

# Incorporation of phenyl-substituted pentadienyl ligands in (pentamethylcyclopentadienyl)ruthenium complexes†

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The reactions of the  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  tetramer with 2,4-diphenylpenta-1,3-diene or 3-phenyl- or 1,5-diphenyl-substituted pentadienyl anions lead to the incorporation of the expected phenyl-substituted pentadienyl ligands into the respective symmetric  $\text{Ru}(\text{C}_5\text{Me}_5)(\text{Pdl})$  products ( $\text{Pdl} = 2,4\text{-Ph}_2\text{C}_5\text{H}_5$ ;  $3\text{-PhC}_5\text{H}_6$ ;  $1,5\text{-Ph}_2\text{C}_5\text{H}_5$ ). The reaction of the tetramer with a mixture of 2-methyl-4-phenylpenta(-1,3- or -2,4-)dienes led to the  $\text{Pdl} = 2\text{-Me-4-PhC}_5\text{H}_5$  complex. In contrast, the reaction of the tetramer with 3-phenylpenta-1,3-diene led to simple incorporation of the  $\eta^4$ -diene ligand. Structural confirmation of the formulations of the four  $\eta^5$ -pentadienyl complexes has been achieved, allowing for a number of comparisons to be made regarding the structural effects of phenyl substitution on the (1,5), (2,4) and 3 positions of the open diene ligand.

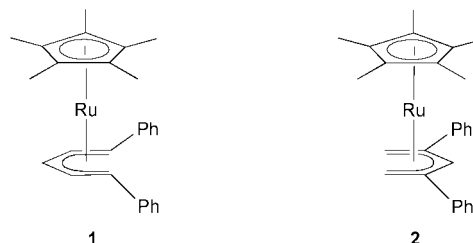
## Introduction

Metal pentadienyl compounds have proven to be interesting in terms of their structures and bonding,<sup>1</sup> as well as reaction chemistry<sup>2</sup> and potential applications.<sup>3</sup> In many of these aspects, the ability to incorporate a wide variety of substituents would clearly be advantageous, whether for probing the effects of such substituents on physical properties, or to expand upon the range of targets that can be prepared from them synthetically. To date,  $\text{Ru}(\text{C}_5\text{Me}_5)(\text{Pdl})$  complexes ( $\text{Pdl}$  = various pentadienyl groups) have been found capable of tolerating a number of different substituents, including alkyl,  $\text{CF}_3$  and siloxy groups<sup>4</sup> (trialkylsilyl substituents having been incorporated in other systems).<sup>5</sup> Aromatic substituents should be of particular interest, owing to the possibility of conjugation with the pentadienyl fragment, and of coordinating additional metal centers to the complex.<sup>6</sup> Indeed, a few, typically highly specialized, phenyl-substituted pentadienyl complexes of chromium,<sup>7</sup> rhodium,<sup>8</sup> iron<sup>9</sup> and rhenium<sup>10</sup> have previously been described, although general systematic routes to symmetrically mono- and disubstituted complexes have not been developed. Herein we report the syntheses and full characterizations of  $\text{Ru}(\text{C}_5\text{Me}_5)(\text{Pdl})$  complexes having symmetrically ( $\text{Pdl} = 1,5\text{-Ph}_2\text{C}_5\text{H}_5$ , **1**;  $2,4\text{-Ph}_2\text{C}_5\text{H}_5$ , **2**;  $3\text{-PhC}_5\text{H}_6$ , **3**) or unsymmetrically ( $\text{Pdl} = 2\text{-Me-4-PhC}_5\text{H}_5$ , **4**) disposed phenyl substituents.

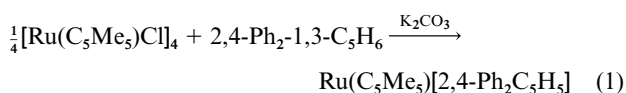
## Results and discussion

### Diene and symmetric diene complexes

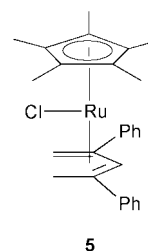
The preparation of  $\text{Ru}(\text{C}_5\text{Me}_5)(1,5\text{-Ph}_2\text{C}_5\text{H}_5)$  **1** from the reaction of  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  with the 1,5-diphenylpentadienyl anion has been previously described.<sup>4a</sup> The other possible symmetrically disubstituted complex,  $\text{Ru}(\text{C}_5\text{Me}_5)(2,4\text{-Ph}_2\text{C}_5\text{H}_5)$  **2**, can be prepared in variable yield (35–65%) from the reaction of  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  with 2,4-diphenylpenta-1,3-diene in the pres-



ence of  $\text{K}_2\text{CO}_3$  [eqn. (1)]. In this reaction it is likely that a



$\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}(\eta^4\text{-diene})$  complex is first formed, such as **5**, from which  $\text{HCl}$  may be extracted by virtue of the presence of an *endo*-oriented methyl group on a diene terminus.<sup>11</sup>



Such methyl group orientations are a normal consequence of a 2,4-disubstitution pattern in a pentadiene or pentadienyl fragment,<sup>1,12</sup> and formal deprotonations have been found to be quite facile in a number of complexes similar to **5**.<sup>4,13</sup> As a related 3-phenylpenta-1,3-diene complex would instead be expected to have an *exo*-oriented methyl group, its conversion to an  $\eta^5$ -dienyl complex should not occur so readily. In fact, a similar reaction of the tetramer and this diene led to the anticipated  $\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}(\eta^4\text{-3-PhC}_5\text{H}_6)$  complex **6**, one of many

† Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday.

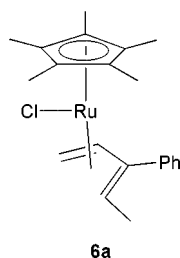
**Table 1**  $^1\text{H}$  NMR Resonances for selected  $\text{Ru}(\text{C}_5\text{Me}_5)(\text{Pdl})$  complexes

Pdl	$\delta[\text{H-3}]$	$\delta[\text{H-2,4}]$	$\delta[\text{H-1,5}(\text{exo})]$	$\delta[\text{H-1,5}(\text{endo})]$	$\text{C}_5\text{Me}_5$
$\text{C}_5\text{H}_7$	4.82	4.02	2.30	0.32	1.72
$3\text{-C}_6\text{H}_9$	—	3.88	2.30	0.38	1.70
$2,4\text{-C}_7\text{H}_{11}$	4.78	—	2.16	0.36	1.68
$3\text{-PhC}_5\text{H}_6$	—	4.48	2.39	0.54	1.65
$2,4\text{-Ph}_2\text{C}_5\text{H}_5$	6.35	—	2.73	0.51	1.37
$1,5\text{-Ph}_2\text{C}_5\text{H}_5$	4.79	4.95	—	2.28	1.19
$2\text{-Me-4-PhC}_5\text{H}_5$	5.62	—	2.28, 2.72	0.19, 0.74	1.52

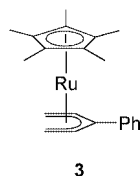
**Table 2** Summary of structure determinations

Compound	1	2	3	4
Chemical formula	$\text{C}_{27}\text{H}_{30}\text{Ru}$	$\text{C}_{27}\text{H}_{30}\text{Ru}$	$\text{C}_{21}\text{H}_{26}\text{Ru}$	$\text{C}_{22}\text{H}_{28}\text{Ru}$
$M$	455.56	455.56	388.53	402.56
Crystal system	Monoclinic	Hexagonal	Monoclinic	Rhombohedral
Space group	$Cc$	$P6_3cm$	$P2_1/c$	$R\bar{3}$
$\mu/\text{cm}^{-1}$	7.37	6.34	8.59	8.30
$a/\text{\AA}$	11.833(1)	24.266(5)	16.169(6)	36.617(11)
$b/\text{\AA}$	25.685(3)	24.266(5)	7.689(2)	36.617(11)
$c/\text{\AA}$	7.4492(6)	7.364(2)	14.598(4)	7.301(3)
$\beta/^\circ$	107.750(5)	120	91.33(2)	90 ( $\gamma = 120$ )
$V/\text{\AA}^3$	2156.3(3)	3755(2)	1814.4(11)	8482(6)
$T/\text{K}$	195	298	298	233
$Z$	4	6	4	18
Reflections collected	8614	3876	3469	4148
Independent reflections	1923	1418	3341	2954
$R(F)$	0.041	0.038	0.034	0.072
$R(wF)$	0.045	0.064	0.049	0.172

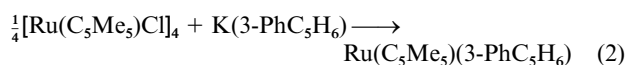
examples of  $\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}(\eta^4\text{-diene})$  compounds.<sup>14</sup> Characterization of the resulting yellow–orange product was achieved straightforwardly through analytical and spectroscopic data. Since these, and other,  $\text{Ru}(\text{II})$  complexes could have either  $\eta^4\text{-cis}$  or  $\eta^4\text{-trans}$  diene coordination,<sup>14,15</sup> it is not completely certain which mode would hold for **6**, although the presence of the 3-phenyl substituent would likely provide a steric influence in favor of the *cis* isomer **6a**.



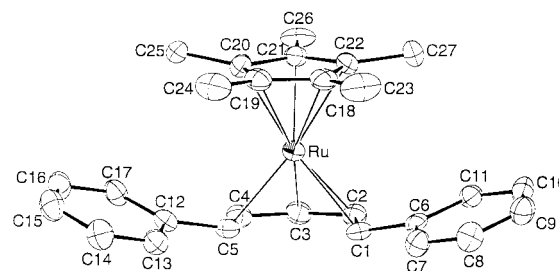
Owing to the reluctance of **6** to undergo loss of  $\text{HCl}$ , the preparation of the  $\eta^5\text{-3-phenylpentadienyl}$  complex **3** required



a direct reaction of  $[\text{Ru}(\text{C}_5\text{Me}_5)_4\text{Cl}]_4$  with the dienyl anion [eqn. (2)]. The resulting product, like **1** and **2**, is a yellow crystal-



line compound, relatively air-stable in the solid state, but significantly more air-sensitive in solution. These compounds have been characterized through routine analytical and spectro-

**Fig. 1** Perspective view of  $\text{Ru}(\text{C}_5\text{Me}_5)(1,5\text{-Ph}_2\text{C}_5\text{H}_5)$  **1**.

scopic methods (see Experimental section), and some particularly interesting comparisons may be made from the NMR spectroscopic data. For each dienyl complex, the presence of the expected formal mirror plane symmetry was evident, which in the case of **3** requires at least a rapid partial oscillation around the dienyl–aryl C–C bond. That a full rotation is also a facile process can be recognized from the  $^{13}\text{C}$  NMR spectra for complexes **1–4**, which reveal a single resonance for the *ortho* carbon atoms, and for the *meta* carbon atoms as well. The  $^{13}\text{C}$  NMR spectra are strikingly similar to those of the corresponding methyl-substituted analogs. Thus, replacement of H by either Me or Ph leads to significant and surprisingly comparable downfield shifts for the attached carbon atoms, the greatest difference in chemical shifts being *ca.* 5 ppm for the dienyls' C-3 resonance of the 3-substituted complexes (3-H, 92.1; 3-Me, 100.9 ppm; 3-Ph, 105.8 ppm). On the other hand, the  $^1\text{H}$  NMR spectra are significantly different, with large downfield shifts of up to *ca.* 2 ppm resulting from phenyl substitution (Table 1), whereas methyl substitution leads to nearly no change.

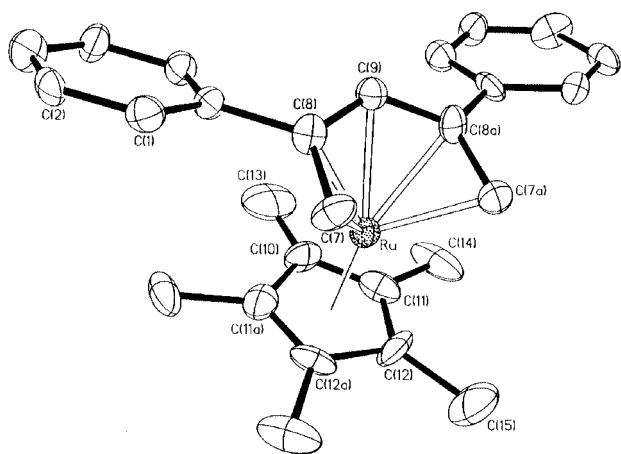
Structural confirmation has been obtained for the symmetric 1,5-diphenyl, 2,4-diphenyl and 3-phenyl substituted  $\text{Ru}(\text{C}_5\text{Me}_5)(\text{Pdl})$  complexes, **1–3**, as well as for  $\text{Ru}(\text{C}_5\text{Me}_5)(2\text{-Me-4-PhC}_5\text{H}_5)$  (Tables 2–6, Figs. 1–3). Although reasonable discrepancy indices were obtained for the symmetric structures, the fair to poor diffracting natures of the diphenyl substituted complexes have led to relatively poor precision in some of the

**Table 3** Selected bond distances (Å) and angles (°) for **1**

Ru–C1	2.307(11)	C1–C6	1.468(16)
Ru–C2	2.170(8)	C5–C12	1.489(18)
Ru–C3	2.169(9)	C18–C23	1.505(12)
Ru–C4	2.161(8)	C19–C24	1.499(12)
Ru–C5	2.197(16)	C20–C25	1.531(15)
Ru–C18	2.213(8)	C21–C26	1.490(12)
Ru–C19	2.203(9)	C22–C27	1.455(17)
Ru–C20	2.149(15)	C6–C7	1.416(12)
Ru–C21	2.201(8)	C6–C11	1.397(11)
Ru–C22	2.259(12)	C7–C8	1.373(12)
C1–C2	1.453(14)	C8–C9	1.377(13)
C2–C3	1.398(11)	C9–C10	1.377(14)
C3–C4	1.416(12)	C10–C11	1.378(12)
C4–C5	1.427(15)	C12–C13	1.401(12)
C18–C19	1.421(12)	C12–C17	1.380(12)
C18–C22	1.483(15)	C13–C14	1.366(13)
C19–C20	1.397(16)	C14–C15	1.400(14)
C20–C21	1.437(16)	C15–C16	1.361(14)
C21–C22	1.431(15)	C16–C17	1.399(12)
C1–C2–C3	123.2(8)	C5–C12–C13	118.4(8)
C2–C3–C4	126.0(8)	C5–C12–C17	124.8(9)
C3–C4–C5	123.7(9)	C18–C19–C20	108.1(8)
C2–C1–C6	121.2(10)	C19–C20–C21	109.7(10)
C4–C5–C12	121.1(11)	C20–C21–C22	108.2(9)
C1–C6–C7	117.1(7)	C21–C22–C18	105.6(10)
C1–C6–C11	126.1(8)	C22–C18–C19	108.3(8)

**Table 4** Selected bond distances (Å) and angles (°) for **2**

Ru–C7	2.170(16)	C11–C14	1.541(25)
Ru–C8	2.158(11)	C12–C15	1.536(17)
Ru–C9	2.174(16)	C7–C8	1.428(22)
C6–C8	1.544(11)	C8–C9	1.398(16)
C10–C13	1.439(27)	C10–C11	1.391(17)
Ru–C10	2.233(20)	C11–C12	1.378(29)
Ru–C11	2.218(15)	C12–C12a	1.500(23)
Ru–C12	2.171(15)		
C1–C6–C8	119.2(7)	C11–C10–C13	126.4(11)
C5–C6–C8	120.7(7)	C10–C11–C12	111.3(15)
C6–C8–C7	119.6(11)	C10–C11–C14	123.9(18)
C6–C8–C9	119.1(12)	C12–C11–C14	124.7(13)
C7–C8–C9	120.9(10)	C11–C12–C12a	105.4(6)
C8–C9–C8a	128.4(16)	C11–C12–C15	127.8(13)
C11–C10–C11a	106.6(19)	C12a–C12–C15	126.5(13)

**Fig. 2** Molecular structure of Ru(C<sub>5</sub>Me<sub>5</sub>)(2,4-Ph<sub>2</sub>C<sub>5</sub>H<sub>3</sub>) **2**.

bonding parameters. Nevertheless, there are still a number of useful comparisons that can be drawn from these data. For simplicity, pertinent averaged bonding parameters are presented in Table 7, using brackets to designate general pentadienyl positions, e.g., C[1,5] for the terminal carbon atoms of a pentadienyl ligand.

**Table 5** Selected bond distances (Å) and angles (°) for **3**

Ru–C1	2.175(5)	C3–C11	1.505(5)
Ru–C2	2.144(4)	C4–C15	1.421(6)
Ru–C3	2.198(4)	C12–C13	1.418(6)
Ru–C4	2.130(5)	C12–C16	1.438(6)
Ru–C5	2.165(5)	C13–C14	1.427(6)
Ru–C12	2.184(4)	C14–C15	1.418(5)
Ru–C13	2.176(4)	C15–C16	1.414(6)
Ru–C14	2.195(4)	C12–C17	1.494(7)
Ru–C15	2.199(4)	C13–C18	1.510(6)
Ru–C16	2.191(4)	C14–C19	1.498(6)
C1–C2	1.420(7)	C15–C20	1.519(7)
C2–C3	1.426(6)	C16–C21	1.507(7)
C3–C4	1.422(6)		
C1–C2–C3	124.4(4)	C12–C13–C18	125.8(4)
C2–C3–C4	122.1(4)	C14–C13–C18	125.0(4)
C2–C3–C11	119.0(4)	C13–C14–C15	107.0(3)
C4–C3–C11	118.1(4)	C13–C14–C19	126.2(4)
C3–C4–C5	124.3(4)	C15–C14–C19	126.5(4)
C3–C11–C6	121.3(2)	C14–C15–C16	109.0(4)
C3–C11–C10	118.7(2)	C14–C15–C20	124.2(4)
C13–C12–C16	107.2(4)	C16–C15–C20	126.7(4)
C13–C12–C17	126.6(5)	C12–C16–C15	107.8(4)
C16–C12–C17	126.1(4)	C12–C16–C21	125.7(4)
C12–C13–C14	109.0(4)	C15–C16–C21	126.5(4)

**Table 6** Selected bond distances (Å) and angles (°) for **4**

Ru–C1	2.208(10)	C12–C13	1.425(14)
Ru–C2	2.208(9)	C12–C22	1.531(16)
Ru–C3	2.191(10)	C13–C14	1.423(14)
Ru–C4	2.177(10)	C14–C15	1.455(13)
Ru–C5	2.218(10)	C14–C16	1.489(13)
Ru–C11	2.195(10)	C1–C6	1.497(15)
Ru–C12	2.142(10)	C2–C7	1.501(14)
Ru–C13	2.186(9)	C3–C8	1.494(14)
Ru–C14	2.172(9)	C4–C9	1.520(14)
Ru–C15	2.183(10)	C5–C10	1.509(15)
C1–C2	1.453(15)	C16–C17	1.394(13)
C1–C5	1.382(15)	C16–C21	1.394(13)
C2–C3	1.398(14)	C17–C18	1.389(14)
C3–C4	1.447(14)	C18–C19	1.371(16)
C4–C5	1.439(15)	C19–C20	1.391(16)
C11–C12	1.424(16)	C20–C21	1.367(14)
C1–C2–C3	108.3(9)	C13–C14–C15	121.8(9)
C1–C5–C4	108.9(11)	C11–C12–C22	120.3(10)
C2–C1–C5	108.0(10)	C13–C12–C22	115.9(11)
C2–C3–C4	107.8(9)	C13–C14–C16	117.9(8)
C3–C4–C5	107.0(10)	C15–C14–C16	119.9(9)
C11–C12–C13	123.8(11)	C14–C16–C17	122.8(9)
C12–C13–C14	125.2(9)	C14–C16–C21	120.5(9)

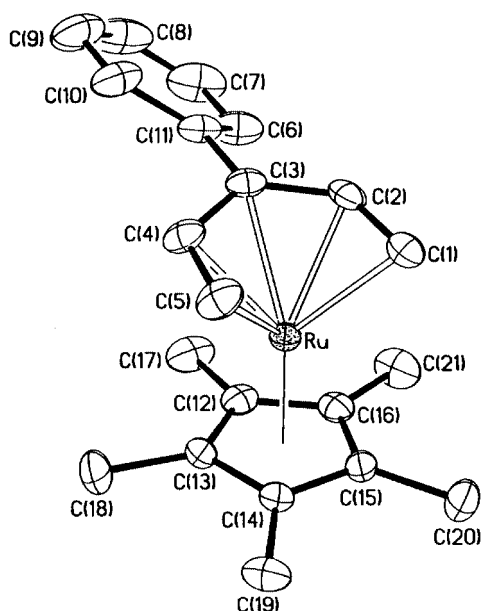
Within the statistical limits, the Ru–C(C<sub>5</sub>Me<sub>5</sub>) bonding for the three compounds appears similar (Table 7), and not unlike that in Ru(C<sub>5</sub>Me<sub>5</sub>)(3-C<sub>6</sub>H<sub>9</sub>) [C<sub>6</sub>H<sub>9</sub> = methylpentadienyl, Ru–C(av) 2.193(8) Å]. The Ru–C[1,5], –C[2,4] and –C[3] distances of 2.164(2), 2.126(2) and 2.187(2) Å in Ru(C<sub>5</sub>Me<sub>5</sub>)(3-C<sub>6</sub>H<sub>9</sub>) are all shorter than the respective distances in **3**, suggesting that phenyl substitution hinders the extent of metal–pentadienyl interaction relative to methyl substitution. Such an effect could easily be steric in origin, although for **1** and **3** the phenyl groups could significantly stabilize the formally negatively charged 1, 3 and/or 5 positions, thereby reducing the metal–pentadienyl interaction electronically. In fact, in both **1** and **3**, the Ru–C distances for the phenyl-substituted carbon atoms are significantly longer than those for the other carbon atoms, while for **2** this is not the case. Also pertinent in this regard is the fact that for **1**, with two phenyl groups stabilizing the negative charge, at least the Ru–C[1,2,4,5] distances appear substantially longer than their counterparts in **2** and **3**, presumably reflecting weaker bonding for complex **1**.<sup>16a,b</sup>

As has been the case for methyl-substituted complexes,<sup>17</sup> phenyl substituents decrease delocalized C–C(Ph)–C bond

**Table 7** Comparison of pertinent structural parameters for **1**, **2**, **3** and **4**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Ru–C(Cp*)/Å	2.205(18)	2.202(9)	2.189(4)	2.200(7)
Ru–C[1,5]/Å	2.252(10)	2.170(16)	2.170(4)	2.189(7)
Ru–C[2,4]/Å	2.166(6)	2.158(11)	2.137(3)	2.157(7)
Ru–C[3]/Å	2.169(9)	2.174(16)	2.198(4)	2.186(9)
C[1]–C[2]/Å	1.440(10)	1.428(22)	1.421(4)	1.440(10)
C[2]–C[3]/Å	1.407(8)	1.398(16)	1.424(4)	1.424(10)
C[1]–C[2]–C[3]/°	123.4(6)	120.9(10)	124.4(3)	122.8(7)
C[2]–C[3]–C[4]/°	126.0(8)	128.4(16)	122.1(4)	125.2(9)
C[1]...C[5]/°	2.847(21)	2.789(27)	2.774(8)	2.813(15)
Ph tilt <sup>a</sup> /°	11.0, 10.3	12.2, 17.4	1.4, 1.0	10.8, 15.4
Ph twist <sup>b</sup> /°	19.6(1.6, 12.4)	30.5, 29.0	34.1, 34.0	30.4, 30.5
Interligand angle <sup>c</sup> /°	3.7	11.8	7.5	8.4
Ru–PdI/Å	1.611	1.557	1.553	1.561
Ru–Cp*/Å	1.836	1.846	1.824	1.837

<sup>a</sup> The first tilt angle  $\theta$  is defined by  $\sin(\theta) = d/d$ , for which  $d$  is the deviation of the dienyl-bound substituent atom from the dienyl plane, and  $d$  is the C(dienyl)–substituent bond distance. The second tilt angle is defined by the torsion angle generated by a dienyl-attached substituent atom and any three carbon atom dienyl chain to which it is attached. <sup>b</sup> The first twist angle is equal to the angle between the phenyl and PdI planes, while the other values derive from torsion angles involving two dienyl and two phenyl carbon atoms. For **1** the latter definition led to two values due to a deformation of the phenyl group, through which C(1) and C(5) no longer lie in the phenyl group's plane. <sup>c</sup> Determined from the least-squares planes of the two ligands, such that an angle of 0° would reflect a parallel orientation.



**Fig. 3** Perspective view of Ru(C<sub>5</sub>Me<sub>5</sub>)(3-PhC<sub>5</sub>H<sub>6</sub>) **3**.

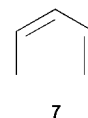
angles. Thus, in **2** the C[1]–C[2]–C[3] angle is smaller than the C[2]–C[3]–C[4] angles, while for **3**, the reverse trend is observed. Such angular contractions are common in delocalized species.<sup>18</sup> Interestingly, siloxy substituents have been found to bring about the opposite effect,<sup>4b,d</sup> apparently by increasing the amount of s character available for the other bonds of the siloxy-substituted carbon atom.

Several other parameters related to the ligand planes are of interest. Due to the combination of the similarity of the Ru–C bond lengths for the two ligands, and the wider nature of the ligands PdI, the metal atoms in these mixed sandwich complexes are required geometrically to lie closer to the pentadienyl ligand plane. The values for **2** and **3** are similar to those for Ru(C<sub>5</sub>Me<sub>5</sub>)(3-C<sub>6</sub>H<sub>5</sub>) (1.557, 1.553 and 1.567 Å for ligands PdI vs. 1.846, 1.824 and 1.834 Å for C<sub>5</sub>Me<sub>5</sub>, respectively), while for **1**

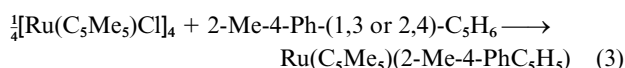
the ruthenium center is 1.611 Å from the plane of PdI. The longer Ru–PdI separation for **1** seems to be the result of some anomalous distortions present in **1** (*vide infra*), which also appear reflected by the small interligand angle in **1** [3.7°, *cf.*, 8.0° for Ru(C<sub>5</sub>Me<sub>5</sub>)(3-C<sub>6</sub>H<sub>5</sub>)]. This can further be seen in the values of the twist angles between the phenyl and pentadienyl planes. The values for **2** and **3** of *ca.* 29–34° are reasonable, much as would be expected for biphenyls.<sup>20</sup> For **1**, however, one observes a smaller twist, whose actual value is quite dependent on definition. Both of these observations are direct results of other, unexpected deformations. The first of these involves a 6–8° asymmetry in the non-ring angles about the *ipso* carbon atoms of the phenyl groups, *e.g.*, C1–C6–C(7 vs. 11) and C5–C12–C(13 vs. 17). Much smaller or negligible distortions (*ca.* 2°) of this sort are displayed by **2** and **3**. The second distortion involves a flexing of the phenyl groups such that the attached dienyl carbon atoms (C[1,5]) do not lie in the phenyl planes. In fact, flexings of 1.6 and 3.7° are observed for the two phenyl groups of **1**, in opposite directions (a smaller deformation of 1.4° is found for **2**, toward ruthenium, while the distortion in **3** is negligible). Thus, the first phenyl group is tilted away from the ruthenium center, but the second one toward it. Quite possibly these deformations relieve steric interactions between hydrogen atoms sufficiently that less of a twist is required between the dienyl and each of the two phenyl planes, perhaps leading to better conjugation between them. However, it is also possible that the distortions arise from an effort to optimize C–H– $\pi$  interactions between the phenyl groups and the methyl substituents on the C<sub>5</sub>Me<sub>5</sub> ligands, or to optimize intermolecular  $\pi$ – $\pi$  interactions between phenyl groups (*vide infra*). There are in fact some data that suggest the presence of C–H– $\pi$  interactions.<sup>21</sup> In particular, one sees significant upfield shifts for the methyl substituents on the C<sub>5</sub>Me<sub>5</sub> ligands for **1** and **2**, but not for **3** (Table 1), the shift being especially pronounced for **1**. Additionally, for both **1** and **2** one observes significant tilting toward the C<sub>5</sub>Me<sub>5</sub> ligands by the phenyl groups (Table 7), while for **3** the tilting is minimal. While it is normal for the tilting of a substituent in the 3 position to be smaller than for the other positions,<sup>17</sup> the magnitude of the phenyl tilting in **2** appears greater than would be expected, in line with the idea of an attractive C–H– $\pi$  interaction. Presumably the tilting in **1** does not need to be as pronounced as alternative modes of distortion are available to enhance the interaction (*vide supra*).

### Unsymmetric dienyl complexes

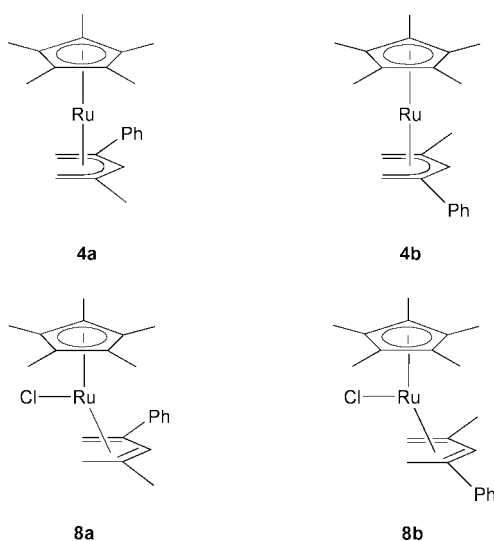
There are some situations in which electronic effects of a substituent may not be apparent as a result of a symmetric disubstitution pattern. For example, stabilization of negative charge by a phenyl substituent on a terminal carbon atom should lead to a long–short–long–short pattern in the dienyl's carbon framework, as in **7**. Obviously, however, with 1,5-disubsti-



tution by phenyl groups one would have cancelling effects at each bond. Thus it was of interest to obtain complexes with unsymmetric mono(phenyl)substitution, especially at the 2 position, since some 1-phenylpentadienyl complexes have been reported.<sup>7–10</sup> A straightforward synthesis of such a species was readily accomplished from the reaction of 2-methyl-4-phenylpentadienes with [Ru(C<sub>5</sub>Me<sub>5</sub>)Cl]<sub>4</sub> [eqn. (3)]. As in the



case of the preparation of **2**, these reactions presumably go through  $\eta^4$ -diene intermediates, **8a,b**, whose *endo*-oriented methyl groups then facilitate loss of HCl, leading to the formation of **4**, as a mixture of planar chiral enantiomers. Com-



pound **4** was readily characterized, and its  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were found to be quite as expected based upon those of  $\text{Ru}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$  ( $\text{C}_7\text{H}_{11}$  = dimethylpentadienyl) and **2**.

The structural characteristics of **4** (Fig. 4) are generally similar to those exhibited by **1–3**. However, while a change from  $\text{Ru}(\text{C}_5\text{Me}_5)(3\text{-C}_6\text{H}_9)$  ( $\text{C}_6\text{H}_9$  = methylpentadienyl) to **3** led to an apparent enhancement of the  $\text{Ru}\text{--}\text{C}_5\text{Me}_5$  bonding at the expense of the  $\text{Ru}\text{--}\text{Pdl}$  bonding, the change from **4** to **2** (also involving replacement of Me by Ph) does not seem to bring about the same effect, but rather perhaps the opposite (Table 7). Owing to the greater tiltings experienced by substituents in the 2,4 vs. 3 positions (*vide supra*), one would expect steric problems involving the phenyl groups to be relieved in **4** relative to **2**; furthermore, the location of phenyl groups at the formally uncharged 2 and 4 positions would not lead to nearly as much resonance stabilization of a free dienyl anion's  $\pi$  system as would occur for 3 substitution, so that the less stabilized 2-phenyl or 2,4-diphenyl substituted anions would be expected on an electronic basis to be at least more comparable to, if not actually better than, their methyl-substituted counterparts regarding the favorability of their binding to a given metal center. It therefore appears entirely reasonable that the  $\text{Ru}\text{--}\text{C}(\text{Pdl})$  bonding in **2** could be quite competitive to that in **4** or even perhaps in  $\text{Ru}(\text{C}_5\text{Me}_5)(2,4\text{-C}_7\text{H}_{11})$  ( $\text{C}_7\text{H}_{11}$  = dimethylpentadienyl). With respect to substituent tilting, the presence of both methyl and phenyl substituents in **4** allows for a direct comparison of their inherent preferences. Perhaps not surprisingly, the tilt by the phenyl substituent is greater than that by the methyl substituent,  $10.8^\circ$  vs.  $8.8^\circ$ .

Finally, one can make some general observations regarding all four phenyl-substituted complexes. Concerning the extent of conjugation between the phenyl and pentadienyl planes, one can note that for **1** and **4** the lengths of the  $\text{C}\text{--}\text{C}$  bonds connecting the two aromatic systems are, within their uncertainties, indistinguishable from the value of *ca.*  $1.484\text{ \AA}$  observed in a large number of biphenyl structures.<sup>19b</sup> The values of  $1.505(5)\text{ \AA}$  for **3** and  $1.544(11)\text{ \AA}$  for **2** appear slightly to somewhat longer. However, in those cases it was necessary to refine the phenyl rings as rigid groups, which could lead to systematic errors in these distances, rendering them less credible. Thus, it would appear reasonable to expect all of these species to be fairly similar to biphenyls in their degrees of conjugation. Interestingly, it has been observed that the inter-ring  $\text{C}\text{--}\text{C}$  distances in biphenyls appear to be independent of the twist between the two rings.<sup>19b</sup>

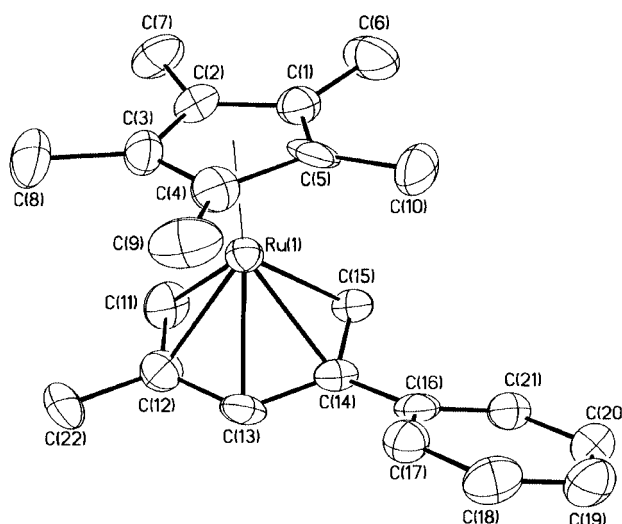


Fig. 4 Perspective view of  $\text{Ru}(\text{C}_5\text{Me}_5)(2\text{-Me-4-PhC}_5\text{H}_5)$  **4**.

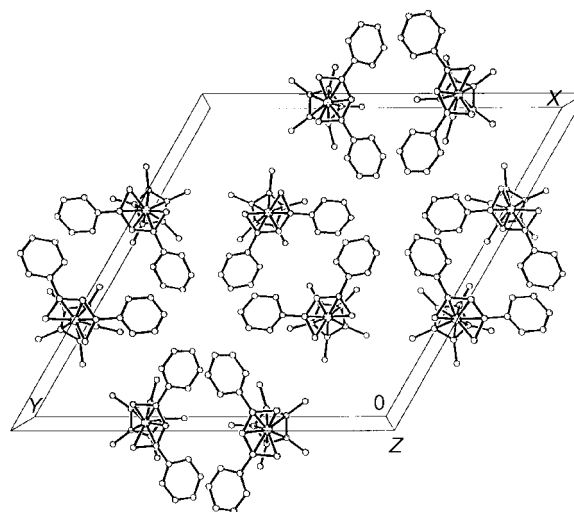


Fig. 5 Solid state packing for  $\text{Ru}(\text{C}_5\text{Me}_5)(2,4\text{-Ph}_2\text{C}_5\text{H}_5)$  **2**.

It is of some interest that the presence of the phenyl groups in **2** and **4** has a significant effect on the solid state packing of these molecules. As can be seen in Figs. 5 and 6, apparently favorable intermolecular stacking interactions between the phenyl groups result in interesting modes of association of the molecules, which may be responsible for the compounds' adoption of relatively uncommon hexagonal and rhombohedral space groups. Of course,  $\pi\text{--}\pi$  stacking interactions are commonly observed in a variety of compounds,<sup>21</sup> and some of the ways by which these and various  $\text{C}\text{--}\text{H}\text{--}\pi$  interactions can lead to hexagonal and rhombohedral symmetries have been explicitly described.<sup>22</sup>

With the development of straightforward routes to the rather general incorporation of phenyl substituents into metal pentadienyl compounds, a fairly complete series of electronically tuned pentadienyl ligand substituent patterns has now become available, and the incorporation of phenyl substituents into pentadienyl ligands has been found to lead to significant spectroscopic as well as electronic effects. Structural data suggest that at least when phenyl substitution occurs on the formally charged 1, 3 and/or 5 positions, thereby stabilizing the formal dienyl anion, the metal–pentadienyl bonding is weakened. Significant twisting exists between the phenyl and pentadienyl ligands, which would seem to hinder conjugation and communication between the  $\pi$  systems; however, the fact that such interactions do occur in similarly twisted biphenyls suggests that conjugation effects in phenylpentadienyl ligands are not

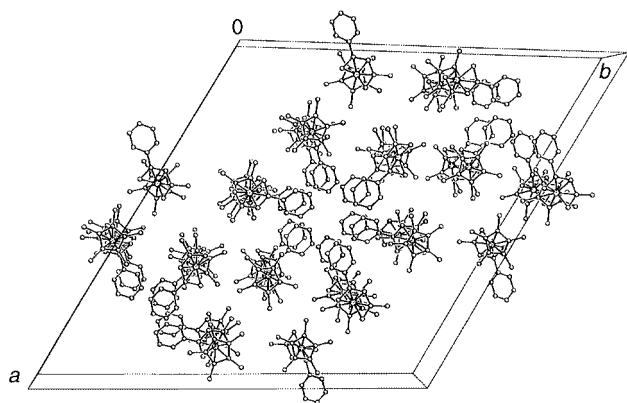


Fig. 6 Solid state packing for  $\text{Ru}(\text{C}_5\text{Me}_5)(2\text{-Me-4-PhC}_5\text{H}_5)$  **4**.

precluded. Of course, such could also be the case for phenyl-substituted cyclopentadienyl ligands; however, to date most such species have contained adjacent phenyl groups,<sup>23</sup> which would further diminish if not prevent conjugation with the ligand fragment. In any event, the fact that there are significant differences between the natures of the pentadienyl positions (e.g., the charged 1,5 vs. 3 vs. uncharged 2,4 carbon atoms) leads to an added dimension and potentially greater diversity in properties for the open pentadienyl systems. It can be expected that much remains to be learned through comparative physical studies on variously substituted pentadienyl complexes, and additional efforts in these directions are continuing.

## Experimental

All procedures were carried out under a nitrogen atmosphere using standard Schlenk apparatus and techniques. Solvents were dried and deoxygenated under a nitrogen atmosphere using sodium benzophenone ketyl. Phenylacetaldehyde was obtained commercially, and converted to phenylcrotonaldehyde and subsequently to 3-phenylpenta-1,3-diene by reported procedures;<sup>24</sup> 2,4-diphenylpenta-1,3-diene was also prepared by a reported procedure from dypnone,<sup>25</sup> except that the use of flash chromatography (silica column, 3 cm diameter  $\times$  10 cm, hexane eluent) allowed for higher yields (up to ca. 65%).  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  and  $\text{Ru}(\text{C}_5\text{Me}_5)(1,5\text{-Ph}_2\text{C}_5\text{H}_5)$  **1** were also prepared as previously described.<sup>7</sup> Spectroscopic studies were carried out as reported earlier,<sup>26</sup> while analytical data were obtained from Robertson or E + R Laboratories.

### $\alpha$ -Phenylcrotonaldehyde

$^1\text{H}$  NMR (neat):  $\delta$  9.54 (s, 1H, CHO), 7.1–7.4 (m, 5H,  $\text{C}_6\text{H}_5$ ), 6.83 (q, 1H, vinyl,  $J = 7.2$  Hz), 1.99 (d, 3H, Me,  $J = 7.2$  Hz).

### 2,4-Diphenylpenta-1,3-diene

$^1\text{H}$  NMR: major isomer (neat):  $\delta$  7.2–7.5 (m, 10H, Ph), 6.55 (q, 1H, C-3,  $J = 1.5$  Hz), 5.67 (d, 1H, H-1,  $J = 1.5$  Hz), 5.23 (t, 1H, H-1a,  $J = 1.5$  Hz), 2.12 (d, 3H, Me,  $J = 1.5$  Hz). The minor (ca. 10%) geometric isomer was evidenced in solution by characteristic peaks at  $\delta$  6.24 (t, 1H,  $J = 1.4$  Hz), 5.28 (d, 1H,  $J = 1.6$  Hz), 4.88 (t, 1H,  $J = 1.5$  Hz), 2.19 (d, 3H,  $J = 1.5$  Hz).

### 2-Methyl-4-phenylpenta-(1,3 and 2,4)-dienes

A mixture of these dienes was prepared from the reaction of mesityl oxide with freshly prepared phenylmagnesium bromide (commercial solutions gave poorer results), using a procedure analogous to that used for 2,4-dimethylpenta-1,3-diene.<sup>27</sup> After the reaction had been quenched with aqueous ammonium chloride, and the organic products extracted with diethyl ether, GC analysis indicated that some dehydration of the alcohol had already taken place. A few small crystals of iodine were then

added to the stirred ether solution, whose composition was monitored by GC. After ca. 10 h, dehydration of the alcohol was complete, and small portions of aqueous sodium hydrogensulfite were added, until the iodine had been reduced to iodide. The diethyl ether solution was then dried over  $\text{MgSO}_4$ , and the ether removed *in vacuo*, providing a mixture of the dienes in a yield of 78%. Vacuum transfer of the dienes yielded a product of ca. 95% purity. Further purification is possible,<sup>28</sup> but was found unnecessary for the subsequent reaction with  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$ . Spectroscopic data were identical to those previously reported.<sup>28</sup>

### (Pentamethylcyclopentadienyl)(3-phenylpentadienyl)-ruthenium(II), $\text{Ru}(\text{C}_5\text{Me}_5)(3\text{-PhC}_5\text{H}_5)$ , **3**

To a solution of 0.35 g of  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  (1.4 mmol of Ru) in 30 mL of THF at  $-78^\circ\text{C}$ , a solution of 0.40 g (1.4 mmol) of the potassium salt of the 3-phenylpentadienyl anion in 20 mL of THF was slowly added. The resulting red solution was stirred at  $-78^\circ\text{C}$  for 30 min and thereafter slowly warmed to room temperature. The red solution was stirred overnight, and the solvent removed *in vacuo*. The crude product was extracted with  $3 \times 25$  mL of pentane, and the mixture was filtered through alumina. After concentration to a volume of ca. 5–10 mL, the yellow solution was cooled to  $-90^\circ\text{C}$ , yielding a yellow air-stable (as solid) crystalline compound (mp  $59\text{--}60^\circ\text{C}$ , 31% yield).

Anal. Calc. for  $\text{C}_{21}\text{H}_{26}\text{Ru}$ : C, 66.45; H, 6.91. Found: C, 64.82; H, 7.01%.  $^1\text{H}$  NMR (toluene- $d_8$ , ambient):  $\delta$  7.1–7.4 (m, 5H, Ph), 4.48 (t, 2H, H-2,4,  $J = 8.8$  Hz), 2.39 (dd, 2H,  $\text{H}_{\text{exo-1,5}}$ ,  $J = 2.3$ , 8.9 Hz), 1.65 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 0.54 (dd, 2H,  $\text{H}_{\text{endo-1,5}}$ ,  $J = 2.3$ , 8.9 Hz).  $^{13}\text{C}$  NMR (toluene- $d_8$ , ambient):  $\delta$  142.7 (s, Ph), 128.2 (d, Ph,  $J = 159$  Hz), 126.9 (d, Ph,  $J = 159$  Hz), 123.8 (d, Ph,  $J = 159$  Hz), 105.8 (s, C-3), 90.1 (s,  $\text{C}_5\text{Me}_5$ ), 82.7 (d, C-2,  $J = 157$  Hz), 44.6 (t, C-1,  $J = 156$  Hz), 10.6 (q,  $\text{C}_5\text{Me}_5$ ,  $J = 122$  Hz). Mass spectrum (EI, 17 eV) [ $m/z$  (relative intensity)]: 379 (100), 365 (51), 363 (30), 351 (4), 231 (10), 189 (6), 128 (6), 91 (3%).

### (Pentamethylcyclopentadienyl)(2,4-diphenylpentadienyl)-ruthenium(II), $\text{Ru}(\text{C}_5\text{Me}_5)(2,4\text{-Ph}_2\text{C}_5\text{H}_5)$ , **2**

To a THF solution containing 0.30 g of  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  (1.1 mmol of Ru) and 0.30 g of  $\text{K}_2\text{CO}_3$  (2.2 mmol) was slowly added 0.50 g of 2,4-diphenylpenta-1,3-diene (2.2 mmol). The red-brown solution was stirred for 24 h, during which time it turned to yellow. The solvent was removed from the yellow solution. The residue was extracted with  $2 \times 30$  mL of pentane, and the mixture was filtered through Celite. The yellow filtrate was concentrated to a volume of ca. 5–10 mL and cooled to  $-90^\circ\text{C}$ , yielding yellow air-stable (as solid) crystals (mp  $59\text{--}60^\circ\text{C}$ , 37–65% yield). Anal. Calc. for  $\text{C}_{27}\text{H}_{30}\text{Ru}$ : C, 71.18; H, 6.64. Found: C, 70.36; H, 6.76%.  $^1\text{H}$  NMR (toluene- $d_8$ , ambient):  $\delta$  7.1–7.6 (m, 10H, Ph), 6.35 (s, 1H, H-3), 2.73 (d, 2H,  $\text{H}_{\text{exo-1,5}}$ ,  $J = 2$  Hz), 1.37 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 0.51 (d, 2H,  $\text{H}_{\text{endo-1,5}}$ ,  $J = 2$  Hz).  $^{13}\text{C}$  NMR (toluene- $d_8$ , ambient):  $\delta$  144.5 (s, Ph), 128.8 (d, Ph,  $J = 159$  Hz), 128.2 (d, Ph,  $J = 159$  Hz), 126.9 (d, Ph,  $J = 159$  Hz), 93.1 (d, C-3,  $J = 155$  Hz), 92.9 (s, C-2,4), 90.9 (s,  $\text{C}_5\text{Me}_5$ ), 41.5 (t, C-1,5,  $J = 157$  Hz), 10.1 (q,  $\text{C}_5\text{Me}_5$ ,  $J = 126$  Hz). Mass spectrum (EI, 17 eV) [ $m/z$  (relative intensity)]: 454 (100), 439 (59), 379 (5), 314 (11), 228 (37), 203 (13), 115 (10), 91 (19), 57 (7), 41 (3%).

### ( $\eta^5$ -Pentamethylcyclopentadienyl)( $\eta^4$ -3-phenylpenta-1,3-diene)-ruthenium(II) chloride, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\eta^4\text{-3-Ph-1,3-C}_5\text{H}_7)\text{Cl}]$ **6**

To a THF solution (20 mL) containing  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  (0.08 g, 0.3 mmol of Ru) was added an excess of potassium carbonate and 3-phenylpenta-1,3-diene (0.04 g, 0.3 mmol). The original dark brown solution immediately turned a clearer yellow-brown. After 4 h stirring, the solvent was removed *in vacuo*. The yellow residue was extracted with  $2 \times 20$  mL pentane and

filtered through Celite. The yellow filtrate was concentrated *in vacuo* until incipient crystallization, and cooled to  $-20^{\circ}\text{C}$ , resulting in the formation of air-stable (as solid) yellow–orange crystals (0.09 g, 70% yield, mp  $95\text{--}97^{\circ}\text{C}$ , decomp.). Refluxing the mixture for several hours did not result in any new compound. Anal. Calc. for  $\text{C}_{21}\text{H}_{27}\text{RuCl}$ : C, 60.64; H, 6.54. Found: C, 60.66; H, 6.67%.  $^1\text{H}$  NMR (chloroform- $d$ , ambient):  $\delta$  7.66–7.40 (m, 5H, Ph), 4.60 (dd, 1H, H-2,  $J = 7.7, 9.5$  Hz), 2.97 (dd, 1H, H-1,  $J = 7.7, 2.3$  Hz), 2.11 (q, 1H, H-4,  $J = 6.8$  Hz), 1.80 (d,  $\text{CH}_3$ ,  $J = 6.8$  Hz), 1.60 (dd, 1H, H-1,  $J = 9.5, 2.3$  Hz), 1.42 (s, 15H,  $\text{C}_5\text{Me}_5$ ).  $^{13}\text{C}$  NMR (chloroform- $d$ , ambient):  $\delta$  137.6 (s, Ph), 130.7 (d, Ph,  $J = 158$  Hz), 129.1 (d, Ph,  $J = 158$  Hz), 126.8 (d, Ph,  $J = 158$  Hz), 110.1 (s, C-3), 94.9 (s,  $\text{C}_5\text{Me}_5$ ), 83.1 (dd, C-2,  $J = 162, 5$  Hz), 69.6 (d, C-4,  $J = 158$  Hz), 50.9 (t, C-1,  $J = 156$  Hz), 15.7 (q, Me,  $J = 127$  Hz), 9.1 (q,  $\text{C}_5\text{Me}_5$ ,  $J = 128$  Hz). IR (Nujol mull): 1732s, 1599w, 1504w, 1261s, 1120w, 1074ms, 1024ms, 893w, 800m, 781m, 705s  $\text{cm}^{-1}$ . Mass spectrum (EI, 17 eV) [ $m/z$  (relative intensity)]: 544 (49), 543 (47), 542 (35), 467 (14), 145 (15), 144 (89), 143 (19), 129 (100), 128 (23%).

**(Pentamethylcyclopentadienyl)(2-methyl-4-phenylpentadienyl)-ruthenium(II),  $\text{Ru}(\text{C}_5\text{Me}_5)(2\text{-Me-4-PhC}_5\text{H}_5)$  4**

To a THF solution (40 mL) containing  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{Cl}]_4$  (2.50 g, 2.3 mmol) was added an excess of potassium carbonate and a mixture of 2-methyl-4-phenylpenta-1,3-diene and 2-methyl-4-phenylpenta-2,4-diene (1.45 g, 9.2 mmol) in 10 mL of THF. The original dark brown solution turned a clearer yellow–brown after stirring overnight. The volatiles were removed *in vacuo* and the residue was extracted with  $3 \times 20$  mL pentane and filtered through alumina. The yellow filtrate was concentrated to a volume of ca. 5 mL and cooled to  $-90^{\circ}\text{C}$ , yielding yellow air-stable (as solid) crystals (1.70 g, mp  $81\text{--}82^{\circ}\text{C}$ , 47% yield). Higher quality crystals for X-ray analysis were obtained by slowly cooling a saturated pentane solution to  $-30^{\circ}\text{C}$ . Anal. Calc. for  $\text{C}_{22}\text{H}_{28}\text{Ru}$ : C, 67.15; H, 7.17. Found: C, 66.97; H, 7.26%.  $^1\text{H}$  NMR (benzene- $d_6$ , ambient):  $\delta$  7.1–7.5 (m, 5H, Ph), 5.62 (s, 1H, H-3), 2.72 (d, 1H,  $\text{H}_{\text{exo-1}}$ ,  $J = 2.6$  Hz), 2.28 (d, 1H,  $\text{H}_{\text{exo-5}}$ ,  $J = 2.3$  Hz), 1.83 (s, 3H, Me), 1.52 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 0.74 (d, 1H,  $\text{H}_{\text{endo-5}}$ ,  $J = 2.3$  Hz), 0.19 (d, 1H,  $\text{H}_{\text{n-1}}$ ,  $J = 2.6$  Hz).  $^{13}\text{C}$  NMR (benzene- $d_6$ , ambient):  $\delta$  144.5 (s, Ph), 128.7 (d, Ph), 128.6 (d, Ph), 127.1 (d, Ph), 92.7 (s, C-2), 92.5 (d, C-3,  $J = 159$  Hz), 92.1 (s, C-4), 90.7 (s,  $\text{C}_5\text{Me}_5$ ), 46.7 (t, C-5,  $J = 153$  Hz), 40.4 (t, C-1,  $J = 156$  Hz), 26.5 (q, Me, 126 Hz), 10.8 (q,  $\text{C}_5\text{Me}_5$ ,  $J = 125$  Hz). Mass spectrum (EI, 80 eV) [ $m/z$  (relative intensity)]: 396 (40), 395 (40), 394 (100), 393 (89), 392 (96), 391 (83), 390 (45), 389 (32), 388 (21), 387 (10), 381 (22), 380 (12), 379 (56), 378 (30), 377 (50), 376 (32), 375 (20), 374 (14), 373 (11), 233 (11), 232 (11), 231 (13), 230 (11%).

**X-Ray structural determinations**

Single crystals of the symmetrically substituted compounds were obtained by slowly cooling their concentrated solutions in hexane  $[\text{Ru}(\text{C}_5\text{Me}_5)(1,5\text{-Ph}_2\text{C}_5\text{H}_5)$  **1**,  $\text{Ru}(\text{C}_5\text{Me}_5)(3\text{-PhC}_5\text{H}_6)$  **3**] or diethyl ether  $[\text{Ru}(\text{C}_5\text{Me}_5)(2,4\text{-Ph}_2\text{C}_5\text{H}_5)$  **2**] to  $-20^{\circ}\text{C}$ . Crystallographic data are collected in Table 2. The crystals were mounted in glass capillaries. For **1**, systematic absences were consistent with either the  $Cc$  or  $C2/c$  space group, but a solution could only be achieved for the former. Data were processed using bioteX<sup>29</sup> and teXsan<sup>30</sup> program packages, while the structure was solved by direct methods (SIR92).<sup>31</sup>

For **2** the crystals were found to possess  $6/mmm$  Laue symmetry. Systematic absences in the data were compatible with three space groups:  $P6_3cm$  (185),  $P6c2$  (188) or  $P6_3/mcm$  (193). Since  $Z = 6$  and the only symmetry element **2** can accommodate is a mirror plane,  $P6_3cm$  becomes the only plausible choice. For **3**,  $2/m$  symmetry was indicated and absences uniquely defined the space group. For **4**,  $\bar{3}$  Laue symmetry was observed, compatible with space groups  $R\bar{3}$ ,  $R\bar{3}2$ ,  $R\bar{3}m$  and  $R\bar{3}m$ . The centrosymmetric  $R\bar{3}$  yielded chemically reasonable and com-

putationally stable results. In the above cases, the Ru atoms were located from Patterson syntheses. For all structures, non-hydrogen atoms were anisotropically refined and hydrogen atoms were treated as idealized contributions. SHELXTL<sup>32</sup> (ver. 4.2 and 5.1) software was used in the solution and refinement of **2** and **3**.

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