

# Ambi-Valence Taken Literally: Ruthenium vs Iron Oxidation in (1,1'-Diphosphinoferrocene)ruthenium(II) Hydride and Chloride Complexes as Deduced from Spectroelectrochemistry of the Heterodimetallic "Mixed-Valent" Intermediates<sup>†</sup>

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Combining two different redox-active organometallic moieties, we prepared the compounds [(Cym)- $RuCl(dpf)](PF_6)$ , with Cym = p-cymene = 1-isopropyl-4-methylbenzene, and the diphosphinoferrocenes (dpf) 1,1'-bis(diphenylphosphino)ferrocene (dppf; complex 3), 1,1'-bis(diisopropylphosphino)ferrocene (dippf; complex 4), and 1,1'-bis(diethylphosphino)ferrocene (depf; complex 5) as well as the structurally characterized hydride complex  $[(C_5Me_5)RuH(dippf)]$  (2). In contrast to the case for 2, with an approximately staggered ferrocene conformation, the chloride complexes 3-5 exhibit a syn-periplanar ferrocene arrangement due to a  $Cl \cdots H(C_5H_4)$  interaction in the solid and in solution. The related new compounds  $[(Cym)RuH(dppf)](PF_6)$  (6) and trinuclear  $(\mu - dpf)[(Cym)RuCl_2)]_2$  (7–9) were also obtained and identified by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. The redox behavior of 2-6 and of the known  $[(C_5Me_5)RuH(dppf)]$  (1) was investigated using cyclic voltammetry, spectroelectrochemistry in the UV/ vis/near-IR and IR regions, and, in part, by EPR. The first oxidation of the areneruthenium compounds 3-6 occurs reversibly at the ferrocene site, while the reduction proceeds via an ECE two-electron pattern under chloride dissociation. These results are compared to those obtained for the pentamethylcyclopentadienide/hydride complexes 1 and 2, which demonstrate unambiguously the ruthenium center as the site of the first electron loss. The different results for the two kinds of heterodimetallic  $d^5/d^6$  mixed-valent intermediates,  $Fe^{II}Ru^{III}$  for 1<sup>+</sup> and 2<sup>+</sup> and  $Fe^{III}Ru^{II}$  for 3<sup>+</sup>-6<sup>+</sup>, are discussed with respect to the possible uses of such heterodinuclear systems in H<sub>2</sub> conversion catalysis.

#### Introduction

The +III/+II oxidation state change of the group 8 elements in their compounds is a most common and well-investigated elementary reaction. This holds not only for the atoms in solid-state materials or classical metal complexes but also for organometallic systems.<sup>1</sup> Whereas the lightest homologue, iron, is best established through the remarkably stable ferrocenium/ferrocene pair,<sup>2,3</sup> the more inert bonds

formed by a heavier homologue, ruthenium, help to tolerate formally uncharged ligands such as arenes.<sup>4,5</sup> With regard to the application potential, the ferrocenes have found much interest not only as one-electron transfer and storage moieties<sup>2,3,6</sup> but also as molecular scaffolds for catalytically relevant structures (involving, for example, the 1,1'-disubstituted derivatives).<sup>7</sup> On the other hand, the organoruthenium complex fragments  $[Ru(C_nR_n)]^x$ , n = 5, 6, can have both a direct catalytic function in coordination compounds<sup>8</sup> and

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exhibit physiological effects in the field of anticancer activity.

Combining ferrocene (Fc) and organoruthenium moieties within one molecular entity raises the question of the electron transfer sequence for the two M<sup>III/II</sup> transitions. This sequence, which would involve heterodimetallic mixed-valent intermediates  $Fc^+/Ru^{II}$  or  $Fc/Ru^{III}$ , is not a priori obvious; it depends on the molecular configuration and environment, and it is of significance for the expected overall reactivity.<sup>10</sup> Following previous exploratory studies on Os/Fc and Ru/Fc examples,<sup>11</sup> we now present a more comprehensive report on the heterometallic complexes 1-9, as obtained from reactions between 1,1'-bis(diorganophosphino)ferrocenes and organoruthenium complex fragments.



A catalysis of the energy-producing dihydrogen oxidation to H<sup>+</sup> or of the reversed process is of interest, both for technical processes, especially fuel cell reactions, and for microbiological activity.<sup>12</sup> Biochemically, this reaction is catalyzed by hydrogenase enzymes, several of which were shown to possess oligometal active sites such as Fe,Ni-heterodimetallic structures.<sup>13</sup> Synthetic efforts for molecular systems effecting the reaction  $H_2 \rightarrow 2H^+ + 2e^-$  via "redox-switch" models have been described, <sup>10a,d,e,h</sup> involving inter alia the Fe,Ru-heterodimetallic hydride complex  $[(C_5Me_5)RuH(dppf)]$  (1; dppf=1,1'-bis(diphenylphosphino)ferrocene), which was shown to reduce methylviologen with H<sub>2</sub>.<sup>10a</sup> In that work by Hembre et al. it was suggested that the oxidation of 1, which is crucial for the catalytic process, involves the ruthenium and not the ferrocene iron.<sup>10a</sup>

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Our earlier studies<sup>11</sup> confirmed this claim, and similar assertions were made recently for the halide species [(C5Me5)RuX- $(dpf)]^{n+.10b,c}$ 

Herein we present further spectroelectrochemical and EPR evidence and describe another derivative, [(C<sub>5</sub>Me<sub>5</sub>)RuH-(dippf)] (2; dippf = 1,1'-bis(diisopropylphosphino)ferrocene). Compound 2 has been structurally characterized, as have the complexes  $[(Cym)RuCl(dpf)](PF_6)$  (Cym = p-cymene = 1-isopropyl-4-methylbenzene) with dpf = dppf (complex 3),<sup>14</sup> dippf (complex 4), and 1,1'-bis(diethylphosphino)ferrocene (depf; complex 5) with a neutral arene instead of a cyclopentadienide coligand at ruthenium. Complexes of the (Cym)ClRu<sup>+</sup> fragment with  $\alpha$ -diimine chelate ligands were reported to exhibit a characteristic ECE reduction behavior with loss of chloride,<sup>5</sup> while the dpf ligand family may be described as "noninnocent",<sup>15</sup> exhibiting the potential for redox activity.

The compounds  $[(Cym)RuH(dppf)](PF_6)$  (6) and  $(\mu$ -dpf)- $[(Cym)RuCl_2)]_2$  (7–9; dpf = dppf, depf, dippf) were also obtained and identified by NMR spectroscopy. Complex 7 was reported earlier,<sup>16</sup> but claims of a reduction to Ru<sup>0</sup> species could not be substantiated spectroscopically. The osmium analogue [(Cym)OsCl(dppf)](PF<sub>6</sub>) (10) of the known<sup>11a,14</sup> 3 has been described previously.<sup>11b</sup>

## **Experimental Section**

**Instrumentation.** EPR spectra in the X band were recorded with a Bruker System ESP 300. <sup>1</sup>H and <sup>31</sup>P NMR spectra were taken on a Bruker AC 250 spectrometer. IR spectra were obtained using a Philips PU 9800 FT-IR instrument. UV/vis/ near-IR absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> solution using a three-electrode configuration (glassy-carbon working electrode, Pt counter electrode, Ag reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple served as internal reference. Electron consumption was assessed by comparing integrated peak areas. Spectroelectrochemistry was performed using an optically transparent thin-layer elec-trode (OTTLE) cell.<sup>17a</sup> A two-electrode capillary served to generate intermediates for X-band EPR studies.<sup>1</sup>

generate intermediates for X-band EPK studies. Syntheses. The dpf ligands were obtained by an established procedure<sup>19b</sup> unless they were commercially available. Complex 1 was prepared according to the literature.<sup>10a</sup>  $[(C_5Me_5)RuH(dippf)]^{10b}(2)$ . A 53 mg amount (0.086 mmol) of  $[(C_5Me_5)RuCl_2]_2^{18}$  and 60 mg (0.199 mmol) of aluminum bronze were suspended in 5 mL of degassed toluene and stirred with 86 mg (0.206 mmol) of dippf<sup>19</sup> for 3 days at room temperature. The filtrate obtained after separation was treated with 27 mg (1.21 mmol) of sodium in 5 mL of methanol, and the mixture was heated to reflux for 4 h. Removal of solvent, redissolution in a very small amount of toluene, layering with CH<sub>3</sub>OH, and cooling to -17 °C produced an orange precipitate

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(82 mg, 73%). Anal. Calcd for  $C_{32}H_{52}FeP_2Ru$  (655.63 g/mol): C, 58.62; H, 7.99. Found: 58.63; H, 7.99. For NMR see Tables S1 and S2 (Supporting Information).

[(Cym)RuCl(dpf)](PF<sub>6</sub>) (3-5). A suspension containing 200 mg (0.328 mmol) of [(Cym)RuCl<sub>2</sub>]<sub>2</sub> in 20 mL of a CH<sub>3</sub>OH/ CH<sub>3</sub>CN mixture was treated with 174 mg (0.653 mmol) of TINO<sub>3</sub>. After it was stirred for 30 min, this preparation was added to 0.685 mmol of the corresponding dpf ligand, dissolved in 30 mL of methanol (depf, dippf) or THF (dppf). After 1 h and the removal of most solvent the oily residue was redissolved in methanol and precipitated with diethyl ether and the residue this time was dissolved in ethanol/water (4/1). Excess ammonium hexafluorophosphate precipitated the product, which was washed with wet ethanol and water and dried in vacuo.

 $dpf = dppf (3; 298 mg, 56\%).^{14}$  Anal. Calcd for  $C_{44}H_{42}ClF_{6}$ -FeP<sub>3</sub>Ru (934.34 g/mol): C, 54.48; H, 4.36. Found: 54.00; H, 4.39. For NMR see Tables S1 and S2.

dpf = dippf (4; 248 mg, 52%). Anal. Calcd for  $C_{32}H_{50}ClF_{6}$ -FeP<sub>3</sub>Ru (834.03 g/mol): C, 46.08; H, 6.04. Found: 45.37; H, 6.26. For NMR see Tables S1 and S2.

dpf = depf(5; 255 mg, 49%). Anal. Calcd for  $C_{28}H_{42}ClF_6Fe$ -P<sub>3</sub>Ru (777.92 g/mol): C, 43.23; H, 5.44. Found: 42.78; H, 5.32. For NMR see Tables S1 and S2.

 $[(Cym)RuH(dppf)](PF_6)$  (6). An orange solution of 301 mg (310 mmol) of  $3^{14}$  in 50 mL of THF was cooled to 205 K and treated with 0.39 mL of a commercially available 1 M LiBEt<sub>3</sub>H solution in THF for 1 h. Warming to room temperature, stirring for 4 h, removing the solvent in vacuo, washing three times with 15 mL of water and 3 mL of diethyl ether each, dissolving in acetonitrile, filtering over Celite, and eventual drying under vacuum yielded 248 mg (0.265 mmol, 86%) of 6 as a yellow solid. Anal. Calcd for C44H43F6FeP3Ru (935.64 g/mol): C, 56.48; H, 4.63. Found: C, 56.16; H, 4.90. MS: m/z 791.12  $[M - PF_6]^+$ . UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 320 (sh), 440 (sh) nm.

 $(\mu-dpf)[(Cym)RuCl_2)]_2$  (7–9). A mixture containing 78 mg (0.126 mmol) of [(Cym)RuCl<sub>2</sub>]<sub>2</sub> and 0.120 mmol of the dpf ligand were stirred for 6 h in 20 mL of CH<sub>3</sub>OH (dippf, depf) or acetone (dppf). The resulting precipitate was collected by filtration, washed with methanol, and dried in vacuo.

dpf = dppf (7) was reported earlier.<sup>16</sup> For NMR see Tables S1 and S2.

dpf = depf (8; 24 mg, 24%). Anal. Calcd for  $C_{38}H_{56}Cl_4Fe$ -P<sub>2</sub>Ru<sub>2</sub> (974.60 g/mol): Č, 46.83; H, 5.79. Found: 46.05; H, 5.95. For NMR see Tables S1 and S2.

dpf = dippf (9; 46 mg, 22%). Anal. Calcd for  $C_{42}H_{64}Cl_4Fe$ -P<sub>2</sub>Ru<sub>2</sub> (1030.70 g/mol): C, 48.94; H, 6.26. Found: 48.71; H, 6.31. For NMR see Tables S1 and S2.

Crystallography. Single crystals were obtained by layering a toluene solution of 2 with methanol at 256 K, by cooling of a saturated methanol solution of 4 to 276 K, or by slowly evaporating a methanolic solution of 5 at room temperature. The crystals were analyzed using a Syntex P21 diffractometer at 173 K with graphitemonochromated Ka radiation (0.71073 A). Direct method refinement using available programs<sup>20a</sup> was used; the C-H hydrogen atoms were included in calculated positions. In 2 the metal hydride H atom was located but refined at a realistic<sup>21</sup> distance of 159 pm at last refinement. For complex 4 with two independent molecules in the unit cell an absorption correction procedure<sup>20b</sup> led to significant improvement. Complex 5 exhibited a disorder of the  $PF_6^-$  ions involving two edge-sharing octahedra.

#### **Results and Discussion**

Synthesis and NMR Spectroscopy. Different from a recent report, <sup>10b</sup> the neutral hydride compound 2 was prepared here



Figure 1. Molecular structure of 2 in the crystal state.

in analogy to the dppf complex 1 reported by Hembre et al.<sup>10a</sup> The areneruthenium hydride complex 6 was prepared from the chloride complex 3 using LiBEt<sub>3</sub>H; other approaches were unsuccessful. The heterotrinuclear compounds 7, <sup>16</sup> 8, and 9 were obtained from [Ru(Cym)Cl<sub>2</sub>]<sub>2</sub> and the corresponding 1,1'-diphosphinoferrocenes in a 1:1 ratio under mild conditions. Using higher temperatures or activation with silver or thallium(I) salts, followed by  $Cl^{-}/PF_{6}^{-}$  anion exchange, produced the hetero-dinuclear systems 3–5. The NMR spectra of 3–5, 7–9, and the hydride complexes 2 and 6 confirm the composition of the compounds (Tables S1 and S2) and shed light on the P-substituent (Ph, <sup>i</sup>Pr, Et) and Ru-ligand effects (H vs Cl). The <sup>1</sup>H and <sup>31</sup>P chemical shifts not only reflect the lowered symmetry of the dinuclear systems 1-6 and the anticipated substituent effects, e.g. Cl<sup>-</sup> vs more electron-rich hydride, cymene vs more electronrich pentamethylcyclopentadienide, P-phenyl vs more electronrich P-isopropyl, but also point to specific inter- and intramolecular interactions. One such case is the Cl···H attraction between chlororuthenium and two H(cyclopentadienyliron) atoms, which causes <sup>1</sup>H NMR deshielding of one set of protons and is attributed to a crystallographically confirmed (cf. below) intramolecular bridging, as illustrated in Figure 4.

Structures. The compounds 2-5 could be crystallized for structure analysis. Complex 3 and its structure were reported previously.<sup>14a</sup> Crystallographic data of compounds 2, 4, and 5 are summarized in Table S3, and selected bond parameters are given in Tables S4 and S5 (Supporting Information). Figures 1-4 and Figure S2 (Supporting Information) illustrate the structural situation in the hydride 2 and in two of the cymene/chloride complex salts: viz., complexes 5 and 4.

Compounds 2-5 all contain ruthenium chelated by the 1,1'-diphosphinoferrocene ligands with the hydride/chloride and  $(C_5Me_5^{-})/(Cym)$  6e ligands in an approximately perpendicular position. The chelate bite angles P-Ru-P are ca. 95°, and the P-Ru-Cl angles for complexes 3-5 are between 81 and 88°, in agreement with the preferential "octahedral" coordination of the 4d<sup>6</sup> center ruthenium(II). The Ru-Cl bond lengths do not vary significantly; the Ru···Fe and Ru-P distances are longer for the dippf complexes with the space-demanding isopropyl groups.

The structure characterization of compound 2 allowed us to find the hydride ligand at a reasonable Ru-H distance of about 159 pm.<sup>21</sup> Figure S1 (Supporting Information)

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Figure 2. View along the Cp–Fe–Cp axis in the molecular structure of 2.



Figure 3. Molecular structure of 5 in the crystal state.

illustrates the particular position of the hydride in compound 2 and its shielding by the isopropyl groups. Figures 1 and 2 show that the ferrocene-cyclopentadienide rings are a little less staggered (27°) in 2 than in the related 1 (33°; 36° is the value for "ideal" staggering). Whereas the hydride compounds 1 and 2 thus show near staggering of the ferrocene-cyclopentadienide rings, the chloride complex ions exhibit an almost synperiplanar arrangement with twist angles below 6°. This conformation is favored because of an intramolecular  $H \cdots Cl \cdots H$  bridging which has already been mentioned in the discussion of solution <sup>1</sup>H NMR results. Cl-H distances of about 270 pm and the particular conformation (Figure 4) point to a weak but structure-determining interaction.

The cymene ligands in **4** and **5** are nearly planar and show the isopropyl group oriented toward the chloride ligand.

**Cyclic Voltammetry.** The complexes 1-6 exhibit characteristic cyclic voltammograms in solution involving two oxidation processes and, in the case of chloro derivatives, a reduction coupled to a chloride release (cf. below). Figures 5



Figure 4. Cl····H interactions in the molecular structure of 5 (M = Ru; P substituents omitted for clarity).



Figure 5. Cyclic voltammogram of 4 at 298 K in 0.1 M  $Bu_4NPF_6/THF$ .



Figure 6. Cyclic voltammogram of 6 at 298 K in 0.1 M  $Bu_4NPF_6/CH_3CN$ .

and 6 show two such typical responses, and Table S6 (Supporting Information) summarizes the potentials.

According to our experiments the cyclopentadienide/hydride complexes 1 and 2 first exhibit a reversible one-electron oxidation, followed by irreversible processes. The reversibility of the second oxidation (to "Ru<sup>IV</sup>") and the quasireversibility of the third oxidation of 1 as reported by Hembre et al.<sup>10a</sup> could not be reproduced. Changing the  $\pi$ accepting *P*-phenyl to the more  $\sigma$  donating *P*-isopropyl groups in going from 1 to 2 causes a decrease of the oxidation potential by about 270 mV.

The cymene/chloride complexes also exhibit a first reversible oxidation, albeit at higher potentials. The difference



(tentative oxidation state assignments)

#### Scheme 2

${(\mu-dpf)[(Cym)Ru^{II}Cl_2]_2}^{\circ}$	E1, -e <sup>-</sup> E2, +e <sup>-</sup>	$\{(\mu\text{-dpf}^+)[(Cym)Ru^{II}Cl_2]_2\}^+$
${(\mu-dpf^+)[(Cym)Ru^{II}Cl_2]_2}^+$	E3 -2e <sup>-</sup>	$\{(\mu\text{-}dpf^{+})[(Cym)Ru^{III}Cl_{2}]_{2}\}^{3+}$
{(µ-dpf)[(Cym)Ru <sup>II</sup> Cl <sub>2</sub> ] <sub>2</sub> }°	E4 +2e	${(\mu-dpf)[(Cym)RuCl_2]_2}^{2-}+2Cl_2$

between the dppf and dippf complexes (3 vs 4) amounts to only 110 mV. Whereas no reduction of the hydride complexes 1 and 2 was observed within the available potential range, the cationic chloride complexes 3-5 are reduced in a two-electron fashion with a back-oxidation in cyclic voltammetry at less negative potentials.<sup>11</sup> The underlying ECE reductive elimination/EEC oxidative addition mechanism between [M(C<sub>n</sub>R<sub>n</sub>)Cl(L)]<sup>+</sup> and [M(C<sub>n</sub>R<sub>n</sub>)(L)] forms is wellknown for such complexes (Scheme 1).<sup>5,22</sup>

The hydrido complex cation **6** exhibits a well-behaved reversible one-electron oxidation near that of the chloride precursor **3**, which is attributed to a  $Ru^{II}$ -ferrocenium configuration on the basis of EPR silence and absorption spectrum (cf. below). A second wave for irreversible oxidation with double intensity (Figure 6) is assigned to a proton-releasing oxidation of ruthenium. The trinuclear complexes **7–9** show a similar behavior on the anodic side; they are also reduced in an irreversible multielectron step (Scheme 2). as was noted before for compound **7**.<sup>16</sup>

**EPR Spectroscopy.** To identify the site of electron removal on oxidation, we have employed EPR spectroscopy. Although both iron(II) in ferrocene and ruthenium(II) centers are oxidized fairly easily, the resulting EPR signals in glassy frozen solution will differ significantly. Whereas organometallic ruthenium(III) centers in a coordination environment as in the complexes described here should lead to relatively small g anisotropy,  $\Delta g = g_1 - g_3$ , with individual g components between 1.5 and 3.0,<sup>23</sup> the ferrocenium system with its special symmetry and d orbital splitting is distinguished by broad EPR signals, often observable only at 4 K, with large g anisotropy  $\Delta g$ , especially one component at about g = 4; ferrocenium itself has  $g_{1,2} =$ 4.36 and  $g_3 = 1.28$ .<sup>24</sup>

Figure 7 shows the low-temperature (4 K) spectrum for the cyclopentadienide/hydride cation  $2^+$ , taken from in situ electrolytic oxidation of the precursor complex in THF/0.1 M Bu<sub>4</sub>NPF<sub>6</sub>. A representative EPR spectrum of the oxidized cymene/chloride complex  $3^+$  at 4 K has been shown earlier;<sup>11a</sup> the cymene/hydride system  $6^+$  did not exhibit an



Figure 7. EPR spectrum of electrogenerated  $2^+$  at 4 K in glassy frozen 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/THF.

EPR response under those conditions. Table S7 (Supporting Information) gives available *g* values.

It is thus obvious from the values in Table S7 that the hydride cations  $1^+$  and  $2^+$  are ferrocene/Ru(III) species, whereas the oxidized complexes  $[(Cym)RuCl(dpf)]^{2+}$  are ferrocenium/Ru<sup>II</sup> systems. The effects of substitution are only small, however, and it is most revealing that the osmium analogue  $10^+$  of  $3^+$  exhibits an almost identical ferrocenium-type EPR response<sup>11b</sup> despite the much higher spin–orbit coupling constant of that metal.

**IR Spectroelectrochemistry.** Infrared spectroelectrochemical studies of metal complexes have often focused on stretching bands of ligands such as CO, CN, and NO with multiple bonds because of the band intensity and the favorable, nonfingerprint spectral region around 2000 cm<sup>-1.25</sup> However, metal-hydride vibrations also occur frequently in that region,<sup>21</sup> albeit with lower intensity. We therefore took advantage of the reversibility of the oxidation processes for the ruthenium hydrides 1, 2, and 6 and studied the response of the M-H stretching band. Unfortunately, complex 6 with (Cym)Ru<sup>2+</sup> exhibited a very low intensity Ru-H stretching absorption at about 1950 cm<sup>-1</sup> which shifted only slightly to about 1975 cm<sup>-1</sup> on spectroelectrochemical oxidation. Compounds 1 and 2 involving electron-rich (C<sub>5</sub>Me<sub>5</sub>)-Ru<sup>+</sup> showed a better response (Figure 8, Table S8 (Supporting Information)), but even in this case the intensity was severely diminished in the oxidized (=dipositive) state, indicating a rather small dipole moment change of the Ru-H vibration. The high-energy shift of about 50 cm<sup>-1</sup> for the Ru-H stretch on oxidation of 1 or 2 reflects the oxidation of ruthenium and the enhanced Coulombic attraction, while the smaller shift for 6 is in agreement with a remote, ferrocene-based oxidation.

UV/Vis/Near-IR Spectroelectrochemistry. Similarly to EPR spectra, absorption spectra of oxidized species should indicate whether the ruthenium(II) center or the ferrocene iron is oxidized. Regular ruthenium(III) centers are expected to exhibit weak long-wavelength (vis/near-IR) ligand-field

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<sup>(23)</sup> Winter, R.; Hornung, F. M. Organometallics 1999, 18, 4005.

<sup>(24)</sup> Elschenbroich, C.; Bilger, E.; Ernst, R. D.; Wilson, D. R.; Kralik, M. S. Organometallics **1985**, *4*, 2068.

<sup>(25)</sup> Best, S. T. In *Spectroelectrochemistry*; Kaim, W., Klein, A., Eds.; RSC: Cambridge, U.K., 2008; p 1.



Figure 8. IR spectroelectrochemical oxidation of 2 at 298 K in  $0.1 \text{ M Bu}_4\text{NPF}_6/\text{THF}$ . Spectra were collected during the potential scan at the first oxidation peak.

(LF) transitions between occupied and unoccupied d orbitals.<sup>26a</sup> Ferrocenium systems, on the other hand, are wellknown to exhibit one weak absorption band at about 600 nm, involving a ligand-to-metal charge transfer (LMCT,  ${}^{2}E_{1u}$ ) transition.<sup>26</sup> The precursors to these oxidations do not interfere with the long-wavelength features because the compounds 1-6have their lowest energy bands in the UV region.

UV/vis spectroelectrochemistry of compounds 1-5 was performed in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> solutions in an optically transparent thin-layer electrolytic (OTTLE) cell. The results are illustrated in Figure 9 and given in Table S9 (Supporting Information).

The data from OTTLE spectroelectrochemistry confirm the results from EPR spectroscopy, assigning on initial ferrocene oxidation for the cymene/chloride and cymene/ hydride complexes ( $\lambda_{max} \sim 630$  nm,  $\varepsilon < 1000 \text{ M}^{-1} \text{ cm}^{-1}$ ) and a first ruthenium oxidation for the hydride compounds 1<sup>+</sup> and 2<sup>+</sup> ( $\lambda_{max} \sim 900$  nm, Figure S3 (Supporting Information)). Hembre et al.<sup>10a</sup> have attributed this latter transition to an intramolecular metal-to-metal charge-transfer (MM'CT) transition from Fe<sup>II</sup> to Ru<sup>III</sup> which would involve a distance of about 440 pm without conjugation. In our view a Rubased ligand field transition<sup>26a</sup> is also plausible.

### Summary

Due to the rigid chelate framework of the dpf ligands and due to their electronic capacity to act as noninnocent ligands (i.e., as dpf or dpf<sup>+</sup>), these systems can stabilize unusual metal configurations,<sup>27a</sup> including copper(I)–quinone



**Figure 9.** UV/vis spectroelectrochemical oxidation of **6** at 298 K in 0.1 M  $Bu_4NPF_6/CH_2Cl_2$ . Spectra were collected during the potential scan at the first oxidation peak.

entities.<sup>27b</sup> In this report we have shown how cationic hydridoruthenium groups can also be stabilized; otherwise, such groups are typically prone to facile decay via proton loss or via disproportionation.<sup>10b,g</sup> The control of the ruthenium and, by implication, of the ferrocene iron oxidation state through the organic 6e ligand  $\eta^n$ -C<sub>n</sub>R'<sub>n</sub> in  $[(\eta^n - C_nR'_n)RuH(dpf)]^k$  is responsible for the unambiguously established ambi-valence,  $Ru^{II} - Fe^{III}$  or  $Ru^{III} - Fe^{II}$ , on oxidation of ruthenium(II)-ferrocene precursors. Electron-rich C<sub>5</sub>Me<sub>5</sub><sup>-</sup> as coligand was found to favor the latter alternative, while complexes with neutral *p*-cymene yielded ruthenium(II)-ferrocenium configurations, both with RuH and RuCl complexes. Reactivity studies of these potential heterodimetallic "redox-switch" catalysts<sup>10a</sup> in either configuration with H<sub>2</sub>, CO<sub>2</sub>, or other relevant targets<sup>10</sup> will be the next research step.

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Supporting Information Available: CIF files giving X-ray crystallographic data for compounds 2, 4 and 5, Scheme S1 (syntheses), Tables S1–S9, and Figures S1 (space-filling model of 2), S2 (molecular structure of 4), and S3 (UV–vis spectrum of  $2^+$ ). This material is available free of charge via the Internet at http://pubs.acs.org.

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