

# IZCp and PZCp: Redox Non-innocent Cyclopentadienyl Ligands as Electron Reservoirs for Sandwich Complexes

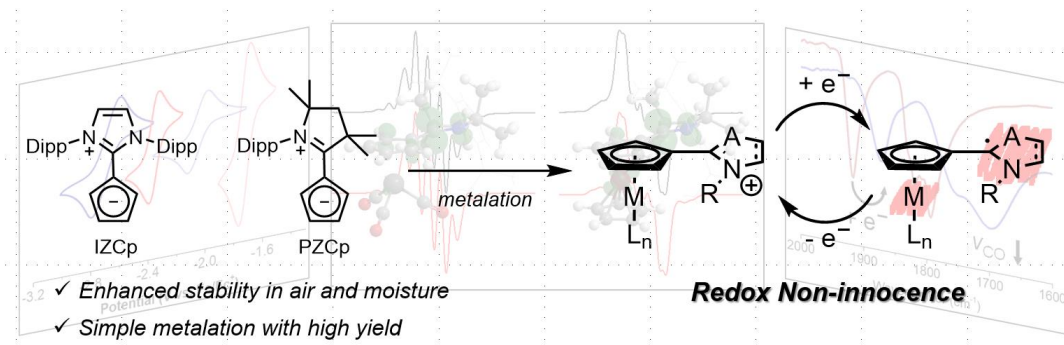
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**ABSTRACT:** Numerous developments in the electronic and steric modification of cyclopentadienyl (Cp) ligands have led to a corresponding growth in their applications. Herein, we present two new redox non-innocent Cp compounds, imidazolium- and pyrrolinium-substituted zwitterionic Cps (IZCp **1a** and PZCp **1b**). The Cps were obtained in high yields and could be handled easily owing to their high stability in air and moisture, unlike other known Cps. The redox non-innocent behavior of the Cp ligands was demonstrated via experimental and computational analyses of their half-sandwich and sandwich complexes. During cyclic voltammetry, the molybdenum half-sandwich (**3a**, **3b**) and ruthenium sandwich ([**4a**]PF<sub>6</sub>, [**4b**]PF<sub>6</sub>) complexes of IZCp and PZCp showed reversible one-electron reduction at a low potential ( $E_{1/2}$  ranging from  $-1.7$  to  $-2.7$  V vs. Fc/Fc<sup>+</sup>). This phenomenon has not been studied previously because of the high instability of the reduced complexes. DFT calculations for the reduced complexes ([**3a**]<sup>-</sup>, [**3b**]<sup>-</sup>, **4a**, and **4b**) confirmed that their spin density was mainly delocalized over the ligand center (70%–90%). EPR analysis of the isolated K[**3b**] and **4b** indicated their ligand-centered radical structures. Furthermore, the CO stretching frequencies of K[**3b**] ( $\nu_{\text{CO}}$  1871.35, 1748.10, and 1698.80 cm<sup>-1</sup>) revealed that the redox non-innocent [PZCp]<sup>-</sup> ligand is the strongest electron-donating Cp ligand among previously reported CpMo(CO)<sub>3</sub> derivatives ( $\nu_{\text{CO}} > 1746$  cm<sup>-1</sup>).



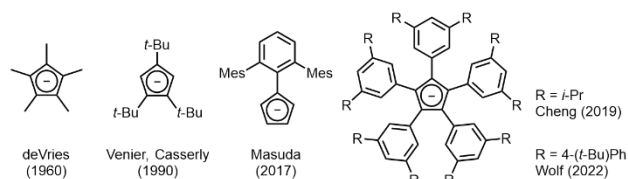
## Introduction

Since the discovery of ferrocene<sup>1</sup>, many different sandwich and half-sandwich complexes containing derivatized cyclopentadienyl (Cp) ligands have been used as catalysts in the syntheses of small molecules<sup>2</sup> or polymers<sup>3</sup> and as novel materials, such as pharmaceuticals<sup>4</sup> and single-molecular magnets.<sup>5</sup> Cp ligands typically form highly stable  $\eta^5$ -coordination with a wide range of transition metals, allowing only the intact chemical transformation of transition metal centers as innocent ligands. A variety of Cp derivatives with desirable electronic<sup>6, 7</sup> and steric<sup>8</sup> properties have been developed (**Figures 1a** and **1b**).

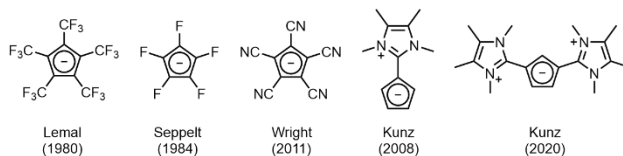
Research on redox non-innocent Cp ligands that can participate cooperatively in the redox chemistry of metal complexes has been relatively less studied. The complexes containing redox non-innocent ligands undergo oxidation state changes in both the corresponding metal and ligand.<sup>9</sup> In contrast, redox reactions in complexes of redox-innocent or

other redox-active ligands only affect metal or ligand, respectively. The development of redox non-innocent Cp ligands is important as they can serve as electron reservoirs to stabilize the high or low oxidation states of their metal complexes, thereby offering a route via which the performance of these complexes in applications, such as single-molecular magnets<sup>10</sup> and energy-storage materials,<sup>11</sup> can be improved. In this context, our group previously reported a novel application of pyrrolinium-substituted persistent zwitterionic ferrocene as an anolyte in redox flow batteries; here, the one-electron reduction of ferrocene, which is known to be highly unstable at room temperature,<sup>12</sup> was stabilized via derivatization with sterically hindered cationic N-heterocycle substituents.<sup>13</sup> However, the synthetic utility of our strategy is highly limited to ferrocene because it requires the direct functionalization of ferrocene via the nucleophilic attack of N-heterocyclic carbenes (NHCs) to access the redox non-innocent Cp ligand. Therefore, we sought to design new redox-innocent ligands by preparing NHC-derived zwitterionic Cp compounds for direct complexation with transition metals.

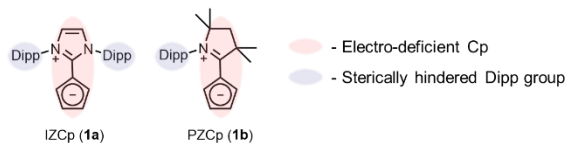
**(a) Examples of sterically congested Cp**



**(b) Examples of electro-deficient Cp**

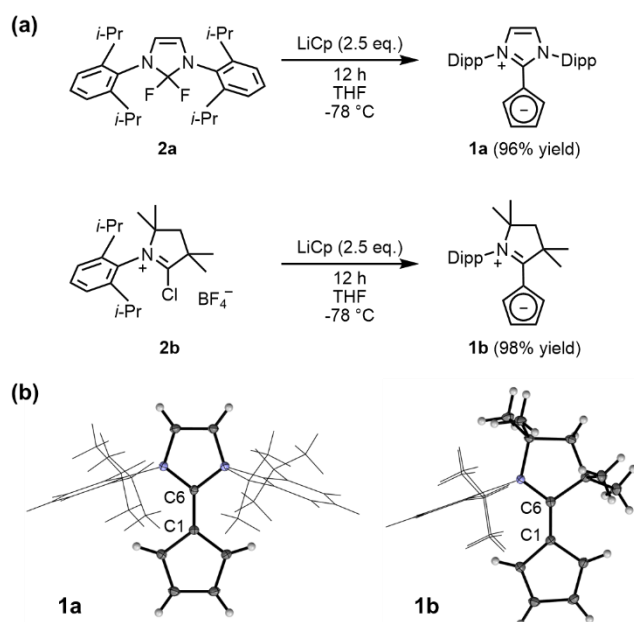


**(c) Redox non-innocent Cp ligands (This work)**



**Figure 1.** Selected examples of (a) sterically congested Cp and (b) electron-deficient Cp. (c) Redox non-innocent IZCp (**1a**) and PZCp (**1b**) ligands (Mes = mesityl, Dipp = 2,6-diisopropylphenyl).

Herein, we report the syntheses and characterization of the imidazolium- and pyrrolinium-substituted zwitterionic cyclopentadienides IZCp (**1a**) and PZCp (**1b**) (**Figure 1c**). Unlike general air-sensitive Cps, **1a** and **1b** showed high stability in air and moisture, which allowed for their easy storage and use. We also obtained their molybdenum half-sandwich (**3a** and **3b**) and ruthenium sandwich ( $[\mathbf{4a}]PF_6$  and  $[\mathbf{4b}]PF_6$ ) complexes. As electron reservoirs, **1a** and **1b** enabled the reversible one-electron reduction of **3a**, **3b**,  $[\mathbf{4a}]PF_6$ , and  $[\mathbf{4b}]PF_6$  at a highly negative potential. These results are especially noteworthy because, although several ZCp derivatives and their transition metal complexes have been reported,<sup>7, 14</sup> their use as redox non-innocent ligands has not been studied.



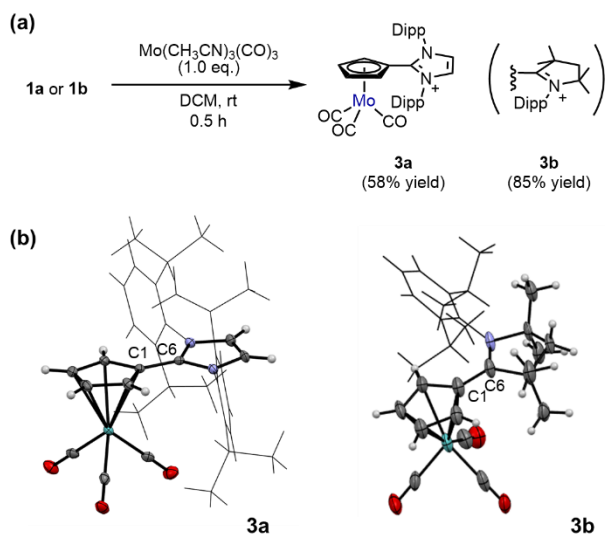
**Figure 2.** (a) Synthesis of the imidazolium-substituted Cp ligands and (b) solid-state structures of **1a** and **1b** determined by single-crystal X-ray crystallography. Selected experimental bond lengths [Å]: C1–C6 1.413(2) (**1a**), 1.389(3) (**1b**). Dipp groups are simplified for clarity.

First, we selected 2-haloimidazolium and 2-halopyrrolinium, which can easily be prepared by halogenating NHCs, as precursors to synthesize **1a** and **1b**. The reaction of 2-chloropyrrolinium (**2b**) with LiCp gave **1b** in high yield, but the reaction of 2-chloroimidazolium with LiCp gave free NHC. Thus, LiCp appears to preferentially react with the electron-deficient chloro group of 2-chloroimidazolium, rather than the aromatic C2 of imidazolium, to produce CpCl. The use of the commercially available reagent PhenoFluor (**2a**) as a precursor allowed the synthesis of **1a** in high yield (**Figure 2a**).

The single crystals of **1a** and **1b** could be obtained by recrystallization in pentane solution at  $-20$  °C. The solid-state structures of the Cps showed a distinct intermediate structure between those of ZCp and fulvene, depending on the  $\pi$ -acidity of their cationic N-heterocycles (**Figure 2b**). The bond length alternation (BLA) parameters of **1a** and **1b** were 0.042 and 0.079 Å, respectively, which lie between those of diphenylfulvene (0.119 Å) and other imidazolium-substituted ZCps (0.021 Å) due to the high  $\pi$ -acidity of their cationic N-heterocycles (**Figure S3**). **1a** showed more shielded Cp–H signals ( $\delta = 5.43$  and 4.94 ppm) than LiCp ( $\delta = 5.54$  ppm) owing to the perpendicular orientation of the two Dipp groups on Cp–H despite their electron-deficient cationic N-heterocycle substituents. The Cp–H signals of **1b** gradually became more shielded as the Dipp group was approached ( $\delta = 6.74, 5.93, 5.64,$  and 4.69 ppm). These results are significantly different from those of diphenylfulvene ( $\delta = 6.59$  and 6.23 ppm) and other cationic N-heterocycle-substituted ZCp ligands,<sup>7</sup> which generally exhibit more deshielded chemical shifts compared with LiCp.

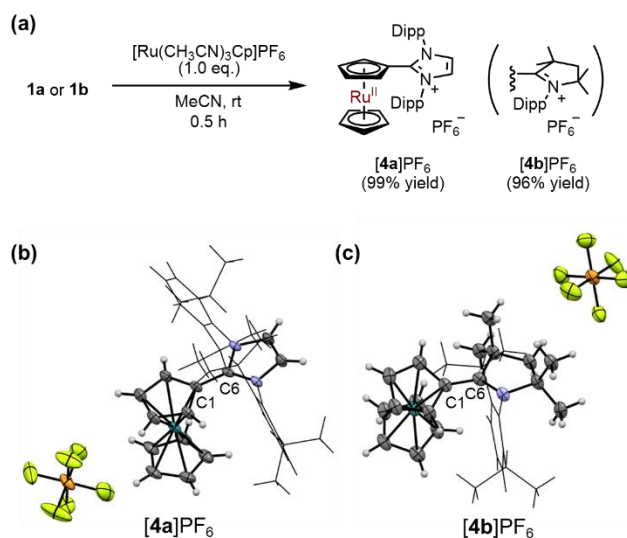
The solids **1a** and **1b** can be stored under air at room temperature for over 1 month without any decomposition. The air and moisture stability of the Cps in aerated solution was also confirmed by  $^1\text{H-NMR}$  monitoring experiments with internal standards (**Figures S17** and **S18**). Conventional Cp anions are well known to be unstable owing to their high reactivity with air and moisture. The air and moisture stability of Cp anion derivatives could be increased by adding an electron-poor substituent (e.g., phosphonium,<sup>15</sup> and pyridinium<sup>16</sup>) to the skeletal carbon of the Cp ring. In a recent study, Kunz's group reported the synthesis of air- and moisture-stable zwitterionic Cp ligands by reducing their nucleophilicity with two or three imidazolium substituents;<sup>7c</sup> in this study, the Cp ligand with only one imidazolium

substituent demonstrated relatively lower reductions in nucleophilicity and was sensitive to air and moisture (**Figure 1b**).<sup>7a</sup>



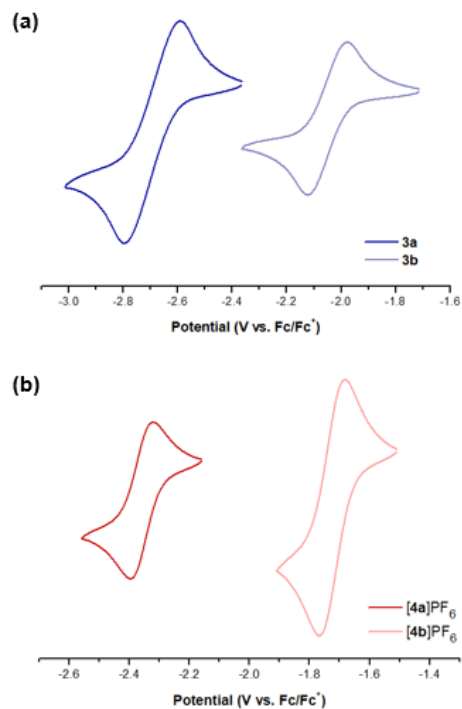
**Figure 3.** (a) Synthesis of **3a** and **3b**. (b) Solid-state structures of **3a** and **3b** determined by single-crystal X-ray crystallography. Selected experimental bond lengths [ $\text{\AA}$ ]: C1–C6 1.457(4) (**3a**), 1.432(9) (**3b**). Dipp groups are simplified and all solvent atoms are omitted for clarity.

Tricarbonyl molybdenum complexes **3a** and **3b** were obtained by the simple metalation of **1a** and **1b** using  $\text{Mo}(\text{MeCN})_3(\text{CO})_3$  as a precursor to investigate the electron-donating properties of **1a** and **1b** to a metal center (**Figure 3a**). The molecular structures of **3a** and **3b** were determined by X-ray crystallographic analysis (**Figure 3b**). The CO stretching frequencies of complexes **3a** ( $\nu_{\text{CO}}$  1902.16, 1797.40, and 1776.86  $\text{cm}^{-1}$ ; ATR) and **3b** ( $\nu_{\text{CO}}$  1916.54, 1817.94, and 1793.29  $\text{cm}^{-1}$ ; ATR) reflected the lower donor properties of ligands **1a** and **1b** compared with those of previously reported ZCp ligands (**Figure S16**).<sup>14c</sup> Because of their weak interaction with the Mo(0) center, **1a** and **1b** dissociated in coordinating solvents such as MeCN. Unlike **3a**, which was obtained as a tawny solid similar to the existing (ZCp)Mo(CO)<sub>3</sub> complex,<sup>14c</sup> **3b** exhibited an inherent deep-purple color. The red-shifted and stronger UV absorbance of **3b** at 514 nm compared with that of **3a** at 436 nm reflects favorable metal-to-ligand charge transfer (MLCT) owing to the stronger  $\pi$ -accepting redox domain of the pyrrolinium substituent compared with that of the imidazolium substituent (**Figure S5**).



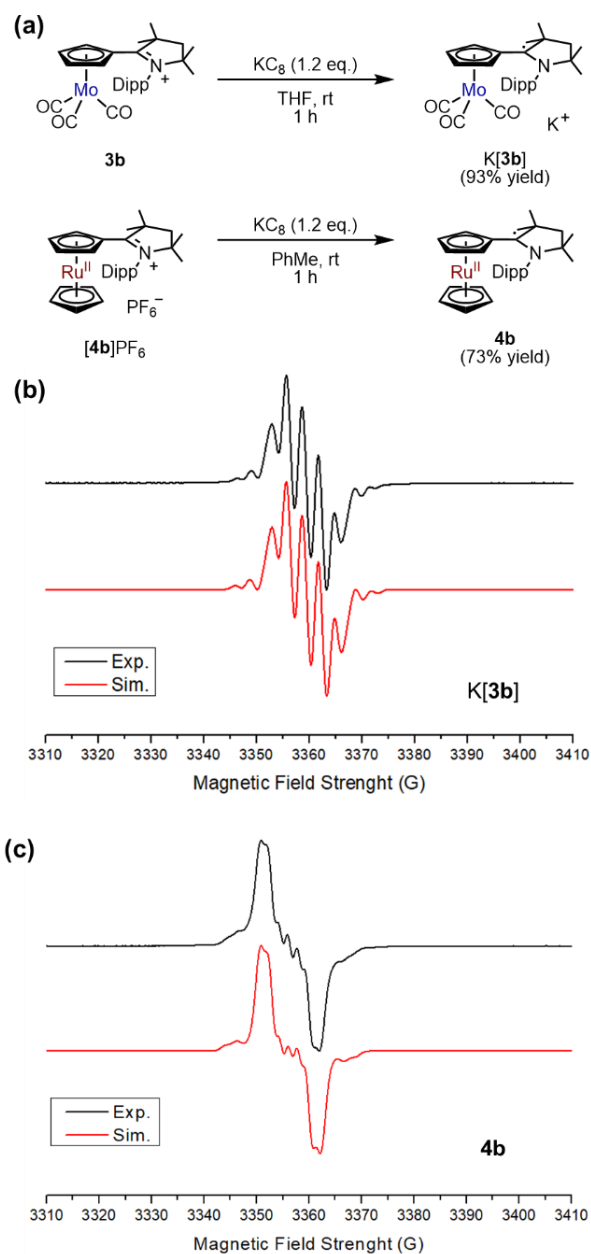
**Figure 4.** (a) Synthesis of  $[4a]PF_6$  and  $[4b]PF_6$ . (b) Solid-state structures of  $[4a]PF_6$  and  $[4b]PF_6$  determined by single-crystal X-ray crystallography. Selected experimental bond lengths ( $\text{\AA}$ ): C1–C6 1.454(4) ( $[4a]PF_6$ ), 1.451(6) ( $[4b]PF_6$ ). Dipp groups are simplified and all solvent atoms are omitted for clarity.

Based on our previous report on zwitterionic ferrocenate derivatives,<sup>13</sup> we expected that the sterically hindered ZCP ligands **1a** and **1b** could be applied to the reversible reduction of other sandwich complexes as redox non-innocent ligands. Thus, we synthesized the ruthenocene derivatives  $[4a]PF_6$  and  $[4b]PF_6$  by the simple reaction of **1a** and **1b** with  $[Ru(CH_3CN)_3Cp]PF_6$  to investigate their ligand properties;  $[4a]PF_6$  and  $[4b]PF_6$  were obtained in high yield (**Figure 4**). The molecular structures of the crystalline solids of  $[4a]PF_6$  and  $[4b]PF_6$  were determined by X-ray crystallographic analysis (**Figure 4b**).



**Figure 5.** Cyclic voltammograms of (a) **3a** and **3b** in 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub>/THF and (b) [**4a**]PF<sub>6</sub> and [**4b**]PF<sub>6</sub> in 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub>/MeCN (vs. Fc/Fc<sup>+</sup>, scan rate = 0.1 V s<sup>-1</sup>).

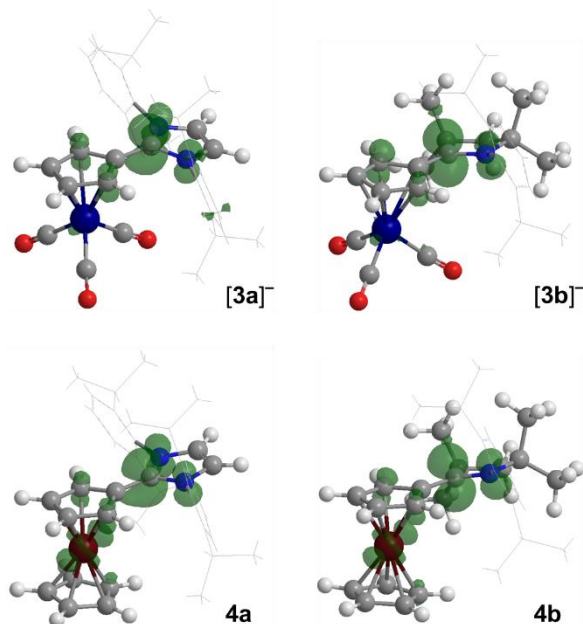
Next, we investigated the reduction properties of half-sandwich and sandwich complexes bearing the ZCp ligands. Because of the low stability of **3a** and **3b** in MeCN, their cyclic voltammograms were characterized in THF. Interestingly, despite the weak binding of the ZCp ligands to Mo(0), **3a** and **3b** showed reversible one-electron reduction peaks at  $E_{1/2} = -2.70$  V ( $i_{pa}/i_{pc} = 0.95$ ) and  $E_{1/2} = -2.05$  V ( $i_{pa}/i_{pc} = 0.99$ ) (vs Fc/Fc<sup>+</sup>) in 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub>/THF solution, respectively (**Figures 5a, S9, and S10**). Previous examples of ruthenocene derivatives with one and more imidazolium substituents showed irreversible one-electron reduction,<sup>7c</sup> but the cyclic voltammograms of [**4a**]PF<sub>6</sub> and [**4b**]PF<sub>6</sub> demonstrated reversible one-electron reduction at  $E_{1/2} = -2.36$  V ( $i_{pa}/i_{pc} = 0.96$ ) and  $E_{1/2} = -1.72$  V ( $i_{pa}/i_{pc} = 0.95$ ) (vs. Fc/Fc<sup>+</sup>) in 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub>/MeCN solution, respectively (**Figures 5b, S11, and S12**). These results are fairly similar to the reduction potentials of our previous ferrocene derivatives bearing ZCp ligands ([ (IZCp)FeCp]PF<sub>6</sub>: -2.40 V and [(PZCp)FeCp]PF<sub>6</sub>: -1.69 V vs. Fc/Fc<sup>+</sup>),<sup>13</sup> thereby implying ZCp ligand-centered reduction for M(II)-metallocene derivatives. Unfortunately, the one-electron oxidation of [**4a**]PF<sub>6</sub> and [**4b**]PF<sub>6</sub> was irreversible ( $E_{pc} = 0.77$  V for [**4a**]PF<sub>6</sub> and 0.75 V for [**4b**]PF<sub>6</sub> vs. Fc/Fc<sup>+</sup>) even in non-coordinating media, such as [Bu<sub>4</sub>N][BAR<sup>F</sup><sub>4</sub>] electrolyte in DCM, to prevent the decomposition pathway of ruthenocenium (**Figure S13**).<sup>17</sup>



**Figure 6.** (a) Stoichiometric reduction of **3a** and **[4b]PF<sub>6</sub>**, (b) EPR spectra of **K[3b]** in 2-MeTHF [ $g_{\text{iso}} = 2.00318$ ,  $A(\text{Mo}) = 7.74940$ ,  $A(\text{N}) = 8.87312$ ,  $A(\text{H}) = 8.13907$ ,  $A(\text{H}) = 5.76264$  MHz] at room temperature, and (c) EPR spectra of **4b** in toluene [ $g_{\text{iso}} = 2.00814$ ,  $A(\text{Ru}) = 7.56448$ ,  $A(\text{N}) = 9.60461$ ,  $A(\text{H}) = 5.02136$ ,  $A(\text{H}) = 4.61759$  MHz] at room temperature.

We also attempted to characterize the reduced complexes **[3a]<sup>-</sup>**, **[3b]<sup>-</sup>**, **4a**, and **4b** generated by the stoichiometric reduction of **3a**, **3b**, **[4a]PF<sub>6</sub>**, and **[4b]PF<sub>6</sub>** using **KC<sub>8</sub>** (**Figure 6a**). The reduction of **3b** in THF afforded an EPR-active dark-brown solid **K[3b]** in 93% yield, but the reduction of **3a** did not yield any EPR-active product. The reduction of **[4b]PF<sub>6</sub>** in toluene also produced a brown oily solid (73% yield) that was highly soluble in pentane and toluene, indicating a neutral complex; however, the reduction of **[4a]PF<sub>6</sub>** in toluene did not produce the same results. These findings indicate that, in contrast to the relatively high stability of the second-row transition metal complex of IZCp,<sup>13</sup> the one-electron-reduced third-row transition metal complexes introduced with IZCp (**3a** and **[4a]PF<sub>6</sub>**) are difficult to

isolate despite their electrochemically reversible reduction. The X-band EPR spectra of the corresponding products gave a narrow  $g$ -value, thereby confirming the ligand-centered radical character of these complexes (**Figures 6b** and **6c**).<sup>9b</sup> The EPR spectra of K[**3b**] in 2-MeTHF and **4b** in toluene at room temperature showed isotropic hyperfine couplings with Mo and Ru isotopes, respectively. These results could be reproduced by DFT calculations for their optimized structures using ORCA at the B3LYP/ZORA-def2-TZVP (C, N, O, H)/SARC-def2-TZVP (Ru, Mo) levels (**Table S7**). Notably, the CO stretching frequencies of complex K[**3b**] ( $\nu_{\text{CO}} = 1871.35, 1748.10, 1698.80 \text{ cm}^{-1}$ , **Figure S16**) are among the lowest obtained for known neutral<sup>14a, 14c</sup> and anionic<sup>18</sup> CpMo(CO)<sub>3</sub> complexes ( $\nu_{\text{CO}} > 1746 \text{ cm}^{-1}$ ). This result indicates that the redox non-innocent [PZCp]<sup>-</sup> ligand has the strongest electron-donating property toward the Mo(0) center among the Cp ligands reported thus far.



**Figure 7.** Visualized Mulliken spin densities of [3a]<sup>•-</sup>, [3b]<sup>•-</sup>, 4a, and 4b (Gaussian 16, B3LYP/Def2-SVP, isovalue = 0.05 (electrons/bohr<sup>3</sup>)<sup>1/2</sup>).

Finally, we attempted to theoretically confirm the electronic properties of the one-electron reduced derivatives [3a]<sup>•-</sup>, [3b]<sup>•-</sup>, 4a, and 4b. According to the DFT calculation results, most of the spin densities of complexes [3a]<sup>•-</sup>, [3b]<sup>•-</sup>, 4a, and 4b are delocalized on ZCp ligands (spin densities on the metal center/ZCP ligand: 5.2%/93.7% for [3a]<sup>•-</sup>, 4.9%/91.1% for [3b]<sup>•-</sup>, 21.4%/72.9% for 4a and 16.1%/79.1% for 4b, **Figure 7**). These results show that ZCp ligands **1a** and **1b**, as redox non-innocent ligands, have a small effect on the redox state of the transition metal center. By comparison, the spin densities of the ruthenocene groups ((C<sub>3</sub>H<sub>4</sub>)RuCp) for 4a and 4b radicals were 35.3% and 23.5%, respectively, which are lower than the total spin densities of the ferrocene groups ((C<sub>5</sub>H<sub>4</sub>)FeCp) for (IZCp)FeCp (44.8%) and (PZCp)FeCp (28.0%) radicals.<sup>13</sup> These findings indicate that the zwitterionic metallocenate character of 4a and 4b is lower than that of (IZCp)FeCp and (PZCp)FeCp radicals.

In summary, the new Cp ligands imidazolium-/pyrrolinium-substituted zwitterionic cyclopentadienide (IZCp **1a**, PZCp **1b**) were synthesized in high yield and fully characterized. **1a** and **1b** showed not only remarkable stability in air and moisture, in contrast to conventional Cps, but also easy metalation ability. These new ligand systems were then used to synthesize molybdenum half-sandwich complexes and ruthenocene derivatives (for IZCp: **3a** and [4a]PF<sub>6</sub>; for PZCp: **3b** and [4b]PF<sub>6</sub>), which were obtained in high yield and also fully characterized. The reversible one-electron reduction of these complexes at low potentials ( $E_{1/2} = -2.69 \text{ V}$  (**3a**),  $-2.05 \text{ V}$  (**3b**),  $-2.36 \text{ V}$  ([4a]PF<sub>6</sub>), and  $-1.72 \text{ V}$  ([4b]PF<sub>6</sub>) vs. Fc/Fc<sup>+</sup>) could be attributed to the steric bulkiness and  $\pi$ -accepting ability of the imidazolium-/pyrrolinium-substituents. The stoichiometric reduction of **3b** and [4b]PF<sub>6</sub> using KC<sub>8</sub> proceeded to yield K[**3b**] and **4b** radical



complexes. The mainly ligand-centered radical character of these complexes was confirmed by EPR analysis and supported by DFT calculations. The results collectively indicate the utility of our IZCp and PZCp ligands as redox non-innocent Cp ligands that could preserve the structure of sandwich and half-sandwich complexes. Further studies on the applications of IZCp and PZCp ligands to develop new single-molecular magnets are currently underway in our laboratory.

**Supporting Information.** Experimental details, X-ray crystallographic analysis, Computational details, and other characterization data. The crystallographic data for **2a**, **2b**, **3a**, **3b**, [**4a**]PF<sub>6</sub>, and [**4b**]PF<sub>6</sub> are deposited in the Cambridge Crystallographic Data Centre (CCDC) with deposition numbers CCDC 2208136–2208141.

## Acknowledgments

X-ray crystallographic analysis with synchrotron radiation was performed at the Pohang Accelerator Laboratory (PLS-II BL2D SMC beamline). This work was supported by (1) the National Research Foundation of Korea (NRF-2019R1A2C2010732, NRF-2019M1A2A2067940), (2) Samsung Science and Technology Foundation (SSTF-BA2002-09), (3) National Supercomputing Center with supercomputing resources, including technical support (KSC-2019-CRE-0162), and (4) the postdoctoral research fellowship of the POSTECH Initiative for fostering the Unicorn of Research & Innovation (PIURI) project.

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