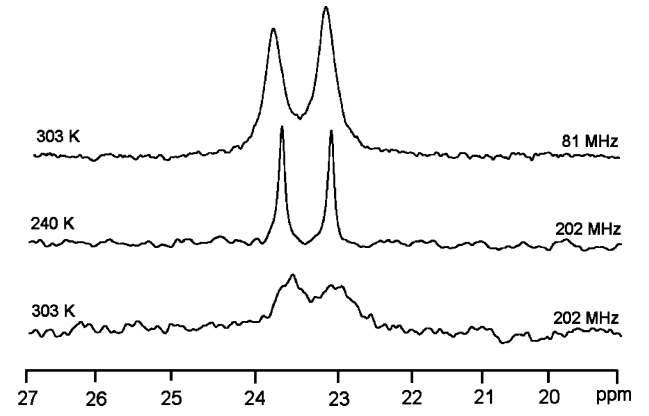


Fig. 7. Field strength and temperature dependence of the ^{31}P-NMR lineshape for 5a.

The exact cause of this behaviour has not been established, but the data suggest that it is the result of the influence of the chemical shift anisotropy (CSA) relaxation mechanism. The shape of the ^{31}P lines improves at lower field, which could be attributable either to the decreased spin–spin (T_2) relaxation due to the CSA of the phosphorus, or to reduced scalar relaxation from the CSA-induced T_1 of the rhodium. CSA relaxation is also implied by the asymmetry of the doublet, which is characteristic of a relaxation cross-term between dipolar coupling and CSA. This is a well-established effect [59] that has recently become important as the basis for the TROSY experiment in the structure determination of large biological macromolecules [60]. The unusual effect of the sharpening of the phosphorus lines at lower temperatures suggests that the rhodium T_1 may be below its temperature minimum, and may be getting longer with a reduction in both temperature and motion. Direct NMR measurements of the rhodium would be necessary to establish this proposition. This effect is not present at low temperature, thus does not impede the observation of splitting behaviour.

3. Conclusions

The incorporation of naphthyl substituents into cyclopentadienone–rhodium complexes results in the formation of mixtures of rotamers in which the naphthyls can adopt either proximal or distal orientations. In the dimers **4a** and **4b**, slowed naphthyl rotation can be detected by observation of the acetylacetonate ^{1}H-NMR methyl resonances. In the phosphine complexes **5a** and **5b**, the variable-temperature ^{31}P-NMR spectra yield enthalpies of activation for naphthyl rotation of 8.2 ± 0.5 kcal mol^{-1}. Efforts are continuing to synthesize poly-arylated ligands in which all the peripheral substituents are naphthyls, and these will be the subject of future reports.

4. Experimental

4.1. General methods

All reactions involving organometallic reagents were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. Tetrahydrofuran solvent was dried according to standard procedures before use [61]. Silica gel (particle size 20–45 μm) was employed for flash column chromatography. ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker Avance DRX-500 spectrometer at 500.13 and 125.76 MHz, respectively, and were referenced to the residual proton signal, or ^{13}C signal, of the solvent. Assignments were based on standard ^{1}H–^{1}H and ^{1}H–^{13}C two-dimensional techniques. ^{31}P-NMR spectra were acquired at 202.46 MHz and were externally referenced to the ^{31}P signal of 85% H_3PO_4 in D_2O. As a result of the poor resolution and asymmetry of the ^{31}P peaks at room temperature (r.t.) (as discussed above), the spectral data quoted below were collected at 243 and 163 K, which allowed for accurate peak assignment and coupling constant determination in both **5a** and **5b**. Mass spectra were measured on a Finnigan 4500 spectrometer by direct electron impact (DEI) or direct chemical ionization (DCI) with NH_3, as well as electrospray (ESI). Infrared spectra were recorded on a Bio-Rad FTS-40 spectrometer. Melting points (m.p.) (uncorrected) were determined on a Fisher–Johns melting point apparatus. Elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ont., Canada.

The reagents β-naphthaldehyde and 1,3-diphenylpropanone were used as received from commercial sources. (Acetylacetonato)bis(ethylene)rhodium(I) [62], (acetylacetonato)(2,3,4,5-tetra-phenylcyclopentadienone) rhodium(I) (**4c**) [29a] and 1,3-bis(*m*-xylyl)propanone [17] were prepared according to literature procedures.

4.2. 1,2-Di-(β-naphthyl)-2-hydroxyethanone, β-naphthoin (*1*)

In an adaptation of the literature procedure for the synthesis of benzoin [63], β-naphthaldehyde (10.12, 0.06) and NaCN (1.92 g, 0.04 mmol) were dissolved in 20 ml H_2O and 40 ml ethanol, then stirred under reflux for ca. 30 min, resulting in the formation of a thick, yellow precipitate, which was filtered by suction and dried to give **1** (8.23 g, 0.03 mol; 88%) as a pale yellow powder, m.p. 124–126 °C (lit. [64] 125–126 °C). Further concentration of the reaction mixture gave an additional 0.77 g of product, resulting in an overall yield of 96%. ^{1}H-NMR (200 MHz, CD_2Cl_2): δ 8.53 (s, 1H, naphthyl-H_1), 8.03–7.44 (m, 13H, naphthyl rings), 6.31 (s, 1H, CH), 4.68 (br, 1H, OH). ^{13}C-NMR (50 MHz, CD_2Cl_2): δ 199.3 (CO), 137.2, 136.1, 133.8, 133.5, 132.6, 131.3 (naphthyl C's), 131.6, 130.0, 129.4, 128.9, 128.3, 128.0, 127.7, 127.3, 126.9, 125.2, 124.5 (naphthyl CH's), 76.7 (CH–OH). MS (DEI; *m/z* (%)): 312 [M^+, 2%], 155 ($C_{10}H_7CO$, 99), 127 ($C_{10}H_7$, 100), 101 (C_8H_5, 13), 77 (C_6H_5, 24). MS (DCI; *m/z* (%)): 330 ($M+H+NH_3$, 1%), 313 (M+H, 37), 312 [M^+, 22], 295 (M–OH, 100), 267 ($C_{21}H_{15}$, 4), 201 ($C_{16}H_9$, 15), 155 ($C_{10}H_7CO$, 26), 128 ($C_{10}H_8$, 4), 77 (C_6H_5, 1).

4.3. 1,2-Di-(β-naphthyl)ethan-1,2-dione, β-naphthil (*2*)

The literature procedure for the synthesis of benzil [65] was modified for the preparation of **2**. Thus, $CuSO_4$ (8.76 g, 0.05 mol) was added to 13 ml pyridine and 25 ml H_2O in a 250 ml round-bottom flask. When all the $CuSO_4$ was dissolved, 1,2-di-(β-naphthyl)-2-hydroxyethanone (**1**) (8.23 g, 0.03 mol) was added and the reaction mixture was stirred under reflux for ca. 2 h, then left to cool overnight. The blue aqueous layer was decanted, leaving a yellow solid that was washed with water, then with hot HCl (10%). The product was filtered, then dissolved in CH_2Cl_2, dried over $MgSO_4$, filtered and the solvent was removed under vacuum to give **2** (7.53 g, 0.02 mol; 93%) as a yellow powder, m.p. 157–160 °C (lit. [64] 158–159 °C). ^{1}H-NMR (200 MHz, CD_2Cl_2): [assignments are quoted with respect to the normal labeling for a β-naphthyl substituent] δ 8.47 (s, 1H, naphthyl-H_1), 8.15 (dd, 1H, *J*(HH) 8.6 Hz, 1.52 Hz, naphthyl-H_4), 8.04–7.92 (m, 3H, naphthyl-$H_{3,5,8}$), 7.67 (dt, 1H, *J*(HH) 5.9 Hz, 1.2 Hz, naphthyl-H_6), 7.58 (dt, 1H, *J*(HH) 7.65 Hz, 1.2 Hz, naphthyl-H_7); (assignments for naphthyl-H_6 and H_7 may be interchanged). ^{13}C-NMR (50 MHz, CD_2Cl_2): δ 195.2 (CO), 136.8, 132.7, 130.8 (naphthyl C's), 133.9, 130.2, 129.9, 129.5, 128.3, 127.6, 123.9 (naphthyl CH's). MS (DEI; *m/z* (%)): 310 [M^+, 6%], 155 ($C_{10}H_7CO$, 100), 127 ($C_{10}H_7$, 97), 101 (C_8H_5, 10), 77 (C_6H_5, 19). MS (DCI; *m/z* (%)): 328 ($M+NH_3+H$, 37%), 311 (M+H, 69), 310 [M^+, 15], 190 (17), 172 ($C_{11}H_8O_2$, 52), 155 ($C_{10}H_7CO$, 100), 144 ($C_{10}H_8O$, 19), 80 (40).

4.4. 3,4-Di-(β-naphthyl)-2,5-di-phenylcyclopentadienone (*3a*)

Analogous to the synthesis of tetracyclone [66], β-naphthil (**2**) (4.73 g, 0.02 mol) and 1,3-diphenylpropanone (3.51 g, 0.02 mol) were dissolved in 125 ml of hot ethanol with stirring. Once the reaction mixture began to reflux, KOH (0.85 g, 0.02 mol) dissolved in ca. 10 ml hot ethanol, was added dropwise through the top of the condenser to the stirring mixture. The solution darkened immediately from yellow to deep red, eventually turning very dark red–purple. The solution was stirred for ca. 30 min, then cooled and the solvent was removed under vacuum to leave **3a** (4.42 g, 9.13 mmol; 61%) as a dark purple powder, m.p. 227–230 °C (lit. [30c] 227–229 °C). Calc. for $C_{37}H_{24}O\cdot H_2O$: C, 88.41; H, 5.22. Found: C, 88.21; H, 4.68%. IR (CH_2Cl_2): ν_{max} (cm^{-1}) at 1710 (CO). ^{1}H-NMR (500 MHz, CD_2Cl_2): [assignments are quoted with respect to the normal labeling for a β-naphthyl substituent] δ 7.76 (d, 2H, *J*(HH) 7.9 Hz, naphthyl-H_5), 7.62 (d, 2H, *J*(HH) 8.3 Hz, naphthyl-H_4), 7.49 (d, 2H, *J*(HH) 8.8 Hz, naphthyl-H_8), 7.48 (s, 2H, naphthyl-H_1), 7.46 (dd, 2H, *J*(HH) 7.5 Hz, 7.5 Hz, naphthyl-H_6), 7.37 (dd, 2H, *J*(HH) 7.2 Hz, 7.2 Hz, naphthyl-H_7), 7.30 (s, 6H, phenyl-$H_{2,4,6}$), 7.25 (s, 4H, phenyl-$H_{3,5}$), 7.11 (d, 2H, *J*(HH) 8.2 Hz, naphthyl-H_3). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 200.9 (CO), 155.2 (naphthyl-C_2, cyclopentadienone-C_3), 133.6 (naphthyl-C_{4a}), 133.4 (naphthyl-C_{8a}), 131.7 (phenyl-C_1), 131.5 (cyclopentadienone-C_2), 130.9 (phenyl-$C_{2,6}$), 129.7 (naphthyl-C_1), 128.8 (naphthyl-C_8), 128.6 (phenyl-$C_{3,4,5}$), 128.3 (naphthyl-C_5), 128.1 (naphthyl-C_4), 127.4 (naphthyl-$C_{6,3}$), 126.9 (naphthyl-C_7); (assignments for naphthyl-H,C_5 and H,C_8, naphthyl-H,C_6 and H,C_7 and naphthyl-C_{4a} and C_{8a} may be interchanged). MS (DEI; *m/z* (%)): 484 [M^+, 2%], 280 ($C_{10}H_7CHCHC_{10}H_7$, 10), 228 ($C_{10}H_7C{\equiv}CC_6H_5$, 4), 140 ($C_{10}H_7CH$, 12), 125 (15), 85 (62), 84 (100). MS (DCI; *m/z* (%)): 485 (M+H, 17%), 228 ($C_{10}H_7C{\equiv}CC_6H_5$, 2), 136 (14), 125 (100).

4.5. 3,4-Di-(β-naphthyl)-2,5-di(m-xylyl)cyclopentadienone (*3b*)

As with **3a**, β-naphthil (**2**) (0.76 g, 2.0 mmol) and 1,3-bis(3,5-dimethylphenyl)propanone (1.047 g, 3.8 mmol) were dissolved in 125 ml of hot ethanol with stirring. While the mixture was refluxing, KOH (0.3 g, 5.4 mmol) dissolved in 10 ml hot ethanol was added dropwise through the top of the condenser, and the solution darkened to a red–purple colour. The solution was stirred for ca. 30 min, then cooled, resulting in the formation of a dark purple solid which was collected by vacuum filtration to give **3b** (0.88 g, 1.6 mmol; 82%),

m.p. 285–288 °C. Calc. for $C_{42}H_{32}O$: C, 91.08; H, 5.97. Found: C, 90.65; H, 6.09%. IR (CH_2Cl_2): ν_{max} (cm^{-1}) at 1708 (CO). ^{1}H-NMR (500 MHz, CD_2Cl_2): [assignments are quoted with respect to the normal labeling for a β-naphthyl substituent] δ 7.75 (dd, 2H, J(HH) 8.1 Hz, 1.2 Hz, naphthyl-H_5), 7.60 (d, 2H, J(HH) 8.4 Hz, naphthyl-H_4), 7.48 (d, 2H, J(HH) 8.1 Hz, naphthyl-H_8), 7.44 (s, 2H, naphthyl-H_1), 7.43 (ddd, 2H, J(HH) 7.5 Hz, 6.9 Hz, 1.3 Hz, naphthyl-H_6), 7.35 (ddd, 2H, J(HH) 8.1 Hz, 6.9 Hz, 1.2 Hz, naphthyl-H_7), 7.10 (dd, 2H, J(HH) 8.5 Hz, 1.7 Hz, naphthyl-H_3), 6.88 (s, 6H, xylyl-$H_{2,4,6}$), 2.16 (s, 12H, xylyl-CH_3). ^{13}C-NMR (50 MHz, CD_2Cl_2): δ 201.2 (C=O), 154.8 (naphthyl-C_2), 138.1 (xylyl-$C_{3,5}$), 133.6 (naphthyl-C_{4a}), 133.3 (naphthyl-C_{8a}), 131.7 (cyclopentadienone-C_2), 131.5 (cyclopentadienone-C_3), 129.9 (xylyl-C_4), 129.6 (naphthyl-C_1), 128.7 (naphthyl-C_8), 128.5 (xylyl-$C_{2,6}$), 128.2 (naphthyl-C_5), 127.9 (naphthyl-C_4), 127.5 (naphthyl-C_3), 127.2 (naphthyl-C_6), 127.0 (xylyl-C_1), 126.7 (naphthyl-C_7), 21.6 (xylyl-CH_3); (assignments for naphthyl-H,C_5 and H,C_8, naphthyl-H,C_6 and H,C_7 and naphthyl-C_{4a} and C_{8a} may be interchanged). MS (DEI; m/z (%)): 540 [M^+, 27%], 512 (M–CO, 4), 278 ($C_{10}H_7C{\equiv}CC_{10}H_7$, 11), 256 ($C_{10}H_7C{\equiv}CC_6(CH_3)_2H_3$, 25), 239 (6), 128 ($C_{10}H_8$, 4), 84 (100). MS (DCI; m/z (%)): 557 (M+NH_3, 8%), 541 (M+H, 100), 279 ($C_{10}H_7C{\equiv}CC_{10}H_7$+H, 8), 396 (M–$C_{10}H_7$–OH, 8), 256 ($C_{10}H_7C{\equiv}CC_6(CH_3)_2H_3$, 17), 86 (24).

4.6. (Acetylacetonato)(3,4-di-(β-naphthyl)-2,5-diphenylcyclopentadienone)rhodium(I), (**4a**)

(Acetylacetonato)bis(ethylene)rhodium(I) (0.22 g, 0.87 mmol) and **3a** (0.26 g, 0.54 mmol) were dissolved in 30 ml dry THF and stirred under gentle reflux for ca. 2 h. The volume of the solution was reduced to half under vacuum, and 10 ml of hexanes was added, resulting in the formation of a red precipitate, which was collected by vacuum filtration to give **4a** (0.29 g, 0.42 mmol; 78%) as a red powder, m.p. 267 °C (dec). Calc. for $C_{42}H_{31}O_3Rh$: C, 73.47; H, 4.55. Found: C, 73.95; H, 4.34%. IR (CH_2Cl_2): ν_{max} (cm^{-1}) at 1640 (CO). ^{1}H-NMR (500 MHz, CD_2Cl_2): [assignments are quoted with respect to the normal labeling for a β-naphthyl substituent] δ 7.95 (s, 2H, naphthyl-H_1), 7.83 (dd, 4H, J(HH) 7.2 Hz, 1.3 Hz, phenyl-$H_{2,6}$), 7.73 (dd, 2H, J(HH) 8.1 Hz, 1.3 Hz, naphthyl-H_5), 7.59 (d, 2H, J(HH) 8.5 Hz, naphthyl-H_4;), 7.56 (d, 2H, J(HH) 8.2 Hz, naphthyl-H_8), 7.50 (dd, 2H, J(HH) 8.5 Hz, 1.2 Hz, naphthyl-H_3), 7.45 (ddd, 2H, J(HH) 8.1 Hz, 6.9 Hz, 1.3 Hz, naphthyl-H_6), 7.38 (ddd, 2H, J(HH) 8.1 Hz, 6.9 Hz, 1.3 Hz, naphthyl-H_7), 7.33 (tt, 2H, J(HH) 7.2 Hz, 1.3 Hz, phenyl-H_4), 7.26 (dd, 4H, J(HH) 7.8 Hz, 7.2 Hz, phenyl-$H_{3,5}$), 5.50 (s, 1H, acac-γH), 2.13 (s, 6H, acac-CH_3). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 188.1 (acac-CO), 163.6 (C=O), 133.5 (naphthyl-C_{4a}), 133.3 (naphthyl-C_{8a}), 131.3 (phenyl-$C_{2,6}$, naphthyl-C_1), 128.5 (naphthyl-$C_{8,3}$), 128.4 (phenyl-$C_{3,4,5}$), 128.3 (naphthyl-C_5), 128.1 (naphthyl-C_4), 127.3 (naphthyl-C_6), 127.0 (naphthyl-C_7), 99.5 (acac-γC), 95.5 (cyclopentadienone-C_3), 95.4 (naphthyl-C_2), 76.1 (cyclopentadienone-C_2), 76.1 (phenyl-C_1), 27.7 (acac-CH_3); (assignments for naphthyl-H,C_5 and H,C_8, naphthyl-H,C_6 and H,C_7 and naphthyl-C_{4a} and C_{8a} may be interchanged). MS (ESI; m/z (%)) 687 [M^+, 4%], 669 (M–H_2O, 100).

4.7. (Acetylacetonato)[3,4-di-(β-naphthyl)-2,5-di(m-xylyl)cyclopentadienone]rhodium(I), (**4b**)

As with **4a**, (acetylacetonato)bis(ethylene)rhodium(I) (0.41 g, 1.6 mmol) and **3b** (0.82 g, 1.5 mmol) were dissolved in 30 ml dry THF and stirred under gentle reflux for ca. 2 h. The volume of the solution was reduced under vacuum to ca. 15 ml, then 10 ml of hexanes was added dropwise, resulting in the formation of a precipitate of **4b** (1.00 g, 1.4 mmol; 90%) as a red powder which was collected by vacuum filtration, m.p. 244–247 °C. Calc for $C_{46}H_{39}O_3Rh$: C, 74.39; H, 5.29. Found: C, 73.85; H, 5.70%. IR (CH_2Cl_2): ν_{max} (cm^{-1}) at 1638 (CO). ^{1}H-NMR (500 MHz, CD_2Cl_2): [assignments are quoted with respect to the normal labeling for a β-naphthyl substituent] δ 7.99 (s, 2H, naphthyl-H_3), 7.73 (d, 2H, J(HH) 8.1 Hz, naphthyl-H_8), 7.58 (s, 2H, naphthyl-H_1), 7.58 (d, 2H, J(HH) 7.8 Hz, naphthyl-H_5), 7.54 (s, 2H, naphthyl-H_4), 7.52 (s, 4H, xylyl-$H_{2,6}$), 7.44 (dd, 2H, J(HH) 7.0 Hz, 7.0 Hz, naphthyl-H_7), 7.37 (dd, 2H, J(HH) 7.2 Hz, 7.2 Hz, naphthyl-H_6), 6.97 (s, 2H, xylyl-H_4), 5.53 (s, 1H, acac-γH), 2.24 (s, 12H, xylyl-CH_3), 2.16 (s, 6H, acac-CH_3). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 188.0 (acac-CO), 164.0 (C=O), 133.4 (naphthyl-C_{4a}), 133.3 (naphthyl-C_{8a}), 131.2 (naphthyl-C_3), 130.0 (xylyl-C_4), 129.6 (xylyl-$C_{3,5}$), 129.1 (xylyl-$C_{2,6}$), 128.5 (naphthyl-C_4), 128.5 (naphthyl-C_1), 128.3 (naphthyl-C_8), 127.9 (naphthyl-C_5), 127.2 (naphthyl-C_7), 126.9 (naphthyl-C_6), 99.5 (acac-γC), 95.6 (cyclopentadienone-C_3), 95.5 (naphthyl-C_2), 76.8 (cyclopentadienone-C_2), 76.7 (xylyl-C_1), 27.7 (acac-CH_3), 21.5 (xylyl-CH_3); (assignments for naphthyl-H,C_5 and H,C_8, naphthyl-H,C_6 and H,C_7 and naphthyl-C_{4a} and C_{8a} may be interchanged). MS (ESI; m/z (%)) 743 [M^+, 2%], 725 (M–H_2O, 100), 684 (M–CO–2CH_3–H, 11).

4.8. (Acetylacetonato)(3,4-di-(β-naphthyl)-2,5-diphenylcyclopentadienone)(triphenylphosphine)rhodium(I), (**5a**)

Triphenylphosphine (0.06 g, 0.23 mmol) was dissolved in 10 ml dry THF and added by syringe to a stirring solution of **4a** (0.13 g, 0.20 mmol) in 30 ml dry THF. The mixture was stirred under reflux for 1 hour, and the solvent was reduced to half under vacuum. Hexanes (10 ml) was added, resulting in the formation of a yellow precipitate, which was collected by vacuum filtration to

give **5a** (0.19 g, 0.19 mmol; 98%) as a yellow powder, m.p. 185–188 °C. Calc. for $C_{60}H_{46}O_3PRh\cdot CH_2Cl_2$: C, 70.92; H, 4.69. Found: C, 70.60; H, 4.15%. IR (CH_2Cl_2): ν_{max} (cm^{-1}) at 1635 (CO). ^{1}H-NMR (500 MHz, CD_2Cl_2): [assignments are quoted with respect to the normal labeling for a β-naphthyl substituent] δ 8.03 (s, 2H, naphthyl-H_1), 7.70 (d, 4H, J(HH) 7.5 Hz, phenyl-$H_{2,6}$), 7.64 (dd, 2H, J(HH) 7.0 Hz, 1.6 Hz, naphthyl-H_5), 7.62 (dd, 2H, J(HH) 7.1 Hz, 1.8 Hz, naphthyl-H_8), 7.45 (d, 2H, J(HH) 8.6 Hz, naphthyl-H_4), 7.37 (dd, 2H, J(HH) 7.9 Hz, 6.9 Hz, naphthyl-H_6), 7.36 (dd, 2H, J(HH) 7.9 Hz, 1.8 Hz, naphthyl-H_7), 7.27 (d, 2H, J(HH) 8.5 Hz, naphthyl-H_3), 7.21 (d, 6H, J(HH) 8 Hz, PPh_3–phenyl-$H_{2,6}$), 7.21 (t, 3H, J(HH) 8 Hz, PPh_3–phenyl-H_4), 7.17 (t, 2H, J(HH) 7.4 Hz, phenyl-H_4), 7.02 (dd, 4H, J(HH) 7.7 Hz, 7.7 Hz, phenyl-$H_{3,5}$), 6.97 (dd, 6H, J(HH) 6.5 Hz, 6.9 Hz, PPh_3–phenyl-$H_{3,5}$), 5.13 (s, 1H, acac-γH), 1.80 (s, 6H, acac-CH_3). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 188.4 (acac-CO), 170.2 (C=O), 134.6 (d, J(CCP) 10.6 Hz, PPh_3–phenyl-C_2), 133.2 (naphthyl-C_{4a}), 133.0 (naphthyl-C_{8a}), 131.6 (naphthyl-C_1), 131.3 (d, J(CP) 50.7 Hz, PPh_3–phenyl-C_1), 131.0 (phenyl-$C_{2,6}$), 129.8 (PPh_3–phenyl-C_4), 128.8 (naphthyl-C_3), 128.5 (naphthyl-C_5), 128.1 (naphthyl-C_8), 128.0 (d, J(CCCP) 12.9 Hz, PPh_3–phenyl-$C_{3,5}$), 127.9 (phenyl-$C_{3,5}$), 127.8 (naphthyl-C_6), 127.1 (naphthyl-C_4), 126.8 (naphthyl-C_7), 126.6 (phenyl-C_4), 104.7 (naphthyl-C_2, cyclopentadienone-C_3), 101.7 (acac-γC), 64.2 (phenyl-C_1, cyclopentadienone-C_2), 28.7 (acac-CH_3); (assignments for naphthyl-H,C_5 and H,C_8, naphthyl-H,C_6 and H,C_7 and naphthyl-C_{4a} and C_{8a} may be interchanged). ^{31}P-NMR (202 MHz, CD_2Cl_2, 243 K): δ 22.5 (d, J(RhP) 165.6 Hz, Rh–PPh_3); (202 MHz, CD_2Cl_2, 163 K): δ 23.5 (d, J(RhP) 159.8 Hz, Rh–PPh_3), 22.9 (d, J(RhP) 156.8 Hz, Rh–PPh_3). MS (ESI; m/z (%)): 949 [M^+, 3%], 890 (M–CO–2CH_3–H, 7), 849 (M+H-acac, 83), 557 ($C_4(C_6H_5)_2(C_{10}H_7)_2$Rh–H, 9), 277 ($C_{10}H_7C{\equiv}CC_{10}H_6$, 100).

4.9. (Acetylacetonato)(3,4-di-(β-naphthyl)-2,5-di-m-xylylcyclopentadienone)(triphenylphosphine) rhodium(I), (**5b**)

Triphenylphosphine (0.29 g, 1.1 mmol) was dissolved in 10 ml dry THF and added by syringe to a stirring solution of **4b** (0.80 g, 1.1 mmol) in 30 ml dry THF. The mixture was stirred under reflux for 1 h, and the solvent was reduced to half under vacuum. Ca. 10 ml of hexanes was added, creating a yellow–orange precipitate of **5b**, (0.93 g, 0.92 mmol; 84%), which was collected by vacuum filtration, m.p. 188–191 °C. Calc. for $C_{64}H_{54}O_3PRh\cdot 2H_2O$: C, 73.84; H, 5.62. Found: C, 73.44; H 6.45%. IR (CH_2Cl_2): ν_{max} (cm^{-1}) at 1626 (CO). ^{1}H-NMR (500 MHz, CD_2Cl_2): [assignments are quoted with respect to the normal labeling for a β-naphthyl substituent] δ 8.14 (s, 2H, naphthyl-H_1), 7.68 (d, 4H, J(HH) 7 Hz, naphthyl-$H_{5,8}$), 7.51 (d, 2H, J(HH) 8.5 Hz, naphthyl-H_4), 7.41 (s, 4H, xylyl-$H_{2,6}$), 7.39 (d, 2H, J(HH) 6.8 Hz, naphthyl-H_6), 7.38 (d, 2H, J(HH) 7 Hz, naphthyl-H_7), 7.37 (d, 2H, J(HH) 8.9 Hz, naphthyl-H_3), 7.31 (dd, 6H, J(HH) 8.6 Hz, 8.6 Hz, PPh_3–phenyl-$H_{2,6}$), 7.27 (t, 3H, J(HH) 7.3 Hz, PPh_3–phenyl-H_4), 7.05 (dd, 6H, J(HH) 6.7 Hz, 6.9 Hz, PPh_3–phenyl-$H_{3,5}$), 6.87 (s, 2H, xylyl-H_4), 5.20 (s, 1H, acac-γH), 2.15 (s, 12H, xylyl-CH_3), 1.85 (s, 6H, acac-CH_3), (couplings for naphthyl-$H_{5,7,8}$ were not well resolved due to overlap). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 188.1 (acac-CO), 170.2 (C=O), 137.1 (xylyl-$C_{3,5}$), 134.7 (d, J(CCP) 17.6 Hz, PPh_3–phenyl-$C_{2,6}$), 133.2 (naphthyl-C_{4a}), 133.0 (naphthyl-C_{8a}), 131.6 (naphthyl-C_1), 131.5 (d, J(CP) 43.2 Hz, PPh_3–phenyl-C_1), 130.0 (naphthyl-C_7), 129.7 (PPh_3–phenyl-C_4), 129.2 (xylyl-C_2), 128.3 (xylyl-C_4), 128.2 (naphthyl-C_5), 128.1 (naphthyl-C_8), 127.9 (d, J(CCCP) 9.2 Hz, PPh_3–phenyl-$C_{3,5}$), 127.0 (naphthyl-C_4), 126.7 (naphthyl-C_3), 126.5 (naphthyl-C_6), 104.4 (naphthyl-C_2, cyclopentadienone-C_3), 101.4 (acac-γC), 64.3 (xylyl-C_1, cyclopentadienone-C_2), 28.8 (acac-CH_3), 21.5 (xylyl-CH_3); (assignments for naphthyl-H,C_5 and H,C_8, naphthyl-H,C_6 and H,C_7 and naphthyl-C_{4a} and C_{8a} may be interchanged). ^{31}P-NMR (202 MHz, CD_2Cl_2, 243 K): δ 23.4 (d, J(RhP) 167.3 Hz, Rh–PPh_3); (202 MHz, CD_2Cl_2, 163 K): δ 23.5 (d, J(RhP) 164.2 Hz, Rh–PPh_3), 23.2 (d, J(RhP) 158.4 Hz, Rh–PPh_3). MS (ESI; m/z (%)): 1005 [M^+, 7], 946 (M–CO–2CH_3–H, 38), 905 (M–Hacac, 18), 743 (M–PPh_3, 11), 725 (M–PPh_3–H_2O, 100), 684 (M–PPh_3–CO–2CH_3, 9), 631 (13).

4.10. (Acetylacetonato)(2,3,4,5-tetraphenylcyclopentadienone)(triphenylphosphine) rhodium(I), (**5c**)

As with **5a**, triphenylphosphine (0.22 g, 0.84 mmol) was dissolved in 10 ml dry THF and added dropwise by syringe to a stirring solution of **4c** (0.25 g, 0.42 mmol) in 30 mL dry THF. After refluxing for 1 h, the solvent was removed under vacuum to give **5c** (0.13 g, 0.15 mmol, 36%) as a yellow–orange powder, m.p. 136 °C (dec). Calc. for $C_{52}H_{42}O_3PRh\cdot CH_2Cl_2$: C, 68.23; H, 4.76. Found: C, 68.10; H, 5.06%. IR (CH_2Cl_2): ν_{max} (cm^{-1}) at 1627 (CO). ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.65, 7.29 (d, 8H, J(HH) 7.6 Hz, phenyl-$H_{2,6}$), 5.94 (m, 9H, PPh_3), 7.14 (t, 4H, J(HH) 7.0 Hz, phenyl-H_4), 7.08, 7.05 (dd, 8H, J(HH) 7.40 Hz, 8.5 Hz, phenyl-$H_{3,5}$), 6.97 (s, 6H, PPh_3), 4.98 (s, 1H, acac-γH), 1.75 (s, 6H, acac-CH_3). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ 188.1 (acac-CO), 170.0 (C=O), 135.5, 134.6, 134.5, 132.7, 131.6, 131.0, 129.7, 128.0, 127.9, 127.8, 126.5 (aromatic rings), 101.6 (acac-γC), 28.8 (acac-CH_3). ^{31}P-NMR (81 MHz, CD_2Cl_2): δ 21.1 (d, J(RhP) 162.5 Hz, Rh–PPh_3). MS (ESI; m/z (%)): 849 [M^+, 0.7%], 790 (M–CO–2CH_3–H, 9), 749 (M–Hacac, 100), 279 ($C_4(C_6H_5)_3$, 6).

4.11. Lineshape analysis

NMR simulations were carried out using the program MEXICO [67] (available from Alex Bain). This program does an iterative least-squares fit of the calculated lineshape to the experimental data, and is capable of varying all the parameters: shifts, couplings and rates. This was a standard, non-mutual (non-degenerate) exchange problem. In this analysis, the chemical shift difference and rate were varied (using a simplex algorithm) to obtain the best fit. The calculation of errors in a multi-parameter fit is a difficult problem. For this case, they were estimated by changing the parameters and visually monitoring the fit to the experimental data. The errors quoted correspond to a clear and obvious mismatch between calculated and observed. Full details can be found in [68].

4.12. Crystallographic data for *4a*, *4b*, *5a* and *5b*

X-ray crystallographic data for **4a**, **4b**, **5a** and **5b** (Table 2) were collected from a suitable sample mounted with epoxy on the end of a thin glass fiber. For **4a**, the rapid lattice solvent evaporation was minimized by the mounting of a suitable crystal in an atmosphere saturated with solvent, and quickly freezing it to 173 K on the diffractometer. Data were collected on a P4 Bruker diffractometer equipped with a Bruker SMART 1K CCD area detector (employing the program SMART) [69] and a rotating anode utilizing graphite-monochromated Mo–Kα radiation ($\lambda = 0.710.73$ Å). Data processing was carried out by use of the program SAINT [70], while the program SADABS [71] was utilized for the scaling of diffraction data, the application of a decay correction and an empirical absorption correction based on redundant reflections. Structures were solved by using the direct-methods procedure in the Bruker SHELXL [72] program library and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined using anisotropic thermal parameters, with the exception of **5b**, in which the crystal did not diffract beyond 1 Å, creating difficulties in refining anisotropically on the carbon atoms. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded. In the course of the refinement process for **4a** and **4b**, several dichloromethane solvent molecules were located in the asymmetric unit, and a satisfactory refinement of the solvate atomic positions was not attained, though the diffraction data allowed for complete anisotropic refinement of the target molecules. As a result, the values for the residual electron density in the region of the solvent molecules and the refinement statistics associated with the structures are high.

5. Supplementary material

Supporting Information Available: Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC numbers 175627 (**4a**), 175628 (**4b**), 175629 (**5a**) and 175630 (**5b**). 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). Fully labeled thermal ellipsoid plots are also available (four pages).

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