

# Molecular Structure of Ru( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)( $\eta$ -C<sub>5</sub>F<sub>5</sub>) by Gas-Phase Electron Diffraction and Density Functional Theory

Blair F. Johnston, David W. H. Rankin,\* and Heather E. Robertson

Department of Chemistry, University of Edinburgh, West Mains Road,  
Edinburgh, Scotland EH9 3JJ, U.K.

Russell P. Hughes\* and Jeffrey R. Lompfrey

Department of Chemistry, 6128 Burke Laboratory, Dartmouth College,  
Hanover, New Hampshire 03755-3564

Received July 10, 2002

The structure of Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>) has been determined by gas-phase electron diffraction and density functional theory. Comparison structures of the known compounds Ru(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> and Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>), as well as the unknown compound Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub>, have also been determined by density functional theory.

## Introduction

The effects of fluorination on the structure, bonding, and chemical reactivity of ligands bound to transition metal centers have been of considerable interest for several years.<sup>1</sup> While the  $\sigma$ -electron-withdrawing and  $\pi$ -electron-donating substituent effects of fluorine in simple organic molecules have been thoroughly studied and reviewed,<sup>2</sup> the corresponding effects on organometallic systems are less well understood, and far fewer examples of direct hydrocarbon and fluorocarbon analogues are available for comparison. The first reported example of a compound containing a fluorinated cyclopentadienyl ligand, [Mn( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>F)(CO)<sub>3</sub>], appeared in 1965,<sup>3</sup> but the compound was poorly characterized. Monofluoroferrrocene, first reported by Hedberg and Rosenberg<sup>4</sup> and later by Popov et al.,<sup>5</sup> was prepared by a direct introduction of fluorine onto an already coordinated cyclopentadienyl ring, a method not generally applicable to the synthesis of perfluorinated systems. Attempts to prepare perfluorinated cyclopentadienyl rings in a manner analogous to that used to make perchlorinated analogues have not been successful,<sup>6–8</sup> and while the C<sub>5</sub>F<sub>5</sub><sup>−</sup> anion is known,<sup>9</sup> attempts to use it as a precursor to transition metal complexes also proved to be frustratingly unrewarding.<sup>10</sup>

The successful synthetic approach to the perfluorocyclopentadienyl ligand involved use of substrates in

which all necessary carbon–fluorine bonds were in place before complexation of the ligand and utilized a flash vacuum thermolysis induced decarbonylation of  $\eta^5$ -pentafluorophenoxide complexes to give the corresponding pentafluorocyclopentadienyl compounds [Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>)] and [Ru(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>)].<sup>11,12</sup> Subsequently, the complete set of isomeric partially fluorinated cyclopentadienyl ligands were prepared in a similar fashion.<sup>13</sup> The effects of fluorination on the electronic properties of the cyclopentadienyl ligand and its ruthenium complexes were evaluated in two ways. The gas-phase ionization free energy of [Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>)] was shown to be 18.5 kcal/mol higher than that of [Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>)], confirming that perfluorination of a Cp ligand does increase its electron-withdrawing ability, although the effects of  $\sigma$ -electron withdrawal are strongly attenuated by  $\pi$ -donation from the fluorines.<sup>14</sup> Effects of added fluorines were also shown to be approximately additive.<sup>15</sup> Comparisons of the photoelectron spectra of [Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>)] and its analogues [Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>)] and [Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>Cl<sub>5</sub>)] resulted in similar conclusions.<sup>16</sup>

While various physical techniques have been applied successfully to evaluate the substituent effects of fluorination in these ruthenocene derivatives, only one compound, [Ru(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>)], yielded metric parameters via X-ray crystallographic studies.<sup>12</sup> Unfortunately crystals of the pentamethylcyclopentadienyl analogue exhibited a ring for ring disorder that made a resolution of the solid state structural parameters impossible. Due to the volatility of this compound, we turned to a gas-phase structural study using electron diffraction techniques.

- (1) Hughes, R. P. *Adv. Organomet. Chem.* **1990**, *31*, 183.
- (2) Smart, B. E. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1983; Chapter 14. Smart, B. E. *Organofluorine Chemistry, Principles and Applications*; Banks, R. E., Smart, B. E., Tatlow, J. L., Eds; Plenum: New York, 1994; Chapter 3.
- (3) Cais, M.; Narkis, N. *J. Organomet. Chem.* **1965**, *3*, 269.
- (4) Hedberg, F. L.; Rosenberg, H. *J. Organomet. Chem.* **1971**, *28*, C14.
- (5) Popov, V. I.; Lib, M.; Hass, A. *Ukr. Khim. Zh.* **1990**, *56*, 1115.
- (6) Hedberg, F. L.; Rosenberg, H. *J. Am. Chem. Soc.* **1970**, *92*, 3239.
- (7) Hedberg, F. L.; Rosenberg, H. *J. Am. Chem. Soc.* **1973**, *95*, 870.
- (8) Winter, C. H.; Han, Y.; Ostrander, R. L.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1161.
- (9) Paprott, G.; Seppelt, K. *J. Am. Chem. Soc.* **1984**, *106*, 4060.
- (10) Paprott, G.; Lehmann, S.; Seppelt, K. *Chem. Ber.* **1988**, *121*, 727.

- (11) Curnow, O. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1992**, *114*, 5895.
- (12) Hughes, R. P.; Zheng, X.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 1567.
- (13) Hughes, R. P.; Zheng, X.; Morse, C. A.; Curnow, O. J.; Lompfrey, J. R.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1998**, *17*, 457.
- (14) Richardson, D. E.; Ryan, M. F.; Geiger, W. E.; Chin, T. T.; Hughes, R. P.; Curnow, O. J. *Organometallics* **1993**, *12*, 613.
- (15) Richardson, D. E.; Lang, L.; Eyley, J. R.; Zheng, X.; Morse, C. A.; Hughes, R. P. *Organometallics* **1997**, *16*, 149.
- (16) Lichtenberger, D. L.; Elkadi, Y.; Gruhn, N.; Hughes, R. P.; Curnow, O. J.; Zheng, X. *Organometallics* **1997**, *16*, 5209.

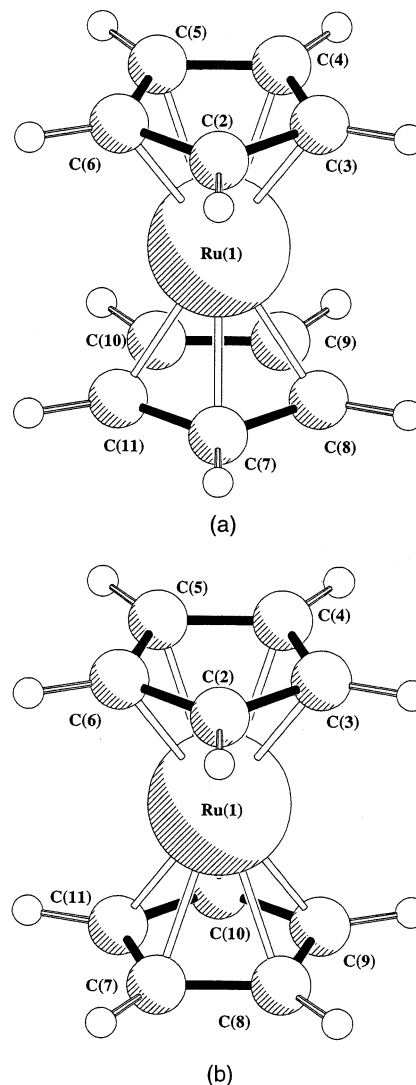
Sandwich compounds, such as ferrocene and ruthenocene, are ideal subjects for study by gas-phase electron diffraction. Heavy metal atom distances, such as Fe–C and Ru–C, are well defined by the data and can be refined very accurately. The C–C ring distances are also well defined, although data on the longer C...C inter-ring distances may be lost to an extent among the intense background atomic scattering from the metal center (particularly in the case of ruthenocene).<sup>17</sup> As a result, conformational analysis can be difficult. We anticipated that the compound Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) would benefit from the substitution of ring hydrogens by heavier fluorine and methyl groups, which contribute significantly more to the molecular scattering and should allow determination of substituent tilting out of the plane of the cyclopentadienyl rings.

Here we report the structure of Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) determined by gas-phase electron diffraction and density functional theory (DFT), along with results of DFT calculations for Ru(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>), and Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub>.

### Experimental Section

**Synthesis.** Samples of Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) (**3**) were prepared as previously described.<sup>11,13</sup>

**Theoretical Methods.** All calculations were performed on a Dec Alpha 1000 4/200 workstation using the Gaussian 98 program.<sup>18</sup> An extensive search of the potential energy surfaces of ruthenocene, ruthenium(cyclopentadienyl)(pentafluorocyclopentadienyl), and bis(perfluorocyclopentadienyl)ruthenium was undertaken at the B3PW91<sup>19–24</sup>/LanL2DZ<sup>25–27</sup> level in order to locate all minima. The B3PW91 DFT method was chosen for the calculations in light of the failings of the Hartree–Fock (HF) and Møller–Plesset (MP) methods for predicting the structures of sandwich compounds.<sup>28,29</sup> For Ru(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> and Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub> the eclipsed conformation (*D*<sub>5h</sub> symmetry) was the potential minimum, and there was a transition state of *D*<sub>5d</sub> symmetry at the staggered conformation. For Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>) the eclipsed conformation was again the minimum, although both this and the staggered transition state



**Figure 1.** DFT calculated structures of ruthenocene in (a) *D*<sub>5h</sub> and (b) *D*<sub>5d</sub> symmetry.

have *C*<sub>5v</sub> symmetry. A similar search of the potential energy surface of Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) was undertaken at the B3PW91/SDD level in order to locate all minima. In this case, the larger Stuttgart basis set<sup>30</sup> was used in conjunction with a pseudopotential on the ruthenium atom. The change in basis set was required in order to achieve convergence on an energy minimum, as calculations on this compound using the LanL2DZ basis set were found to run indefinitely despite efforts to tighten the convergence criteria within Gaussian 98. Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) was found to adopt a *C*<sub>5</sub> structure very close to an eclipsed *C*<sub>5v</sub> structure. Vibrational frequencies, from all calculations carried out, were used to determine the nature of the stationary points and to provide estimates of amplitudes of vibration (*u*) for use in the gas-phase electron diffraction (GED) refinements. The structures and numbering schemes of the compounds Ru(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>), Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub>, and Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) are shown in Figures 1–4, and the potential energy curves are shown in Figure 5.

**Gas-Phase Electron Diffraction.** Data were collected for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) using the Edinburgh gas diffraction apparatus.<sup>31</sup> An accelerating voltage of 40 kV (electron wavelength ca. 6.0 pm) was used, with sample and nozzle temper-

(17) A. Haaland, J. Nilsson, *Acta Chem. Scand.* **1968**, *22*, 2653.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzales, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(20) Burke, K.; Perdew, J. P.; Wang, Y. *Electronic Density Functional Theory: Recent Progress and New Directions*; Plenum: New York, 1998.

(21) Perdew, J. P. *Electronic Structures of Solids '91*; Akademie Verlag: Berlin, 1991; p 11.

(22) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1996**, *46*.

(23) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1993**, *48*.

(24) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533.

(25) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

(26) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

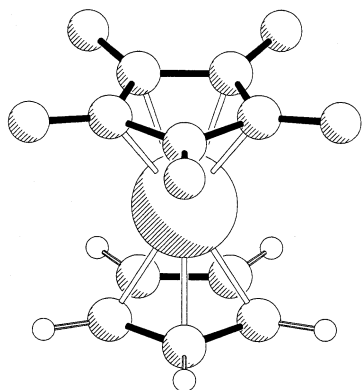
(27) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(28) Luthi, H. P.; Ammeter, J.; Almqvist, J.; Korsell, K. *Chem. Phys. Lett.* **1980**, *69*, 54.

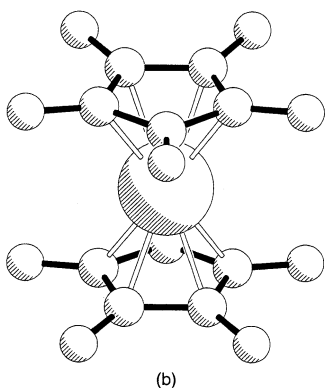
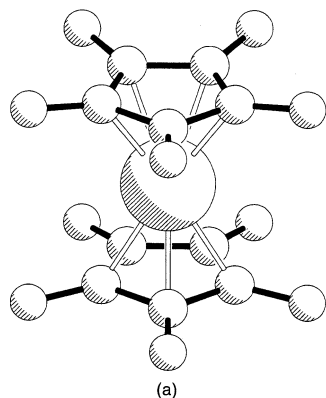
(29) Klopffer, W.; Luthi, H. P. *Chem. Phys. Lett.* **1996**, *262*, 546.

(30) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

(31) Huntley, C. M.; Laurenson, G. S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1980**, 954.



**Figure 2.** DFT calculated structure of  $\text{Ru}(\text{C}_5\text{F}_5)(\text{C}_5\text{H}_5)$ . The structure has  $C_{5v}$  symmetry.

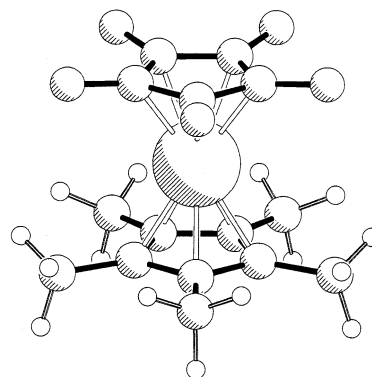


**Figure 3.** DFT calculated structures of  $\text{Ru}(\text{C}_5\text{F}_5)_2$  in (a)  $D_{5h}$  and (b)  $D_{5d}$  symmetry.

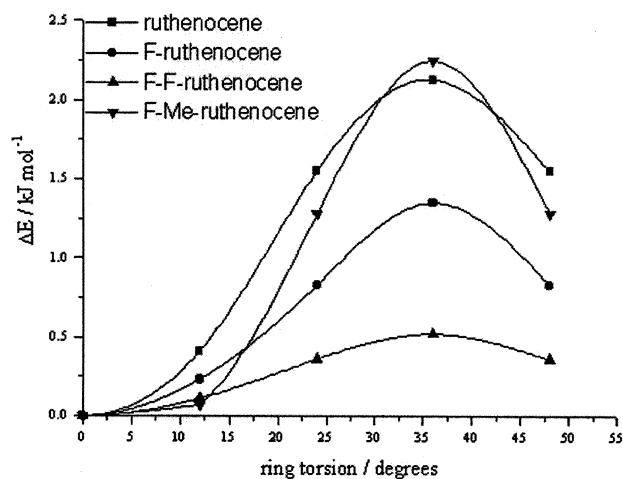
atures of 404 and 454 K, respectively. Scattering intensities were recorded at nozzle-to-plate distances of 89.17 and 261.51 mm on Kodak electron image plates. The weighting points for the off-diagonal weight matrixes, correlation parameters, and scale factors for the two camera distances are given in Table 1, together with electron wavelengths, which were determined from the scattering patterns of benzene vapor recorded immediately after the patterns of  $\text{Ru}(\text{C}_5\text{F}_5)(\text{C}_5\text{Me}_5)$  and analyzed in exactly the same way, to minimize systematic errors in wavelengths and camera distances. A PDS densitometer at the Institute of Astronomy in Cambridge was used to convert the intensity patterns into digital form using a scanning program described elsewhere.<sup>32</sup> Data reduction and least-squares refinements were carried out using the new 'ed@ed' program,<sup>33</sup> employing the scattering factors of Ross et al.<sup>34</sup>

(32) Lewis, J. R.; Brain, P. T.; Rankin, D. W. H. *Spectrum* **1997**, 15, 7.

(33) Johnston, B. F.; Rankin, D. W. H.; Turner, A. Unpublished work.



**Figure 4.** DFT calculated structure of  $\text{Ru}(\text{C}_5\text{F}_5)(\text{C}_5\text{Me}_5)$ . The structure has  $C_5$  symmetry as a result of the two rings being very slightly twisted from an eclipsed conformation.



**Figure 5.** Torsional potential energies for  $\text{Ru}(\text{C}_5\text{H}_5)_2$ ,  $\text{Ru}(\text{C}_5\text{F}_5)(\text{C}_5\text{H}_5)$ ,  $\text{Ru}(\text{C}_5\text{F}_5)_2$ , and  $\text{Ru}(\text{C}_5\text{F}_5)(\text{C}_5\text{Me}_5)$ .

**Table 1.** Nozzle-to-Plate Distances (mm), Weighting Functions ( $\text{nm}^{-1}$ ), Correlation Parameters, Scale Factors, and Electron Wavelengths (pm) Used in the Electron-Diffraction Study of  $\text{Ru}(\text{C}_5\text{F}_5)(\text{C}_5\text{Me}_5)$

nozzle-to-plate distance <sup>a</sup>	89.17	261.51
$\Delta S$	4	2
$S_{\text{min}}$	80	20
$S_{\text{w1}}$	100	40
$S_{\text{w2}}$	304	128
$S_{\text{max}}$	356	150
correlation parameter	0.450	0.415
scale factor <sup>b</sup>	0.902(37)	0.974(13)
electron wavelength	6.016	6.016

<sup>a</sup> Determined by reference to the scattering pattern of benzene vapor. <sup>b</sup> Values in parentheses are the estimated standard deviations.

## Results

**Density Functional Theory Calculations.** Molecular orbital calculations were carried out with the DFT hybrid functional B3PW91 method in light of the success this had predicting the iron to cyclopentadienyl ring distance in ferrocene.<sup>35</sup> In this study it was found that the Hartree–Fock method overestimates the iron-to-

(34) Ross, A. W.; Fink, M.; Hilderbrandt, R. *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C, p 245.

(35) Morrison, C. A.; Bone, S. F.; Rankin, D. W. H.; Robertson, H. E.; Parsons, S.; Coxall, R.; Fraser, S. *Organometallics* **2001**, 20, 2309.

**Table 2. Calculated Geometric Parameters for Ruthenocene (distances in pm, angles in deg) from the B3PW91/LanL2DZ DFT Study**

	eclipsed ( $D_{5h}$ )	staggered ( $D_{5d}$ )
Ru–ring center	183.7	183.2
Ru–C	220.4	220.0
C–C	143.1	143.1
C–H	108.2	108.2
C–C–H	126.0	126.0
H out-of-plane bend <sup>a</sup>	0.2	0.2
energy difference		+2.14 kJ mol <sup>-1</sup>

<sup>a</sup> Positive tilt angles indicate that the ring substituent is pointing away from the Ru center.

**Table 3. Calculated Geometric Parameters for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>) ( $C_{3v}$  Symmetry) (distances in pm, angles in deg) from the B3PW91/LanL2DZ DFT Study**

	fluorine ring (X = F)	hydrogen ring (X = H)
Ru–ring center	179.5	186.2
Ru–C	216.9	222.4
C–C	143.2	143.0
C–X	133.3	108.2
C–C–X	125.8	126.0
X out-of-plane bend <sup>a</sup>	6.1	0.6

<sup>a</sup> Positive tilt angles indicate that the ring substituent is pointing away from the Ru center.

**Table 4. Calculated Geometric Parameters for Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub> (distances in pm, angles in deg) from the B3PW91/LanL2DZ DFT Study**

	eclipsed ( $D_{5h}$ )	staggered ( $D_{5d}$ )
Ru–ring center	183.0	183.2
Ru–C	219.8	220.0
C–C	143.1	143.1
C–F	132.7	132.7
C–C–F	125.8	125.8
F out-of-plane bend <sup>a</sup>	5.6	5.6
energy difference		+0.31 kJ mol <sup>-1</sup>

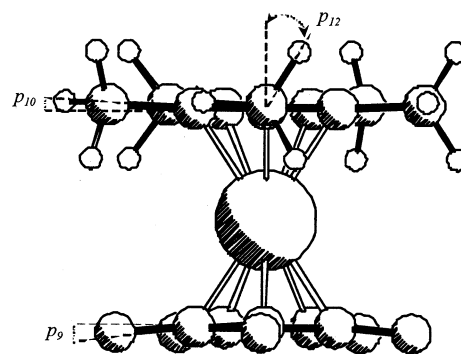
<sup>a</sup> Positive tilt angles indicate that the ring substituent is pointing away from the Ru center.

ring distance by as much as 20 pm as a result of neglecting the important electron correlation. On the other hand, the second-order Møller–Plesset (MP2) calculations overestimated the effects of electron correlation and predicted metal-to-ring distances short by 20 pm.<sup>36</sup> Success has been achieved predicting this distance at the CCSD(T) level with a large basis set.<sup>37</sup> However, such calculations are particularly computationally demanding and are, currently, beyond the capabilities of most research groups,<sup>35</sup> particularly for the much more demanding metal atom and ligands in the present study.

The LanL2DZ basis set was chosen for the calculations, as it provides a pseudo-potential for the ruthenium atom (considering relativistic effects become important with heavier atoms) and reduces the time required for the calculation (as the number of electrons that need to be considered is reduced).

A selection of the molecular geometries from the DFT calculations can be found in Tables 2–5.

**Gas-Phase Electron Diffraction Study.** On the basis of the DFT calculations described above, a model with  $C_5$  symmetry was written for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>). The

**Figure 6.** Diagrammatic representation of the out-of-plane bending parameters  $p_9$  and  $p_{10}$ . Positive values signify bending away from the ruthenium atom. The methyl twist parameter,  $p_{12}$ , is also included and in this instance is shown with a value of 30°.

only other assumption made in the model was that the C-methyl groups had local  $C_{3v}$  symmetry. In total, 12 geometric parameters were required to model Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>). Seven parameters, two average bond lengths, two differences between distances within the averages, and three unique bond lengths were required to describe the bonds in the molecule. These were the average Ru–C<sub>(cyclopentadienyl)</sub>,  $p_1$ , the difference between the two Ru–C<sub>(cyclopentadienyl)</sub> distances (Me minus F),  $p_2$ , the average C–C ring distance,  $p_3$ , the difference between the C–C ring distances (Me minus F),  $p_4$ , and the C–C<sub>(methyl)</sub>, C–H, and C–F bond lengths,  $p_5$ ,  $p_6$ , and  $p_7$ . Three angle parameters were required: the C–C–H angle,  $p_8$ , the bend of the C–F bond out of the plane of the cyclopentadienyl ring,  $p_9$ , and the corresponding bend of the C–C<sub>(methyl)</sub> bonds out of the cyclopentadienyl ring plane,  $p_{10}$ . These were defined as being positive for displacement away from the ruthenium atom. Two torsional parameters were required: clockwise twisting of the two cyclopentadienyl rings from a position in which they are eclipsed,  $p_{11}$ , and a clockwise methyl twist from a position in which one of the methyl hydrogen atoms points directly upward (away from the ruthenium atom),  $p_{12}$ . Figure 6 shows the out-of-plane angle parameters,  $p_9$  and  $p_{10}$ , and the methyl twist,  $p_{12}$ .

Starting values for the  $r_a$  refinement were taken from the theoretical geometry calculated by DFT (see Table 5). An  $r_a$  refinement was not undertaken because the low-lying, ring-twisting torsional vibration modes result in large and unreliable perpendicular correction terms. Amplitudes of vibration were obtained from an internal coordinate analysis of the theoretical Cartesian force constants using the program ASYM40, which has been modified to work on molecules containing more than 40 atoms.<sup>38</sup> All geometric parameters were subsequently refined.

In total 12 geometric parameters and 21 vibrational amplitudes were refined. Flexible restraints were employed, using the SARACEN method,<sup>39</sup> for four of the geometrical parameters and 10 of the vibrational am-

(38) Hedberg, L.; Mills, I. M. *ASYM40, Program for Force Constants and Coordinate Analysis*, Version 3.0. See also: Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(39) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.* **1996**, *100*, 12280. Brain, P. T.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1996**, 4589.

(36) Klopper, W.; Lüthi, H. P. *Chem. Phys. Lett.* **1996**, *26*, 35.

(37) Koch, H.; Jørgensen, P. *J. Chem. Phys.* **1996**, *104*, 9528.

**Table 5. Refined and Calculated Geometric Parameters for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) (distances in pm, angles in deg) from the GED Study<sup>a</sup>**

no.	parameter	GED ( <i>r</i> <sub>a</sub> )	B3PW91/SDD	restraint
<i>p</i> <sub>1</sub>	(Ru–C <sub>methyl ring</sub> + Ru–C <sub>fluorine ring</sub> )/2	217.8(2)	217.0	
<i>p</i> <sub>2</sub>	Ru–C <sub>methyl ring</sub> – Ru–C <sub>fluorine ring</sub>	5.3(8)	5.0	5.0(10)
<i>p</i> <sub>3</sub>	(C–C <sub>methyl ring</sub> + C–C <sub>fluorine ring</sub> )/2	142.9(3)	143.6	
<i>p</i> <sub>4</sub>	C–C <sub>methyl ring</sub> – C–C <sub>fluorine ring</sub>	1.2(6)	0.9	1.0(10)
<i>p</i> <sub>5</sub>	C–C <sub>methyl gp.</sub>	149.0(8)	149.8	
<i>p</i> <sub>6</sub>	C–H	109.6(4)	109.6	109.6(5)
<i>p</i> <sub>7</sub>	C–F	132.9(3)	133.8	
<i>p</i> <sub>8</sub>	C–C–H	111.3(4)	111.3	111.3(5)
<i>p</i> <sub>9</sub>	C–F/ring plane tilt <sup>b</sup>	4.2(6)	6.3	
<i>p</i> <sub>10</sub>	C–C <sub>Me</sub> /ring plane tilt <sup>b</sup>	2.1(11)	3.4	
<i>p</i> <sub>11</sub>	ring twist	–1.7(63)	0.7	
<i>p</i> <sub>12</sub>	methyl twist	–32(13)	0.0	

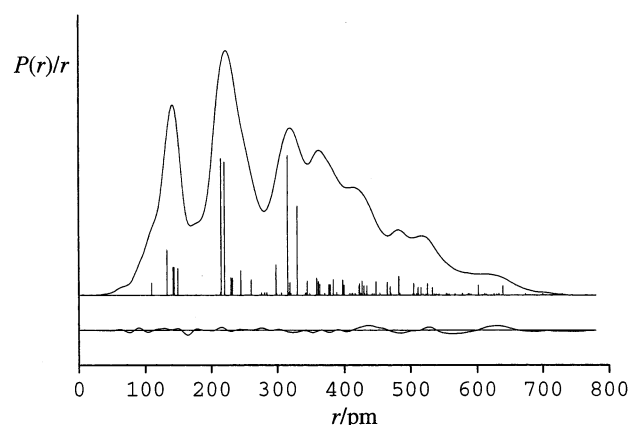
<sup>a</sup> Figures in parentheses are the estimated standard deviations of the last digits. See text for parameter definitions. <sup>b</sup> Positive tilt angles indicate that the ring substituent is pointing away from the Ru center.

**Table 6. Interatomic Distances (*r*/pm) and Amplitudes of Vibration (*u*/pm) for the Restrained GED Structure of Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>)<sup>a</sup>**

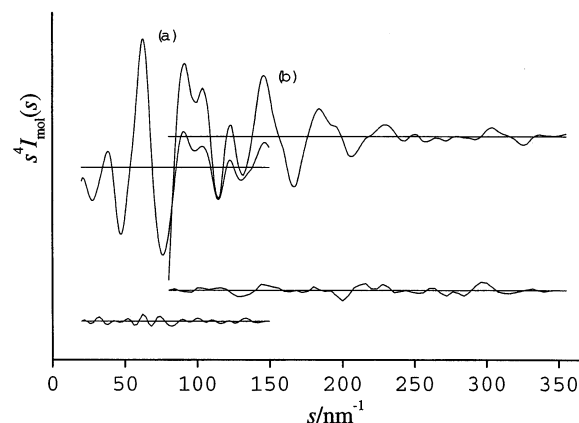
no.	atom pair	<i>r</i> <sub>a</sub> /pm	<i>u</i> /pm <sup>b</sup>	restraint <sup>c</sup>
<i>u</i> <sub>1</sub>	H(17)–C(12)	109.6(4)	7.6(fixed)	
<i>u</i> <sub>2</sub>	F(32)–C(3)	132.9(3)	4.2(3)	4.4(4)
<i>u</i> <sub>3</sub>	C(5)–C(3)	142.2(3)	4.1(6)	
<i>u</i> <sub>4</sub>	C(4)–C(2)	143.6(5)	4.1(tied to <i>u</i> <sub>7</sub> )	
<i>u</i> <sub>5</sub>	C(12)–C(2)	149.1(8)	4.6(4)	4.9(5)
<i>u</i> <sub>6</sub>	C(3)–Ru(1)	215.3(4)	6.4(5)	
<i>u</i> <sub>7</sub>	C(2)–Ru(1)	220.6(4)	6.2(tied to <i>u</i> <sub>2</sub> )	
<i>u</i> <sub>8</sub>	C(7)···C(3)	230.2(5)	6.1(4)	5.5(6)
<i>u</i> <sub>9</sub>	C(6)···C(2)	232.4(8)	6.0(4)	
<i>u</i> <sub>10</sub>	F(32)···C(5)	245.1(2)	7.0(6)	
<i>u</i> <sub>11</sub>	F(32)···C(11)	245.1(2)	7.0(tied to <i>u</i> <sub>10</sub> )	
<i>u</i> <sub>12</sub>	C(12)···C(4)	260.8(4)	7.4(5)	7.0(7)
<i>u</i> <sub>13</sub>	C(12)···C(10)	260.8(4)	7.4(tied to <i>u</i> <sub>18</sub> )	
<i>u</i> <sub>14</sub>	F(33)···F(32)	298.1(3)	11.8(8)	11.8(12)
<i>u</i> <sub>15</sub>	F(32)···Ru(1)	315.7(6)	10.1(8)	
<i>u</i> <sub>16</sub>	C(13)···C(12)	318.8(6)	12.0(fixed)	
<i>u</i> <sub>17</sub>	C(12)···Ru(1)	329.8(15)	10.0(7)	10.2(10)
<i>u</i> <sub>18</sub>	H(17)···Ru(1)	344.4(77)	27.1(fixed)	
<i>u</i> <sub>19</sub>	F(32)···C(7)	358.7(3)	6.6(4)	
<i>u</i> <sub>20</sub>	F(32)···C(9)	358.7(3)	6.6(tied to <i>u</i> <sub>15</sub> )	
<i>u</i> <sub>201</sub>	H(27)···Ru(1)	361.3(120)	27.4(tied to <i>u</i> <sub>17</sub> )	
<i>u</i> <sub>22</sub>	C(3)···C(2)	363.4(9)	13.5(fixed)	
<i>u</i> <sub>23</sub>	C(12)···C(6)	377.0(5)	6.5(fixed)	
<i>u</i> <sub>24</sub>	C(12)···C(8)	377.0(5)	6.5(fixed)	
<i>u</i> <sub>25</sub>	C(4)···C(3)	378.9(23)	24.3(fixed)	
<i>u</i> <sub>26</sub>	F(32)···C(12)	383.6(36)	36.1(23)	31.8(32)
<i>u</i> <sub>27</sub>	F(32)···C(2)	397.5(17)	21.8(15)	21.1(21)
<i>u</i> <sub>28</sub>	C(12)···C(3)	398.8(26)	22.1(fixed)	
<i>u</i> <sub>29</sub>	C(5)···C(2)	399.7(26)	23.4(fixed)	
<i>u</i> <sub>30</sub>	C(6)···C(3)	422.3(20)	14.6(fixed)	
<i>u</i> <sub>31</sub>	H(22)···Ru(1)	423.0(15)	11.5(fixed)	
<i>u</i> <sub>32</sub>	F(32)···C(4)	426.7(45)	42.9(fixed)	
<i>u</i> <sub>33</sub>	C(12)···C(11)	429.6(55)	44.6(fixed)	
<i>u</i> <sub>34</sub>	C(7)···C(2)	434.0(9)	15.1(fixed)	
<i>u</i> <sub>35</sub>	F(32)···C(13)	447.9(97)	80.6(fixed)	
<i>u</i> <sub>36</sub>	F(32)···C(10)	464.7(45)	39.5(fixed)	
<i>u</i> <sub>37</sub>	C(12)···C(5)	469.5(47)	42.7(fixed)	
<i>u</i> <sub>38</sub>	F(34)···F(32)	482.3(4)	7.9(4)	7.3(7)
<i>u</i> <sub>39</sub>	F(32)···C(6)	504.9(36)	24.1(fixed)	
<i>u</i> <sub>40</sub>	C(14)···C(12)	515.9(9)	8.1(fixed)	
<i>u</i> <sub>41</sub>	F(32)···C(16)	525.2(86)	78.2(fixed)	
<i>u</i> <sub>42</sub>	F(32)···C(8)	525.2(15)	23.1(fixed)	
<i>u</i> <sub>43</sub>	C(12)···C(7)	532.8(20)	25.3(fixed)	
<i>u</i> <sub>44</sub>	F(32)···C(14)	601.9(70)	38.1(fixed)	
<i>u</i> <sub>45</sub>	F(32)···C(15)	639.3(25)	39.5(fixed)	

<sup>a</sup> Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses. <sup>b</sup> Amplitudes not refined were fixed at the values obtained using the B3PW91/SDD force field. <sup>c</sup> A restraint was also applied to the ratio *u*<sub>13</sub>/*u*<sub>14</sub> [1.020(21)]. Uncertainties are 5% of the amplitude ratios or 10% of absolute values of amplitudes.

plitudes. Six vibrational amplitude constraints were also used. All of these can be found in Tables 5 and 6.



**Figure 7.** Experimental and difference (experimental – theoretical) radial-distribution curve,  $P(r)/r$ , for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>). Before Fourier inversion the data were multiplied by  $s \exp(-0.00002s^2)/[(Z_{\text{Ru}} - f_{\text{Ru}})/(Z_{\text{F}} - f_{\text{F}})]$ .



**Figure 8.** Experimental and final weighted difference (experimental – theoretical) molecular-scattering intensities for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) at camera distances 262 mm (a) and 89 mm (b).

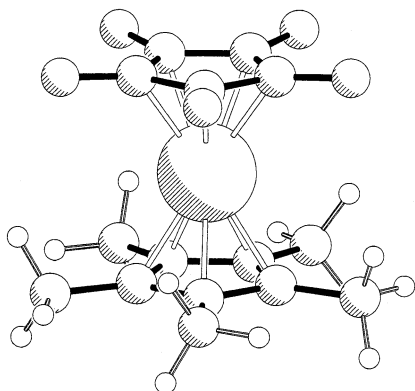
The success of the final refinement, for which  $R_G = 0.097$  ( $R_D = 0.066$ ), can be assessed on the basis of the radial distribution curve (Figure 7) and the molecular scattering intensity curves (Figure 8).

Final refined parameters are listed in Table 5, the least-squares correlation matrix is shown in Table 7, and interatomic distances and the corresponding amplitudes of vibration are given in Table 6. In the SARACEN analysis, because all parameters are refining, the error estimates are realistic. We therefore quote

**Table 7. Least-Squares Correlation Matrix ( $\times 100$ ) for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>)<sup>a</sup>**

	<i>p</i> <sub>5</sub>	<i>p</i> <sub>9</sub>	<i>p</i> <sub>12</sub>	<i>u</i> <sub>1</sub>	<i>u</i> <sub>4</sub>	<i>u</i> <sub>7</sub>	<i>u</i> <sub>14</sub>
<i>p</i> <sub>3</sub>	-60						
<i>p</i> <sub>4</sub>	-74						54
<i>p</i> <sub>5</sub>							-50
<i>p</i> <sub>8</sub>		-60	58				
<i>p</i> <sub>9</sub>				-78			
<i>p</i> <sub>11</sub>					-55		
<i>u</i> <sub>13</sub>							84

<sup>a</sup> Only elements with absolute values  $\geq 50\%$  are shown.

**Figure 9.** GED refined structure of Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>).

the estimated standard deviations and do not need to add any further allowance for fixed parameters. Figure 9 shows a perspective view of Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) in the optimum refinement of the GED data.

### Discussion

For all compounds discussed here, measurements, unless stated otherwise, are for the conformer calculated as being the global minimum structure. Convergence of the DFT calculations, particularly for the compound Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>), proved tricky, and tightening of the default Gaussian 98 convergence criteria was required in all cases. For all four compounds the barriers to rotation were calculated to be 2.2 kJ mol<sup>-1</sup> or less (see Figure 5), so rotation of the rings relative to one another would be more or less free.

Looking first at features common to all of the compounds studied, it can be seen that the ruthenium-to-ring distance is significantly affected by the nature of the ring substituents. In simple unsubstituted ruthenocene this distance is 183.7 pm. If one of the cyclopentadienyl rings is replaced by a perfluorocyclopentadienyl ring [Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>)], then variations in the ruthenium-to-ring distances are seen. The ruthenium-to-perfluorocyclopentadienyl ring distance shortens by 4.2 pm to 179.5 pm, and the ruthenium-to-cyclopentadienyl ring distance lengthens by 2.5 pm to 186.2 pm. If both of the cyclopentadienyl rings are replaced with perfluorocyclopentadienyl rings [Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub>], then the ruthenium-to-ring distance is found to be shorter by 0.7 pm (183.0 pm) than in the ruthenocene case. Fluorine substituents, while  $\sigma$ -electron withdrawing in nature, donate to the ring's  $\pi$ -system, resulting in shorter ruthenium-to-ring distances. A gas-phase free energy ionization study of Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>) and Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>) found the electron-withdrawing nature of the ring to increase on perfluorination.<sup>14</sup> As a result, less electron

density will be available for bonding between the ruthenium and the cyclopentadienyl or pentamethylcyclopentadienyl ligand, and the calculated increase in this ruthenium-to-ring distance is seen. Curiously, the X-ray diffraction study<sup>12</sup> found no significant change in the ruthenium-to-cyclopentadienyl ring distance within the family of compounds Ru(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>X<sub>5</sub>) for X = Me and F. A similar effect is observed in the compound Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>). The ruthenium-to-perfluorocyclopentadienyl ring distance is, again, shorter (176.6 pm) than in ruthenocene, and the ruthenium-to-permethylcyclopentadienyl ring distance is also slightly shorter (182.2 pm). Direct comparisons between the distances calculated using DFT for this particular compound and the others would be invalid, as the basis sets used are different. Nonetheless the general differences from the experiment can be considered as valid. The methyl group and fluorine substituents therefore both act to strengthen the bonding between the ruthenium atom and the C<sub>5</sub> ring. The GED analysis of Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) supports the trends predicted by DFT with ruthenium-to-perfluorocyclopentadienyl ring distances and ruthenium-to-permethylcyclopentadienyl ring distances of 177.9(2) and 183.6(2) pm, respectively. It should also be noted that although the difference between the two ruthenium-to-ring distances has been restrained in the GED analysis, the associated esd is smaller than the uncertainty placed on the value of the difference (see Table 5). This would suggest that there is real information about the different distances in the GED data.

The DFT calculated C–C ring distances are, in comparison to the Ru–Cp distance, insensitive to the type of substituent on the ring. For ruthenocene, the C–C distance is 143.1 pm (cf. 144.1(9) pm in the X-ray diffraction study<sup>12</sup>) and for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>) it is 143.2 and 143.0 pm for the perfluoro and Cp rings, respectively (cf. 139.9(10) and 138.0(10) pm in the X-ray diffraction study<sup>12</sup>). In Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub> the C–C distance is found to be 143.1 pm and for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) it is 143.1 and 144.0 pm for the perfluoro and permethyl rings, respectively. The GED study provides values of 142.3(9) and 143.5(9) pm for the respective C–C distances.

DFT calculations show the substituents on the rings to bend away from the ruthenium atom in all cases. For ruthenocene the hydrogen atoms bend out of the ring plane by 0.2°, and for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>) they bend by 0.6°. Fluorine atoms in the compound Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>) bend by 6.1° and by 5.7° in Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub>. In the compound Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) they bend by 6.3° and the methyl groups bend by 3.4°.

C–F distances, calculated by DFT, in the compounds Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>), Ru(C<sub>5</sub>F<sub>5</sub>)<sub>2</sub>, and Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) are found to be 133.3, 132.7, and 133.8 pm, respectively. The GED refinement value for Ru(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>Me<sub>5</sub>) is 132.9(3) pm, almost 1 pm shorter than the theoretical value, even though an experimental *r*<sub>a</sub> distance will be slightly longer than the *r*<sub>e</sub> distance.

The C–C<sub>(Me)</sub> bond length is calculated by DFT as 149.8 pm and refines to 149.0(8) pm in the GED analysis.

The GED refinement was unable to determine accurately the conformation of the two rings relative to one another, suggesting that the rings are indeed

rotating more or less freely in the experiment. However, the two rings did tend to favor a more eclipsed geometry throughout the refinement process, and the unrestrained final refined torsion value of  $1.7(63)^\circ$  would appear to support a more eclipsed conformation over a staggered one (in which case the torsion would be in the region of  $32^\circ$ ) despite a relatively large esd of  $6.3^\circ$ .

It would appear that the theoretical B3PW91 calculations have provided fairly reliable geometries once again. The tricky ruthenium-to-ring distances were found to be within 1.5 pm of the values determined by GED, a good result given the unreliability of Hartree–Fock and Møller–Plesset theory in related compounds (20 pm errors for this distance in ferrocene). The relative tilting of the fluorine and methyl group substituents also seems to have been reliably calculated by DFT with tilt values of  $6.3^\circ$  and  $3.4^\circ$  for the fluorine and methyl substituents respectively (cf.  $4.2(6)^\circ$  and  $2.1(11)^\circ$  in the unrestrained GED refinement of these parameters). Theoretical C–C ring distances have been shown to be

particularly good, with values lying within one esd of the experimental GED values. Perhaps the only slightly disappointing DFT value is that of the C–F distance. GED predicts this to be around 1 pm shorter than theory (although the DFT value lies within three esd's of the GED value). A larger basis set for the fluorine atoms (perhaps with more diffuse and polarization functions) would probably reduce this discrepancy greatly.

**Acknowledgment.** We thank the UK Engineering and Physical Sciences Research Council for a studentship (B.F.J.) and for support of the electron diffraction service (grant GR/K44411), and the U.K. Computational Chemistry Facility (admin: Department of Chemistry, King's College London, Strand, London WC2R 2LS) for the computing time on Columbus. R.P.H is grateful to the National Science Foundation and to the donors of Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

OM0205501