Synthesis of (η^5-Pentamethylcyclopentadienyl)ruthenium π-Complexes of Heterocycles by Nucleophilic Substitution†

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*Summary: Cp*Ru$^+$ π-complexes of 1,2-dihalo- and 1,2,4,5-tetrahaloaromatics are readily prepared by reaction of the arenes with Cp*Ru(CH$_3$CN)$_3^+$OTf$^-$. The π-complexes undergo nucleophilic substitutions with 1 or 2 equiv of 1,2-disubstituted aromatic nucleophiles, leading to symmetrically and unsymmetrically substituted organometallic heterocycles.*

Introduction

Recently we demonstrated the outstanding ability of Cp*Ru$^+$ (Cp* = pentamethylcyclopentadienyl) to form π-complexes with highly electron deficient aromatics such as 1,3,5-trichloro-, 1,2,4,5-tetrachloro-, pentachloro-, and hexachlorobenzene.[1] The π-arene syntheses proceed by ligand exchange with [Cp*Ru(CH$_3$CN)$_3$]$^+$OTf$^-$ in polar solvents under mild reaction conditions. We also reported the extraordinary activating ability of the Cp*Ru$^+$ moiety, as shown by rapid and quantitative nucleophilic substitution reactions of the tri- and tetrachlorobenzene π-complexes with preformed potassium salts of phenols or thiophenols.[2,3] Overall, the Cp*Ru$^+$ fragment acts as an activating group and also as a solubilizing agent[4] and provides a versatile organometallic tool for construction of highly functionalized arene architectures.

We now report extensions of this Cp*Ru$^+$ complexation, activation, and nucleophilic substitution chemistry to the synthesis of a series of symmetrically and unsymmetrically substituted organometallic heterocycles.[5]

Results and Discussion

Synthesis and Characterization of Cp*Ru$^+$ π-Complexes. Synthesis of Cp*Ru$^+$ π-complexes **1**-**4** is accomplished by the ligand exchange reaction of [Cp*Ru(CH$_3$CN)$_3$]$^+$OTf$^-$ with an excess of the corresponding haloaromatic in THF or dioxane under mild reaction conditions (see Scheme 1).[6] The remarkable π-complexing ability of Cp*Ru$^+$[7] allows the direct solution synthesis of even highly fluorinated arene π-complexes such as 1,2,4,5-tetrafluorobenzene (**4**). 1,2-Dihaloaromatics **1** and **2** provide a platform for reaction with 1 equiv of a 1,2-disubstituted nucleophile, while 1,2,4,5-tetrahaloaromatics **3** and **4** can react with 2 equiv of a 1,2-disubstituted nucleophile.

Unoptimized reactions afford dihaloaromatic complexes **1** and **2** in excellent yield (92−94%) and tetrahaloaromatic complexes **3** and **4** in good yield (78%). As we noted previously, the yields can be increased substantially if very large excesses (10−15 equiv) of the haloaromatic are used. The ^{1}H and ^{13}C NMR spectra, positive-ion fast atom bombardment (FAB) mass spectral analyses, and elemental microanalyses of compounds **1**−**4** confirm the Cp*Ru$^+$ π-complexation (see Experimental Section).

Nucleophilic Substitution of Cp*Ru$^+$ π-Complexes. The activating ability of the Cp*Ru$^+$ moiety is demonstrated by nucleophilic displacement reactions of π-arenes **1**−**4** with 1,2-disubstituted nucleophiles to afford organometallic heterocycles **5**−**10**. The nucleophiles are the dipotassium salts of catechol and 1,2-benzenedithiol and the potassium salts of 2-aminophenol and 2-aminothiophenol. The reactions occur under very dilute conditions in CH$_3$CN or DMSO solvent at 60−85 °C for 5−18 h. The Cp*Ru$^+$ complexes of dibenzodioxin (**5**), thianthrene (**6**) and the corresponding bis(dibenzodiozin) (**9**) and bis(thianthrene) species (**10**) arise from nucleophilic displacement by symmetrically substituted nucleophiles, while complexes of phenoxazine (**7**) and phenothiazine (**8**) are formed from reactions with unsymmetrically substituted nucleophiles.

Specifically, the symmetrical heterocycles **5** and **6** are prepared by reaction of the dichlorobenzene Cp*Ru$^+$ π-complex **1** with 1 equiv of the corresponding dipotassium salts of catechol or 1,2-benzenedithiol in CH$_3$CN

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(1) (a) Dembek, A. A.; Fagan, P. J. *Organometallics* **1995**, *14*, 3741. (b) Dembek, A. A. U.S. Patent 5,386,044, 1994.

(2) For background on transition-metal-activated nucleophilic aromatic substitution, see: (a) Pearson, A. J. *Metallo-Organic Chemistry*; Wiley: New York, 1985; Chapter 9, and references therein. (b) Watts, W. E. The Organic Chemistry of Metal-Coordinated Cyclopentadienyl and Arene Ligands. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, Chapter 59, and references cited therein.

(3) For specific examples of transition-metal-activated nucleophilic substitution, see: (a) Pearson, A. J.; Park, J. G.; Yang, Y. S.; Chuang, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1363. (b) Pearson, A. J.; Park, J. G.; Zhu, P. Y. *J. Org. Chem.* **1992**, *57*, 3583. (c) Pearson, A. J.; Zhu, P. Y.; Youngs, W. J.; Bradshaw, J. D.; McConville, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 10376. (d) Pearson, A. J.; Gelormini, A. M. *Macromolecules* **1994**, *27*, 3675. (e) Pearson, A. J.; Gelormini, A. M. *J. Org. Chem.* **1994**, *59*, 4561. (f) Abd-El-Aziz, A. S.; Schriemer, D. C.; de Denus, C. R. *Organometallics* **1994**, *13*, 374. (g) Abd-El-Aziz, A. S.; de Denus, C. R. *J. Chem. Soc., Chem. Commun.* **1994**, 663.

(4) (a) Dembek, A. A.; Fagan, P. J.; Marsi, M. *Macromolecules* **1993**, *26*, 2992. (b) Dembek, A. A.; Marsi, M. U.S. Patent 5350832, 1994. (c) Dembek, A. A.; Fagan, P. J.; Marsi, M. *Polym. Mater. Sci. Eng.* **1994**, *71*, 158.

(5) (a) Simonsen, S. H.; Lynch, V. M.; Sutherland, R. G.; Piorko, A. *J. Organomet. Chem.* **1985**, *290*, 387. (b) Sutherland, R. G.; Piorko, A.; Gill, U. S.; Lee, C. C. *J. Heterocycl. Chem.* **1982**, *19*, 801. (c) Abboud, K. A.; Lynch, V. M.; Simonsen, S. H.; Piorko, A.; Sutherland, R. G. *Acta Crystallogr.* **1990**, *C46*, 1018.

(6) The 1,2,4,5-tetrachlorobenzene π-arene **3** was reported in our previous paper.[1]

(7) (a) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981. (b) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. (c) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485. (d) Glatzhofer, D. T.; Liang, Y.; Khan, M. A.; Fagan, P. J. *Organometallics* **1991**, *10*, 833. (e) Moriarty, R. M.; Gill, U. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157. (f) Glatzhofer, D. T.; Liang, Y.; Funkhouser, G. P.; Khan, M. A. *Organometallics* **1994**, *13*, 315.

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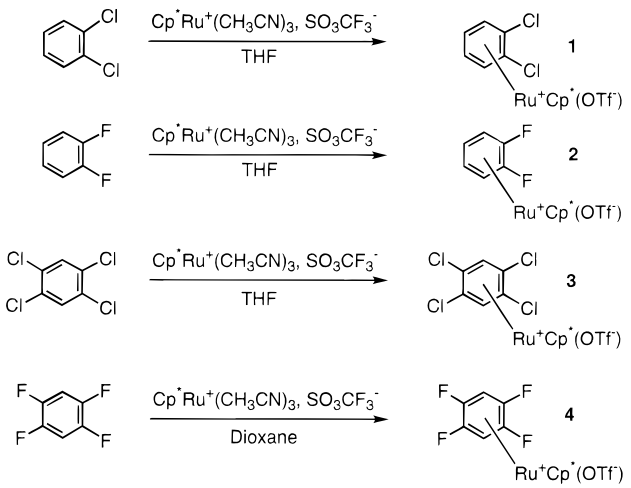
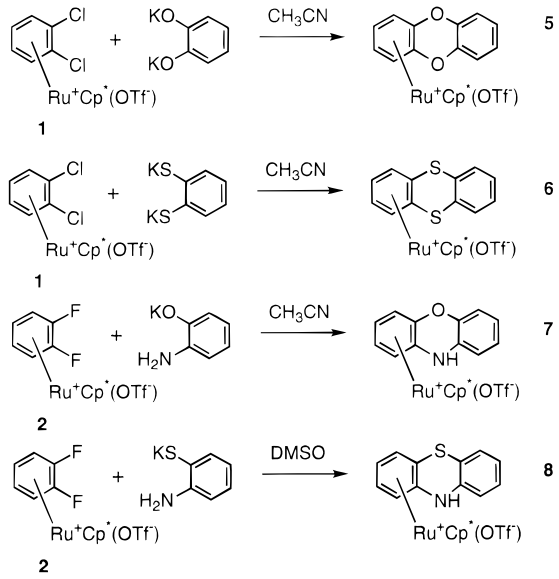
Scheme 1



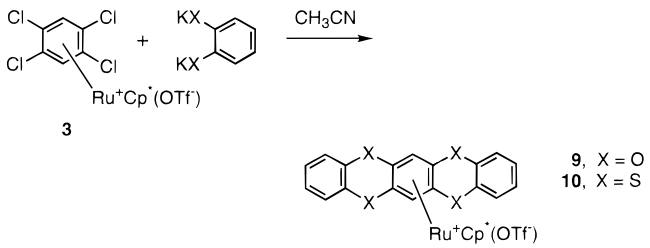
Scheme 2



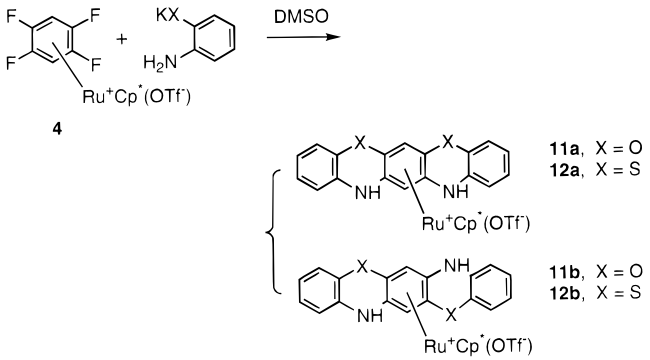
(see Scheme 2). The unsymmetrical heterocycles **7** and **8** are prepared by reaction of the 1,2-difluorobenzene complex **2** with 2-aminophenoxide and 2-aminothiophenoxide in CH_3CN and DMSO, respectively. Typically, we found that quantitative nucleophilic substitution with aromatic amines as one component of the nucleophile requires using the more highly activated *fluoro*-aromatic electrophiles, higher temperatures, and longer reaction times. For compounds **7** and **8**, the phenoxide/thiophenoxide nucleophile is likely the first nucleophile to add,[8] which is a nice selectivity feature. Reaction of **2** with 1,2-diaminobenzene under a variety of reaction conditions does not effect complete C−F displacement to afford the corresponding symmetrical heterocycle phenazine.

In general, the reaction mixtures for **5**−**8** are heterogeneous due to the limited solubility of the preformed potassium salt and are highly colored. Dilute concentrations promote formation of the desired heterocycle and eliminate reaction of the nucleophile with two different Cp*Ru$^+$ dihalobenzene π-complexes. ^{1}H NMR spectroscopy using CH_3CN-d_3 or DMSO-d_6 as the reaction solvent shows quantitative conversion of the starting π-arene to the desired product, as evidenced by an upfield shift in the aromatic resonances of the Cp*Ru$^+$ π-complex. The isolated yields of compounds **5**−**8** are 56−76% due to unavoidable product losses during the aqueous extraction in the purification scheme. Characterization of the recrystallized compounds by ^{1}H and ^{13}C NMR spectroscopy, FAB mass spectral analysis and elemental microanalysis support the heterocycle structure.

Scheme 3



Scheme 4



The Cp*Ru$^+$ tetrachlorobenzene π-complex **3** reacts with 2 equiv of the dipotassium salt of catechol or 1,2-benzenedithiol in dilute CH_3CN to afford the corresponding organometallic bis(dibenzodioxin) (**9**) and bis(thianthrene) (**10**) derivatives (see Scheme 3). These syntheses further exemplify the extraordinary activating ability of the Cp*Ru$^+$ moiety. Monitoring the reaction by ^{1}H NMR spectroscopy in CH_3CN-d_3 shows complete conversion of arene **3** to the tetrasubstituted product. Specifically, the ^{1}H NMR spectra (DMSO-d_6) of **9** and **10** show singlet resonances at 6.98 and 7.00 ppm, respectively, for the tetrasubstituted Cp*Ru$^+$ π-complexed arene. Product losses during isolation and purification lower the final yields to 63 and 51%, respectively.

The analogous reaction of Cp*Ru$^+$ tetrafluorobenzene π-complex **4** with 2 equiv of 2-aminophenoxide or 2-aminothiophenoxide in dilute DMSO at 120 °C for 16 h affords a mixture of the *cis* and *trans* tetrasubstituted heterocycles **11** and **12** (see Scheme 4). The progress of the reaction is monitored by ^{1}H NMR spectroscopy using DMSO-d_6 as the reaction solvent. Preliminary ^{1}H and ^{13}C NMR spectroscopy and FAB mass spectral analysis on the product mixtures support formation of the tetrasubstituted heterocycles. However, complete separation and purification of the series of *cis*/*trans* isomers for **11** and **12** was not accomplished, and characterization data are not included in this paper.

A portion of pure compound **11a** was isolated by selective recrystallization from a CH_3CN/THF mixed-solvent system. ^{1}H NMR spectroscopy (DMSO-d_6)

(8) Lee, C. C.; Zhang, C. H.; Abd-El-Aziz, A. S.; Piorko, A.; Sutherland, R. G. *J. Organomet. Chem.* **1989**, *364*, 217.

shows two singlet resonances at 5.47 and 6.10 ppm, which correspond to the two inequivalent protons on the Cp^*Ru^+ π-complexed arene and a singlet resonance at 9.17 ppm for the NH resonance, supporting the *cis* heterocycle formation.

Decomplexation of the Cp^*Ru^+ heterocycles **5**−**10** was explored by traditional arene displacement reactions (decomplexation thermally in DMSO at 160 °C for 2 h or photochemically (450 W) in CH_3CN for 1 h). No decomplexation was detected. This result was expected and was observed previously in our attempts to decomplex tri- and tetrafunctionalized π-arenes containing electron-donating substituents.[1] Overall, the outstanding π-complexing ability of the Cp^*Ru^+ moiety, especially to highly electron rich aromatics and heterocycles, limits use of traditional decomplexation chemistry.

Experimental Section

General Procedures. All procedures were carried out in a glovebox under a nitrogen atmosphere or in Schlenk-type glassware on a vacuum line. Tetrahydrofuran (THF) was dried and distilled from sodium metal under nitrogen before use. All other solvents, purchased as anhydrous grade from Aldrich, were stored over 3 Å molecular sieves under nitrogen before use. $Cp^*Ru^+(CH_3CN)_3OTf^-$ was prepared by using the procedures described previously.[7] All reagents (Aldrich) were used as received. The potassium salts of catechol, 1,2-benzenedithiol, 2-aminophenol, and 2-aminothiophenol were prepared by reaction of the corresponding phenolic/thiophenolic compound with potassium *tert*-butoxide (1.00 equiv/OH or SH) in THF at 66 °C for 6 h. In general, the salts were THF insoluble and were collected by filtration under nitrogen, dried in vacuo at 60 °C for 16 h and powdered before use.

^1H (300.0 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a QE300 GE spectrometer using DMSO-d_6 as solvent with tetramethylsilane as an external standard. Positive-ion atom fast atom bombardment (FAB) mass spectra were taken with a VG ZAB-E double-focusing instrument equipped with a Xe-gas ionization gun. Elemental analyses were preformed by MicroAnalysis, Inc., Wilmington, DE.

[Cp*Ru(η^6-1,2-dichlorobenzene)]$^+$OTf$^-$ (1). A 100 mL Schlenk flask was charged with 1,2-dichlorobenzene (1.3 g, 8.78 mmol, 1.5 equiv) and $Cp^*Ru^+(CH_3CN)_3OTf^-$ (3.0 g, 5.85 mmol) in THF (60 mL). The reaction mixture was stirred and heated at 66 °C for 16 h and allowed to cool to room temperature. Diethyl ether (ca. 30 mL) was added to the solution to precipitate a white solid that was collected by filtration, washed twice with 10 mL portions of diethyl ether, and dried in vacuo. Yield: 94%. ^1H NMR (DMSO-d_6): 6.66−6.62 (m, 2 H, arene), 6.16−6.12 (m, 2 H, arene), 1.89 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 103.5, 97.8, 88.5, 87.8, 9.0 ppm. MS (positive FAB): calcd *m*/*z* cation 382.99; found *m*/*z* cation 383.02. Anal. Calcd for $C_{17}H_{19}O_3SCl_2F_3Ru$: C, 38.35; H, 3.60. Found: C, 38.04; H, 3.36.

[Cp*Ru(η^6-1,2-difluorobenzene)]$^+$OTf$^-$ (2). Compound **2** was prepared by the same procedure described for **1** using 1.5 equiv of 1,2-difluorobenzene. Yield: 92%. ^1H NMR (DMSO-d_6): 6.79−6.75 (m, 2 H, arene), 6.00−5.96 (m, 2 H, arene), 1.97 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 126.3 (d, $^1J_{CF}$ = 279 Hz), 97.8, 85.6, 78.2 (m), 9.5 ppm. MS (positive FAB): calcd *m*/*z* cation 351.05, found *m*/*z* cation 351.04. Anal. Calcd for $C_{17}H_{19}O_3SF_5Ru$: C, 40.88; H, 3.83. Found: C, 40.27; H, 3.53.

[Cp*Ru(η^6-1,2,4,5-tetrachlorobenzene)]$^+$OTf$^-$ (3). Compound **3** was prepared by the same procedure described for **1** using 1.3 equiv of 1,2,4,5-tetrachlorobenzene. Yield: 78%. ^1H NMR (DMSO-d_6): 7.66 (s, 2 H, arene), 1.82 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 130.2, 99.3, 88.5, 8.0 ppm. MS (positive FAB): calcd *m*/*z* cation 450.9, found *m*/*z* cation 450.9. Anal. Calcd for $C_{17}H_{17}Cl_4RuSO_3F_3$: C, 33.96; H, 2.85. Found: C, 33.83; H, 2.66.

[Cp*Ru(η^6-1,2,4,5-tetrafluorobenzene)]$^+$OTf$^-$ (4). A 50 mL Schlenk flask was charged with 1,2,4,5-tetrafluorobenzene (1.2 g, 7.87 mmol, 4.0 equiv) and $Cp^*Ru^+(CH_3CN)_3OTf^-$ (1.0 g, 1.97 mmol) in dioxane (20 mL). The reaction mixture was stirred, heated to 85 °C for 16 h, and to cooled to room temperature. The solids that precipitated during the reaction and on cooling were collected by filtration, washed twice with 10 mL portions of diethyl ether, and dried in vacuo. Yield: 78%. ^1H NMR (DMSO-d_6): 8.02−8.00 (m, 2 H, arene), 2.00 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 122.6 (d, $^1J_{CF}$ = 270 Hz), 98.3 (d, J = 220 Hz), 69.0 (m), 9.3 (d, J = 27 Hz) ppm. MS (positive FAB): calcd *m*/*z* cation 387.03, found *m*/*z* cation 387.03. Anal. Calcd for $C_{17}H_{17}O_3SF_7Ru$: C, 38.13; H, 3.20. Found: C, 37.62; H, 3.00.

[Cp*Ru(η^6-dibenzodioxin)]$^+$OTf$^-$ (5). A 50 mL Schlenk flask was charged with **1** (0.25 g, 0.47 mmol) and the dipotassium salt of catechol (0.105 g, 0.56 mmol, 1.2 equiv) in CH_3CN (25 mL). The heterogeneous reaction mixture was stirred at 25 °C for 3 h and warmed to 60 °C for 16 h. The solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 (15 mL), this solution was extracted with water (2 × 20 mL), and the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was dissolved in CH_3CN (ca. 8 mL). Slow addition of diethyl ether (ca. 10 mL) precipitated a white solid that was collected by filtration and dried in vacuo. Yield: 57%. ^1H NMR (DMSO-d_6): 7.20−7.12 (m, 4 H, Ar H), 6.31−6.28 (m, 2 H, arene), 5.87−5.84 (m, 2 H, arene), 1.82 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 139.0, 125.9, 117.2, 115.8, 96.6, 84.7, 76.8, 9.9 ppm. MS (positive FAB): calcd *m*/*z* cation 421.1, found *m*/*z* cation 421.1. Anal. Calcd for $C_{23}H_{23}O_5F_3SRu$: C, 48.50; H, 4.07. Found: C, 48.42; H, 3.88.

[Cp*Ru(η^6-thianthrene)]$^+$OTf$^-$ (6). Compound **6** was prepared by the same procedure described for **5** using 1.2 equiv of the dipotassium salt of 1,2-benzenedithiol. Yield: 56%. ^1H NMR (DMSO-d_6): 7.64−7.61 (m, 2 H, Ar H), 7.48−7.44 (m, 2 H, Ar H), 6.44−6.41 (m, 2 H, arene), 6.08−6.06 (m, 2 H, arene), 1.70 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 130.5, 129.4, 128.8, 101.6, 96.9, 86.6, 86.2, 9.4 ppm. MS (positive FAB): calcd *m*/*z* cation 453.0, found *m*/*z* cation 453.0. Anal. Calcd for $C_{23}H_{23}O_3S_3F_3Ru$: C, 45.91; H, 3.85. Found: C, 45.91; H, 3.64.

[Cp*Ru(η^6-phenoxazine)]$^+$OTf$^-$ (7). A 50 mL Schlenk flask was charged with **2** (0.25 g, 0.501 mmol) and the potassium salt of 2-aminophenol (0.077 g, 0.526 mmol, 1.05 equiv) in CH_3CN (35 mL). The heterogeneous reaction mixture was warmed to 80 °C for 5 h. The solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 (25 mL), this solution was extracted with water (2 × 25 mL), and the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was dissolved in CH_3CN (ca. 8 mL). Slow addition of diethyl ether (ca. 10 mL) precipitated a white solid that was collected by filtration and dried in vacuo. Yield: 68%. ^1H NMR (DMSO-d_6): 8.8 (br s, 1H, NH), 6.99−6.65 (m, 4 H, Ar H), 5.94−5.47 (m, 4 H, arene), 1.80 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 140.0, 128.9, 125.1, 122.6, 116.0, 115.4, 115.1, 107.0, 95.2, 83.8, 82.1, 75.8, 73.0, 9.8 ppm. MS (positive FAB): calcd *m*/*z* cation 420.10, found *m*/*z* cation 420.18. Anal. Calcd for $C_{23}H_{24}O_4NF_3SRu$: C, 48.59; H, 4.25; N, 2.46. Found: C, 48.35; H, 4.10; N, 2.45.

[Cp*Ru(η^6-phenothiazine)]$^+$OTf$^-$ (8). A 50 mL Schlenk flask was charged with **2** (0.25 g, 0.501 mmol) and the potassium salt of 2-aminothiophenol (0.086 g, 0.526 mmol, 1.05 equiv) in DMSO (25 mL). The reaction mixture was warmed to 85 °C for 5 h. The DMSO was distilled in vacuo from the reaction mixture to concentrate the reaction volume to ca. 5 mL. The concentrated DMSO solution was dissolved in CH_2Cl_2 (70 mL) and extracted with water (2 × 50 mL), and the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was dissolved

with warming in CH_3CN (10−15 mL). Slow addition of diethyl ether (15 mL) precipitated a white solid that was collected by filtration and dried in vacuo. Yield: 76%. ^{1}H NMR (DMSO-d_6): 9.11 (br s, 1H, NH), 7.16−6.75 (m, 4 H, Ar H), 5.88−5.66 (m, 4 H, arene), 1.75 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 138.6, 128.1, 126.6, 123.4, 116.3, 113.1, 112.4, 95.3, 88.6, 85.4, 83.1, 83.0, 74.6, 9.6 ppm. MS (positive FAB): calcd *m*/*z* cation 436.07, found *m*/*z* cation 436.03. Anal. Calcd for $C_{23}H_{24}O_3NF_3S_2Ru$: C, 47.25; H, 4.14; N, 2.40. Found: C, 47.04; H, 3.95; N, 2.47.

[Cp*Ru(η^6-bis(dibenzodioxin))]$^+$OTf$^-$ (9). A 50 mL Schlenk flask was charged with **3** (0.25 g, 0.42 mmol) and the dipotassium salt of catechol (0.170 g, 0.91 mmol, 2.2 equiv) in CH_3CN (25 mL). The heterogeneous reaction mixture was stirred at 25 °C for 3 h and warmed at 60 °C for 16 h. The solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 (15 mL), this solution was extracted with water (2 × 20 mL), and the organic layer was dried over $MgSO_4$. After filtration, the solvent was removed in vacuo and the residue was dissolved in CH_3CN (ca. 8 mL). Slow addition of diethyl ether (ca. 10 mL) precipitated a white solid that was collected by filtration and dried in vacuo. Yield: 63%. ^{1}H NMR (DMSO-d_6): 7.22−7.13 (m, 8 H, Ar H), 6.98 (s, 2 H, arene), 1.70 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 138.3, 126.1, 117.0, 112.8, 97.2, 66.7, 9.4 ppm. MS (positive FAB): calcd *m*/*z* cation 527.1, found *m*/*z* cation 527.1. Anal. Calcd for $C_{29}H_{25}O_7SF_3Ru$: C, 51.55; H, 3.73. Found: C, 51.59; H, 3.96.

[Cp*Ru(η^6-bis(thianthrene))]$^+$OTf$^-$ (10). Compound **10** was prepared by the same procedure described for **9** using 2.2 equiv of the dipotassium salt of 1,2-benzenedithiol. Yield: 51%. ^{1}H NMR (DMSO-d_6): 7.60−7.57 (m, 4 H, Ar H), 7.43−7.40 (m, 4 H, Ar H), 7.00 (s, 2 H, arene), 1.50 (s, 15 H, CH_3) ppm. ^{13}C NMR (DMSO-d_6): 130.2, 129.7, 129.2, 101.6, 97.7, 84.2, 8.9 ppm. MS (positive FAB): calcd *m*/*z* cation 591.0, found *m*/*z* cation 591.0. Anal. Calcd for $C_{29}H_{25}O_3S_5F_3Ru$: C, 47.08; H, 3.41. Found: C, 46.60; H, 3.33.

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