

Doubly N-Functionalized Pentafulvenes and Redox-Responsive [N,N]- and [N,C,N]-Pincer Bis(imidoyl)pentamethylruthenocene Metalloligands

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New doubly functionalized pentafulvenes are easily obtained by a regioselective one-pot reaction of sodium cyclopentadienide with imidoyl chlorides of different electrophilicity. Under thermodynamic control, benzimidoyl chlorides as electrophiles afford hydrogen-bridged 6-arylamino-2-benzimidoylfulvenes, whereas under kinetic control trifluoroacetimidoyl chlorides afford nonhydrogen-bridged 6-arylamino-3-imidoylfulvenes. Structurally, these [N,N]H fulvenes exist either as pairs of rapidly interconverting tautomers (fulvenes with intramolecular hydrogen bridges) or as regular fulvenes (fulvenes without intramolecular but with intermolecular hydrogen bridges) in solution and in the solid state, as shown by NMR studies and single-crystal X-ray diffraction. Both types of fulvenes represent interesting ambidentate [N,N]H ligands per se as well as precursors to novel doubly functionalized bis(imidoyl)metallocenes. Synthetically, after deprotonation of these acceptor-substituted [N,N]H-fulvenes, 1,2- or 1,3-bis(imidoyl)pentamethylruthenocenes are easily accessible by reaction with [Cp*Ru(CH₃CN)₃]PF₆ as a source of the electron-rich Cp*Ru⁺-synthon. Structurally, these new [N,N]-pentamethylruthenocene metalloligands are related to diazabutadienes or bis(imino)-[N,C,N]H pincer ligand systems, respectively. Electrochemical investigations show that the bis(imidoyl)(pentamethyl)ruthenocenes are novel redox-active metalloligands and reveal the strongly electron-withdrawing effect of the appended imine moieties. All new compounds were fully characterized by spectroscopic methods and by a total of 11 single-crystal X-ray analyses.

Introduction

Functionalized pentafulvenes represent very useful reagents for the synthesis of η^5 -cyclopentadienyl early to late transition metal complexes that are inaccessible by common methodology.1 The donor-substituted metallocenes derived from these fulvenes have numerous applications in catalysis, supramolecular chemistry, medicinal chemistry, and electrochemical sensor techniques. Whereas pentafulvenes with one functionality are well-known, doubly functionalized

examples are very scarce, with few representatives bearing [O,O]H,² [N,O]H,³ and [N,N]H⁴ groups. A common structural feature of all these fulvenes is their 1,2-substitution pattern enforced by a stabilizing intramolecular O-H-O, O-H-N, or N-H-N hydrogen bond.

In this contribution (Scheme 1), we report on (i) an improved, modular, and simple synthetic approach to 6-amino-2-imidoylpentafulvenes A, (ii) the first synthesis of the regioisomeric 6-amino-3-imidoylpentafulvenes **B**, (iii) the synthesis and properties of new pentamethylruthenocenes of types

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Scheme 1. Doubly N-Functionalized Pentafulvenes and Their η^5 Complexes

C and D, and (iv) the first results of electrochemical studies on bis(imidoyl)pentamethylruthenocenes C and D. It is quite obvious that, starting from these different classes of compounds, a rich coordination chemistry can be developed. Fulvenes A may be considered "fulvenologous" β -diimines; these compounds are ambidentate ligands, forming either κ^2 [N,N] metal complexes^{4j,5} or η^5 -[1,2-bis(imidoyl)]metallocenes⁵ C, depending on the electron richness of the metal center. Fulvenes A may be termed "γ-diketiminato" ligands, resembling the popular β -diketiminato ("nacnac") ligands, but their N-donor sites are conjugated through the annelated fulvene moiety and their metal chelates are seven-membered instead of six-membered. Metallocenes C derived from fulvenes A are redox-responsive bis(imino)metalloligands resembling the well-known diazabutadiene⁷ ("dab") ligands. Pentafulvenes B are novel [N,N]H fulvenes without precedence in the literature. They are especially interesting as precursors to η^5 -[1,3-bis(imidoyl)]metallocenes **D** that are promising new ligand frameworks for electrochemically active new bis(imino) [N,C,N]-pincer complexes. The direct synthesis of 1,3-disubstituted metallocenes from fulvenes **B** is an attractive, as-short-as-possible route to metallocenes with this substitution pattern. Traditional methods require tedious multistep procedures involving consecutive directed ortho metalations and removal of protecting groups.8

Results and Discussion

Synthesis of 6-Arylamino-2-/3-imidoylpentafulvenes. Historically, the first synthetic work in the chemistry of 6-amino-2-imidoyl-pentafulvenes was reported in 1963 by Hafner^{4a,b} and later in 1970 by Müller-Westerhoff.^{4c} At that time rather cumbersome preparations of 6-aminofulvene-2-aldimines starting from 6-dimethylaminofulvene had been developed. However, these procedures are too limited for our purposes. Therefore, we devised a much more convenient synthetic protocol to such [N,N]H fulvenes, inspired by the simple one-pot preparation of the [O,O]H analogue 2-benzoyl-6-phenyl-6-hydroxyfulvene reported in 1957 by Linn and Sharkey^{2a} and in 1969 by Lloyd and Preston.^{2b}

Mechanistically, this reaction consists of a regioselective, 2-fold acylation of a cyclopentadienide salt; the regioselectivity is enforced by the formation of an intramolecular O—H—O hydrogen bond. Analogously, [N,N]H fulvenes are now accessible in a convenient one-pot reaction by interaction of cyclopentadienide with *imidoyl chlorides* as the electrophilic reagents (Scheme 2).

The key starting materials, stable N-aryl-substituted imidoyl chlorides, can easily be prepared according to published procedures: benzimidoyl chlorides9 are made from N-arylbenzamides by dehydration and chlorination with thionyl chloride, and trifluoroacetimidoyl chlorides 10 are made from trifluoroacetic acid, aniline, and carbon tetrachloride in a one-pot reaction in the presence of triethylamine and triphenylphosphine. A noteworthy feature of these N-aryl-substituted imidovl chlorides is their variable substitution pattern. Because their N-aryl group is synthetically introduced via the corresponding aniline, almost any desired substituent is possible from the large pool of commercially available anilines. For our purposes, 2,6-disubstituted N-aryl substituents are the most interesting species, due to their stereoelectronic influence on the donor properties of the corresponding [N,N] ligands.

Overall, the reaction of sodium cyclopentadienide with N-arylimidoyl chlorides depends critically on the electrophilicity of the imidoyl reagents. With benzimidoyl chlorides the expected 6-arylamino-2-imidoylpentafulvenes 1-4 are formed in yields of 11-36%, albeit only under microwave activation in a pressure-controlled microwave synthesis reactor. Standard reaction conditions such as reflux at high temperatures and/or extended reaction periods gave mostly monosubstituted fulvenes and only very low yields (< 2%) of isolable [N,N]H-fulvenes. In contrast, reactions of the more electrophilic trifluoroacetimidoyl chlorides afford the regioisomeric 6-arylamino-3-imidoylpentafulvenes 5 and 6 in isolated yields of 33-35% in a comparatively fast reaction (approximately 2 h) at room temperature without the necessity of microwave activation. Hence, fulvenes 1-4 are formed under thermodynamic control, whereas 5 and 6 are products of kinetically controlled reactions. Practically, fulvenes 1-6 are bright yellow-orange solids which crystallize easily, an advantageous property for their isolation and

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Scheme 2. Modular One-Pot Synthesis of 6-Arylamino-2-/3-imidoylpentafulvenes

purification. Mechanistically, the reaction can be envisaged by the following intermediates: first, 1 equiv of cyclopentadienide is monosubstituted by an imidoyl chloride to give an intermediate imidoylcyclopentadiene. Second, this acceptorsubstituted cyclopentadiene is deprotonated by another 1 equiv of sodium cyclopentadienide to a sodium imidoylcyclopentadienide. Third, in the case of benzimidoyl chlorides, electrophilic substitution with a second equivalent of imidoyl chloride affords 1,2-bis(imidoyl)cyclopentadienes which tautomerize to the final fulvenes 1-4 containing an intramolecular N-H-H hydrogen bond. Alternatively, in the case of trifluoroacetimidoyl chlorides, electrophilic attack of the second equivalent of imidoyl chloride at the less hindered 3-position of the cyclopentadienide moiety gives 1,3-bis-(imidoyl)cyclopentadienes which tautomerize to the final products 5 and 6, containing no intramolecular N-H-N hydrogen bond.

Structure of 6-Arylamino-2-imidoylpentafulvenes. In solution, [N,N]H-fulvenes 1-4 exist as the rapidly equilibrating tautomers depicted in Scheme 2. NMR spectra are consistent with $C_{2\nu}$ -symmetric molecules with nondistinguishable enamine/imine functionalities (1-4: $\delta_{C=N/C-N}$ 164.5-166.8 ppm) and a simple AB₂ spin system for the three fulvene hydrogens (1–4: $\delta_{\text{fulvene-H-4}} = 6.28-6.34 \text{ ppm}$; $\delta_{\text{fulvene-H-3/5}}$ 6.63-6.76 ppm). The N-aryl and imine/enamine-phenyl substituents are magnetically equivalent, consistent with $C_{2\nu}$ symmetry of these compounds. Interestingly, the hydrogen of the intramolecular N-H-N hydrogen bond is detected only for 3 (δ_{NH} 15.6 ppm). Positive mode FAB mass spectrometry shows signals of the molecular ions of all four compounds, further corroborating the identity of these pentafulvenes.

All these fulvenes crystallize extremely well, and singlecrystal X-ray structures are available for all of them (Supporting Information). Figure 1 shows the molecular structure of 4 as an instructive example. The pentafulvene ring and the two imine/enamine functionalities with their

N-H-N hydrogen bond form one conjugated planar structure, as expected. The peripheral phenyl substituents at the imine/enamine carbons and the N-2,6-dichlorophenyl substituents are more or less orthogonal with respect to this plane, due to steric congestion. The carbon-carbon bond distances as well as the two carbon-nitrogen distances of the enamine/imine functionalities are alternating between bond lengths of single and double bonds, and the hydrogen of the N-H-N hydrogen bond is localized at one nitrogen, indicating no tautomeric equilibrium in the solid state. The molecular structures of the other representatives 1-3 are in general similar; only minor differences of the tilt angles of the peripheral aryl substituents and variances in their steric shielding are evident, caused by the different 2,6-substituents of the N-aryl groups. Due to crystallographic symmetry, fulvenes 2 and 3 display averaged, nonalternating bond lengths. In contrast, representative 1 is a crystallographically nonsymmetric molecule which displays averaged single and double bonds, indicative of rapid interconversion of the two tautomeric forms in the solid state.

Due to the proximity of the two nitrogens enforced by the molecular framework of a 2-imidovl-6-aminopentafulvene. this N-H-N hydrogen bridge is a special case of a pseudoseven-membered ring system in comparison to common pseudo-six-membered hydrogen-bonded ring systems. The "true" nature of such N-H-N hydrogen bonds in the corresponding aldimines 4a-c,j has been addressed by a number of authors; 4c,d,f-i their congruent opinion is the existence of an ultrafast (microsecond-to-picosecond), low-barrier hydrogen bond with a double-well potential, in solution as well as in the solid state. An analogous tautomeric equilibrium is equally observed in the solid-state structure of the related [O,O]H-fulvene 2-benzoyl-6-hydroxy-6-phenylpentafulvene. 11 In contrast, our findings show that only

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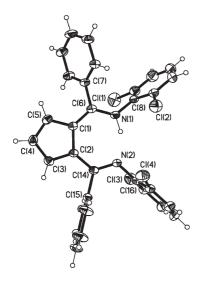


Figure 1. Molecular structure of **4**. Selected bond distances (Å) and angles (deg): C(1)-C(2)=1.470(3), C(2)-C(3)=1.398(3), C(3)-C(4)=1.393(3), C(4)-C(5)=1.369(3), C(1)-C(5)=1.430(3), C(1)-C(6)=1.402(3), C(1)-C(6)=1.337(3), C(2)-C(14)=1.429(3), C(2)-C(14)=1.307(3); dihedral angle of plane C(1)-C(6)-C(14)=1.307(3); dihedral angle of plane C(1)-C(14)-C(14)=1.307(3); dihedral angle of plane C(1)-C(14)-C(14)=1.307(3); dihedral angle of plane C(2)-C(14)-C(14)=1.307(3); dihedral angle of plane C(2)-C(14)-C(14)=1.307(3); dihedral angle of plane C(2)-C(14)-C(14)=1.307(3); versus C(16)-aryl group 84.4(1).

[N,N]H-ketimine 4 exists in the solid state as a regular fulvene without equilibrating tautomeric forms; for 2 and 3 this question cannot be solved due to crystallographic symmetry, and for 1 an averaged bonding situation is observed. We can offer no simple explanation for this incongruent behavior; one reason for this difference between [N,N]H aldimines and ketimine 4 might be the increased basicity of the latter caused by decreased tilt angles of the aryl groups and increased conjugation with concomitant stronger and localized bonding of the hydrogen of the N-H-N hydrogen bond.

Structure of 6-Arylamino-3-imidoylpentafulvenes. In contrast to compounds 1-4, both regioisomeric fulvenes 5 and 6 exist in solution as well as in the solid state as "regular" fulvenes without an equilibrium between the two formal tautomeric forms depicted in Scheme 2. Accordingly, in the solution NMR spectra all hydrogens and carbons are magnetically inequivalent. The enamine hydrogens give rise to broad signals at rather high field (5, $\delta(^{1}H)$ 8.42 ppm; 6, $\delta(^{1}H)$ 8.62 ppm), indicative of a lack of intermolecular N-H-N hydrogen bridging. A single-crystal structure analysis is available for 5 (Supporting Information, Figure 2). Overall, the fulvene core structure of C(1)-C(6) and its 6-amino and 3-imidoyl substituents is planar with alternating single and double bonds. The two peripheral N-phenyl groups are tilted with respect to this plane, most likely due to crystal-packing effects and/or steric congestion. The hydrogen is located at one nitrogen without intramolecular hydrogen bonding but with intermolecular hydrogen bonding.

Synthesis of 1,2-/1,3-Bis(imidoyl)pentamethylruthenocenes. 6-Arylamino-2-imidoylpentafulvenes 1–4 and 6-arylamino-3-imidoylpentafulvenes 5 and 6 are ambidentate [N,N]H ligand systems. After depronation by suitable bases, they are capable of forming either κ^2 or η^5 metal complexes, depending on the hard/soft character of the metal electrophile. In this contribution, we focus on the use of 1–6 as

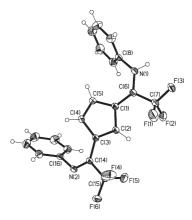


Figure 2. Molecular structure of **5**. Selected bond distances (Å): C(1)-C(2) = 1.438(2), C(2)-C(3) = 1.371(2), C(3)-C(4) = 1.453(2), C(4)-C(5) = 1.347(2), C(1)-C(5) = 1.446(2), C(1)-C(6) = 1.381(2), N(1)-C(6) = 1.338(2), C(3)-C(14) = 1.460(2), N(2)-C(14) = 1.275(2).

precursors of new metalloligands incorporating an electroresponsive ruthenocene backbone, whereas the coordination chemistry of 1-6 with hard metal centers to κ^2 metal complexes will be addressed in future work. As has been published by Bailey and co-workers in 2007, a fulvene aldimine $[N,N]H^4$ with a structure analogous to that of the 6-arylamino-2-imidoylpentafulvenes 1-4 can be converted to 1,2-bis(formimidoyl)pentamethylruthenocenes by reaction of the corresponding $[N,N]_2Zn$ or $[N,N]_2Pd$ complexes with $Cp*Ru(CH_3CN)_3^+PF_6^-$, either with loss of the N,N-coordinated zinc or with formation of a trimetallic Ru_2Pd complex. On the basis of our recent report on related [N,O]H pentafulvenes we report here on the direct transmetalation of [N,N] fulvene ketiminates to bis(imidoyl)pentamethylruthenocenes (Scheme 3).

6-Arylamino-2-imidoylpentafulvenes 1-4 are easily deprotonated by *n*-butyllithium or potassium hydride in THF solution at low temperature, and subsequent reaction with Cp*Ru(CH₃CN)₃+PF₆ at room temperature gives 1,2-bis-(imidoyl)pentamethylruthenocenes 7–9 in isolated yields of approximately 50% after aqueous workup and chromatographic purification. Note that the ruthenocene based on starting fulvene 1 is not included in this work, because only in this case was partial hydrolysis of the imino groups encountered, thereby hampering isolation of a pure product (vide infra). The choice of deprotonating agent is based on convenience; other reagents such as potassium hydride or diethylzinc gave comparable results without any advantages in comparison to n-butyllithium. The chemoselectivity of this reaction— η^5 versus κ^2 coordination—is governed by the electron-rich, soft pentamethylruthenium(II) cation, a synthon of known affinity for $6-\pi$ -aromatic systems such as benzene or cyclopentadienide. 12 Bis(imidoyl)pentamethylruthenocenes 7-9 are air-stable, yellow compounds with a high tendency to crystallize, an advantageous property for their purification and subsequent characterization. Chemically, these 1,2-bis(imidoyl)pentamethylruthenocenes are rather strong Brønsted bases, due to formation of a sevenmembered hydrogen-bridged chelate upon protonation; therefore, care must be taken to avoid acidic conditions.

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Scheme 3. Synthesis of Bis(imidoyl)pentamethylruthenocenes

By accident, in one of the syntheses of 7 its conjugate acid (7H⁺PF₆⁻) was obtained, and its structure is discussed below. On the other hand, this high basicity is clearly indicative of a highly electron-donating [N,N] ligand system, a property that will be exploited in future work addressing the coordination chemistry of these metalloligands. We also note that the facile hydrolysis of the ruthenocene based on starting fulvene 1 is without doubt due to the lack of steric protection (2,6- R_2 -phenyl substituents of 1 (R = H) versus those of 2-4 (R = CH₃, CH(CH₃)₂, Cl)) with concomitant easier attack by a proton and increased basicity of the nitrogens due to more conjugating, less tilted N-phenyl groups.

Starting from the regioisomeric 6-arylamino-3-imidoylpentafulvenes 5 and 6, the corresponding 1,3-bis(imidoyl)pentamethylruthenocenes 10 and 11 are accessible in a similar transmetalation reaction in isolated yields of 87% and 48%, respectively. The 1,3-substitution pattern of these novel ruthenocenes rules out formation of an intramolecular seven-membered hydrogen chelate; therefore, these compounds are less basic than the former 1,2-bis(imidoyl)pentamethylruthenocenes, as is exemplified by the unproblematic isolation of ruthenocene 10 with its lesser steric protection by the peripheral N-phenyl substituents. In addition, this inferior steric shielding allows isolation of 10 in 87% yield, whereas all other ruthenocenes with more bulky N-phenyl groups containing 2,6-substituents are obtained in approximately 50% yield. Physically, 1,3-bis(imidoyl)pentamethylruthenocenes 10 and 11 are yellow, air-stable compounds that crystallize readily, similarly as in the case of the former 1,2-bis(imidoyl)pentamethylruthenocenes 7-9.

Structures of 1,2-/1,3-Bis(imidoyl)pentamethylruthenocenes. In solution, the structure of ruthenocenes 7-11 is most clearly evidenced by characteristic low-field NMR signals for the imidoyl functionalities (13 C: $\delta_{C=N}$ 166.5– 171.7 ppm) and strong signals for the five magnetically equivalent methyl substituents of the Cp* moiety (1 H: δ_{CH} , 1.74–2.06 ppm; 13 C: δ_{CH_3} 10.9–12.1 ppm). The disubstituted Cp group gives rise to two ¹H signals in the ratio of 1:2

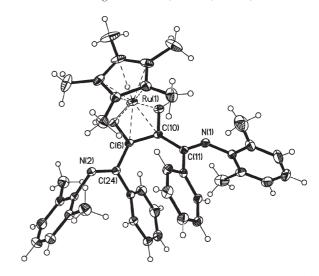


Figure 3. Molecular structure of 7. Selected bond distances (Å) and torsion angles (deg): C(11)-N(1) = 1.283(2), C(24)-N(2) = 1.283(2)1.282(2); C(6)-C(10)-C(11)-N(1) = 152.4(2), C(10)-C(6)-C(24)-N(2) = 147.3(2).

and to three (7, 10, 11) or five (8, 9) 13C resonances, indicating restricted rotation of the substituents in the latter cases. In addition, 1,3-bis(trifluoracetylimidoyl)pentamethylruthenocenes 10 and 11 show the expected ${}^{1}H-{}^{19}F$ and ¹³C-¹⁹F coupling patterns (vide infra, Experimental Section). Overall, these bis(imidoyl)ruthenocenes behave in solution as normal, regular metallocenes with quite similar spectral features for both regioisomers. By positive mode FAB or ESI mass spectrometry the (protonated) molecular ions of all compounds are detected.

The bis(imidoyl)pentamethylruthenocenes have a high tendency to crystallize, and single-crystal structures are available for all of them (Supporting Information). Figure 3 shows the molecular structure of 7 as a representative example of the 1,2-bis(imidoyl)pentamethylruthenocenes, and Figure 4 shows the structure of its conjugate acid, 7H⁺PF₆⁻, which was obtained by accident under overly acidic workup conditions. The solid-state structure of 7 consists of a regular pentamethylruthenocene with two bulky imidoyl substituents that are oriented in a transoid sense with regard to the imine functionalities. These two groups deviate from the plane of the cyclopentadienyl ring by 28° (C=N(1)) and 33° (C=N(2)), respectively, and the imine-phenyl and peripheral N-aryl substituents are tilted as well, obviously a result of steric crowding. The two more or less coplanar phenyl groups of the imine functionalities look at first sight like stacked, π -bonded aryl groups, but there is no such π -stacking because one phenyl group is oriented to the front and the second occupies a space in the back. The molecular structures of representatives 8 and 9 (Supporting Information) are similar to the structure of 7, except for conformational differences due to their different N-aryl substituents. The observation of a transoid bis-imine in the solid-state structure of 7 does not impede the ability of 1,2-bis(imidoyl)pentamethylruthenocenes to act as chelating [N,N]-metalloligands with cisoid N-donor sites, as can be inferred from the structure of its conjugate acid, $7H^+PF_6^-$ (Figure 4). In this molecule, the 1,2-imidoyl substituents of the regular pentamethylruthenocene are in a cisoid conformation, due to intramolecular N(1)-H-N(2) hydrogen bonding. The hydrogen of this N-H-H hydrogen bond is located at both

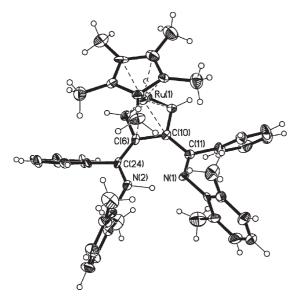


Figure 4. Molecular structure of the cation of $7H^+PF_6^-$. Selected bond distances (Å) and torsion angles (deg): C(11)-N(1) = 1.298(15), C(24)-N(2) = 1.318(11); C(6)-C(10)-C(11)-N(1) = -23(1), C(10)-C(6)-C(24)-N(2) = 5(1).

nitrogens, indicating an equilibrium between two tautomeric forms in the solid state. The bond distances of the two imines are more or less similar to those in 7, and the deviation of the planes of the imine functionalities C=N(1) and C=N(2)from the cyclopentadienide plane are also in the same range $(-23^{\circ} \text{ and } 5^{\circ})$. The N-2,6-dimethylphenyl substituents are roughly orthogonal to the imine planes, thereby providing axial steric shielding of the seven-membered chelate ring. In addition, due to the presence of the 2,6-dimethyl groups, the pentamethylruthenocene is in an eclipsed conformation with one methyl group of the pentamethylcyclopentadienyl ring being positioned atop the seven-membered chelate, thereby effectively blocking one axial site. The phenyl substituents of the imine functionalities are tilted as well, due to steric reasons. Overall, this structure shows that 1,2-bis(imidoyl)pentamethylruthenocenes are exceptionally bulky diimine ligand systems with not only peripheral but also axial steric shielding.

Figure 5 shows the molecular structure of 11 as a representative example of the 1,3-bis(imidoyl)pentamethylruthenocenes. In the solid-state structure of 11 a regular pentamethylruthenocene is observed with its two 1,3-trifluoroimidoyl substituents oriented in a cisoid conformation of the trifluoromethyl and imino moieties. The deviations of the π -imine planes from the cyclopentadienyl ring are 17° (C=N(1)) and 21° (C=N(2)), respectively. As observed in all the other structures, the N-aryl substituents are tilted as well, thereby avoiding steric congestion. With regard to the anticipated use of 1,3-bis(imidoyl)pentamethylruthenocenes as a precursors of [N,C,N]-pincer metal complexes containing the N(1)-C(6)-N(2) donor set, the solid-state structure shows the "wrong" backward orientation of the two imine pincer clip; however, in solution rotation of the imidoyl substituents seems possible. The molecular structure of representative 10 (Supporting Information) is quite similar; only minor conformational differences are observed.

Electrochemistry of Bis(imidoyl)pentamethylruthenocenes. The anodic electrochemistry of ruthenocenes tends to be complicated. The parent ruthenocenium ion, Cp_2Ru^+ , is

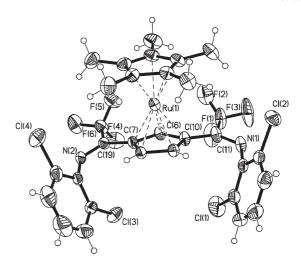


Figure 5. Molecular structure of **11**. Selected bond distances (Å) and torsion angles (deg): C(11)-N(1)=1.269(4), C(19)-N(2)=1.270(4); C(6)-C(10)-C(11)-N(1)=-162.5(4), C(6)-C(7)-C(19)-N(2)=159.0(3).

easily attacked by even modest nucleophiles to render addition products Cp_2Ru - $X^{(1-n)+}$ (n=0 for X= neutral ligand such as CH_3CN , n=1 for X= anionic ligand). The exceptionally high electrophilicity of Cp_2Ru^+ is illustrated by the fact that it rapidly abstracts F^- from the BF_4^- or PF_6^- counterions of popular, traditional supporting electrolytes. Being more electron rich than the parent ruthenocenium ion itself, Cp_2Ru - X^{n+} is then subject to further oxidation at the potential of the $Cp_2Ru^{0/+}$ couple or undergoes disproportionation. The result is a net two-electron-oxidation process as expressed in eqs 1-4, with Ru(IV) species as the ultimate products. I^3

$$Cp_2Ru \leftrightharpoons Cp_2Ru^+ + e^-$$
 (1)

$$Cp_2Ru^+ + X^{n-} \leftrightharpoons Cp_2Ru - X^{(1-n)+}$$
 (2)

$$Cp_2Ru-X^{(1-n)+} \Longrightarrow Cp_2Ru-X^{(2-n)+} + e^-$$
 (3)

$$2Cp_2Ru-X^{(1-n)+} \iff Cp_2Ru-X_2^{(2-n)+} + Cp_2Ru$$
 (4)

Pentamethylruthenocene shows a qualitatively similar behavior in the CH_2Cl_2/NBu_4ClO_4 electrolyte. ¹⁴ In permethylated Cp^*_2Ru ($Cp^* = \eta^5 \cdot C_5Me_5$) or $Cp^*Ru(\eta^5 \cdot Indenyl)$ steric protection and electron donation from the alkyl substituents combine to render the oxidation a chemically reversible one-electron process. ¹⁵ When fluorinated tetrarylborates such as $B(C_6F_5)_4^-$ and $B[(1,3\cdot CF_3)_2C_6H_3]_4^-$ are used as supporting electrolyte counterions in non-nucleophilic solvents, none of the above reactions 2–4 prevail. ¹⁶

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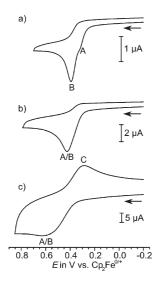


Figure 6. Cyclic voltammetry of complex 9 (0.1 M NBu₄PF₆/ CH_2Cl_2 , room temperature) at (a) v = 0.05 V/s, (b) v = 0.4 V/s, and (c) v = 10 V/s.

Instead, Cp₂Ru⁺ engages in an equilibrium with its Ru–Rubonded dimer [Cp₂Ru-RuCp₂]²⁺.¹⁷

The present set of ruthenocenes featuring two differently substituted Cp rings allow us to study how the combined effects of only partial steric protection and electronic modification by two different bis(iminoyl) substitution patterns (1,2 versus 1,3) affect their anodic behavior in the CH₂Cl₂/NBu₄PF₆ electrolyte system, where the parent ruthenocenium cation is highly reactive. These studies also pertain to the bis(imidoyl)ruthenocenes 7-11 as novel metalloligands containing redox-active, conjugated ruthenocene and imine functionalities. To this end, cyclic voltammetry on the selected representatives 9-11 was per-

The overall anodic behavior of compounds 9 and 10 is qualitatively similar: at room temperature, and at sweep rates of 20 mV/s to several V/s, the first anodic oxidation peak A is followed by an additional minor peak B at slightly more positive potentials (see Figures 6 and 7). Increasing the sweep rate has the effect of first broadening the secondary peak and decreasing its height and then merging all anodic features into a single, heavily broadened peak (Figure 6). The reverse scan features inflections at the positions where the counterpeak of oxidation B should be located. Under appropriate conditions, the back-reduction of the respective ruthenocenium ion appears as peak C (see Figures 6c and 7). Peak C is also present when the sweep is clipped immediately after traversing through peak A, which adds further evidence that A/C constitute the associated peaks of an electrochemical couple. The ratio of cathodic to anodic peak currents generally increases with increasing sweep rate or as the temperature is lowered. Wave A/C has the diagnostic features of a chemically partially reversible and electrochemically quasireversible one-electron event. Thus, forward peak half-widths and peak-to-peak separations are consistently larger than that of the ferrocene standard under identical conditions. Deviations from ideality become ever more apparent as the sweep rate is increased or the temperature is lowered, in

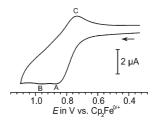


Figure 7. Cyclic voltammogram of complex 10 (0.1 M NBu₄- PF_6/CH_2Cl_2 ,room temperature) at v = 0.1 V/s.

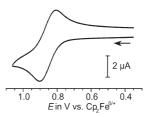


Figure 8. Cyclic voltammogram of complex **11** (0.1 M NBu₄PF₆/ CH_2Cl_2 , room temperature) at v = 0.1 V/s.

keeping with sluggish electron-transfer kinetics. Half-wave potentials $E_{1/2}$ are estimated as +0.42 V for 9 and +0.83 V for 10 against the ferrocene/ferrocenium standard. Despite its significantly higher half-wave potential, complex 10 shows partial reversibility even at room temperature and at low sweep rates, while for 9 low temperatures (see Figure S1 of the Supporting Information) or sweep rates of 5 V/s or higher are required in order to observe peak C (Figures 6c and 7). Better resolution of oxidation peaks A and B is obtained in square wave voltammetry, as is illustrated in Figures S2 and S3 of the Supporting Information. Compound 11 exhibits a single chemically reversible and electrochemically quasireversible wave at $E_{1/2} = +0.855 \text{ V}$ (Figure 8). Upon scanning to higher potentials, a second irreversible anodic peak at $E_p = +1.08 \text{ V}$ (v = 0.20 V/s) is seen for complex 9. An associated reduction peak at -1.47 V, which is otherwise absent, appears on the cathodic reverse scan (Figure S4 of the Supporting Information). No such features were observed for 10 or 11, where the additional oxidation probably lies outside the accessible potential window. Likewise, no reduction waves of 9-11 were found within the cathodic limit of the NBu₄PF₆/CH₂Cl₂ electrolyte.

On comparison to the reversible half-wave potential of pentamethylruthenocene (Cp*CpRu, $E_{1/2} = +0.22$ V in $CH_2Cl_2/NBu_4^+B[(1,3-CF_3)_2C_6H_3]_4^-)$ it becomes evident that the imine functionalities on the second substituted Cp ring exert a sizable (9) or strong (10, 11) electron-withdrawing effect. Thus, the half-wave potential of 9 resembles that of $Cp*(\eta^5-C_5H_4COMe)Ru$ (+0.46 V), while the potential of **10** is similar to that of $Cp^*(\eta^5-C_5Cl_5)Ru$ (0.94 V). ^{16b} The rather similar half-wave potentials of 10 and 11 demonstrate that the aryl substituents on the imine nitrogens exert rather little influence on their redox potential. This may arise from the strong tilt between the cyclopentadienyl and the aryl substituent planes. The substituents on the conjugated imine carbon atoms and, possibly, the mutual disposition of the imine functionalities have, however, a profound influence, with the CF₃-substituted 1,3-isomers being harder to oxidize but giving chemically more stable radical cations than the phenyl-substituted 1,2-isomers.

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Conclusions

By a modular one-pot reaction of sodium cyclopentadienide with various imidoyl chlorides, new fulvenes with two N-functionalities are easily accessible in isolated yields of 11–35%. Starting from benzimidoyl chlorides, 6-arylamino-2-imidoylpentafulvenes are formed in a microwave-assisted synthesis under thermodynamic control, whereas from trifluoroacetimidoyl chlorides regioisomeric 6-arylamino-3-imidoylpentafulvenes are formed under kinetic control. Mechanistically, this reaction is a regioselective 2-fold imidoacylation of cyclopentadienide with a dual role for cyclopentadienide, first as a nucleophile and second as a Brønsted base for the deprotonation of the monoimidoacylated intermediate, thereby requiring a stochiometric ratio of 1:1 for sodium cyclopentadienide and imidoyl chloride. Structurally, these fulvenes exist either as rapidly interconverting pairs of tautomers of N-H-N hydrogen-bridged structures in solution and in the solid state or as regular fulvenes without structural dynamics, depending on their substitution pattern. These fulvenes are ambidentate [N,N]H ligand systems capable of forming either κ^2 N,N- or η^5 -cyclopentadienyl complexes, depending on the hardness or softness of the metal electrophile. Reaction of the deprotonated fulvenes with "arenophilic" pentamethylcyclopentadienylruthenium(II) hexafluorophosphate affords 1,2or 1,3-bis(imidoyl)pentamethylruthenocenes in isolated yields of 48-87%. These bis(imidoyl)metallocenes represent novel [N,N]-metalloligands composed of an electroresponsive pentamethylruthenocenyl moiety and two directly attached imine functionalities with tunable steric protection and adjustable regiochemistry. NMR spectroscopy and single-crystal structure analyses show that these ruthenocenes behave as normal, regular metallocenes with quite similar spectral features for both regioisomers. Cyclic voltammetry reveals partially reversible oxidations of these ruthenocenes and differing stability of their radical cations, depending on their substitution pattern.

In future work we will address the coordination chemistry of these new [N,N]-metalloligands and the electrochemistry and potential catalytic applications of their metal complexes: 1,2-bis(imidoyl)pentamethylruthenocenes will most likely give access to new κ^2 N,N-metal complexes, whereas 1,3-bis-(imidoyl)pentamethylruthenocenes are possible precursors to novel κ^3 N,C,N-pincer complexes. In both types of complexes, the focus of our interest will be on the steric and electronic influence of the directly attached pentamethylruthenocene core, as well as its potentially beneficial role in catalytic and/or photophysical applications.

Experimental Section

General Considerations. All reactions and manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of dry argon using Schlenk techniques or in a conventional dinitrogen-filled glovebox (UNIlab mBraun). Solvents such as toluene, THF, diethyl ether, and *n*-hexane were dried over and distilled from Na under an argon atmosphere prior to use; dichloromethane was dried over Siccapent. All solvents and other reagents were commercially obtained and used as received. Microwave-assisted syntheses were performed in an Anton Paar Synthos 3000 microwave reactor. NMR spectra were recorded on a Bruker Avance DPX 300 (300 MHz) spectrometer, and ¹H and ¹³C shifts are reported in ppm relative to Si(CH₃)₄ and were referenced internally with respect to the protio solvent ¹³C resonances. IR spectra were recorded on a

THERMO Nicolet 5700 ATR-FT-IR spectrometer. Melting points were measured on a Leica Galen Kofler-microscope. Mass spectra were recorded on a Finnegan MAT 95 mass spectrometer. Single-crystal structure analysis was carried out on a Nonius Kappa CCD diffractometer. Electrochemical work was performed on a BAS CV50 potentiostat in a home-built vacuumtight one-compartment cell using a 1.6 mm diameter Pt-disk working electrode from BAS, a platinum spiral as the counter electrode, and a silver spiral as a pseudoreference electrode. Each of the spiral-shaped electrodes was welded to Vycon wire and sealed into a glass tube. Counter and reference electrodes were introduced into the cell by appropriate fittings in the side wall and sealed via a Quickfit screw. Potential calibration was performed by adding an appropriate amount of ferrocene to the analyte solution and repeating all necessary scans previously performed on the pure analyte in the presence of the standard.

Representative Procedure for the Synthesis of 6-Arylamino-2imidoylpentafulvenes: 1-[5-[1-[N-(Phenyl)amino-1-phenylmethylene]cyclopenta-1,3-dienyl]phenylmethylene]aniline (1). Two microwave linears were each charged with 4 mL of tetrahydrofuran (THF), 1 equiv of a 2.0 M solution of sodium cyclopentadienide in THF (3.0 mL, 6 mmol), and 1.1 equiv of a THF solution of N-phenylbenzimidoyl chloride⁹ (10 mL, 6.6 mmol). The microwave program was run under the following conditions: three times of irradiation at 400 W for 25 min, maximum temperature 120 °C, maximum pressure 2.2 bar. Workup: THF was removed on a vacuum line, and the crude product was extracted into diethyl ether at neutral pH. The combined ethereal layers were washed with water, saturated aqueous ammonium chloride solution, and saturated aqueous sodium chloride solution, and the organic phase was dried with anhydrous sodium sulfate. Volatile materials were removed on a rotary evaporator to afford the crude brown to orange product. Chromatography on silica with dichloromethane as eluent and subsequent removal of solvents and crystallization from n-hexane/diethyl ether yielded the pure product as light orange crystals in 35.7% yield. Mp: 219 °C. ¹H NMR (CDCl₃): δ 6.28 (t, 1H, J = 3.9 Hz, fulvene-H-4), 6.63 (d, 2H, J = 3.9 Hz, fulvene-H-3/5), 6.79 (m, 4H, phenyl), 6.94 (t \times t, 2H, $^{1}J = 1.2$ Hz, $^2J = 7.4$ Hz, phenyl), 7.09 (m, 4H, phenyl), 7.33–7.42 (m, 10H, phenyl), no signal for the tautomerizing H. 13 C NMR (CDCl₃): δ 118.6, 123.8, 124.2, 124.3, 128.0, 128.8, 128.8, 129.9, 135.6, 137.2, 144.2, 164.5 (imine/enamine). MS (FAB pos): m/z 425.15 (M + H) $^{+}$. IR (ATR; cm $^{-1}$) 560.7 s, 601.9 w, 627.9 w, 687.1 vs, 700.2 s, 712.0 s, 749.5 m, 779.9 w, 884.6 w, 898.1 w, 1001.6 m, 1024.5 m, 1046.9 m, 1073.3 m, 1134.6 m, 1162.6 s, 1239.7 m, 1330.9 s, 1358.6 s, 1441.7 s, 1482.3 s, 1530.5 m, 1577.6 m, 1650.7 w, 2850.7 w, 2923.5 w, 3021.6 w, 3056.5 w, 3075.5 w. Anal. Calcd for $C_{31}H_{24}N_2$ (424.55): C, 87.70; H, 5.70; N, 6.60. Found: C, 87.94; H, 5.72; N, 6.84. Single-crystal X-ray structure: Supporting Information.

1-[5-[1-[N-(2,6-Dimethylphenyl)amino-1-phenylmethylene]cyclopenta-1,3-dienyl]phenylmethylene]-2,6-dimethylaniline (2). Starting materials: 8.0 mmol of NaCp, 8.8 mmol of N-2,6-dimethylphenylbenzimidoyl chloride. 9 Yield: 20.8%. Mp: 252 °C. 1H NMR (CDCl₃): δ 2.25 (s, 12H, CH₃), 6.28 (t, 1H, J = 3.8 Hz, fulvene-H-4), 6.59 (d, 2H, J = 3.8 Hz, fulvene-H-3/5), 6.81–6.89 (m, 6H, aryl), 7.22-7.29 (m, 6H, aryl), 7.38-7.41 (m, 4H, aryl), no signal for the tautomerizing H. 13 C NMR (CDCl₃): δ 19.3 (aryl-CH₃), 117.3, 123.4, 125.3, 127.3, 128.0, 128.6, 128.8, 131.7, 134.5, 137.4, 141.3, 166.8 (imine/enamine). MS (FAB pos): m/z 480.38 (M⁺). IR (ATR; cm⁻¹) 504.3 w, 545.2 w, 582.8 w, 600.0 m, 666.3 w, 697.1 s, 740.8 m, 758.5 s, 773.6 m, 890.3 m, 958.1 w, 1027.4 w, 1047.9 w, 1089.0 m, 1135.3 w, 1160.6 m, 1227.4 w, 1257.0 w, 1347.0 w, 1439.3 w, 1470.9 w, 1538.6 w, 1581.8 w, 1596.9 w, 2851.8 w, 2916.6 w, 2942.4 w, 3021.5 w, 3114.8 w. Anal. Calcd for C₃₅H₃₂N₂ (480.65): C, 87.46; H, 6.71; N, 5.83. Found: C, 87.71; H, 6.74; N, 5.67. Single-crystal X-ray structure: Supporting Information.

1-[5-[1-[*N*-(2,6-Diisopropylphenyl)amino-1-phenylmethylene]-cyclopenta-1,3-dienyl]phenylmethylene]-2,6-diisopropylaniline (3). Starting materials: 8.0 mmol of NaCp, 8.8 mmol of

N-2,6-diisopropylphenylbenzimidoyl chloride. Yield: 10.5%. Mp: $208 \,^{\circ}$ C. ¹H NMR (CDCl₃): $\delta 0.85$ (d, 12H, CH₃, J = 7 Hz), 1.05 (d, 12H, CH₃, J = 7 Hz), 3.24 (sept, 4H, CH(CH₃)₂, J = 7Hz), 6.34 (t, 1H, fulvene-4-H, J = 4 Hz), 6.76 (d, 2H, fulvene-H-3/5, J = 4 Hz), 6.94-7.05 (m, 6H, aryl), 7.27-7.29 (m, 6H, aryl), 7.41–7.44 (m, 4H, aryl), 15.58 (s, 1H, NH). ¹³C NMR (CDCl₃): δ 23.5 (CH₃), 24.8 (CH₃), 28.5 (CH(CH₃)₂), 117.6, 123.8, 124.3, 126.1, 127.3, 129.0, 130.4, 134.9, 137.1, 139.7, 141.5, 166.4 (imine/enamine). MS (FAB pos): m/z 592.43 (M⁺). IR (ATR; cm⁻¹) 504.3 m, 545.4 m, 582.6 m, 599.9 vs, 666.5 m, 697.1 vs, 740.6 s, 758.1 vs, 773.5 s, 843.3 w, 889.3 m, 957.8 m, 1027.4 m, 1048.0 m, 1088.8 m, 1135.3 m, 1160.0 m, 1210.7 m, 1227.2 m, 1257.1 m, 1348.6 m, 1439.3 m, 1471.0 m, 1536.8 m, 1600.0 w, 2853.8 w, 2917.2 w, 2942.5 w, 3018.5 w, 3113.5 w, 3632.7 w. Anal. Calcd for C₄₃H₄₈N₂ (592.87): C, 87.11; H, 8.16; N, 4.73. Found: C, 87.42; H, 8.18; N, 4.79. Single-crystal X-ray structure: Supporting Information.

1-[5-[1-[N-(2,6-Dichlorophenyl)amino-1-phenylmethylene]cyclopenta-1,3-dienyl]phenylmethylene]-2,6-dichloroaniline (4). Starting materials: 8.0 mmol of NaCp, 8.8 mmol of N-2,6-dichlorophenylbenzimidoyl chloride.⁹ Yield: 27.9%. Mp: 170 °C. ¹H NMR (CDCl₃): δ 6.29 (t, 1H, fulvene-H-4, J = 4 Hz), 6.30 (d, 2H, fulvene-H-3/5, J = 4 Hz), 6.81-6.86 (m, 2H, aryl), 7.10 (s, 2H, aryl), 7.13 (s, 2H, aryl), 7.24–7.30 (m, 6H, aryl), 7.55–7.57 (m, 4H, aryl), no signal for the tautomerizing H. 13 C NMR (CDCl₃): δ 119.1, 123.9, 126.6, 127.4, 128.2, 128.7, 129.2, 131.4, 137.0, 137.3, 140.3, 167.8 (imine/enamine). MS (FAB pos): m/z 562.06 (M⁺). IR (ATR; cm⁻¹): 586.9 w, 673.8 m, 697.9 s, 764.7 s, 898.4 m, 1031.9 m, 1174.3 w, 1241.0 w, 1338.9 w, 1432.5 m, 1485,8 w, 1557.0 w, 1641.5 m, 1668.2 w, 2847.5 w, 2927.6 w, 2954.3 w, 3056.6 w. Anal. Calcd for C₃₁H₂₀Cl₄N₂ (562.33): C, 66.21; H, 3.58; N, 4.98. Found: C, 66.38; H, 3.60; N, 5.19. Single-crystal X-ray structure: Figure 1, Supporting Information.

Representative Procedure for the Synthesis of 6-Arylamino-3imidoylpentafulvenes: 2,2,2-Trifluoro-1-[3-1-[2,2,2-trifluoro-1-N-[(phenylamino)ethylene]cyclopenta-1,4-dienyl]ethylene]aniline (5). A Schlenk vessel was charged with 8 mL of dry THF and 1 equiv of a 2.0 molar solution of sodium cyclopentadienide in THF (2.0 mL, 4.0 mmol). At 0 °C, 0.9 equiv of N-phenyltrifluoroacetimidovl chloride 10 (0.80 g, 3.9 mmol) was added via syringe, and the color of the solution changed from violet to yellow-brown. The mixture was then stirred at ambient temperature for 2 h. Workup: THF was removed on a vacuum line and the crude, now green product was extracted into diethyl ether at neutral pH, accompanied by a color change from green to a bright orange. The combined ethereal layers were washed with water, saturated aqueous ammonium chloride solution, and saturated aqueous sodium chloride solution, and the organic phase was dried with anhydrous sodium sulfate. Volatile materials were removed on a rotary evaporator to afford the crude brown to orange product. Chromatography on silica with diethyl ether/n-pentane (1/4 v/v) and crystallization yielded the slightly light- and air-sensitive product as bright orange crystals in 35.4% yield (289 mg). Mp: 133 °C. ¹H NMR (CD₃CN): δ 5.59 (s, 2H, fulvene-H), 6.41 (s, 1H, fulvene-H), 6.99–7.02 (m, 4H, aryl), 7.24–7.28 (m, 2H, aryl), 7.36–7.41 (m, 4H, aryl), 8.42 (s, broad, NH). 13 C NMR (CDCl₃): δ 117.6, 118.8, 119.1, 119.3, 121.6, 124.8, 125.0, 125.3, 126.2, 127.6, 128.5, 128.8, 129.2, 129.4, 129.6, 130.5, 130.9, 138.4, 149.4, 149.8, 151.6, 151.8. MS (ESI pos): m/z 408.11 (M⁺), 431.07 (M + Na)⁺. IR (ATR; cm⁻¹): 491.8 m, 574.1 m, 605.8 m, 691.3 s, 719.8 m, 760.9 m, 830.6 m, 879.2 s, 890.7 m, 912.1 m, 924.1 m, 985.8 s, 1074.4 m, 1106.1 s, 1131.4 vs, 1169.4 s, 1245.4 s, 1359.4 m, 1470.9 m, 1517.4 m, 1548.1 s, 1571.5 s, 1600.0 m, 1631.7 w, 2895.0 w, 3034.3 w, 3183.1 w. Anal. Calcd for C₂₁H₁₄F₆N₂ (408.35): C, 61.77; H, 3.46; N, 6.86. Found: C, 62.04; H, 3.44; N, 6.72. Single-crystal X-ray structure: Figure 2, Supporting Information.

2,2,2-Trifluoro-1-[3-1-[2,2,2-trifluoro-1-*N*-[(2,6-dichlorophenylamino)ethylene]cyclopenta-1,4-dienyl]ethylene]-2,6-dichloroaniline (6). Starting materials: 6.0 mmol of NaCp, 6.9 mmol of N-2,6dichlorophenyltrifluoroacetimidoyl chloride. 10 Yield: 32.6%.

Mp: 154 °C. 1 H NMR (CD₃CN): δ 5.84 (s, 2H, fulvene-H), 6.17 (s, 1H, fulvene-H), 7.28-7.33 (m, 2H, aryl), 7.46-7.49 (m, 4H, aryl), 8.62 (s, 1H, NH). ¹³C NMR (CDCl₃): δ 118.5, 118.8, 122.9, 124.5, 126.0, 127.1, 129.0, 129.2, 129.7, 131.2, 132.3, 141.6, 155.6. MS (ESI pos): *m/z* 546.95 (M⁺). IR (ATR; cm⁻¹): 698.1 m, 738.2 w, 790.0 m, 871.9 m, 894.1 m, 978.5 m, 1018.5 m, 1095.5 s, 1137.1 s, 1178.7 m, 1232.1 m, 1281.1 m, 1321.1 m, 1374.5 m, 1432.6 s, 1516.9 m, 1563.9 s, 1583.7 m, 1628.2 m, 2851.9 w, 2976.5 w, 3038.8 w, 3163.4 w. Anal. Calcd for C₂₁H₁₀Cl₄F₆N₂ (546.13): C, 46.19; H, 1.85; N, 5.13. Found: C, 46.09; H, 1.84; N, 5.07.

Representative Procedure for the Synthesis of 1,2-/1,3-Bis-(imidoyl)pentamethylruthenocenes: 1,2-Bis[1-[N-(2,6-dimethylphenyl)imino]-1-phenylmethyl]-1',2',3',4',5'-pentamethylruthenocene (7). A Schlenk tube was charged under an atmosphere of argon with 2 (240 mg, 0.50 mmol), 20 mL of dry THF, and a stirring bar. At a temperature of -60 °C, 1.1 equiv of a 1.6 M n-butyllithium solution in hexane (0.34 mL, 0.55 mmol) was added, and the solution darkened as it was heated to ambient temperature. After the mixture was stirred for 24 h, Cp*Ru-(CH₃CN)₃PF₆ (250 mg, 0.50 mmol) was added all at once at -60 °C, accompanied by further darkening of the solution. The solution was stirred overnight at ambient temperature; afterward, solvents were removed on a vacuum line. Workup: the reaction mixture was hydrolyzed by addition of water, the organic materials were extracted three times with diethyl ether, and the organic layers were combined and dried over extraction with brine and addition of Na₂SO₄. The volatile materials were removed on a rotary evaporator. Chromatography on silica with dichloromethane (elution of unreacted ligand), followed by elution of the product with diethyl ether, yielded the pure product as yellow crystals in 46.9% yield (168 mg). ¹H NMR (CDCl₃): δ 1.68 (s, 6H, aryl-CH₃), 1.98 (s, 6H, aryl-CH₃), 2.05 (s, 15H, Cp*CH₃), 4.40 (unresolved m, 1H, Cp-H), 4.70 (unresolved m, 2H, Cp-H), 6.66–6.71 (m, 2H, aryl), 6.76–6.81 (m, 2H, aryl), 7.03–7.13 (m, 10H, aryl). 13 C NMR (CDCl₃): δ 12.1 (Cp*CH₃), 18.4 (aryl-CH₃), 18.9 (aryl-CH₃), 74.5, 78.8, 87.5, 90.4, 121.9, 125.2, 126.7, 127.4, 127.5, 127.6, 128.5, 138.6, 149.7, 166.5 (C=N). MS (FAB pos): m/z 717.32 (M + H)⁺. IR (ATR; ${\rm cm}^{-1}) : 447.8 \, {\rm m}, 507.5 \, {\rm w}, 669.6 \, {\rm m}, 678.0 \, {\rm m}, 696.6 \, {\rm s}, 758.6 \, {\rm s}, 775.6$ m, 806.3 w, 827.1 m, 895.7 w, 960.5 m, 1026.8 m, 1081.4 m, 1155.9 w, 1205.7 m, 1252.9 m, 1279.6 m, 1347.0 w, 1374.5 m, 1445.4 m, 1469.2 m, 1571.1 m, 1588.2 m, 1736.1 w, 2852.5 m, 2919.5 m, 2952.0 m, 3050.1 w. Anal. Calcd for C₄₅H₄₆N₂Ru (715.94): C, 75.49; H, 6.48; N, 3.91. Found: C, 75.77; H, 6.50; N, 3.94. Single-crystal X-ray structure: Figure 3, Supporting Information.

1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl)imino]-1-phenylmethyl]-1,2-Bis[1-[N-(2,6-diisopropylphenyl]imino]-1,21',2',3',4',5'-pentamethylruthenocene (8). Starting materials: 0.54 mmol of 3, 0.49 mmol of Cp*Ru(CH₃CN)₃PF₆. Yield: 47.1%. Mp: 210 °C. ¹H NMR (CD₂Cl₂): δ 0.76 (s, 12H, isopropyl), 1.08-1.17 (m, 12H, isopropyl), 2.06 (s, 15H, Cp*CH₃), 2.60 (s, 2H, isopropyl-CH), 2.82 (s, 2H, isopropyl-CH), 4.40 (s, 1H, Cp-H), 5.04 (s, 2H, Cp-H), 6.82-7.00 (m, 16H, aryl). ¹³C NMR (CDCl₃): δ 11.7 (Cp*CH₃), 15.5 (isopropyl-CH₃), 21.8 (isopropyl-CH₃), 22.7 (isopropyl-CH₃), 23.8 (isopropyl-CH₃), 25.2 (isopropyl-CH₃), 27.7 (isopropyl-CH₃), 28.0 (isopropyl-CH₃), 30.0 (isopropyl-CH₃), 66.0, 75.6, 79.7, 87.3, 91.0, 122.7, 122.8, 123.0, 127.3, 128.3, 129.6, 135.7, 136.1, 137.7, 147.3, 166.4 (imine/ enamine), 166.5 (imine/enamine). MS (ESI pos): m/z 828.48 (M⁺). IR (ATR; cm⁻¹): 506.8 w, 694.0 s, 759.2 s, 773.3 m, 827.2 w, 898.4 m, 960.7 w, 1030.0 m, 1152.0 w, 1249.9 w, 1281.1 m, 1321.1 w, 1361.2 w, 1423.5 m, 1459.1 m, 1573.1 m, 1586.7 m, 1598.6 m, 1726.1 w, 2865.3 m, 2918.7 m, 2959.9 m, 3056.6 w. Anal. Calcd for C₅₃H₆₂N₂Ru (828.16): C, 76.87; H, 7.55; N, 3.38. Found: C, 77.02; H, 7.52; N, 3.31. Single crystal X-ray structure: Supporting Information.

1,2-Bis[1-[N-(2,6-dichlorophenyl)imino]-1-phenylmethyl]-1',2',3', 4',5'-pentamethylruthenocene (9). Starting materials: 0.49 mmol of 4, 0.49 mmol of Cp*Ru(CH₃CN)₃PF₆. Yield: 49.8%. Mp: 227 °C. ¹H NMR (CD₂Cl₂): δ 2.00 (s, 15H, Cp*CH₃), 4.45 (s, 1H, Cp-H),

4.85 (s, 2H, Cp-H), 6.71 $^-$ 6.73 (unresolved t, 2H, aryl), 7.05 (unresolved m, 14H, aryl). 13 C NMR (CD₂Cl₂): δ 11.9 (Cp*CH₃), 66.0, 75.2, 79.6, 88.1, 89.3, 123.0, 124.6, 125.5, 27.5, 128.0, 128.4, 128.9, 138.2, 147.0, 171.7 (C=N). MS (ESI pos): m/z 798.09 (M + H) $^+$. IR (ATR; cm $^{-1}$): 671.4 m, 701.1 s, 746.3 s, 764.5 s, 791.6 m, 827.2 m, 840.5 w, 898.4 m, 956.2 m, 1027.4 m, 1063.0 w, 1156.5 w, 1227.7 m, 1254.4 m, 1281.1 m, 1347.8 w, 1379.0 w, 414.6 m, 1454.6 w, 1494.7 w, 1548.1 m, 1565.9 m, 1597.3 s, 1650.4 w, 1721.6 w, 2847.5 w, 2900.9 w, 2954.3 w, 3061.1 w. Anal. Calcd for C₄₁H₃₄-Cl₄N₂Ru (797.62): C, 61.74; H, 4.30; N, 3.51. Found: C, 61.56; H, 4.29; N, 3.40. Single-crystal X-ray structure: Supporting Information.

1,3-Bis[2,2,2-trifluoro-1-[*N*-(phenyl)imino]ethyl]-1',2',3',4',5'-pentamethylruthenocene (10). Starting materials: 0.50 mmol of 5, 0.5 mmol of Cp*Ru(CH₃CN)₃PF₆. Yield: 86.7%. Mp: 171 °C. ¹H NMR (CD₃CN): δ 1.74 (s, 15H, Cp*CH₃), 3.86 (s, 2H, Cp-H), 4.22 (s, 1H, Cp-H), 6.71–6.73 (d, 4H, J = 7.4 Hz, phenyl), 7.13–7.17 (t, 2H, J = 7.4 Hz, phenyl), 7.34–7.39 (t, 4H, J = 7.8 Hz, phenyl). ¹³C NMR (CDCl₃): δ 10.9 (Cp*CH₃), 76.6, 76.8, 77.1, 88.6, 114.4, 118.1, 121.9, 125.6 (trifluoromethyl, ¹J(¹³C-¹°F) = 280.5 Hz), 116.9, 124.7, 129.8, 149.6, 153.1, 153.5, 153.9, 154.4 (²J(¹³C-¹°F) = 32.4 Hz, C=N). MS (FAB pos): m/z 644.12 (M⁺). IR (ATR; cm⁻¹): 418.2 m, 440.3 m, 506.5 m, 537.2 w, 693.6 v, 718.7 m, 763.2 vs, 827.0 w, 877.5 m, 902.5 s, 982.2 s, 996.6 s, 1025.6 m, 1069.5 m, 1128.8 vs, 1140.1 vs, 1166.5 s, 1184.5 m, 1216.6 m, 1249.5 m, 1290.2 w, 1371.4 m, 1425.0 w, 1462.3 m, 1482.4 m, 1593.9 m, 1633.3 vs, 2848.5 w, 2912.3 w, 2951.9 w, 2991.4 w, 3064.3 w. Anal. Calcd for C₃₁H₂₈F₆N₂Ru (643.64): C,

57.85; H, 4.38; N, 4.35. Found: C, 57.98; H, 4.40; N, 4.36. Single-crystal X-ray structure: Supporting Information.

1,3-Bis[2,2,2-trifluoro-1-[*N*-(2,6-dichlorophenyl)imino]ethyl]-1',2',3',4',5'-pentamethylruthenocene (11). Starting materials: 0.44 mmol of 6, 0.44 mmol of Cp*Ru(CH₃CN)₃PF₆. Yield: 48.0%. Mp: 195 °C. ¹H NMR (CDCl₃): δ 1.82 (s, 15H, Cp*CH₃), 4.01 (s, 2H, Cp-H), 4.29 (s, 1H, Cp-H), 7.02 (t, 2H, J = 8.1 Hz, aryl), 7.31–7.34 (m, 4H, aryl). ¹³C NMR (CDCl₃): δ 11.1 (Cp*CH₃), 73.8, 75.4, 79.1, 90.0, 117.9, 121.6, 123.0, 123.9, 125.6, 128.8, 129.0, 131.3, 144.0, 159.0 (2 J(13 C $^{-19}$ F) = 34.6 Hz, C=N). MS (ESI pos): *m*/*z* 782.04 (M + H)⁺. IR (ATR; cm⁻¹): 715.9 m, 738.2 s, 769.5 s, 790.5 s, 831.6 w, 880.6 m, 996.3 s, 1144.1 s, 1169.8 m, 1214.3 m, 1249.9 s, 1383.4 w, 1432.4 s, 1476.9 m, 1557.0 w, 1639.7 s, 1677.1 w, 2847.5 w, 2905.3 w, 2958.7 w. Anal. Calcd for C₃₁H₂₄Cl₄-F₆N₂Ru (781.42): C, 47.65; H, 3.10; N, 3.58. Found: C, 47.62; H, 3.07; N, 3.43. Single-crystal X-ray structure: Figure 5, Supporting Information.

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Supporting Information Available: CIF files giving crystal-lographic data for compounds 1-11 (except for 6) and for $7H^+PF_6^-$ and figures giving cyclic and square wave voltammograms of 9 and 10 under different conditions (Figures S1–S4). This material is available free of charge via the Internet at http://pubs.acs.org.