

## An Unusual Rotational Distortion in an $[(\eta\text{-Indenyl})\text{RhL}_2]$ Complex: Molecular Structures of $[(\eta\text{-1,2,3-Me}_3\text{C}_9\text{H}_4)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$ and $[(\eta\text{-C}_9\text{H}_7)\text{Rh}(\text{CO})_2]$

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The molecular structures of  $[(\eta\text{-1,2,3-Me}_3\text{C}_9\text{H}_4)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$  and  $[(\eta\text{-C}_9\text{H}_7)\text{Rh}(\text{CO})_2]$ , barriers to hindered ethylene rotation in a series of indenyl rhodium bis(ethylene) complexes bearing different degrees of indenyl-ring methylation, and the barrier to hindered indenyl-ring rotation in  $[(\eta\text{-1-MeC}_9\text{H}_6)\text{Rh}(\text{CO})_2]$  are reported.

The solid state structures and solution dynamics of  $[(\eta\text{-indenyl})\text{ML}_2]$  complexes (M = Co, Rh, Ir) are of interest owing to their enhanced catalytic activity in intermolecular hydroacylation,<sup>1</sup> alkyne trimerisation to benzenes,<sup>2</sup> and alkyne-nitrile co-trimerisation to pyridines.<sup>3</sup> There are, however, relatively few reports of the solid-state structures of such complexes. Two X-ray structure determinations<sup>4,5</sup> on the parent complex  $[(\eta\text{-C}_9\text{H}_7)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$  (**1**) have now appeared, and the structures of  $[(\eta\text{-C}_9\text{R}_7)\text{M}(\eta^4\text{-1,5-C}_8\text{H}_{12})]$  [**2a**] M = Rh, R = H;<sup>6</sup> [**2b**] R = Me;<sup>6</sup> [**2c**] M = Co, R = H;<sup>3</sup> [**2d**] M = Ir, R = H<sup>7</sup>] and  $[(\eta\text{-C}_9\text{H}_7)\text{RhL}_2]$  [**3**] L = PMe<sub>3</sub>;<sup>5</sup> [**4**] L<sub>2</sub> =  $\eta^4\text{-C}_8\text{F}_8$ <sup>8</sup>] have been reported. In the course of our investigations<sup>1,5,6,8,9</sup> of the reactivity of  $[(\eta\text{-indenyl})\text{RhL}_2]$  complexes, we have recently carried out structure determinations<sup>10</sup> on  $[(\eta\text{-C}_9\text{H}_7)\text{RhL}_2]$  [**5**] L = CO;<sup>11,12</sup> [**6**] L = PPh<sub>2</sub>C≡CBu<sup>t</sup>;<sup>10</sup> [**7**] L = CNBu<sup>t</sup>;<sup>11</sup> [**8**] L<sub>2</sub> = 2,2'-bipyridine<sup>10</sup>] and  $[(\eta\text{-1,2,3-Me}_3\text{C}_9\text{H}_4)\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$  (**9**).<sup>†</sup> We report,

herein, the molecular structures of (**5**) and (**9**), and the ethylene rotational barriers in solution for a series of ring methylated  $[(\eta\text{-C}_9\text{Me}_n\text{H}_{7-n})\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$  ( $n = 3,4,7$ ) com-

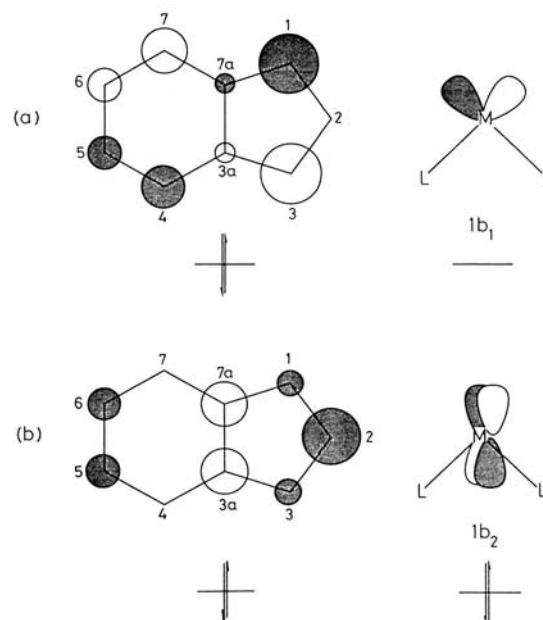
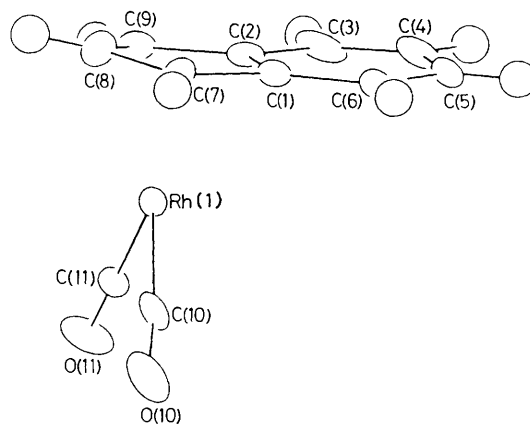


Figure 1. Schematic representations of the HOMO (a) and second HOMO (b) of the indenyl anion (left), and the important frontier molecular orbitals for a d<sup>8</sup>-RhL<sub>2</sub> moiety (right).<sup>13</sup>

<sup>†</sup> The synthesis of complex (**5**) has been reported.<sup>11,12</sup> Complex (**9**) was prepared by BuLi deprotonation of 1,2,3-Me<sub>3</sub>C<sub>9</sub>H<sub>5</sub> and reaction with  $[(\eta\text{-C}_2\text{H}_4)_2\text{Rh}(\mu\text{-Cl})_2]$ . The 1,2,3-Me<sub>3</sub>C<sub>9</sub>H<sub>5</sub> was prepared by a modification of a published procedure: W. G. Miller and C. U. Pittman, Jr., *J. Org. Chem.*, 1974, **39**, 1955. See also: Pl. A. Plattner, A. Fürst, and K. Jerasek, *Helv. Chim. Acta*, 1947, **30**, 1320; C. U. Pittman, Jr., and W. G. Miller, *J. Am. Chem. Soc.*, 1973, **95**, 2947. *Spectroscopic data* for (**9**): <sup>1</sup>H n.m.r. (250 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 7.12 (m, 4H), 2.00 (d, <sup>3</sup>J<sub>Rh-H</sub> 1.5 Hz, 3H, Me), 1.91 (s, 8H, 2 C<sub>2</sub>H<sub>4</sub>), 1.62 (s, 6H, 2 Me); <sup>13</sup>C{<sup>1</sup>H} n.m.r. (63 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 123.03 [s, C(5), C(6)], 117.32 [s, C(4), C(7)], 110.81 [s, C(3a), C(7a)], 106.92 [s, C(2)], 86.48 [s, C(1), C(3)], 48.01 [d, J<sub>Rh-C</sub> 13 Hz, C(11), C(12), C(13), C(14)], 10.91 [s, C(9)], 7.67 [s, C(8), C(10)]. See Figure 3 for carbon numbering.

plexes. The solid state structure of (9) shows an unusual rotational conformation of the  $[\text{Rh}(\eta\text{-C}_2\text{H}_4)_2]$  unit with respect to the indenyl ring which apparently leads to significant asymmetry in the Rh–ring bonding.

Simple molecular orbital arguments predict the preferred ground state structure of  $[(\eta\text{-indenyl})\text{RhL}_2]$  complexes to belong to the  $C_s$  point group, with the  $\text{RhL}_2$  unit straddling the mirror plane. The reasons for this are discussed elsewhere,<sup>4</sup> and are analogous to those used to explain<sup>13</sup> conformational preferences in 1,2-substituted  $\text{C}_5\text{H}_3\text{R}_2$  complexes and other heteroatom substituted  $\pi$ -ligands such as  $[\text{7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$ . In short, the two highest lying filled orbitals for  $[\text{C}_9\text{H}_7]^-$  (Figure 1) are related to the  $e_g$  set of  $[\text{C}_5\text{R}_5]^-$  but are no longer degenerate, the 'diene'-like orbital (a) being higher in energy than the 'ene-enyl' orbital (b). Simple ligand field arguments can be used to predict the ordering of the fragment molecular orbitals for the  $C_{2v}$   $d^8\text{-ML}_2$  moiety (Figure 1). All d orbitals except for  $d_{xz}(1b_1)$  ( $\text{RhL}_2$  lying in the  $xz$  plane,  $z$  being the Rh–ring axis) will be filled and, in particular,  $d_{yz}(1b_2)$ , which, like the  $d_{xz}/p_x$  hybrid, is of  $\pi$  symmetry, is filled. The preferred orientation of the  $d^8\text{-ML}_2$  unit with respect to the indenyl ring will be the one which best stabilises the indenyl HOMO and minimises the other 4-electron destabilising  $\pi$  interaction. This is achieved in the rotational conformation addressed above, and is well illustrated by the molecular structure of (5)<sup>‡</sup> (Figure 2). Rotation of the  $\text{ML}_2$  unit through  $90^\circ$  will switch the  $\pi$  interactions, destabilising the complex and, thus, there will be an energy barrier to such a rotation. We,<sup>5,8,14</sup> and others,<sup>4,15</sup> have measured these barriers [often using the  $(\eta\text{-1-Me-C}_9\text{H}_6)$  ligand to break mirror symmetry] for a number of complexes, and find a correlation between  $\Delta G^\ddagger$  and the degree of ring-slippage [ $\Delta = (\text{average Rh-C-3a,7a}) - (\text{average Rh-C-1,3})$ ]. Larger  $\Delta$  values give rise to increased values of  $\Delta G^\ddagger$ . Interestingly  $\Delta G_{213}^\ddagger$  for  $[(\eta\text{-1-Me-C}_9\text{H}_6)\text{Rh}(\text{CO})_2]$  ( $11.27 \pm 0.09 \text{ kcal mol}^{-1}$ )<sup>§</sup> ( $1 \text{ cal} = 4.184 \text{ J}$ )



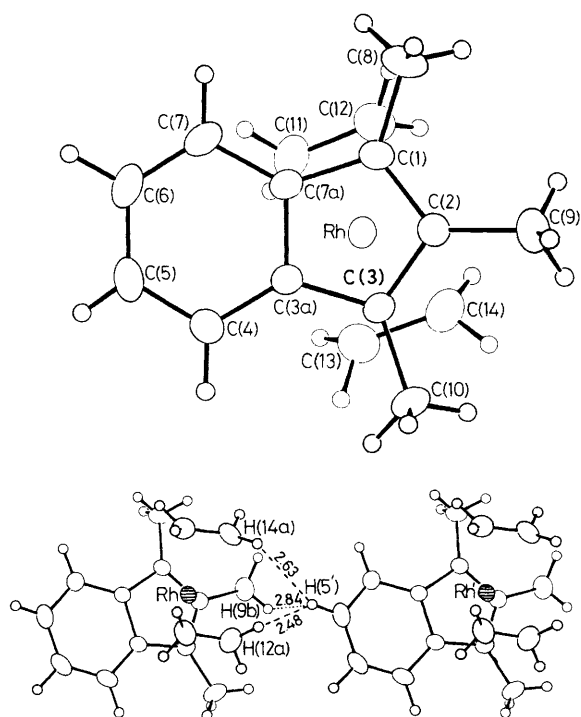
**Figure 2.** Molecular structure of (5). Selected bond distances (Å) and angles ( $^\circ$ ): Rh(1)–C(1) 2.409(7), Rh(1)–C(2) 2.413(7), Rh(1)–C(7) 2.210(11), Rh(1)–C(8) 2.222(8), Rh(1)–C(9) 2.212(7), Rh(1)–C(10) 1.846(6), Rh(1)–C(11) 1.868(10), O(10)–C(10) 1.132(7), O(11)–C(11) 1.132(12), C(1)–C(2) 1.430(9), C(1)–C(7) 1.463(11), C(2)–C(9) 1.447(10), C(8)–C(9) 1.401(11), C(7)–C(8) 1.392(14), C(10)–Rh(1)–C(11) 91.7(7);  $\Delta$  (see text) = 0.20(1) Å; hinge angle =  $9.2^\circ$  between planes C(7), C(8), C(9), and C(7), C(1), C(2), C(9); fold angle =  $10.9^\circ$  between planes C(7), C(8), C(9), and C(1), C(2), C(3), C(4), C(5), C(6).

is insignificantly different from that for  $[(\eta\text{-1-Me-C}_9\text{H}_6)\text{Rh}(\text{PMe}_3)_2]$  ( $11.20 \pm 0.03 \text{ kcal mol}^{-1}$ ).<sup>5</sup> The two values of  $\Delta$ ,<sup>5,6,8,15</sup> the slip-parameter, are also identical (0.20 and 0.20 Å respectively), in keeping with the above correlation.

Thus far, none of the solid state molecular structures determined has a crystallographic mirror plane. There are slight, but generally insignificant, deviations in the Rh–C(1) vs. Rh–C(3) and Rh–C(3a) vs. Rh–C(7a) distances. A single-crystal structure determination on (9),<sup>‡</sup> however, yielded the surprising observation (Figure 3) that in the solid state, the projection of the  $\text{Rh}(\eta\text{-C}_2\text{H}_4)_2$  unit onto the indenyl ring plane is rotated through an angle of  $21.2^\circ$  with respect to the normal to the plane perpendicular to the trimethylindenyl ring and passing through C(2) and the midpoints of C(3a,7a) and C(5,6). The two ethylene ligands are still essentially parallel, although the Rh–C(14) distance is significantly shorter than that of the remaining 3 Rh–C(ethylene) bonds. It is not yet entirely clear why (9) adopts this configuration in the solid state. In solution, indenyl ring rotation is quite rapid as evidenced by the apparent mirror symmetry of the complex in both  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  n.m.r. spectra. An analysis of the existing and potential short contacts between hydrogen atoms on C(8) and C(10) and those on C(11)–C(14) was conducted by examining their vertical distances from a reference plane, e.g. C(1), C(7a), C(3a), and C(3). The average distance below the plane for the 'upper' hydrogens on C(11)–C(14), namely H(11b), H(12b), H(13b), and H(14b), is 2.78 Å, and the average distance below the plane for the 'lower' Me hydrogens, H(8a), H(8b), H(10b), and H(10c), is 0.21 Å. Thus, if the ethylene H's were directly below the Me groups in any  $\text{RhL}_2$  rotamer, the closest contacts would be at least 2.57 Å. In fact, the shortest intramolecular non-bonded distance in (9) is 2.59(8) Å between H(10c) and H(13b). Therefore, it is more likely that intermolecular contacts are responsible for this conformation and the shortest of these are 2.48(5) and 2.60(5) Å respectively, between H(5) and (H12a) and H(14a) on molecules related by the translation  $(1+x, 1+y, z)$ . Thus, if (9) had  $C_s$  symmetry, the packing observed would likely be disrupted by close approach of H(12a) and H(5) on adjacent

<sup>‡</sup> Crystal data, collection and refinement for (5):  $\text{RhO}_2\text{C}_{11}\text{H}_7$ ,  $M = 274.08$ , monoclinic, space group  $P2_1$ ,  $a = 5.949(2)$ ,  $b = 8.452(3)$ ,  $c = 9.838(3)$  Å,  $\beta = 92.83(3)^\circ$ ,  $U = 494.1$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.842 \text{ g cm}^{-3}$ ,  $T = 198 \text{ K}$ ,  $\mu(\text{Mo-K}\alpha) = 16.68 \text{ cm}^{-1}$ . Data were collected from a plate-like crystal of dimensions  $0.10 \times 0.25 \times 0.30 \text{ mm}$  on an Enraf-Nonius CAD4 diffractometer by the  $\omega$  scan method ( $4.2^\circ \leq 2\theta \leq 55.0^\circ$ ). From 2431 data collected, 1050 unique reflections with  $I \geq 3\sigma(I)$ , corrected for absorption (DIFABS), were used in the structure solution (Patterson) and full-matrix least squares refinement which converged at  $R$  and  $R_w$  values of 0.025 and 0.030 respectively. The enantiomorph was chosen from a comparison of relative  $R$  factors. Hydrogen atoms were fixed in calculated positions. For (9):  $\text{RhC}_{16}\text{H}_{21}$ ,  $M = 316.251$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.001(1)$ ,  $b = 7.763(1)$ ,  $c = 14.521(2)$  Å,  $\alpha = 93.10(1)$ ,  $\beta = 104.31(1)$ ,  $\gamma = 112.68(1)^\circ$ ,  $U = 695.7(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.510 \text{ g cm}^{-3}$ ,  $F(000) = 324$ ,  $T = 294 \pm 1 \text{ K}$ ,  $\mu(\text{Mo-K}\alpha) = 11.71 \text{ cm}^{-1}$ . Data were collected from a crystal of dimensions  $0.28 \times 0.29 \times 0.34 \text{ mm}$  on a Syntex  $P2_1$  diffractometer by the  $\theta$ - $2\theta$  scan method ( $3.2^\circ \leq 2\theta \leq 56^\circ$ ). From 3390 data collected, 3135 unique reflections with  $I \geq 3\sigma(I)$  were used in the structure solution (Patterson and Fourier methods) and refinement which converged at  $R$  and  $R_w$  values of 0.024 and 0.028 respectively. All hydrogen atoms were located in difference maps and refined isotropically. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>§</sup> Determined by complete line shape analysis of the variable temperature  $^{13}\text{C}$  n.m.r. spectra using a locally modified version of DNMR3. Activation parameters for ring-rotation are:  $\ln A = 25.4 \pm 2.5$ ;  $E_a = 9.7 \pm 1.1$ ,  $\Delta G_{213}^\ddagger = 11.27 \pm 0.09$ ,  $\Delta H^\ddagger = 9.3 \pm 1.1 \text{ kcal mol}^{-1}$ ; and  $\Delta S^\ddagger = -9.4 \pm 4.8 \text{ cal mol}^{-1} \text{ K}^{-1}$ . Details of additional dynamic Fourier transform n.m.r. studies, particularly of a series of mono- and bi-dentate phosphine complexes, will be published elsewhere in a joint manuscript with the authors in reference 4.



**Figure 3.** Molecular structure of (9). Selected bond distances (Å) and angles (°): Rh-C(1) 2.264(3), Rh-C(2) 2.264(3), Rh-C(3) 2.188(2), Rh-C(3a) 2.310(3), Rh-C(7a) 2.319(3), Rh-C(11) 2.136(4), Rh-C(12) 2.147(4), Rh-C(13) 2.137(4), Rh-C(14) 2.104(4), C(1)-C(2) 1.412(3), C(2)-C(3) 1.433(3), C(3)-C(3a) 1.452(3), C(3a)-C(7a) 1.431(3), C(1)-C(7a) 1.449(3), C(11)-C(12) 1.373(5), C(13)-C(14) 1.388(5),  $\Delta$  (see text) = 0.089(3) Å; hinge angle = 7.12° between planes C(1), C(2), C(3), and C(1), C(7a), C(3a), C(3); fold angle = 7.92° between planes C(1), C(2), C(3), and C(3a), C(4), C(5), C(6), C(7), C(7a); RhL<sub>2</sub> rotation angle (see text) = 21.2°; L-M-L angle {[midpoint of C(11)-C(12)]-Rh-[midpoint of C(13)-C(14)]} = 96.3(1)°; C(11), C(12), and C(13), C(14) are 0.20 and 0.22 Å from the mean planes of H(11a), H(11b), H(12a), H(12b), and H(13a), H(13b), H(14a), H(14b) respectively. Below is a packing diagram showing two molecules related by the translation (1 + x, 1 + y, z).

molecules (Figure 3). Note also that the barrier to the intramolecular process of ethylene rotation is not substantially increased by the presence of the Me groups at C(1) and C(3) (see below). This is consistent with the lack of significant intramolecular steric constraints on the geometry of (9).

Preliminary results of a series of Extended Hückel Molecular Orbital calculations by Albright *et al.* suggested<sup>16</sup> that upon rotation of the RhL<sub>2</sub> unit, the Rh atom would have a tendency to slip off the mirror plane, and this distortion is quite significant for (9). Thus, the Rh-C(3a,7a) distances, 2.310(3) and 2.319(3) Å are insignificantly different as are the Rh-C(1,2) distances of 2.264(3) and 2.264(3) Å. However, Rh-C(3) is unusually short [2.188(2) Å] and differs from Rh-C(1) by 0.078(3) Å. For comparison, in (5), Rh(1)-C(7) and Rh(1)-C(9) are 2.210(11) and 2.212(7) Å respectively. It is clear that further structural studies of substituted indenyl complexes as well as a detailed molecular orbital investigation are required to understand fully the potential energy surface for such species. The molecular structure of (9) has allowed us to capture a 'snap-shot' of the potential surface for hindered indenyl-ring rotation.

Finally, we have measured the barriers to hindered ethylene rotation in [( $\eta$ -4,5,6,7-Me<sub>4</sub>C<sub>9</sub>H<sub>3</sub>)RhL<sub>2</sub>], (9), and [( $\eta$ -

C<sub>9</sub>Me<sub>7</sub>)RhL<sub>2</sub>] (L =  $\eta$ -C<sub>2</sub>H<sub>4</sub>), and obtained  $\Delta G^\ddagger$  values of 10.5  $\pm$  0.4, 10.7  $\pm$  0.4, and 11.1  $\pm$  0.4 kcal mol<sup>-1</sup> respectively, which are similar to the values of 10.3  $\pm$  0.5 and 10.4  $\pm$  0.5 kcal mol<sup>-1</sup> reported for (1)<sup>12</sup> and [( $\eta$ -1-MeC<sub>9</sub>H<sub>7</sub>)Rh( $\eta$ -C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sup>4</sup> respectively. These barriers are all significantly lower than those<sup>17,18</sup> for [( $\eta$ -C<sub>5</sub>R<sub>5</sub>)Rh( $\eta$ -C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (R = H, 15.7  $\pm$  0.2; R = Me, 17.1  $\pm$  0.2 kcal mol<sup>-1</sup>), consistent with weaker Rh-ethylene bonding in the indenyl vs. cyclopentadienyl complexes, a factor which is apparent in the catalytic activity mentioned earlier.

Photoelectron spectroscopic studies of a series of methyl substituted [( $\eta$ -indenyl)RhL<sub>2</sub>] complexes are underway to provide data on the relative donor abilities of the indenyl ligands. These results, and a detailed Extended Hückel Molecular Orbital analysis of the bonding and ligand dynamics, will be reported in due course.<sup>19</sup>

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