

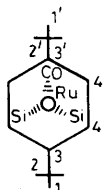
## Ring Tilting and the Barriers to Rotation of Arene Rings $\pi$ -Bonded to Transition Metals

Xiang Hu,<sup>†</sup> John Duchowski, and Roland K. Pomeroy\*

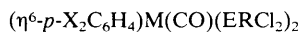
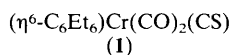
Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Restricted rotation of the arene ring in complexes of the type (arene)M(CO)<sub>3-x</sub>(SiCl<sub>3</sub>)<sub>x</sub> (M = Re, x = 1; M = Ru, Os, x = 2) appears to occur when the ring is prevented from tilting by the presence of two bulky groups on both the arene ring and the transition metal.

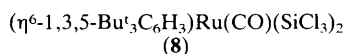
There is currently a controversy as to whether ( $\eta^6$ -C<sub>6</sub>Et<sub>6</sub>)-Cr(CO)<sub>2</sub>(CS) (**1**) exhibits restricted rotation of the arene ring about the metal atom or the changes in the variable



(2)



	M	X	E	R
(2)	Ru	Bu <sup>t</sup>	Si	Cl
(3)	Ru	Bu <sup>t</sup>	Si	Me
(4)	Ru	Bu <sup>t</sup>	Ge	Cl
(5)	Os	Bu <sup>t</sup>	Si	Cl
(6)	Ru	Pr <sup>i</sup>	Si	Cl
(7)	Re	Bu <sup>t</sup>	Si	Cl

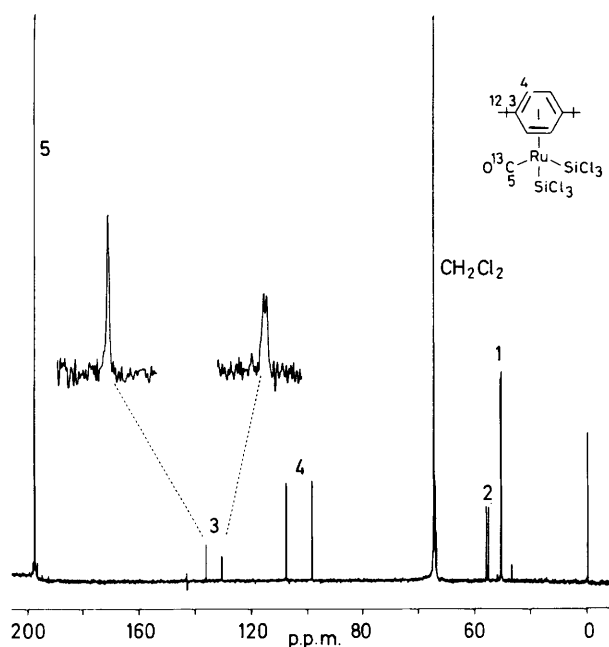


temperature <sup>13</sup>C n.m.r. spectra of the compound can be attributed to rapid equilibration of different conformers of the molecule in solution.<sup>1-3</sup> Previously we studied ( $\eta^6$ -*p*-Bu<sup>t</sup><sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Ru(CO)(SiCl<sub>3</sub>)<sub>2</sub> (**2**), and believe it to be one of the few cases where genuine restricted rotation of an arene ring to a transition metal has been observed by n.m.r. line-broadening techniques.<sup>4</sup> Here we report the important conclusions of studies of molecules related to (**2**) that favour the supposition that the arene ring in (**1**) freely rotates. These studies also give an indication of the geometric requirements necessary in a complex in order to observe restricted rotation of an arene ring  $\pi$ -bonded to a metal.

Nearly forty derivatives<sup>‡</sup> (with a variety of substituted

<sup>‡</sup> Satisfactory C, H analyses and mass spectra were obtained for all new compounds. *Selected spectroscopic data.* I.r. in CH<sub>2</sub>Cl<sub>2</sub>; n.m.r. in CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub>, or CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub>. (**2**)<sup>4</sup> (~90% <sup>13</sup>C enriched) i.r. v (CO) 1959.5 cm<sup>-1</sup>, <sup>13</sup>C{<sup>1</sup>H} n.m.r. (-60 °C)  $\delta$  30.1, 30.4, 98.0, 107.4, 130.2 (d, *J*<sub>cc</sub> 0.8 Hz) 135.8, 197.0 (see text). (**3**) i.r. v (CO) 1977.5 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (25 °C) v 1.10 (SiMe), 1.43 (Bu<sup>t</sup>), 6.52 (br. CH); <sup>13</sup>C{<sup>1</sup>H} n.m.r. (-60 °C)  $\delta$  18.3 (SiMe), 30.2, 30.5 (C-1, C-1', see text), 34.5, 35.1 (C-2, C-2'), 97.9, 106.7 (C-4, C-4'), 128.8, 133.8 (C-3, C-3'), 199.1 (CO). (**4**) i.r. v (CO) 2030 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (25 °C)  $\delta$  1.50, 6.50(br); <sup>13</sup>C{<sup>1</sup>H} n.m.r. (-60 °C)  $\delta$  30.0, 30.6, 35.0, 35.5, 92.6, 104.0, 129.8, 133.7, 194.1 [assignments as for (**3**)]. (**5**) i.r. v (CO) 2002 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (25 °C)  $\delta$  1.49, 6.42(br); <sup>13</sup>C{<sup>1</sup>H} n.m.r. (-60 °C)  $\delta$  30.1, 30.5, 34.7, 35.5, 91.5, 101.2, 125.3, 130.2, 177.2. (**6**) i.r. v (CO) 2008 cm<sup>-1</sup>; <sup>1</sup>H n.m.r.  $\delta$  1.36(d), 3.10 (septet, *J* 6.9 Hz), 6.48; <sup>13</sup>C{<sup>1</sup>H}  $\delta$  15.2, 32.1, 104.7, 129.0, 196.0. (**7**) i.r. v (CO) 1983, 1928 cm<sup>-1</sup>; <sup>1</sup>H n.m.r.  $\delta$  1.34 (s), 6.06(s); <sup>13</sup>C{<sup>1</sup>H} n.m.r.  $\delta$  31.2, 34.7, 90.5, 125.6, 194.4. (**8**) i.r. v (CO) 2006.5 cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (-60 °C)  $\delta$  1.42(s), 6.74(s); <sup>13</sup>C{<sup>1</sup>H} n.m.r.  $\delta$  31.8, 36.4, 103.1, 132.1, 197.6.

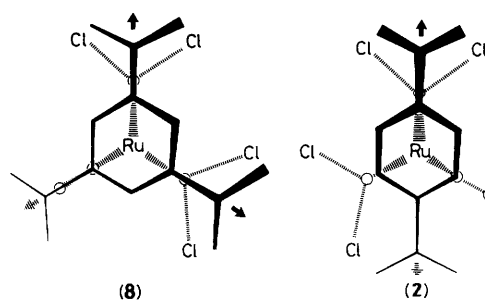
<sup>†</sup> Permanent address: Department of Chemistry, Inner-Mongolian University, Huhehot, Inner-Mongolian Autonomous Region, The People's Republic of China.



**Figure 1.** 100.6 MHz  $^{13}\text{C}\{^1\text{H}\}$  n.m.r. spectrum of  $(\text{dtbb})\text{Ru}(^{13}\text{CO})-(\text{SiCl}_3)_2$  ( $\sim 90\%$   $^{13}\text{C}$ ) in  $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$  (1:5) at  $-60^\circ\text{C}$ . The assignment of signals is shown in the upper right of the figure and discussed in the text.

benzenes) of the type  $(\text{arene})\text{M}(\text{CO})_{3-x}(\text{ERCl}_2)_x$  ( $\text{M} = \text{Re}$ ,  $\text{ERCl}_2 = \text{SiCl}_3$ ,  $x = 1$ ;  $\text{M} = \text{Ru}$ ,  $\text{E} = \text{Si}$ ,  $\text{R} = \text{Cl}$ ,  $\text{Me}$ ,  $\text{E} = \text{Ge}$ ,  $\text{R} = \text{Cl}$ ,  $\text{M} = \text{Os}$ ,  $\text{ERCl}_2 = \text{SiCl}_3$ ,  $x = 2$ ) have been prepared by heating  $\text{M}(\text{CO})_{6-x}(\text{ERCl}_2)_x$  and the appropriate arene at elevated temperatures. Restricted rotation of the arene ring on both the  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. time-scales has been found in three more *p*-di-(*t*-butyl)benzene (dtbb) derivatives: (3), (4), and (5). $\ddagger$  Line shape analyses of the variable temperature  $^1\text{H}$  n.m.r. spectra of molecules (2)—(5) have been carried out and reveal similar activation barriers which range from  $\Delta G^\ddagger_{298} = 53 \pm 3 \text{ kJ mol}^{-1}$  for (3) to  $\Delta G^\ddagger_{298} = 57 \pm 2 \text{ kJ mol}^{-1}$  for (5). Compound (2) labelled with  $^{13}\text{CO}$  ( $\sim 90\%$ ) has also been synthesized. The  $^{13}\text{C}\{^1\text{H}\}$  n.m.r. spectrum of this complex in  $\text{CD}_2\text{Cl}_2$  at  $-60^\circ\text{C}$  (where the arene ring is rigid) is shown in Figure 1. Coupling between the  $^{13}\text{C}$  of the carbonyl ligand and the upfield signal of the two signals assigned to the quaternary carbons (labelled 3) of the arene ring is observed. This indicates that, for these carbons, the upfield signal is due to the carbon (C-3) that is *trans* to the carbonyl group as shown [although the eclipsed configuration is drawn here the solid-state structure of (2) reveals a slightly staggered arrangement]. $\ddagger$  This assignment contrasts with that of McGlinchey and co-workers where the opposite assignment of signals in (1) was inferred from the solid-state n.m.r. spectrum. $\ddagger$  Our assignment is, however, in agreement with those of earlier studies on  $(\text{arene})\text{Cr}(\text{CO})_3$  molecules. $\ddagger$

Of special interest are the derivatives studied here which show unexpectedly low barriers to arene ring rotation by  $^1\text{H}$  n.m.r. spectroscopy. The *p*-di-(isopropyl)benzene complex (6), $\ddagger$  exhibits a singlet in the  $^1\text{H}$  n.m.r. spectrum for the aromatic protons down to  $-120^\circ\text{C}$  ( $\text{CD}_2\text{Cl}_2/\text{CHFCl}_2$  solution). This is consistent with a low barrier to rotation of the ring at this temperature and can be rationalized in terms of a



**Figure 2.** Possible tilting mode so that the barrier to arene rotation is less in (8) than in (2). The bond lengths are drawn approximately to scale (see ref. 5); hydrogen atoms and atoms that point away from the important interactions have been omitted.

gear mechanism: the hydrogen atoms of the isopropyl substituents point towards the trichlorosilyl ligands as the propyl and silyl groups pass by each other. A gear mechanism of this type has been proposed independently by Werner. $\ddagger$  (Gear mechanisms have also been frequently proposed for organic molecules.) $\ddagger$

Another complex that has a low barrier to rotation of the arene ring is the rhenium derivative (7) $\ddagger$ , evidenced by a singlet for the aromatic protons in the  $^1\text{H}$  n.m.r. spectrum of the compound in  $\text{CD}_2\text{Cl}_2/\text{CHFCl}_2$  solution at  $-120^\circ\text{C}$ . We believe that the low barrier to rotation in (7) can be attributed to the ability of the arene ring to tilt so as to allow the *t*-butyl substituents to pass more freely over the single trichlorosilyl ligand. In compounds (2)—(5) this tilting is prevented by the second  $\text{SiCl}_3$  ligand (see below).

Even more remarkable is that complex (8) $\ddagger$  in  $\text{CD}_2\text{Cl}_2$  at  $-60^\circ\text{C}$  exhibits a singlet for the aromatic protons in the  $^1\text{H}$  n.m.r. spectrum consistent with a low barrier to rotation of the arene ring at this temperature. At  $-95^\circ\text{C}$  the signal due to the aromatic protons is partly resolved into the 2:1 pattern expected for restricted rotation of the arene ring. From the spectra an approximate  $\Delta G^\ddagger$  value of  $35 \text{ kJ mol}^{-1}$  may be estimated for the barrier to arene rotation in (8) [the low solubility of (8) has so far limited studies at lower temperatures]. That the barrier to rotation in (8) is much lower than in (2) ( $54 \pm 4 \text{ kJ mol}^{-1}$ ) may be explained by the  $\text{Bu}_3\text{C}_6\text{H}_3$  ring in (8) being able to tilt with one *t*-butyl group down over the small CO ligand which simultaneously lifts the other *t*-butyl substituents over the two  $\text{SiCl}_3$  ligands. Because of the geometry of the ring this tilting is not as favoured in (2) or the other *p*-(di-*t*-butyl)benzene derivatives; this is illustrated in Figure 2.

In conclusion the results reported here indicate that for molecules of the type  $(\text{arene})\text{M}(\text{CO})_{3-x}(\text{SiCl}_3)_x$  ( $x = 1$  or 2) restricted rotation of the arene ring only occurs for those molecules with two large (*t*-butyl) groups on the ring along with two large (trichlorosilyl) ligands attached to the metal so that tilting of the ring is hindered. This is consistent with the observation that  $(\eta^5\text{-}1,3\text{-Bu}_2\text{C}_5\text{H}_3)\text{Co}(\text{PMe}_3)_2$  $\ddagger$  and  $(\eta^6\text{-}p\text{-Bu}_3\text{C}_6\text{H}_4\text{Me})_2\text{Cr}$  $\ddagger$  exhibit this type of restricted rotation and that no evidence for restricted rotation was observed in the  $^1\text{H}$  n.m.r. spectrum of  $(\eta^6\text{-}1,3,5\text{-Bu}_3\text{C}_6\text{H}_3)\text{Cr}(\text{CO})_2(\text{PPh}_3)$  in solution at  $-90^\circ\text{C}$ . $\ddagger$  It is not consistent with the view that (1) has a barrier to arene rotation that is detectable by n.m.r. line-broadening techniques.

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