

## Synthesis and Characterization of 1,2,3,4,5-Pentafluoroferrrocene

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### Supporting Information

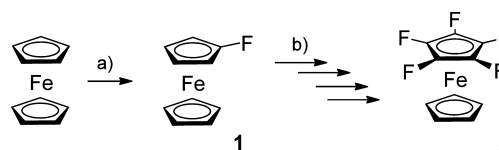
**ABSTRACT:** Starting from ferrocene, pentafluoroferrrocene [Fe(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>)] can be prepared in five steps via a one-pot lithiation–electrophilic fluorination strategy. Pentafluoroferrrocene was characterized by multinuclear NMR and IR spectroscopy, by cyclovoltammetry as well as X-ray (solid) and electron diffraction (gas) and the experimental results compared with DFT calculations.

Ever since the discovery of ferrocene in 1951,<sup>1</sup> this molecule has inspired researchers from many fields of basic and applied chemistry. This multifaceted chemistry has been highlighted on many occasions,<sup>2</sup> and very recently a whole volume of *Organometallics* has been dedicated to its “Beauty and Function”.<sup>3</sup> While most of the “applied research” was focused on the use of ferrocene derivatives as ligands for catalyst design, and more recently in bioorganometallic chemistry and medicinal chemistry, the possibility of inducing high thermal and oxidative stability by proper introduction of substituents has attracted material chemists already over 40 years ago. Thus, the first preparation of decachloroferrrocene in 1969 by Hedberg and Rosenberg<sup>4</sup> and the observed high oxidative stability induced a search for its perfluorinated analogue, which was anticipated to be even more stable and might even find application in military aircrafts.<sup>5</sup> However, while the synthesis of monofluoroferrrocene was reported by the same authors in 1971,<sup>6</sup> no higher fluorinated ferrrocenes could be prepared up to today. A preliminary report filed in 1995 stated: “It has so far not been possible to find that right combination of permetalated metallocene and electrophilic fluorinating agents that gives the perfluorometalocene”.<sup>7</sup> Two articles by King appeared in 2013,<sup>8</sup> stating “...(C<sub>n</sub>F<sub>n</sub>)<sub>2</sub>M sandwich compounds remain unknown...” and “...This suggests that C<sub>5</sub>F<sub>5</sub>–metal chemistry might be quite extensive after suitable methods of introducing the C<sub>5</sub>F<sub>5</sub> group into transition metal complexes are discovered and developed.” Indeed, in 1992 Curnow and Hughes reported [Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>)] as the first transition metal complex containing a perfluorocyclopentadienyl ligand; it was obtained by flash vacuum pyrolysis of a pentafluorophenolate ligand.<sup>9</sup> The corresponding [Ru(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>)] and several less fluorinated ruthenocenes could be prepared by the same method,<sup>10</sup> but it could not be applied to other metallocenes. The electronic and molecular structures of [Ru(C<sub>5</sub>Me<sub>5</sub>)(C<sub>5</sub>F<sub>5</sub>)] have also been examined by photoelectron spectroscopy and gas-phase electron diffraction.<sup>11</sup> There are some theoretical papers about pentafluorocyclopentadienyl complexes, but none of them have been prepared so far.<sup>12</sup> Quite interestingly, it was also not

possible to prepare ferrrocenes and other cyclopentadienides with [C<sub>5</sub>(CF<sub>3</sub>)<sub>5</sub>]<sup>−</sup> or five other perfluoroorganyl substituents,<sup>13</sup> although, similar to (C<sub>5</sub>F<sub>5</sub>)<sup>−</sup>,<sup>14</sup> the “free” ions can be prepared and are relatively stable.

Recently, when we studied the influence of ring substituents on ferrocenylpyridines,<sup>15</sup> we came across a paper by Herberich et al., who reported the successful electrophilic fluorination of a SMP substituted ruthenocene using *N*-fluoro-*N,N*-bis-(benzenesulfonyl)imide.<sup>16</sup> We used this reagent to prepare 1-fluoro-2-(2-pyridyl)-ferrrocene and reasoned that it might also be used for the synthesis of polyfluorinated ferrrocenes. Indeed, when treating the lithiation mixture containing monolithioferrrocene with this *N*-fluoro compound, we obtained monofluoroferrrocene [Fe(C<sub>5</sub>H<sub>4</sub>F)(C<sub>5</sub>H<sub>5</sub>)] (1) (Scheme 1).

### Scheme 1. Synthesis of Pentafluoroferrrocene (2)<sup>a,b</sup>



<sup>a</sup>tert-BuLi/KO<sup>t</sup>Bu/THF; then (PhSO<sub>2</sub>)<sub>2</sub>NF. <sup>b</sup>Four times: <sup>n</sup>BuLi/TMP/THF; then (PhSO<sub>2</sub>)<sub>2</sub>NF.

After chromatographic workup, 1 could be isolated in approximately 50% yield but was still contaminated with 5 to 20% of unreacted ferrocene. This is a substantial improvement over the 10% yield in the original publication<sup>6</sup> and also over the 29% yield reported later by Popov et al.<sup>17</sup> We used the product mixture obtained after chromatography for four further lithiation–electrophilic fluorination sequences. This protocol afforded the title compound pentafluoroferrrocene [Fe(C<sub>5</sub>F<sub>5</sub>)(C<sub>5</sub>H<sub>5</sub>)] (2). It was isolated in pure form in 6.7% overall yield (starting from ferrocene) (Scheme 1).

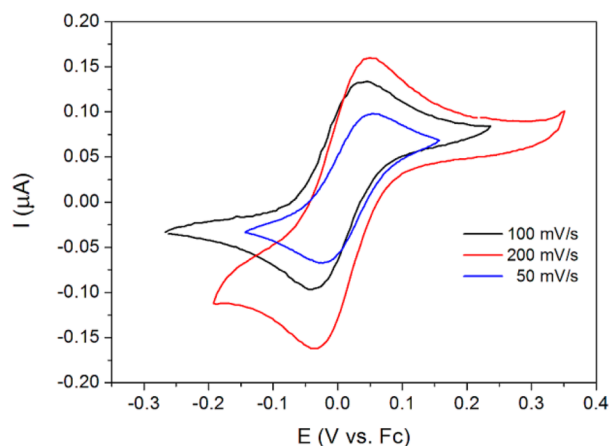
Compound 2 is a yellow-orange crystalline compound that melts at 146 °C in a closed capillary and shows a very high tendency to sublime at room temperature and ambient pressure. The IR spectrum shows the usual ν(C–H), ν(C–C), and δ(C–H) absorptions at 3122, 1414, 1002, and 833 cm<sup>−1</sup>, and the asymmetric C<sub>5</sub>H<sub>5</sub> ring breathing mode at 1107 cm<sup>−1</sup>; two very strong absorptions at 1506 and 939 cm<sup>−1</sup> must be associated with the C<sub>5</sub>F<sub>5</sub> ring since they are not observed with [Fe(C<sub>5</sub>H<sub>5</sub>)(C<sub>5</sub>X<sub>5</sub>)] (X = Cl, Br).<sup>18</sup> The <sup>1</sup>H NMR spectrum (in CD<sub>2</sub>Cl<sub>2</sub>, 400

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MHz) shows a singlet at 4.66 ppm, the  $^{19}\text{F}$  NMR spectrum ( $\text{CDCl}_3$ , 376.5 MHz) a singlet at  $-222.2$  ppm, and the  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ , 100.5 MHz) a singlet at 76.5 ppm for the  $\text{C}_5\text{H}_5$  ring and an  $\text{AXYY'ZZ'}$  multiplet at 107.4 ppm for the  $\text{C}_5\text{F}_5$  ring. The HRMS spectrum ( $\text{EI}^+$  mode) shows the  $\text{M}^+$  peak at  $m/z = 275.9662$  (calcd 275.9661).

**Cyclic Voltammetry.** Compound **2** exhibits a reversible one-electron oxidation ( $\Delta E = 75$  mV) at  $E_0 = 0.01$  V vs  $\text{Fc}/\text{Fc}^+$  at all studied scan rates (Figure 1). This low potential is very



**Figure 1.** Cyclic voltammogram of 0.1 mM  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$ .

surprising, if compared with the CV results obtained with  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{Cl}_5)]$  (**7**)<sup>19</sup> ( $E^0 = +0.77$  eV) and with  $[\text{Cp}^*\text{Ru}(\text{C}_5\text{F}_5)]$ <sup>20</sup> ( $E^0 = +1.07$  eV). This difference and the statement that “ $\text{C}_5\text{Cl}_5$  and  $\text{C}_5\text{F}_5$ ...have very similar overall electronic effects at the metal”,<sup>11</sup> prompted us to investigate the potentials by means of DFT calculations (PBE0/cc-pVTZ/PCM, corrected for  $\text{CH}_3\text{CN}$  solvent effects, strict convergence criteria, and thermal corrections).<sup>21</sup> The calculated free Gibbs reaction enthalpies  $\Delta G^0$  at 25 °C vs  $\text{Fc}/\text{Fc}^+$  are  $-0.04$  eV ( $2/2^+$ ) and  $-0.02$  eV ( $7/7^+$ ), so essentially very similar. A further test of validity was  $\text{Cp}_2\text{Co}/\text{Cp}_2\text{Co}^+$  (in DMF): calculated  $\Delta G^0 = -1.17$  eV vs experiment  $-1.22$  eV.<sup>22</sup> The huge difference between the potentials of  $2/2^+$  and  $7/7^+$  is either due to an extreme case of “perfluoro effect”<sup>23</sup> (meaning a failure of our calculations) or, more likely, due to a deviation of the experimental value reported for  $7/7^+$  as a consequence of the occurrence of irreversible  $2e^-$  oxidations.

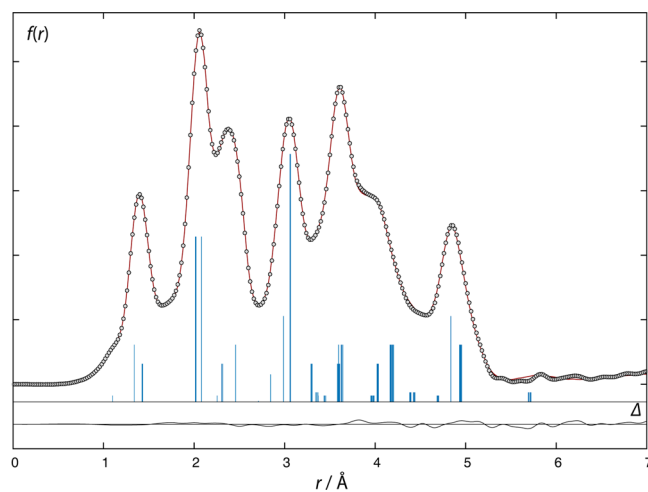
**DFT Calculations.** In order to predict the structural features of  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$ , the geometry of the molecule was calculated at the PBE0 hybrid DFT level of theory,<sup>24</sup> using a correlation consistent, triple- $\zeta$  cc-pVTZ basis set for all atoms.<sup>25</sup> We refrained from performing calculations using second-order perturbation theory methods since they are known to be unreliable for metallocene systems.<sup>26</sup> Structure parameters of  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$  (**2**) were calculated for the eclipsed (see Table 1) and staggered rotamers as well as in five evenly spaced interjacent rotameric forms. Only the eclipsed conformer of  $\text{C}_{5v}$  symmetry is an energetic minimum at this level of theory. All calculations yielded a bending of the fluorine and hydrogen atoms out of their corresponding Cp-planes. The DFT calculations predict the barrier corresponding to internal rotation about the  $\text{X}_\text{F}-\text{Fe}-\text{X}_\text{H}$  connection path to  $2.2$   $\text{kJ mol}^{-1}$ . The structure parameters were also determined by gas electron diffraction and single crystal X-ray diffraction and are discussed in comparison in the crystal structure section below.

**Table 1.** Major Geometrical Parameters [ $\text{\AA}$ , deg] and Rotational Barriers of  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$  (**2**)

	GED <sup>a</sup>		DFT	XRD
	$r_g$	$r_e/\Phi_e$	$r_e/\Phi_e$	$r$
$d[\text{Fe}-\text{C}_\text{H}]$	2.084(1)	2.071(1)	2.054	2.048–2.054
$d[\text{Fe}-\text{C}_\text{F}]$	2.017(1)	2.009(1)	2.012	1.997–2.005
$d[\text{C}-\text{H}]$	1.105(7)	1.085(7)	1.079	0.96–1.12
$d[\text{C}-\text{F}]$	1.340(1)	1.333(1)	1.323	1.331–1.341
$d[\text{C}_\text{H}-\text{C}_\text{H}]$	1.434(1)	1.425(1)	1.420	1.417–1.427
$d[\text{C}_\text{F}-\text{C}_\text{F}]$	1.427(1)	1.419(1)	1.420	1.410–1.416
$a[\text{C}_\text{S}-\text{F}]$		$-3.7(1)$	$-3.0$	$(-3.2)-(-3.8)$
$a[\text{C}_\text{S}-\text{H}]$		$+1.6(2)$	$+1.6$	$+1.7-2.5$
$\Delta E_{\text{rot}}$ ( $\text{kJ mol}^{-1}$ )	2.4(3)		2.2	

<sup>a</sup>Uncertainties are given as  $1 \sigma_{\text{LS}}$ .

**Gas Electron Diffraction (GED).** In order to obtain experimental data for the structure of free molecules of  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$  (**2**) we performed gas electron diffraction experiments. Electron scattering intensities were recorded at 330 K using the Bielefeld GED apparatus.<sup>27</sup> Molecular structure refinements were performed using the UNEX program.<sup>28</sup> Details of the experiment and refinement are provided in the Supporting Information. The radial distribution curve is shown in Figure 2.



**Figure 2.** Experimental (dots) and theoretical (line) radial distribution  $f(r)$  curves and the difference curve (below) for the dynamic GED model of  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$ . Vertical bars indicate the interatomic distances.

In a  $\text{C}_{5v}$ -symmetrical model of  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$ , eight parameters were refined: six distances  $d[\text{Fe}-\text{X}_\text{F}]$ ,  $d[\text{Fe}-\text{X}_\text{H}]$ ,  $d[\text{X}_\text{H}-\text{C}_\text{H}]$ ,  $d[\text{X}_\text{F}-\text{C}_\text{F}]$ ,  $d[\text{C}-\text{F}]$ , and  $d[\text{C}-\text{H}]$  ( $\text{X}_\text{F}$  and  $\text{X}_\text{H}$  define the centers of the  $\text{C}_5\text{F}_5$  and  $\text{C}_5\text{H}_5$  ligands) and two angles  $a[\text{X}_\text{F}-\text{C}-\text{F}]$  and  $a[\text{X}_\text{H}-\text{C}-\text{H}]$ . The first angle describes a bending of the fluorine atoms out of the Cp-plane away from the iron atom, the latter the analogous bending of the hydrogen toward the iron atom. The refinement of the  $a[\text{X}_\text{H}-\text{C}-\text{H}]$  angle was supported by flexible restraints (along the ideas of Bartell et al.<sup>29</sup> and the SARACEN method<sup>30</sup> and implemented in UNEX<sup>31</sup>).

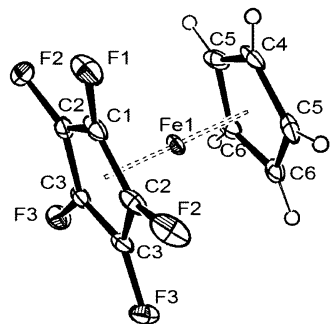
Three different GED models were used for structure refinement: a static model including the eclipsed conformer only, a static model involving refinement of the dihedral angle  $\Phi[\text{C}_\text{F}-\text{X}_\text{F}-\text{X}_\text{H}-\text{C}_\text{H}]$ , and a dynamic model, based on 36 pseudoconformers weighted by a parametrized potential energy curve. The latter resulted in the best fit to the experimental

scattering with an  $R$ -factor of 4.4%. GED data analysis in this way shows the eclipsed rotamer to correspond to the minimum structure. This is congruent with all quantum chemical calculations and structure in the solid state (see below). All bond lengths are in good agreement with the ones derived from the foresaid methods (Table 1). Furthermore, the bending of the fluorine atoms away from the iron atom that was supposed by all quantum chemical calculations could be verified by GED data and structure refinement. Insofar as the Fe–Cp distances are concerned, GED data yield a difference between the two of 0.07 Å, which is slightly higher than the one derived from XRD data and the calculated ones (both 0.05 Å).

The barrier of internal rotation of  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$  could be experimentally determined to 2.4(8) kJ mol<sup>-1</sup> using the dynamic model. This is in very good compliance with the quantum-chemical calculations but significantly smaller than that in  $\text{Fe}(\text{C}_5\text{H}_5)_2$  with 3.9 kJ mol<sup>-1</sup> (also by GED).<sup>32</sup>

According to the choice of the GED model, refinement of a static model, which accounts for the eclipsed conformer only, yielded a larger  $R$ -factor of 5.8% (for radial distribution curve see Figure S3). If the  $\Phi[\text{C}(\text{F})-\text{X}_\text{F}-\text{X}_\text{H}-\text{C}(\text{H})]$  dihedral angle is included in the refinement procedure the  $R$ -factor decreases to 4.8%. In this case, the refined structure of  $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{F}_5)$  shows a twisting of the cyclopentadienide ligands against one another of 15.5(13)°, whereas all other geometrical parameters are well comparable to those derived from the dynamic model.

**Crystal Structure.** Recrystallization of **2** from hexane at -30 °C yielded crystals suitable for X-ray diffraction (monoclinic space group  $P2_1/m$ ,  $Z = 2$ ). The cell metric parameters are very similar to the ones found in the analogous ruthenium compound. The molecular structure is shown in Figure 3.

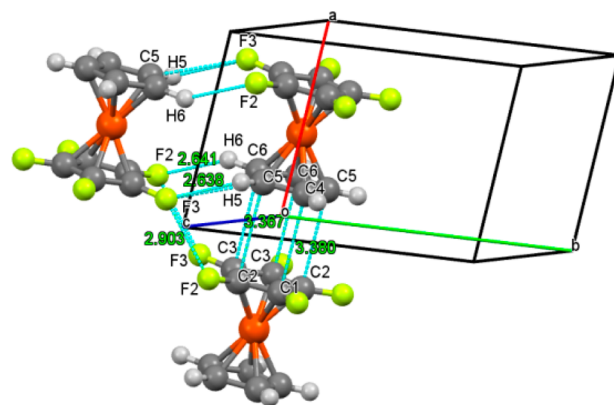


**Figure 3.** Molecular structure of **2**. Displacement ellipsoids drawn at the 30% probability level. The bond angles F–C–C range from 125.4° to 126.4°. Torsion angle C3–Ct(Cp<sub>F</sub>)–Ct(Cp<sub>H</sub>)–C6: 0.1°.

The iron atom of **2** is significantly closer to the fluorinated cyclopentadienyl ring than to the nonsubstituted ring, both in the gas phase and in the solid state. The C–C bonds are longer within the C<sub>5</sub>H<sub>5</sub> ring than in the C<sub>5</sub>F<sub>5</sub> ring. The fluorine substituents are slightly bent away from the iron atom, while the hydrogen atoms are bent toward the iron atom. Also consistent in gas phase and solid state, the two rings are found to be planar and to adopt eclipsed conformation (in the ground state for GED but with noticeable motion but fixed in the crystal lattice).

Some additional interesting features appear in the crystal packing. The molecules of **2** exhibit  $\pi$ -stacking along the  $a$ -direction, with intermolecular distances of neighboring C<sub>5</sub>F<sub>5</sub> and C<sub>5</sub>H<sub>5</sub> rings of ca. 3.37 Å, while the intramolecular distance between the two rings of 3.26 Å is only slightly shorter. Additionally, there are short fluorine–fluorine contacts of 2.90 Å

between inversion related F2–F3 pairs and hydrogen bridges of 2.64 Å between H5...F3 and H6...F2. These important contacts are visualized in Figure 4; more views of the crystal packing can be seen in the Supporting Information.



**Figure 4.** Packing view showing some important intermolecular contacts.

## ■ ASSOCIATED CONTENT

### Supporting Information

Details of the GED experiments, the crystal structure determination, the preparative procedures and analytical data of the new compounds, and results of a different DFT approach. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) (a) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039. (b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632.
- (2) For selected recent reviews see: (a) Philips, E. S. *Ferrocenes: Compounds, Properties 6 Applications (Chemical Engineering Methods and Technology)*; Nova Science Publishers: New York, 2011. (b) Dai, L.-X.; Hou, X. L., Eds. *Chiral Ferrocenes in Asymmetric Catalysis: Synthesis and Applications*; Wiley-VCH: Weinheim, Germany, 2010. (c) Stepnicka, P., Ed. *Ferrocenes: Ligands, Materials and Biomolecules*; John Wiley and Sons: Chichester, U.K., 2008. (d) Butler, I. R.; Thomas, D. A. In *Comprehensive Organometallic Chemistry III*; Elsevier: Amsterdam, The Netherlands, 2006; pp 185 and 629.
- (3) Heinze, K.; Lang, H. *Organometallics* **2013**, *32*, 5623–5625.
- (4) (a) Hedberg, F. L.; Rosenberg, H. *J. Am. Chem. Soc.* **1970**, *92*, 3239–3240. (b) Hedberg, F. L.; Rosenberg, H. *J. Therm. Anal.* **1974**, *6*, 571.

- (5) Rosenberg, H.; Mosteller, J. C. *Ind. Eng. Chem.* **1953**, *45*, 2283–2286.
- (6) Hedberg, F. L.; Rosenberg, H. *J. Organomet. Chem.* **1971**, *28*, C14–C16.
- (7) Winter, C. H. Gov. Rep. Announce Index (U.S.) 1996, 96, Abstr. No. 19-00, 395. CAN 125:276161.
- (8) (a) Deng, J.; Li, Q.; Xie, Y.; King, R. B. *J. Fluorine Chem.* **2013**, *154*, 23. (b) Wang, H.; Li, R.; King, R. B. *J. Fluorine Chem.* **2013**, *153*, 121.
- (9) Curnow, O. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1992**, *114*, 5895–5897.
- (10) (a) Hughes, R. P.; Zheng, X.; Ostrander, R. L.; Rheingold, A. L. *Organometallics* **1994**, *13*, 1567. (b) 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.
- (11) (a) Lichtenberger, D. L.; Elkadi, Y.; Gruhn, N. E.; Hughes, R. P.; Curnow, O. J.; Zheng, X. *Organometallics* **1997**, *16*, 5209. (b) Johnston, B. F.; Rankin, D. W. H.; Robertson, H. E.; Hughes, R. P.; Lompfrey, J. R. *Organometallics* **2002**, *21*, 4840.
- (12) (a) Lima dos Santos, H. F.; L. Pontes, D.; Fime, C. L. *J. Mol. Model.* **2013**, *19*, 2955–2964. (b) Throckmorton, L.; Marynick, D. S. *J. Phys. Chem.* **1988**, *92*, 645.
- (13) (a) Chambers, R. D.; Gray, W. K.; Vaughan, J. F. S.; Korn, S. R.; Medebielle, M.; Batsanov, A. S.; Lehmann, C. W.; Howard, J. A. K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 135. (b) Dinh, L. V.; Gladysz, J. A. *Chem.—Eur. J.* **2005**, *11*, 7211. (c) Deck, P. A. *Coord. Chem. Rev.* **2006**, *250*, 1032–1055. (d) Roemer, M.; Kang, Y. K.; Chung, Y. K.; Lentz, D. *Chem.—Eur. J.* **2012**, *18*, 3371.
- (14) Paprott, G.; Lehmann, S.; Seppelt, K. *Chem. Ber.* **1988**, *121*, 727.
- (15) (a) Sünkel, K.; Weigand, S. *Inorg. Chim. Acta* **2011**, *370*, 224. (b) Sünkel, K.; Weigand, S. *Inorg. Chem. Commun.* **2012**, *21*, 24. (c) Sünkel, K.; Weigand, S. *Polyhedron* **2012**, *44*, 133. (d) Sünkel, K.; Branzan, R.; Weigand, S. *Inorg. Chim. Acta* **2013**, *399*, 193. (e) Sünkel, K.; Budde, H.; Weigand, S. *Z. Anorg. Allg. Chem.* **2013**, *639*, 1242.
- (16) Herberich, G. E.; Englert, U.; Wirth, T. *Eur. J. Inorg. Chem.* **2005**, 4924–4935.
- (17) Popov, V. I.; Lib, M.; Haas, A. *Ukrainskii Khim. Zh.* **1990**, *56*, 1115–1116 CAN 114:185701.
- (18) Phillips, L.; Lacey, A. R.; Cooper, M. K. *J. Chem. Soc., Dalton Trans.* **1988**, 1383.
- (19) Brown, K. N.; Gulyas, P. T.; Lay, P. A.; McAlpine, N. S.; Masters, A. F.; Phillips, L. *J. Chem. Soc., Dalton Trans.* **1993**, 835.
- (20) Richardson, D. E.; Ryan, M. F.; Geiger, W. E.; Chin, T. T.; Hughes, R. P.; Curnow, O. J. *Organometallics* **1993**, *12*, 613.
- (21) A similar approach for calculating redox potentials of metal-locenes was reported in: Baik, M.-H.; Friesner, R. A. *J. Phys. Chem. A* **2002**, *106*, 7407–7412.
- (22) Friesner, R. A.; Baik, M.-H. *J. Phys. Chem. A* **2002**, *106*, 7407.
- (23) (a) Mondal, T.; Mahapatra, S. *J. Chem. Phys.* **2010**, *133*, 084304–1–084304–12. (b) Hitchcock, A. P.; Fischer, P.; Gedanken, A.; Robin, M. B. *J. Phys. Chem.* **1987**, *91*, 531.
- (24) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396. (c) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.
- (25) (a) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (b) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (c) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410. (d) Wilson, A.; van Mourik, T.; Dunning, T. H., Jr. *J. Mol. Struct.* **1997**, *388*, 339.
- (26) Coriani, S.; Haaland, A.; Helgaker, T.; Jørgensen, P. *ChemPhysChem* **2006**, *7*, 245.
- (27) Berger, R. J. F.; Hoffmann, M.; Hayes, S. A.; Mitzel, N. W. *Z. Naturforsch.* **2009**, *64B*, 1259.
- (28) (a) Vishnevskiy, Yu. V. UNEX, v. 1.6.0, 2013; <http://unexprog.org>. (b) Vishnevskiy, Yu. V. *J. Mol. Struct.* **2007**, *871*, 24. (c) Vishnevskiy, Yu. V. *J. Mol. Struct.* **2007**, *833*, 30.
- (29) Bartell, L. S.; Romanesko, D. J.; Wong, T. C. In *Molecular Structure by Diffraction Methods*; Sims, G. A., Sutton, L. E., Eds.; The Chemical Society: London, 1975; Vol. 3, pp 72–79.
- (30) Mitzel, N. W.; Rankin, D. W. H. *Dalton Trans.* **2003**, *16*, 3650.
- (31) Vishnevskiy, Yu. V.; Abaev, M. A.; Rykov, A. N.; Gurskii, M. E.; Belyakov, P. A.; Erdyakov, S. Yu.; Bubnov, Yu. N.; Mitzel, N. W. *Chem.—Eur. J.* **2012**, *18*, 10585.
- (32) Haaland, A.; Nilsson, J. *Acta Chem. Scand.* **1968**, *22*, 2653.