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Synthesis of New Tripodal Tri-Functionalized Hydrotris(indazol-1-yl)borate Ligands and X-ray Structures of Their Cyclopentadieneruthenium Complexes

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Two new tripodal ligands designed to anchor complexes onto surfaces have been synthesized. They integrate ester or thioether functions at the 6-position of the indazoles. Potassium hydrotris[6-(ethoxycarbonyl)indazolyl]borate and potassium hydrotris{6-[(ethylsulfanyl)methyl]indazolyl}borate exhibit three pendant groups oriented to anchor complexes onto an oxide and a metallic surface, respectively. Their complexation with $[RuCp(CH_3CN)_3]PF_6$ yielded two piano-stool-shaped complexes that were characterized by X-ray diffraction. Comparison with the synthesized unfunctionalized analog showed that the three 6-substituted functions do not interfere with the coordination site and are particularly well oriented for surface deposition.

Introduction

In the last decade, the continuous improvement of near-field microscopy techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) has led to the imaging and the study of physicochemical properties of various molecules.[1] These techniques allow the visualization and manipulation of only one molecule and therefore the electrical[2] and mechanical properties[3] of a single molecule deposited on a surface can be investigated. As single-molecule experiments require the control of the shape of the molecule deposited, the design and the synthesis of rigid ligands able to be covalently attached on surfaces with a minimum number of degrees of freedom is an active field of research.[4] In particular, the movement of a molecule can be efficiently restricted by attaching the molecule to a surface with a tripod,[5] which prevents translation. Some rigid organic molecules with three points of attachment have already been used in AFM or STM studies.[6] However, the absence of coordination sites restricts their field of application. Therefore, a structurally rigid bifunctional molecule combining coordinating sites and anchoring groups is of special interest. It would allow the covalent attachment of coordination complexes on a surface, for instance giving rise to surface-mounted molecular gears or motors.[6,7]

Since their discovery by Trofimenko in the late 1960s,[8] the trispyrazolylborate ligands, also known as scorpionate ligands, have been used increasingly in bioinorganic, organometallic, and coordination chemistry.[9] This last aspect has been extensively developed with a particular interest in the modification of the functional groups connected to the pyrazolyl moiety in order to control or modify the steric and electronic environment surrounding the metal center. However its analogue, hydrotris(indazolyl)borate (Tp^{4Bo}), has not stimulated intense studies since its synthesis in 1995.[10] Nevertheless tris(indazolyl)borate bears two advantages over trispyrazolylborate. First it is larger, but the increase in size is not accompanied by a decrease in the rigidity of the molecule. Furthermore, by withdrawing the metal away from the surface, it allows interferences caused by metal–surface interactions to be minimized, which is particularly important for near-field microscopy experiments. The rigidity of its indazolyl fragments, conjugated with its tripodal shape, should make it a good candidate for surface deposition of metal complexes onto surfaces.

Here we report the synthesis of two new scorpionate ligands incorporating functional groups on the indazole, designed to interact with metallic or oxide surfaces. The functionalized borate ligands were designed to have three functional groups pointing in the opposite direction of the coordination site in order not to interfere sterically with it. Each of the three legs of the tripodal unit bears a functional group connected at the 6-position of indazole, which should be the optimal orientation for anchoring on a surface. The ester function has been found to strongly interact with oxide surfaces,[11] spontaneous deprotection yielding carboxylic groups that covalently bind the metallic oxide. In order to interact with a metallic surface, the thioether function was chosen to alleviate the problem encountered with oxidatively unstable thiols. Acetyl-protected thiols were also

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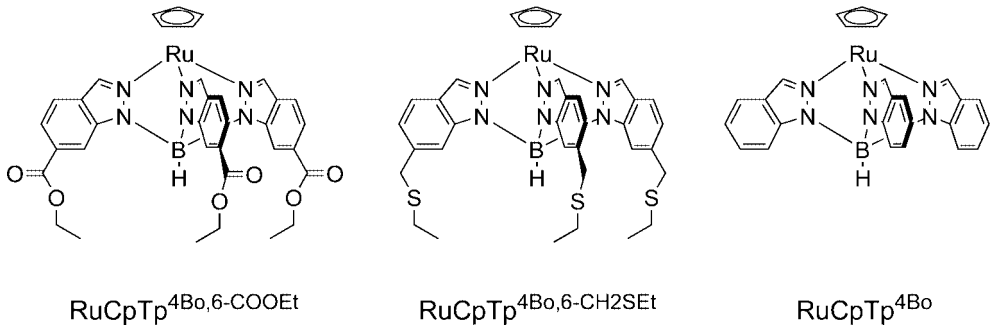


Figure 1. Structure of the triester-functionalized, trithioether-functionalized, and unfunctionalized ruthenium(II) complexes.

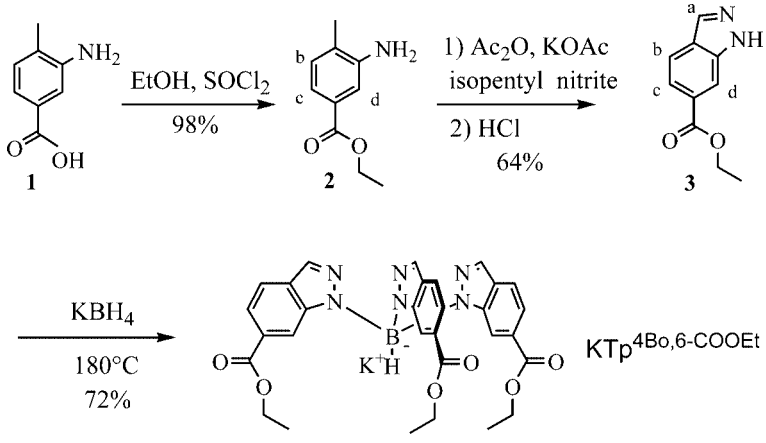
good candidates because of their spontaneous deprotection on a gold surface,[12] but preliminary experiments showed their incompatibility with the last step of the synthesis of the borate ligand, which requires sodium borohydride, yielding the reduction of the acetyl-protected thiol. The thioether group is stable in a wider range of conditions and is also known to interact strongly with a gold surface.[13] The synthesis of the hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate ligand incorporating three ester functions and the hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ligand with three pendant thioether arms is described, followed by the preparation and X-ray structures of the corresponding η^5-cyclopentadienylruthenium complexes with both functionalized tripodal ligands and also with the unfunctionalized ligand. Following Trofimenko's scorpionate nomenclature,[9] the 6-functionalized ligands can be noted as $KTp^{4Bo,6\text{-}COOEt}$ for the ester-functionalized and $KTp^{4Bo,6\text{-}CH2SEt}$ for the thioether-functionalized ligand, and similarly the ruthenium complexes can be noted as $RuCpTp^{4Bo,6\text{-}COOEt}$, $RuCpTp^{4Bo,6\text{-}CH2SEt}$, and $RuCpTp^{4Bo}$ (Figure 1).

Results and Discussion

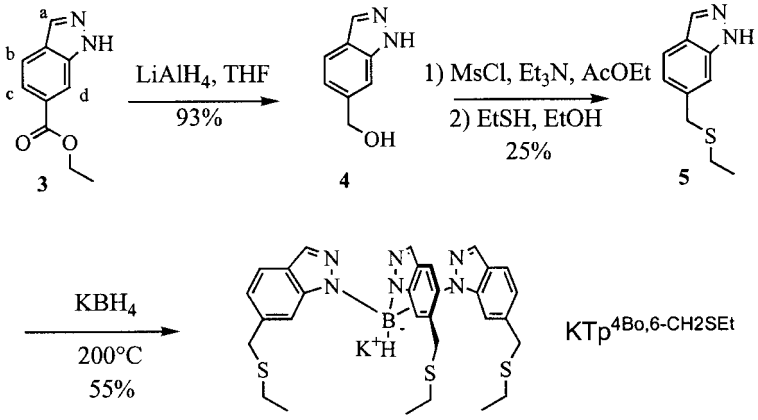
Ligand Syntheses

The strategy we followed consisted in the synthesis of a functionalized indazole in a first step, and its subsequent reaction with potassium borohydride to yield the potassium hydrotris(indazol-1-yl)borate ligand. Purification methods used in classical organic chemistry, such as column chromatography, are not suited to the purification of salts. Trituration with an apolar solvent can selectively dissolve the indazole precursor, and an additional sublimation step provides pure material. Potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate ($KTp^{4Bo,6\text{-}COOEt}$) was synthesized in three steps starting with 3-amino-4-methylbenzoic acid (**1**) (Scheme 1). The esterification of **1** in ethanol mediated by thionyl chloride[14] afforded ethyl 3-amino-4-methylbenzoate (**2**) quantitatively. The conversion of **2** into ethyl indazole-6-carboxylate (**3**) was performed using the Jacobson procedure[15] by reaction of **2** with potassium acetate, acetic anhydride, and isopentyl nitrite in refluxing toluene to give ethyl 1-acetylindazole-6-carboxylate, which was deprotected with HCl, affording **3** in 64% yield.

The formation of the indazolyl ring was demonstrated by ^{1}H NMR where the NH proton resonates with a characteristic signal at δ = 11 ppm. Reaction of **3** at 180 °C for 5 h with potassium borohydride gave the triester-functionalized $KTp^{4Bo,6\text{-}COOEt}$ in 68% yield after purification by repetitive trituration with hot toluene and sublimation of the unreacted ethyl indazole-6-carboxylate. It is noteworthy that by conducting the reaction at 150 °C instead of 180 °C, the bis(indazolyl)borate was mainly obtained. As known from the literature,[16] the signal of the BH proton is very broad and difficult to find but very informative to differentiate the



Scheme 1. Synthesis of potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate.



Scheme 2. Synthesis of potassium hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate.

bis (signal near 3.5 ppm) and tris (δ = 5 ppm) indazolylborates.

Concerning the regiochemistry of the reaction, Trofimenko has shown on the hydrotris(indazol-1-yl)borate ligand[10] that the interplay of steric and electronic factors tilts in favor of the latter, giving a product that is sterically hindered around the boron atom but not on the coordination side. Similarly, we obtained exclusively the product resulting from the fusion of the benzo ring at the 4–5-position (giving the Tp^{4Bo} product) in which the boron atom is bound to the more hindered nitrogen atom and no trace of the 3–4 fusion product (Tp^{3Bo}). This regiospecificity is maintained with ester groups at the 6-position of the indazole, as confirmed by the X-ray structure of the ruthenium complex.

The synthesis of 6-[(ethylsulfanyl)methyl]indazole (**5**) was achieved in two steps from **3** (Scheme 2). Reduction of the ethyl ester function using $LiAlH_4$ gave 6-(hydroxymethyl)-indazole (**4**) with a very good yield. Mesylation of the alcohol followed by reaction with thioethanol allowed the thioether-substituted indazole **5** to be obtained in a one-pot procedure. The same procedure used to obtain $KTp^{4Bo,6\text{-}COOEt}$ was applied to **5**, yielding potassium hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ($KTp^{4Bo,6\text{-}CH2SEt}$).

Complex Formation and Characterization

The coordination chemistry of the two ligands was consistent with the absence of steric hindrance on the metal coordination face. Complexation of KTp^{4Bo}, $KTp^{4Bo,6\text{-}COOEt}$, and $KTp^{4Bo,6\text{-}CH2SEt}$ with $[RuCp(CH_3CN)_3]PF_6$ was performed by heating the scorpionate ligand with 1 equiv. of ruthenium complex in anhydrous and degassed acetonitrile. The η^5-cyclopentadienylruthenium(II) complexes of each tripodal ligand were obtained; η^5-cyclopentadienyl(hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borato)ruthenium(II) ($RuCpTp^{4Bo,6\text{-}CH2SEt}$) and η^5-cyclopentadienyl(hydrotris[6-(ethoxycarbonyl)indazol-1-yl]-borato)ruthenium(II) ($RuCpTp^{4Bo,6\text{-}COOEt}$) were obtained with a lower yield compared to the complex formed with the unfunctionalized ligand. For solubility reasons, the synthesis of $RuCpTp^{4Bo,6\text{-}COOEt}$ required the use of anhydrous DMF as cosolvent. The three complexes were fully characterized.

The cyclic voltammogram of the unfunctionalized complex exhibits a reversible metal-centered oxidation at 0.49 V/SCE, that is 100 mV higher than the pyrazolyl analog in the same conditions (Table 1). This shows that ruthenium(II) is more stabilized in $RuCpTp^{4Bo}$ than in its pyrazolyl analog synthesized by Mann et al.,[17] which can be explained by the more pronounced π-acceptor character of the hydrotris(indazolyl)borate compared to its pyrazolyl analog. In the ruthenium complex $RuCpTp^{4Bo,6\text{-}COOEt}$, which incorporates the triester-functionalized ligand, oxidation occurs at a higher potential: 0.63 V/SCE, the ethoxycarbonyl electron-withdrawing groups stabilizing the ruthenium(II) state further. The ester substituents decrease the σ-donor character and increase the π-acceptor character of the scorpionate ligand. The combination of this low σ-donor character and solubility problems could explain the moderate yield of the coordination step. The coordinating nitrogen of the ester-functionalized scorpionate ligand being less donor than its unfunctionalized analog, is thus less efficient in the displacement of the acetonitrile ligands of the ruthenium precursor. In the ruthenium complex $RuCpTp^{4Bo,6\text{-}CH2SEt}$, which incorporates the thioether functions, oxidation occurs at a slightly lower potential of 0.48 V/SCE, the slightly electron-donating (ethylsulfanyl)-methyl groups destabilizing the ruthenium(II) state.

Table 1. Cyclic voltammetry data.[a]

Compound	$E_{1/2}$(ox) Ru^{II}–Ru^{III} (V/SCE)[b]
$RuCpTp^{4Bo,6\text{-}COOEt}$	0.63
$RuCpTp^{4Bo}$	0.49
$RuCpTp^{4Bo,6\text{-}CH2SEt}$	0.48
RuCpTp	0.39[c]

[a] Cyclic voltammograms were carried out at a scan rate of 100 mV s^{-1} in acetonitrile containing 0.1 M Bu_4NPF_6 as supporting electrolyte. Potentials were measured vs SCE using a Pt working electrode. [b] All couples are reversible. [c] Obtained from ref.[17]

Variable temperature ^{1}H NMR experiments have shown that the rotation of the Cp ligand in the complexes is fast compared to the NMR timescale down to at least –90 °C in deuterated dichloromethane, indicating that the coordination site is not sterically affected by the ethoxycarbonyl or (ethylsulfanyl)methyl substituents.

Crystal Structures of the Complexes

Crystals suitable for X-ray diffraction were grown by the slow diffusion of methanol over a dichloromethane solution of the complex. The ORTEP representations with atom numbering are shown in Figure 2, while selected bond lengths and angles are listed in Table 2.

$RuCpTp^{4Bo,6\text{-}COOEt}$ and $RuCpTp^{4Bo}$ crystallized in the *Pccn* space group while $RuCpTp^{4Bo,6\text{-}CH2SEt}$ crystallized in the $P\bar{1}$ group. The triester-functionalized complex cocrystallized with molecules of methanol (0.5 equiv. per ruthenium complex), which are located on a symmetry axis and are highly disordered. In line with the ^{1}H NMR spectroscopic data, the three complexes have a piano stool shape where the scorpionate ligand binds the ruthenium center in a facial tripodal mode (i.e. κ^3-*N*,*N*′,*N*′′), as shown by Trofimenko for scorpionate complexes. The crystal structure of complexes with the triester- and (ethylsulfanyl)-methyl-functionalized ligands confirmed the regiochemistry of the scorpionate formation, which is the expected Tp^{4Bo} isomer. Moreover, the functional groups at the 6-position of indazole are well oriented, pointing in the opposite direction of the coordination site, which is thus free of any steric hindrance as seen in solution by a variable temperature ^{1}H NMR experiment. The lack of interference between the coordination site and the attaching groups suggests that this molecule can be expected to be truly bifunctional, acting both as ligand and anchor to fix metal complexes onto a surface.

Table 2. Selected bond lengths [Å] and angles [°] in the ruthenium complexes.[a]

	$RuCpTp^{4Bo}$	$RuCpTp^{4Bo,6\text{-}COOEt}$	$RuCpTp^{4Bo,6\text{-}CH2SEt}$
Ru–N(1)	2.141(8)	2.113(4)	2.128(5)
Ru–N(3)	2.108(7)	2.129(4)	2.126(5)
Ru–N(5)	2.099(7)	2.103(4)	2.120(5)
Ru–C(22)	2.141(10)	2.166(5)	2.140(6)
Ru–C(23)	2.156(11)	2.152(5)	2.160(6)
Ru–C(24)	2.166(11)	2.148(5)	2.159(5)
Ru–C(25)	2.145(11)	2.162(5)	2.154(5)
Ru–C(26)	2.131(11)	2.161(5)	2.147(6)
N(1)–Ru–N(3)	84.4(3)	83.46(14)	83.55(18)
N(3)–Ru–N(5)	84.2(3)	84.97(14)	85.87(17)
N(5)–Ru–N(1)	85.6(3)	86.46(14)	84.01(17)
N(2)–B–N(4)	108.3(8)	107.3(4)	107.5(4)
N(4)–B–N(6)	110.2(7)	108.4(4)	108.3(4)
N(6)–B–N(2)	106.8(7)	108.9(4)	108.5(4)

[a] Numbers in parentheses are estimated standard deviations.

It must be noted that these complexes combine a C_5-symmetry cyclopentadienyl ligand and a C_3-symmetry tripodal ligand, and as a result, have a low symmetry. In order to facilitate the discussion and by analogy with ethane, two

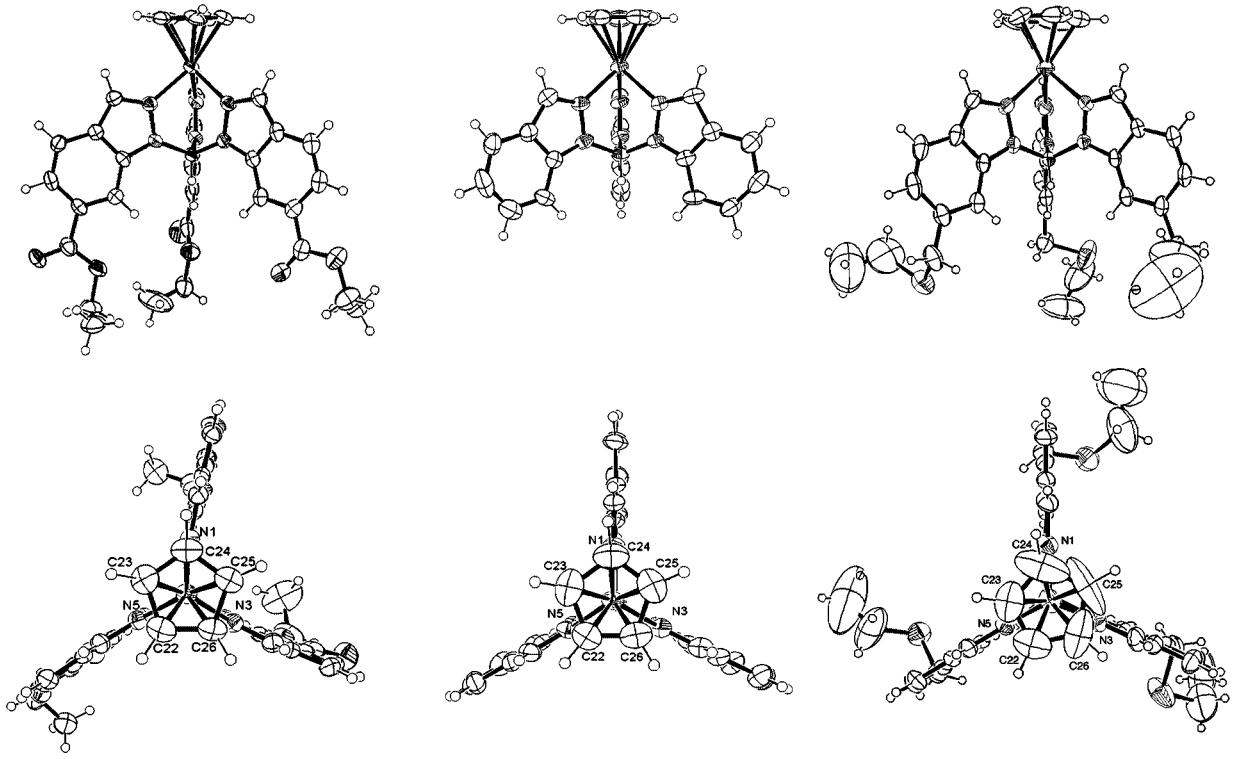


Figure 2. Thermal ellipsoid diagram of ($RuCpTp^{4Bo,6\text{-}COOEt}$) (left), ($RuCpTp^{4Bo}$) (center), and ($RuCpTp^{4Bo,6\text{-}CH2SEt}$) (right), side view (top) and top view (bottom). The ellipsoids are drawn at the 50% probability level and the molecules of cocrystallizing solvent (MeOH) have been removed for clarity.

significant conformations can be defined (Figure 3). The first one can be considered as an eclipsed conformation in which one of the dihedral angles between a CH bond of the cyclopentadienyl ligand and one indazole of the scorpionate ligand is 0°. In the second one, the staggered conformation, two of these dihedral angles are equal to 12°. Because of the symmetry of each ligand, a rotation of 24° is invariant. A 12° rotation of one ligand with respect to the other allows the interconversion between staggered and eclipsed conformations.

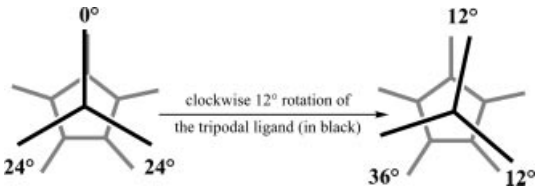


Figure 3. Eclipsed (left) and staggered (right) conformations of a complex containing both C_3- and C_5-symmetry ligands. Interconversion occurs upon a 12° rotation. For symmetry reasons, the staggered conformation appears every 24°.

On purely steric grounds, the staggered conformer is expected to be the most stable, as obtained in the case of the pyrazolyl analog RuCpTp.[15] On the contrary, RuCpTp^{4Bo} adopts an almost eclipsed conformation in the solid state, with a dihedral angle between the C(24)–H(24) bond and the plane of the N(1)-containing indazole equal to 0.3° (Figure 2, bottom view). An explanation for a favored eclipsed conformation must be found in the crystal packing and in the intermolecular forces involved in the solid state. A careful examination of the crystal packing of the unfunctionalized and both functionalized complexes showed π-stacking interactions between the two indazoles of neighboring complexes. As shown for the unfunctionalized complex in Figure 4, the two indazoles face each other in a head-to-tail mode, the electron-rich part of one indazole being exactly above the electron-poor part of the other indazole, which provides further stabilization by donor–acceptor interactions. The distance between the planes of two consecutive indazoles is ideal for stacking: 3.62 Å for the triester complex, 3.59 Å for the tris (ethylsulfanyl)methyl complex, and 3.56 Å for the unfunctionalized complex.

Moreover, average Ru–C distances of 2.15 Å (for cyclopentadienyl) and Ru–N bond lengths of 2.11 Å (for trisindazolylborate) are found in the three complexes, showing that the coordination of the tripodal ligand is not influenced by the presence of the functional groups at the 6-position of the indazole rings. The moderate reactivity of the triester-functionalized ligand towards complexation with $[RuCp(CH_3CN)_3]PF_6$ is thus justified purely by electronic considerations, while steric hindrance due to the ester groups can be ruled out.

Conclusions

In summary, we have described the preparation and coordination of two new tripodal ligands that bear functional groups suitable for surface deposition. The orientation of the three anchoring groups, as shown by the X-ray structures, seems to be ideal for surface deposition of organometallic complexes. Work is underway to anchor these complexes on surfaces and integrate the triester-functionalized ligand into molecular machines such as a molecular rotary motor[7] designed to be studied as a single molecule deposited on an oxide surface.

Experimental Section

All commercially available chemicals were of reagent grade and were used without further purification. $[RuCp(CH_3CN)_3]PF_6$ was purchased from Strem. Potassium hydrotris(indazol-1-yl)borate (KTp^{4Bo}) was prepared according to a literature procedure.[10] NMR spectra were recorded with Bruker AM 250 or Avance 500 spectrometers and full assignments were made using COSY, ROESY, HMBC, and HMQC methods when necessary. The numbering scheme for the indazol derivatives is given in molecule **3** (see Scheme 1 and Scheme 2). Chemical shifts are defined with respect to TMS = 0 ppm for ^1H and ^{13}C NMR spectra and were measured relative to residual solvent peaks. UV/Vis spectra were recorded with a Shimadzu UV-3100 spectrometer. FAB and DCI mass spectrometry was performed using a Nermag R10–10. The melting points were measured on a Kofler Reichert apparatus and are not corrected.

Ethyl 3-Amino-4-methylbenzoate (2): 3-Amino-4-methylbenzoic acid (**1**) (2.00 g, 13.3 mmol, 1 equiv.) was dissolved in absolute eth-

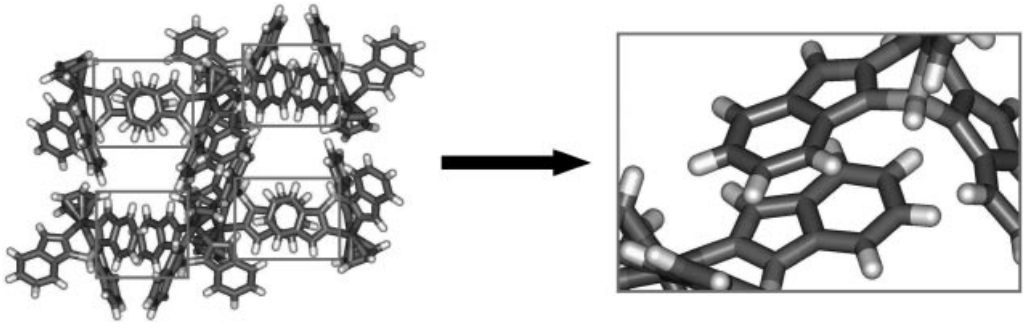


Figure 4. Stabilization in the crystal structure of RuCpTp^{4Bo} by π-stacking interactions between neighboring indazolyl pairs. Zooming in shows the donor–acceptor interactions between two indazolyl groups positioned in a head-to-tail arrangement with an interplane distance of 3.56 Å.

anol (50 mL). Thionyl chloride (2 mL, 27.4 mmol, 2 equiv.) was added dropwise and the reaction mixture was heated at reflux overnight, during which the color of the solution turned from purple to pink. Ethanol was removed under reduced pressure, and the residual oil was dissolved in ethyl acetate (50 mL) and washed with a saturated sodium carbonate solution (3 × 20 mL). The combined aqueous phases were extracted with ethyl acetate (20 mL). Then the combined organic phases were dried with $MgSO_4$ and the solvent removed under reduced pressure to afford ethyl 3-amino-4-methylbenzoate (**2**) (2.33 g, 13.0 mmol, 98%) as a pink oil which was used without further purification. DCI-MS (NH_3): *m*/*z* (%) = 180 [M + H]$^+$, 197 [M + NH_4]$^+$. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.26–7.30 (m, 2 H, H^{c-d}), 6.92 (d, ^3J = 7.8 Hz, 1 H, H^b), 4.31 (q, ^3J = 6.9 Hz, 2 H, CH_2CH$_3$), 3.91 (broad s, 2 H, NH_2), 2.00 (s, 3 H, Me), 1.21 (t, ^3J = 6.9 Hz, 3 H, CH$_2$CH_3) ppm.

Ethyl 1*H*-Indazole-6-carboxylate (3): In a three-necked round-bottomed flask, ethyl 3-amino-4-methylbenzoate (**2**) (2.30 g, 12.8 mmol, 1 equiv.), potassium acetate (1.3 g, 13.2 mmol, 1.1 equiv.), and acetic anhydride (4.4 mL, 47 mmol, 3.6 equiv.) were suspended in toluene (50 mL). Isopentyl nitrite (3.6 mL, 24.6 mmol, 2.1 equiv.) was added dropwise to this suspension over a 15-min period. The gelatinous mixture was heated at reflux overnight giving an orange solution, which was evaporated to dryness. HCl (5 M, 10 mL) and concentrated HCl (5 mL) were added and the red solution was heated at 50 °C for 1 h followed by 10 min at 60 °C. After cooling down, the acid layer was extracted twice with toluene (20 mL) to remove neutral compounds. The red combined organic phases were washed three times with concentrated HCl. The acid phase was then carefully neutralized with ammonia, causing precipitation of the compound. After filtration, the product was dissolved in dichloromethane then dried with $MgSO_4$ and the solvent removed under reduced pressure to afford **3** (1.56 g, 8.2 mmol, 64%) as a brown solid. The product can be sublimed (0.1 Torr, 160 °C) or used without further purification. DCI-MS (NH_3): *m*/*z* (%) = 191 [M + H]$^+$. High resolution LSI calculated [M + H]$^+$: 191.0821 ($C_{10}H_{11}N_2O_2$); found: 191.0827 (100% [M + H]$^+$). M.p. 125 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 11.15 (s, 1 H, NH), 8.27 (d, ^4J = 1 Hz, 1 H, H^a), 8.14 (s, 1 H, H^d), 7.88–7.77 (m, 2 H, H^{b-c}), 4.42 (q, 2 H, ^3J = 7.0 Hz, CH_2CH$_3$), 1.44 (t, 3 H, ^3J = 7.2 Hz, CH$_2$CH_3) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 166.8 (CO), 139.5, 135.0 (C^a), 129.0, 125.7, 121.6 (C^c), 120.7 (C^b), 112.1 (C^d), 61.3 (CH_2), 14.4 (CH_3) ppm. $C_{10}H_{10}N_2O_2$: calcd. C 63.2, H 5.30, N 14.7; found: C 62.8, H 5.11, N 14.5.

Potassium Hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate (KTp$^{4Bo,6-COOEt}$): Ethyl indazole-6-carboxylate (**3**) (700 mg, 3.68 mmol, 3.5 equiv.) and potassium borohydride (56 mg, 1.05 mmol, 1 equiv.) were ground up in a mortar then dried under vacuum and the vessel was filled with argon. The mixture was heated in a sand bath at 180 °C until the gas evolution had ceased (5–6 h). The reaction was then quenched by addition of toluene. The solid was filtered off and purified by trituration with hot toluene, which dissolved the unreacted **3**. After drying under vacuum, the solid was ground in a mortar and any remaining unreacted indazole was removed by sublimation, by heating the sample at 160 °C under vacuum. By repeating alternating trituration and sublimation, potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate (KTp$^{4Bo,6-COOEt}$) (440 mg, 0.712 mmol, 68%) was obtained as a pale yellow solid. FAB-MS (MeOH, Gly-Thio, negative mode): *m*/*z* (%) = 579 [M – K]$^-$. High resolution LSI calculated [M – K]$^-$: 578.2085 ($C_{30}H_{27}BN_6O_6$); found: 578.2099 (100% [M – K]$^-$). ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 8.20 (s, 3 H, H$_a$), 8.15 (d, ^4J = 1 Hz, 3 H, H^d), 7.81 (d, ^3J = 8.5 Hz, 3 H, H^c), 7.59 (dd, ^3J = 8.5 Hz, ^4J = 1 Hz, 3 H, H^b), 4.33 (q, ^3J = 7 Hz, 6 H, CH_2CH$_3$), 1.34 (t, ^3J = 7 Hz, 9 H, CH$_2$CH_3) ppm. ^{13}C NMR (63 MHz, [D$_6$]-DMSO): δ = 166.3 (CO), 144.3, 133.0 (C^a), 126.3, 123.2, 120.6 (C^c), 120.3 (C^b), 112.7 (C$_d$), 61.0 (CH_2), 14.3 (CH_3).

η^5-Cyclopentadienyl(hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borato)ruthenium(II) (RuCpTp$^{4Bo,6-COOEt}$): Potassium hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borate (KTp$^{4Bo,6-COOEt}$) (62 mg, 0.1 mmol, 1 equiv.) was dissolved in dry DMF (2 mL), dry acetonitrile was added (20 mL), and the mixture was purged with argon. [RuCp(CH$_3$CN)$_3$]PF$_6$ (43 mg, 0.1 mmol, 1 equiv.) was added to this solution, which was then refluxed overnight. Evaporation of the solvent followed by a purification by column chromatography (SiO_2: cyclohexane/ethanol 0–20%) afforded η^5-cyclopentadienyl-[hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borato]ruthenium(II) (RuCpTp$^{4Bo,6-COOEt}$) (39 mg, 0.052 mmol, 52%) as a yellow solid. DCI-MS (NH_3): 747 [M + H]$^+$, 764 [M + NH_4]$^+$. High resolution LSI calculated [M + H]$^+$: 747.1676 ($C_{35}H_{34}BN_6O_6Ru$); found: 747.1700 (100% [M + H]$^+$). M.p. 212 °C dec. ^{1}H NMR (250 MHz, CD_2Cl_2): δ = 8.66 (d, ^4J = 0.9 Hz, 3 H, H^a), 8.62 (d, ^4J = 1.2 Hz, 3 H, H^d), 7.69 (dd, ^3J = 8.5 Hz, ^4J = 1.2 Hz, 3 H, H^c), 7.62 (dd, ^3J = 8.5 Hz, ^4J = 0.9 Hz, 3 H, H^b), 4.63 (s, 5 H, Cp), 4.42 (q, ^3J = 7 Hz, 6 H, CH_2CH$_3$), 1.43 (t, ^3J = 7.2 Hz, 9 H, CH$_2$CH_3) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 167.6 (CO), 143.1, 140.2 (C^a), 129.2, 126.8, 122.0 (C^c), 119.7 (C^b), 114.6 (C^d), 72.8 (Cp), 62.0 (CH_2), 15.0 (CH_3) ppm. $E_{Ru^{II}:Ru^{III}}$ (V/SCE): +0.63 rev (sweep rate: 100 mV s^{-1}). UV/Vis (CH_2Cl_2): λ_{max} (ε in L mol^{-1} cm^{-1}) = 222 (60300), 256 (14000), 334 (12800), 418 nm (6900).

η^5-Cyclopentadienyl[hydrotris(indazol-1-yl)borato]ruthenium(II) (RuCpTp^{4Bo}): A solution of potassium hydrotris(indazol-1-yl)borate (KTp^{4Bo}) (81 mg, 0.2 mmol, 1 equiv.) in acetonitrile (20 mL) was purged with argon and [RuCp(CH$_3$CN)$_3$]PF$_6$ (87 mg, 0.2 mmol, 1 equiv.) was added. The solution was refluxed for 1.5 h. The solution, initially yellow, turned to orange-brown. Upon cooling to room temperature, an orange precipitate appeared. Recrystallization from chloroform/methanol gave pure RuCpTp^{4Bo} (70 mg, 0.132 mmol, 65%) as an orange microcrystalline product. DCI-MS (NH_3): *m*/*z* (%) = 548 [M + NH_4]$^+$, 531 [M + H]$^+$. High resolution LSI calculated [M + H]$^+$: 531.1042 ($C_{26}H_{22}BN_6Ru$); found: 531.1061 (100% [M + H]$^+$). M.p. 222 °C dec. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.61 (s, 3 H, H$_a$), 7.90 (d, ^3J = 8.75 Hz, 3 H, H^b), 7.6 (d, ^3J = 7.25 Hz, 3 H, H$_d$), 7.32 (t, ^3J = 7.25 Hz, 3 H, H^c), 7.05 (t, ^3J = 7.25 Hz, 3 H, H^6), 4.56 (s, 5 H, Cp) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 138.9 (C^a), 125.9, 123.7, 120.5 (C^c), 119.2 (C^b), 111.5 (C^d), 70.7 (Cp) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε in L mol^{-1} cm^{-1}) = 231 (21400), 298 (15000), 307 (12200), 325 (9700), 388 nm (4600). CV (CH_3CN, Bu_4NPF_6) $E_{Ru^{II}:Ru^{III}}$ (V/SCE): +0.49 rev (sweep rate: 100 mV s^{-1}).

6-(Hydroxymethyl)-1*H*-indazole (4): $LiAlH_4$ (1.6 g, 42.5 mmol, 4 equiv.) was added carefully in portions to a solution of **3** (2 g, 10.5 mmol, 1 equiv.) in freshly distilled THF (100 mL) at 0 °C. After 2 h of vigorous stirring, TLC analysis showed a complete disappearance of the starting material and the presence of a single product. The reaction mixture was carefully quenched with water (1.6 mL) followed by a 15% NaOH solution (1.6 mL) and then water (4 mL). The mixture was filtered through Celite and the filter cake was washed several times with dichloromethane. The filtrate was dried with $MgSO_4$ and the solvent was removed under reduced pressure, affording 6-(hydroxymethyl)indazole (**4**) (1.45 g, 9.8 mmol, 93%). This compound was used without further purification. ESI-MS: *m*/*z* (%) = 149 [M + H]$^+$. M.p. 159 °C. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 12.97 (s, 1 H, NH), 8.00 (s, 1 H, H^a), 7.65 (d, ^3J = 8.4 Hz, 1 H, H^d), 7.46 (s, 1 H, H^b), 7.04 (d, ^3J = 8.4 Hz, 1 H, H$_c$), 5.28 (br. s, 1 H, OH), 4.61 (d, ^3J = 5.9 Hz, 2 H, CH_2).

6-[(Ethylsulfanyl)methyl]-1*H*-indazole (5): Mesyl chloride (0.65 mL, 8.4 mmol, 1 equiv.) was added dropwise to a solution of 6-(hydroxymethyl)indazole (**4**) (1.24 g, 8.4 mmol, 1 equiv.) and triethylamine (2.5 mL) in ethyl acetate (170 mL) at 0 °C. The mixture was stirred at room temperature for 12 h, the organic phase was washed three times with water (50 mL), and the combined aqueous phases were extracted once with ethyl acetate. The combined organic phases were dried with $MgSO_4$ and the solvent removed under reduced pressure, giving a pale yellow solid that was used without purification in the next step. The mesylate yellow solid was dissolved in dry THF (75 mL) and added dropwise to a solution of ethane thiol (0.62 mL, 8.4 mmol, 1 equiv.) in ethanol (75 mL) with KOH (0.7 g, 12.5 mmol, 1.5 equiv.). The solvent was removed under reduced pressure and the crude material was purified by column chromatography (SiO_2, cyclohexane/Et_2O 40%) to give 6-[(ethylsulfanyl)methyl]indazole (**5**) (400 mg, 2.08 mmol, 25%) as a white solid. DCI-MS (NH_3): *m*/*z* (%) = 193 $[M + H]^+$. High resolution LSI calculated $[M + H]^+$: 193.0799 ($C_{10}H_{13}N_2S$); found: 193.0804 (100% $[M + H]^+$). M.p. 61 °C. ^1H NMR (250 MHz, CD_2Cl_2): δ = 11.35 (s, 1 H, NH), 8.01 (s, 1 H, H^a), 7.68 (d, ^3J = 8.3 Hz, 1 H, H^d), 7.44 (s, 1 H, H^b), 7.08 (d, ^3J = 8.3 Hz, 1 H, H^c), 3.86 (s, 2 H, CH_2), 2.39 (q, ^3J = 7.3 Hz, 2 H, CH_2CH_3), 1.15 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (63 MHz, CD_2Cl_2): δ = 140.4, 138.0 (C^a), 134.4, 122.7 (C^c), 120.8 (C^b), 109.6 (C^d), 36.3 (CH_2S), 25.4 (CH_2), 14.3 (CH_3) ppm. $C_{10}H_{12}N_2S$: calcd. C 62.5, H 6.29, N 14.6; found C 62.2, H 6.14, N 14.5.

Potassium Hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ($KTp^{4Bo,6\text{-}CH2SEt}$): 6-[(Ethylsulfanyl)methyl]indazole (**5**) (300 mg, 1.56 mmol, 3.4 equiv.) and potassium borohydride (25 mg, 46 mmol, 1 equiv.) were ground up in a mortar, dried under vacuum and the vessel was filled with argon. The mixture was heated in a sand bath at 200 °C; 5 h were needed until the gas evolution had ceased. The solid was ground in a mortar and any remaining unreacted indazole was removed by sublimation, by heating the sample at 160 °C under vacuum. By repeating alternating trituration with toluene and sublimation, potassium hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ($KTp^{4Bo,6\text{-}CH2SEt}$) (160 mg, 0.25 mmol, 55%) was obtained as a pale yellow sticky solid. FAB-MS (MeOH, Gly-Thio, negative mode): *m*/*z* (%) = 584 $[M - K]^-$. High resolution LSI calculated $[M - K]^-$: 584.2022 ($C_{30}H_{33}BN_6S_3$); found: 584.2042 (100% $[M - K]^-$). ^1H NMR (250 MHz, $[D_6]$-DMSO): 7.82 (d, ^4J = 1 Hz, 3 H, H^a), 7.52 (d, ^3J = 8.0 Hz, 3 H, H^c), 6.92 (s, 3 H, H^d), 6.84 (dd, ^3J = 8.0 Hz, ^4J = 1 Hz, 3 H, H^b), 3.57 (s, 2 H, CH_2S), 2.05 (q, ^3J = 7.4 Hz, 6 H, CH_2CH_3), 0.97 (t, ^3J = 7 Hz, 9 H, CH_2CH_3), 5.73 (br. s, 1 H, B*H*) ppm. ^{13}C NMR (63 MHz, $[D_6]$DMSO): δ = 143.8, 133.3 (C^a), 131.9, 121.9, 120.0 (C^c), 119.5 (C^b), 112.6 (C^d), 35.2 (CH_2S), 24.0 (CH_2), 14.2 (CH_3) ppm. ^{11}B NMR (160 MHz, $[D_6]$DMSO): –2.57 (s, 1 H) ppm.

η^5-Cyclopentadienyl(hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borato)ruthenium(II) ($RuCpTp^{4Bo,6\text{-}CH2SEt}$): Potassium hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borate ($KTp^{4Bo,6\text{-}CH2SEt}$) (62 mg, 0.1 mmol, 1 equiv.) was dissolved in dry acetonitrile (20 mL) and the mixture was purged with argon. $[RuCp(CH_3CN)_3]PF_6$ (43 mg, 0.1 mmol, 1 equiv.) was added to this solution and it was then refluxed for 2 h. Evaporation of the solvent followed by a purification by column chromatography (SiO_2: cyclohexane/dichloromethane 0–50%) afforded η^5-cyclopentadienyl(hydrotris{6-[(ethylsulfanyl)methyl]indazol-1-yl}borato)ruthenium(II) ($RuCpTp^{4Bo,6\text{-}CH2SEt}$) (10 mg, 0.013 mmol, 13%) as a yellow solid. DCI-MS (NH_3): 753 $[M + H]^+$. High resolution LSI calculated $[M + H]^+$: 753.1613 ($C_{35}H_{40}BN_6RuS_3$); found: 753.1637 (100% $[M + H]^+$). M.p. 206 °C dec. ^1H NMR (500 MHz, CD_2Cl_2): δ = 8.57 (s, 3 H, H^a), 7.78 (s, 3 H, H^d), 7.55 (d, 3 H, ^3J = 8.3 Hz, H^b), 7.08 (d, 3 H, ^3J = 8.3 Hz, H^c), 4.55 (s, 5 H, Cp), 3.87 (s, 6 H, CH_2), 2.15 (q, 6 H, ^3J = 7.3 Hz, CH_2CH_3), 1.22 (t, 9 H, ^3J = 7.3 Hz, CH_2CH_3) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 143.0, 138.9 (C^a), 136.9, 122.7, 122.3 (C^c), 119.3 (C^b), 111.0 (C^d), 70.7 (Cp), 36.4 (CH_2S), 25.2 (CH_2), 14.3 (CH_3) ppm. $E_{Ru^{II}:Ru^{III}}$ (V/SCE): +0.49 rev (sweep rate: 100 mV s^{-1}). UV/Vis (CH_2Cl_2): λ_{max} (ε in L mol^{-1} cm^{-1}) = 231 (30500), 309 (14700), 327 (13500), 390 nm (6200).

X-ray Crystallographic Study: Crystal data for η^5-cyclopentadienyl(hydrotris[6-(ethoxycarbonyl)indazol-1-yl]borato)ruthenium(II) ($RuCpTp^{4Bo,6\text{-}COOEt}$). Orange prismatic crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the complex in a pentane/methanol (1:1) mixture. $C_{35}H_{33}BN_6O_6Ru\cdot 0.5CH_3OH$: M_r = 1523.17, orthorhombic, space group *Pccn*, *a* (Å) = 22.682(6), *b* (Å) = 15.0415(13), *c* (Å) = 19.813(3), *V* (Å^3) = 6760(2), *Z* = 4, $\rho_{calcd.}$ = 1.497 g cm^{-3}, μ(Mo-K_α) (mm^{-1}) = 0.521. Data were collected on a Nonius-Kappa CCD diffractometer using Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å) at 200 K; 3983 reflections having $I > 2\sigma(I)$ were used for structure determination (4.06° < θ < 27.00°). For all computations the Bruker maXus software package was used. Final results: $R(F)$ = 0.0507, $Rw(F)$ = 0.1004, Gof = 1.032.

Crystal Data for η^5-Cyclopentadienyl[hydrotris(indazol-1-yl)borato]-ruthenium(II) ($RuCpTp^{4Bo}$): Orange prismatic crystals suitable for X-ray analysis were obtained by dissolution of the compound in dichloromethane and slow liquid diffusion of methanol. $C_{26}H_{21}BN_6Ru$: M_r = 529.377, orthorhombic, space group *Pccn*, *a* (Å) = 13.2676(12), *b* (Å) = 18.891(2), *c* (Å) = 19.4177(13), *V* (Å^3) = 4866.8(7), *Z* = 8, $\rho_{calcd.}$ = 1.445 g cm^{-3}, μ(Mo-K_α) (mm^{-1}) = 0.67. Data were collected on a Nonius-Kappa CCD diffractometer using Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å) at 298 K; 2103 reflections having $I > 3\sigma(I)$ were used for structure determination (0° < θ < 35.00°). For all computations the Bruker maXus software package was used. Final results: $R(F)$ = 0.047, $Rw(F)$ = 0.108, Gof = 1.055.

Crystal Data for η^5-Cyclopentadienyl(hydrotris{6-[(ethylsulfanyl)-methyl]indazol-1-yl}borato)ruthenium(II) ($RuCpTp^{4Bo,6\text{-}CH2SEt}$): Yellow prismatic crystals suitable for X-ray analysis were obtained by dissolution of the compound in dichloromethane and slow liquid diffusion of methanol. $C_{35}H_{39}BN_6RuS_3$: M_r = 751.81, triclinic, space group $P\bar{1}$, *a* (Å) = 9.883(3), *b* (Å) = 14.032(3), *c* (Å) = 14.889(4), *V* (Å^3) = 1802.7(7), *Z* = 2, $\rho_{calcd.}$ = 1.385 g cm^{-3}, μ(Mo-K_α) (mm^{-1}) = 0.642. Data were collected on a Nonius-Kappa CCD diffractometer using Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å) at 298 K; 3927 reflections having $I > 2\sigma(I)$ were used for structure determination (0° < θ < 27.00°). For all computations the Bruker maXus software package was used. Final results: $R(F)$ = 0.072, $Rw(F)$ = 0.131, Gof = 1.064.

CCDC-254040 (for $RuCpTp^{4Bo}$), -254041 (for $RuCpTp^{4Bo,6\text{-}COOEt}$), and -284359 (for $RuCpTp^{4Bo,6\text{-}CH2SEt}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry: The voltammetric experiments were measured with an AUTOLAB PGSTAT 100 potentiostat using a Pt disc (1 mm diameter) as working electrode and a Pt counter electrode. The reference electrode used was the saturated calomel electrode (SCE). Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) acted as the electrolyte. All solutions were degassed thoroughly for at least 15 min with argon and an inert gas blanket was maintained over the solution during the measurements.

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