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Metal-Templated Hydrogen Bond Donors as "Organocatalysts" for Carbon−Carbon Bond Forming Reactions: Syntheses, Structures, and Reactivities of 2-Guanidinobenzimidazole Cyclopentadienyl Ruthenium Complexes

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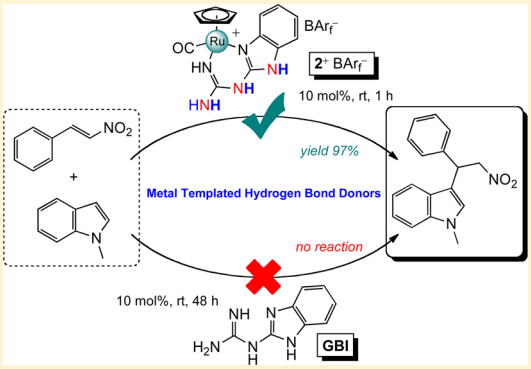
Supporting Information

ABSTRACT: The reaction of 2-guanidinobenzimidazole (GBI) and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(Cl)$ in refluxing toluene gives the chelate $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(GBI)]^+Cl^-$ ($\mathbf{1}^+Cl^-$; 96%). Subsequent anion metatheses yield the BF_4^-, PF_6^-, and BAr_f^- ($B(3,5\text{-}C_6H_3(CF_3)_2)_4^-$) salts (77−85%). Reactions with CO give the carbonyl complexes $[(\eta^5\text{-}C_5H_5)Ru(CO)(GBI)]^+X^-$ ($\mathbf{2}^+X^-$; X^- = Cl^-, BF_4^-, PF_6^-, BAr_f^-; 87−92%). The last three salts can also be obtained by anion metatheses of $\mathbf{2}^+Cl^-$ (77−87%), as can one with the chiral enantiopure anion $P(o\text{-}C_6Cl_4O_2)_3^-$ ((Δ)-TRISPHAT$^-$; 81%). The reaction of $[(\eta^5\text{-}C_5H_5)Ru(CO)(NCCH_3)_2]^+PF_6^-$ and GBI also gives $\mathbf{2}^+PF_6^-$ (81%). The pentamethylcyclopentadienyl analogues $[(\eta^5\text{-}C_5Me_5)Ru(CO)(GBI)]^+X^-$ ($\mathbf{3}^+X^-$; X^- = Cl^-, BF_4^-, PF_6^-, BAr_f^-; 61−84%) are prepared from $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(Cl)$, GBI, and CO followed (for the last three) by anion metatheses. An indenyl complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(GBI)]^+Cl^-$ (96%) is prepared from $(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(Cl)$ and GBI. All complexes are characterized by NMR (^1H, ^{13}C, ^{31}P, ^{19}F, ^{11}B), with 2D spectra aiding assignments. Crystal structures of $\mathbf{1}^+PF_6^-\cdot CH_2Cl_2$ and $\mathbf{1}^+BAr_f^-\cdot CH_2Cl_2$ are determined; the anion is hydrogen bonded to the cation in the former. Complexes $\mathbf{1}$−$\mathbf{3}^+X^-$ are evaluated as catalysts (10 mol %, RT) for condensations of indoles and *trans*-β-nitrostyrene. The chloride salts are ineffective (0−5% yields, 48−60 h), but the BAr_f^- salts exhibit excellent reactivities (97−46% yields, 1−48 h), with the BF_4^- and PF_6^- salts intermediate. Evidence for hydrogen bonding of the nitro group to the GBI ligand is presented. GBI shows no catalytic activity; a BAr_f^- salt of methylated GBI is active, but much less so than $\mathbf{2}$−$\mathbf{3}^+BAr_f^-$.



INTRODUCTION

Hydrogen bonding[1] is a ubiquitous component of numerous recognition[2] and reactivity[3,4] phenomena. In recent years, a great deal of attention has been focused on developing small-molecule hydrogen bond donors capable of catalyzing organic transformations.[3] Macromolecular hydrogen bond donor catalysts are of course well known, as exemplified by enzyme active sites in which peptidic NH or OH linkages activate substrates containing carbonyl groups toward nucleophilic attack.[2c,5]

In designing small-molecule hydrogen bond donor catalysts, modular systems that can be sterically or electronically fine-tuned are advantageous.[2e,6] In this regard, ureas and thioureas have seen extensive use, often in conjunction with chiral substituents and/or auxiliary functionality.[3,6d] This emphasis has been prompted in part by the pioneering studies of Etter, who defined a variety of hydrogen-bonding motifs in the solid state,[7] such as the two 1:1 adducts of simple carbonyl and nitro compounds shown in Figure 1 (**I**, **II**).

We have sought to develop families of metal-containing hydrogen bond donors that are capable of catalyzing organic transformations and manifest the diversity and modularity inherent in organometallic and coordination compounds. In work to date, we have established that the inexpensive, air-stable, and

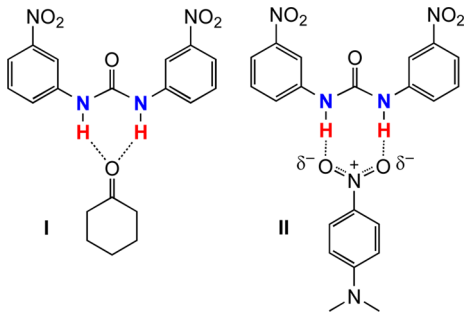


Figure 1. Representative crystallographically characterized adducts of urea hydrogen bond donors and Lewis bases.

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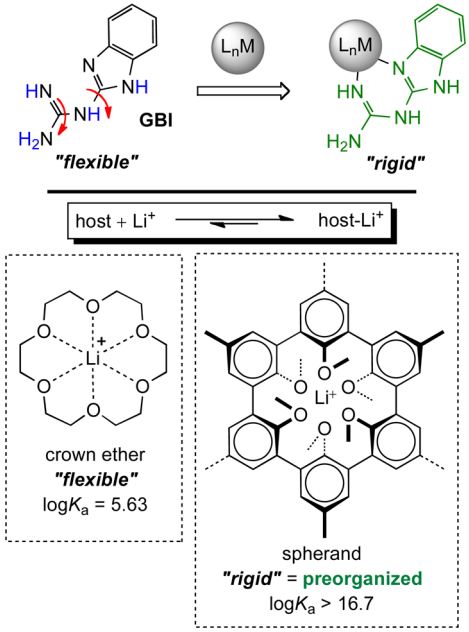
easily synthesized cobalt(III) trication[8] $[Co(en)_3]^{3+}$ and substituted analogues are effective catalysts for Michael additions of malonate anions in the presence of amine bases.[9] Good evidence has been obtained for hydrogen bonding of the Michael acceptors to the NH hydrogen atoms, which would be expected to become more acidic upon coordination to a tricationic spectator metal. Furthermore, NH···X hydrogen bonds are evident in all crystal structures of the salts $[Co(en)_3]^{3+}yX^{z-}$ (y/z = 3:1, 1.5:2, 1:3) that have been reported to date.[10]

An allied approach would involve catalysts with NH hydrogen atoms at positions remote from, as opposed to coordinated to, the metal. Toward this end, our attention was drawn to a chelate ligand that features five NH linkages, is commercially available, and can be synthesized in a single step, namely, 2-guanidinobenzimidazole (GBI; Scheme 1, top).[11] This species

Scheme 1. Structure of GBI and Chelation (Top) and Preorganization Effects in Binding of Li^+ to Cyclic Polyether Hosts (Bottom)



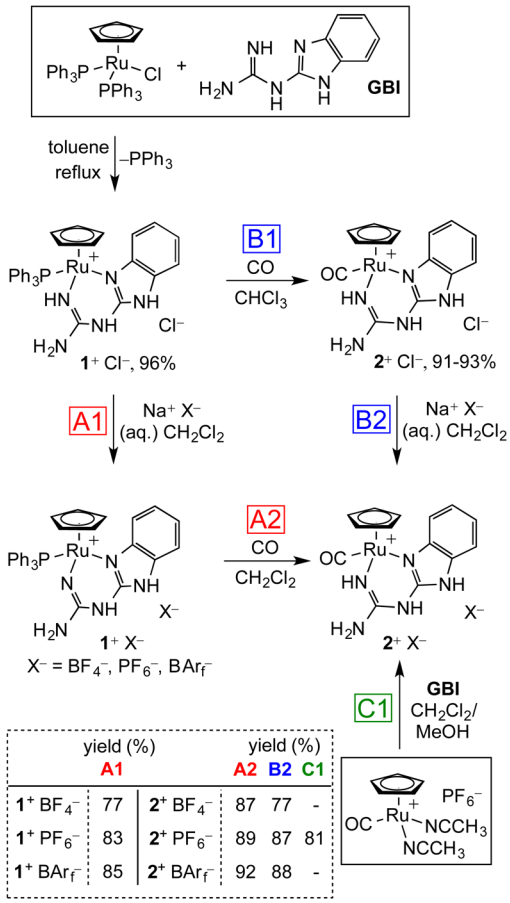
has a well-established coordination chemistry.[12] However, to our knowledge there have never been any applications of its adducts of transition metals, main group elements, or other electrophiles in catalysis. Importantly, coordination reduces the number of conformational degrees of freedom, thereby preorganizing[13] the hydrogen bond donor per Scheme 1 (top). The beneficial effect of preorganization with respect to binding affinities has been demonstrated for complexes of crown ethers and spherands with cations, as illustrated for Li^+ in Scheme 1 (bottom).[14] There would presumably be analogous effects upon reaction rates and catalytic activity.

In this paper, we describe (1) the syntheses, structures, and physical characterization of cationic organoruthenium derivatives of GBI, (2) applications of these adducts as catalysts for condensations of indoles with nitroalkenes, and (3) data that establish the critical importance of hydrogen bonding in the transition-state assemblies and thereby "second coordination sphere" mechanisms. The complexes disclosed herein are chiral but racemic. Related adducts that can be accessed in enantiomerically pure form and applied as catalysts in highly enantioselective transformations are reported in the following companion paper.[15]

RESULTS

1. Syntheses of Cyclopentadienyl GBI Complexes. The ruthenium bis(phosphine) complex $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(Cl)$ was synthesized by a literature method[16] or via a new microwave-mediated procedure (Supporting Information). As shown in Scheme 2, $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(Cl)$ and GBI were reacted in

Scheme 2. Syntheses of Cyclopentadienyl Ruthenium GBI Complexes



refluxing toluene. Workup gave the racemic "chiral-at-metal" cationic monophosphine complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(GBI)]^+Cl^-$ ($\mathbf{1}^+Cl^-$) as a yellow powder in 96% yield. The salt was insoluble in benzene and toluene, slightly soluble in CH_2Cl_2, and soluble in polar solvents such as MeOH, EtOH, and DMSO.

Like most new complexes below, $\mathbf{1}^+Cl^-$ was characterized by NMR (^1H, ^{13}C, ^{31}P), IR, and UV–visible spectroscopy, as summarized in Table 1 and the Experimental Section. The mass spectrum showed a strong ion for the cation $\mathbf{1}^+$. A satisfactory microanalysis was obtained. Together with literature data,[12c,d] 2D NMR experiments (^1H,^1H COSY and ^1H,^{13}C HETCOR) enabled all of the GBI proton and carbon signals to be unambiguously assigned (Supporting Information, Tables s1, s2). These and other data supported the coordination of the benzimidazole C═NAr and guanidine C═NH groups, as verified crystallographically below.

Next, as shown in Scheme 2 (step A1), simple metatheses allowed the chloride anion of $\mathbf{1}^+Cl^-$ to be replaced by the more

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Table 1. C_5H_5 and C_5Me_5 ^{1}H NMR Signals of $1-3^+X^-$[a] and IR ν_{CO} Values (parentheses)[b] for $2-3^+X^-$

	cation		
anion	1^+	2^+	3^+
Cl^-	4.41	5.19 (1938)	1.58 (1915)
BF_4^-	4.43	5.19 (1938)	1.58 (1915)
PF_6^-	4.61	5.20 (1942)[c]	1.58 (1922)
BAr_f^-	5.02	5.30 (1961)	1.56 (1931)

[a] δ, DMSO-d_6, 300 or 400 MHz, ppm. [b] cm^{-1}. [c] Data for $2^+(\Delta)$-TRISPHAT$^-$: 5.18 ppm and 1945 cm^{-1}.

weakly coordinating anions BF_4^-, PF_6^-, and BAr_f^-.[8,17] The new salts 1^+X^- were isolated in 77−85% yields as slightly air sensitive yellow powders with progressively increasing solubilities in CH_2Cl_2. They were similarly characterized, including ^{19}F and ^{11}B NMR spectra. The cyclopentadienyl ^{1}H NMR signals exhibited progressively downfield chemical shifts (Table 1), suggesting the ruthenium center in $1^+BAr_f^-$ to have more cationic character than that in 1^+Cl^-.[18] IR bands associated with the BF_4^- and PF_6^- anions are presented in Table 2, and key features are interpreted below.

Table 2. IR $\nu(BF_4^-)$ and $\nu(PF_6^-)$ Values for Selected BF_4^- and PF_6^- Salts[a]

	anion	
cation	BF_4^-	PF_6^-
Na^+	1015	806[b]
1^+	1089, 1078, 1011	880, 862, 841
2^+	1069, 1015	837[b]
3^+	1093, 1089, 1023, 997	842[b]

[a] Powder film measurements (ATR); values are in cm^{-1}. [b] Asymmetric absorption with unresolved shoulders.

In general, electron-withdrawing substituents lead to stronger hydrogen bond donors. Thus, in the interest of fine-tuning catalyst activity (see below), it was sought to replace the PPh_3 ligand by a more weakly donating or stronger π-accepting ligand. As shown in Scheme 2 (step B1), a solution of 1^+Cl^- was aspirated with a stream of CO or stirred under a static CO atmosphere. Workups gave the substitution product $[(\eta^5\text{-}C_5H_5)Ru(CO)(GBI)]^+Cl^-$ (2^+Cl^-) as an off-white powder in 91−93% yields. Analogous carbonylations were conducted with $1^+BF_4^-$, $1^+PF_6^-$, and $1^+BAr_f^-$ (step A2). These afforded the corresponding salts 2^+X^- as yellow powders in 87−92% yields.

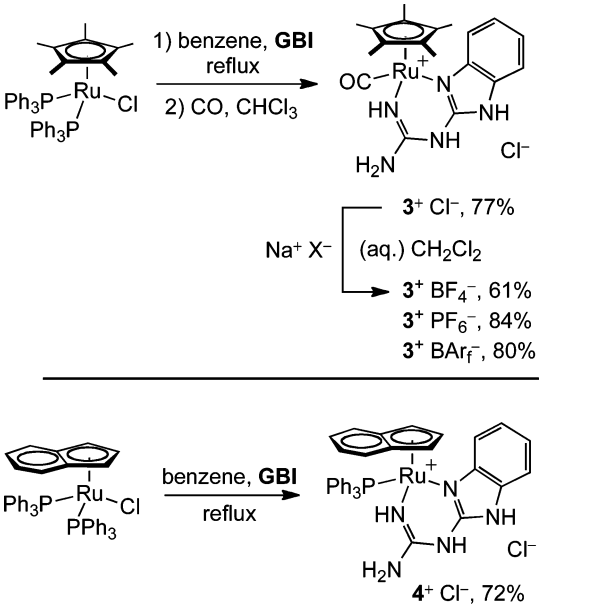
Alternatively, $2^+BF_4^-$, $2^+PF_6^-$, and $2^+BAr_f^-$ could be accessed in 77−88% yields by exchange of the chloride ion of 2^+Cl^-, as shown in Scheme 2 (step B2). Both overall routes from 1^+Cl^- to 2^+X^-, "A" and "B" (Scheme 2), have been repeated by several generations of co-workers, and "B" has been found to be more easily reproducible.[19] Another refinement involves an alternative starting material, the cationic bis(acetonitrile) complex $[(\eta^5\text{-}C_5H_5)Ru(CO)(NCCH_3)_2]^+PF_6^-$ employed in Scheme 2, step Cl. As with the starting material $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(Cl)$, this educt is easily prepared in one step from a commercially available precursor.[20] Addition of GBI directly affords the hexafluorophosphate salt $2^+PF_6^-$ in 81% yield, saving two steps.

The cyclopentadienyl ^{1}H NMR chemical shifts of 2^+X^- were downfield of those of 1^+X^- (δ 5.19−5.30 vs 4.41−5.02; Table 1), suggesting reduced electron density at ruthenium.[18] Accordingly, 2^+X^- exhibited good air stability both in solution and in the solid state; powders showed no noticeable decomposition after five years. Curiously, microanalyses gave consistently low nitrogen values, as summarized in the Experimental Section.

2. Syntheses of Substituted Cyclopentadienyl GBI Complexes. Another possibility for fine-tuning catalytic activity would be to modify the cyclopentadienyl ligands. Accordingly, analogues with bulkier, more electron donating, and more lipophilic pentamethylcyclopentadienyl ligands were sought. The precursor $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(Cl)$[21] was readily available by a new one-pot synthesis using pentamethylcyclopentadiene (Experimental Section). This gave better yields than the two-step literature procedures[21] and avoided handling sensitive ruthenium oligomers.

Reactions of $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(Cl)$ and GBI were carried out under conditions similar to those used for the cyclopentadienyl analogue 1^+Cl^- in Scheme 2. However, as detailed elsewhere,[22] workups did not give the target molecule $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)(GBI)]^+Cl^-$. Thus, the crude product was treated with CO. As shown in Scheme 3 (top), the carbonyl

Scheme 3. Syntheses of Pentamethylcyclopentadienyl (Top) and Indenyl (Bottom) Ruthenium GBI Complexes



complex $[(\eta^5\text{-}C_5Me_5)Ru(CO)(GBI)]^+Cl^-$ (3^+Cl^-) was isolated as an off-white powder in 77% yield. Subsequent anion exchange reactions analogous to those in Scheme 2 gave the salts $3^+BF_4^-$, $3^+PF_6^-$, and $3^+BAr_f^-$ as yellow powders in 61−84% yields. These complexes were air stable in solution and the solid state, were readily soluble in CH_2Cl_2 and other solvents of moderate polarity, and gave correct microanalyses. The IR ν_{CO} values were lower than those of 2^+X^- (1915−1931 vs 1938−1961 cm^{-1}; Table 1), indicative of increased electron density at ruthenium.

The synthesis of an indenyl analogue of 1^+Cl^- was also investigated. As shown in Scheme 3 (bottom), a reaction of $(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(Cl)$[23] and GBI similar to that used for 1^+Cl^- gave the target complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)(GBI)]^+Cl^-$ (4^+Cl^-) as an orange powder in 72% yield. However, 4^+Cl^- decomposed over the course of several days in CH_2Cl_2, as assayed by ^{1}H and ^{31}P NMR. Furthermore, anion exchange and PPh_3/CO substitution reactions were unsuccessful.[22]

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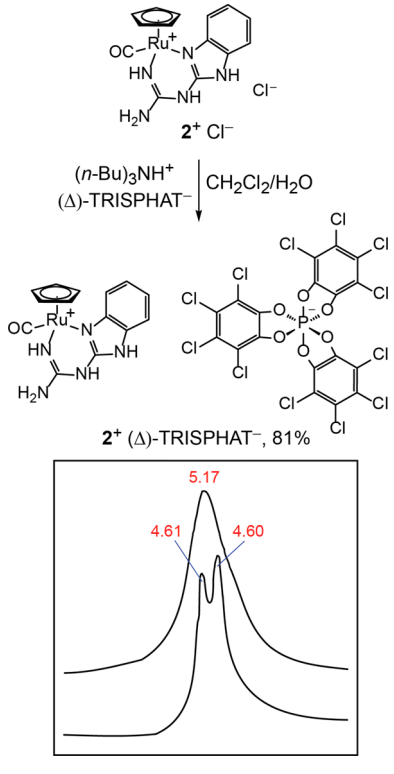
3. Hydration, H/D Exchange, and Nonracemic Complexes. Aqueous conditions (biphasic CH_2Cl_2/water) were used when preparing the tetrafluoroborate salts **1**−**3**$^+BF_4^-$ by anion exchange, and hydrates (2.0−0.5 H_2O) were isolated in all cases. The salt $Na^+BAr_f^-$ is commonly obtained as a hydrate,[24] and **1**−**3**$^+BAr_f^-$ all contained low levels of water (2.0−1.0 H_2O). The water could be removed by crystallization, as illustrated by an X-ray structure below.

When DMSO-d_6 or $CDCl_3$ solutions of **1**−**4**$^+X^-$ were treated with MeOH-d_4 (6 equiv), the NH protons underwent rapid H/D exchange. As shown in the Supporting Information (Figure s1), the NH signals disappeared or coalesced into a single peak and the total integration diminished. Some of the aromatic CH signals became sharper. A variety of cationic coordination compounds of GBI have been quantitatively deprotonated by weak bases such as pyridine, NaOMe, and Na_2CO_3.[12b−d,25] Hence, it is not surprising that rapid exchange can be observed in the absence of added base. Also, the GBI ligand is in principle capable of numerous prototropic equilibria, some of which entail formal 1,3-shifts of protons from the noncoordinating NH/NH_2 moieties to the coordinating C═NAr/C═NH moieties. These may participate in the exchange process, and examples are illustrated in the Supporting Information (Scheme s1).

In order to test the preceding chiral ruthenium complexes as enantioselective catalysts, nonracemic variants would be required. Two possible routes to enantiopure complexes were investigated. The first involved the nonracemic chiral anion (Δ)-TRISPHAT$^-$,[8] the structure of which is depicted in Scheme 4. The chloride salt **2**$^+Cl^-$ and (n-Bu)$_3NH^+$(Δ)-TRISPHAT$^-$[26] were combined in CH_2Cl_2, and a biphasic workup gave the target salt **2**$^+$(Δ)-TRISPHAT$^-$ as a white powder of ca. 95% purity in 81% yield.

Scheme 4. Reaction of 2$^+$Cl$^-$ and (Δ)-TRISPHAT$^-$ (Top): ^{1}H NMR Spectra of the Cyclopentadienyl Signal in DMSO-d_6 (br s) and C_6D_6 (2 × br s) (Bottom)



The new salt was characterized by NMR and IR spectroscopy and mass spectrometry, analogously to **2**$^+X^-$ above. Only one broad cyclopentadienyl ^{1}H NMR signal was observed in DMSO-d_6. In contrast, in the much less polar solvent C_6D_6, two closely spaced signals of equal intensity were apparent, presumably one for each of the diastereomeric salts (Scheme 4). However, all attempts to separate the diastereomers by crystallization were unsuccessful.

The second approach involved the reversible derivatization of one of the NH or NH_2 moieties by the enantiopure chiral cyclopentadienyl rhenium cation [(η^5-C_5H_5)Re(PPh_3)(NO)(CO)]$^+$.[27] Although a series of stable adducts could be prepared, as described elsewhere,[22] the spectroscopic data did not unambiguously reveal which NH or NH_2 group had reacted. Furthermore, only one singlet was observed for each of the ruthenium and rhenium cyclopentadienyl ligands, as opposed to doubled singlets diagnostic of diastereomeric adducts. All attempts to separate the putative diastereomers were unsuccessful.

4. Crystallographic Characterization. During the course of the above syntheses, single crystals of the solvate **1**$^+PF_6^-$·CH_2Cl_2 were obtained. X-ray data were collected and refined as described in the Supporting Information (Table s3) and Experimental Section. The resulting structure is shown in Figure 2. Key metrical parameters are summarized in Table 3. The cation is formally octahedral, with the cyclopentadienyl ligand occupying three coordination sites, as evidenced by P−Ru−N and N−Ru−N bond angles of ca. 90°. The GBI ligand is nearly planar, as reflected by many torsion angles with values near 0° or ±180°. The bond lengths of the coordinated C═NH (C22−N21) and C═NAr (C24−N32) linkages (1.280(4) and 1.314(4) Å) are shorter than the other four carbon−nitrogen bonds about C22 and C24 (1.349(4)−1.385(4) Å). Alternative tautomers of the GBI ligand (Scheme s1) would afford different bond length patterns.

As illustrated in Figure 2, each PF_6^- anion exhibits multiple hydrogen bonding to each of two neighboring cations. All of the NH linkages except for N21−H21 participate. Although the motif about each PF_6^- anion is unsymmetrical, the two cations are related by an inversion center, resulting in identical patterns of bonds to the anions. Curiously, we are only able to locate structures of two other complexes that exhibit hydrogen bonding between NH and PF_6 moieties.[28] In both cases, the PF_6 unit is covalently bound via a M−F−P linkage to the metal fragment. In any case, the F···H, F···N, and P···N distances, which are summarized in Table 4, are in typical ranges for hydrogen bonds.[1b,28]

A CH_2Cl_2 monosolvate of **1**$^+BAr_f^-$ could also be crystallographically characterized. The resulting structure is shown in Figure 3. One CF_3 group was disordered over two positions, the occupancies of which could be refined to a 62:38 ratio. Key metrical data are summarized in Table 3. In this case the GBI ligand is noticeably puckered, with torsion angles that deviate more from 0° or ±180°. However, the carbon−nitrogen bond lengths exhibit similar patterns. No hydrogen-bonding interactions are evident, consistent with the poor acceptor properties of BAr_f^-.[29] The ruthenium−phosphorus distance (2.3154(10) Å) is slightly longer than that in **1**$^+PF_6^-$·CH_2Cl_2 (2.302(3) Å), suggesting that the electron density on ruthenium and back-bonding are enhanced when the anion can engage in hydrogen bonding.

5. Reactions Involving Nitroalkenes. Condensations of indoles (**5**) and *trans*-β-nitrostyrene (**6**) to give 3-substituted indoles (**7**)—sometimes termed Friedel−Crafts alkylations—are often used as benchmarks for hydrogen bond donor

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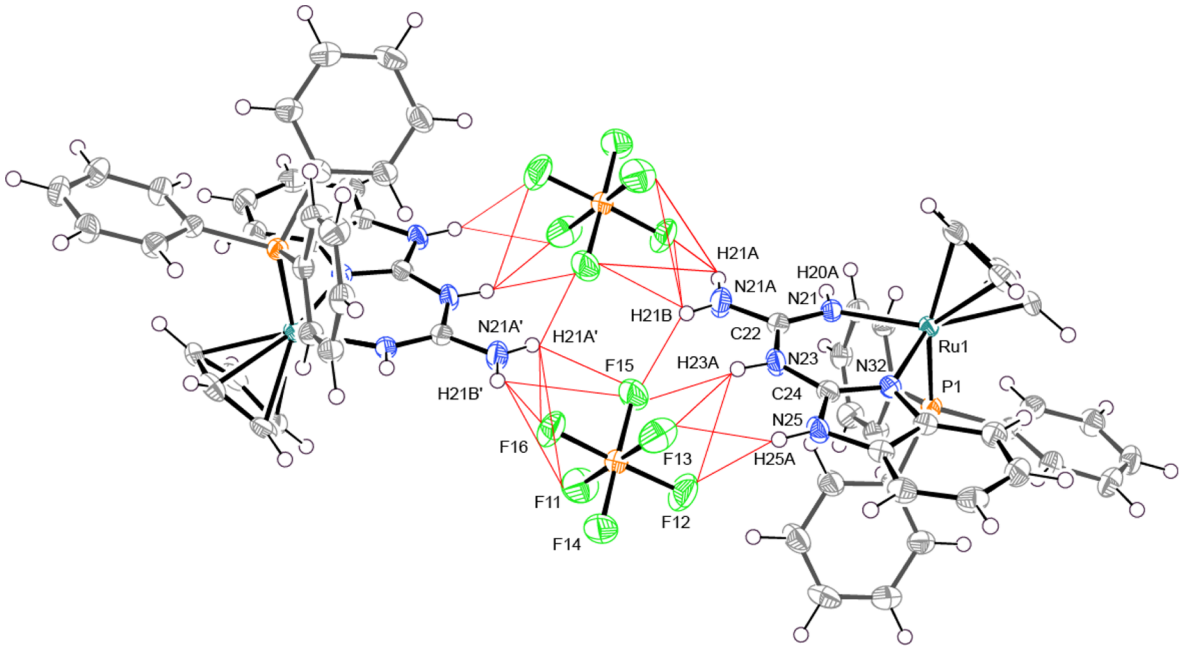

Figure 2. Thermal ellipsoid diagram (50% probability level) showing the structures of two molecules of $\mathbf{1}^{+}PF_6^{-}\cdot CH_2Cl_2$ with solvate molecules omitted and hydrogen bonding between cations and anions.

Table 3. Key Bond Lengths [Å], Torsion Angles [deg], and Bond Angles [deg] for $\mathbf{1}^{+}PF_6^{-}\cdot CH_2Cl_2$ and $\mathbf{1}^{+}BAr_f^{-}\cdot CH_2Cl_2$[a]

	$\mathbf{1}^{+}PF_6^{-}\cdot CH_2Cl_2$	$\mathbf{1}^{+}BAr_f^{-}\cdot CH_2Cl_2$		$\mathbf{1}^{+}PF_6^{-}\cdot CH_2Cl_2$	$\mathbf{1}^{+}BAr_f^{-}\cdot CH_2Cl_2$
Ru1–N21	2.104(2)	2.109(4)	Pl–Ru1–N21	90.49(7)	87.28(11)
Ru1–N32	2.116(2)	2.101(3)	Pl–Ru1–N32	94.04(6)	92.64(9)
Ru1–Pl	2.302(3)	2.3154(10)	N21–Ru1–N32	83.27(9)	82.87(14)
N21–C22	1.280(4)	1.261(6)	Ru1–N21–C22	133.9(2)	131.0(3)
C22–N21A	1.349(4)	1.370(6)	N21–C22–N23	121.2(3)	122.1(4)
C22–N23	1.385(4)	1.376(7)	N21–C22–N21A	125.1(3)	125.2(5)
N23–C24	1.379(4)	1.371(6)	C22–N23–C24	126.5(3)	125.3(4)
C24–N25	1.358(4)	1.365(6)	N23–C24–N32	127.1(3)	126.9(4)
C24–N32	1.314(4)	1.302(6)	N23–C24–N25	119.2(3)	120.4(4)
N25–C26	1.394(4)	1.360(7)	C24–N25–C26	106.43(9)	107.6(4)
C26–C31	1.394(4)	1.395(7)	N25–C26–C31	105.7(2)	105.4(4)
C31–N32	1.405(4)	1.403(5)	C26–C31–N32	109.4(3)	109.3(4)
Pl–Ru1–N21–C22	104.2(7)	116.4(8)	C24–N32–Ru1	127.14(19)	126.0(3)
Pl–Ru1–N32–C24	−99.0(4)	−105.9(7)	C31–N32–Ru1	127.40(19)	128.6(3)
Ru1–N21–C22–N23	−7.2(6)	−13.5(8)	C24–N32–C31	104.9(2)	104.9(4)
Ru1–N21–C22–N21A	171.2(4)	167.6(4)			
Ru1–N32–C24–N23	6.2(1)	6.6(7)			
N21–C22–N23–C24	−1.0(7)	−10.9(9)			
C22–N23–C24–N32	1.2(6)	14.9(9)			

[a]For atom numbering, see Figure 2.

catalysts.[30] Thus, the ruthenium salts $\mathbf{1}-\mathbf{3}^{+}X^{-}$ were screened for activity. Indole or 1-methylindole (**5a** or **5b**; 2.0 equiv) and **6** (1.0 equiv) were combined in CD_2Cl_2 in NMR tubes in the presence of a salt (0.10 equiv; 10 mol %) and an internal standard. Reactions of **5a** were stopped after 48 h, irrespective of the state of completion. Results are summarized in Table 5, and selected rate profiles are given in Figure 4.

With many salts, the 3-substitued indoles **7a**,**b** shown in Table 5 cleanly formed. In all cases, **7b** was produced faster, consistent with an electron-donating effect of the *N*-methyl group. However, the slower rate profiles with **7a** are illustrated in Figure 4, as they allow cleaner reactivity comparisons. As shown in entries 1 and 2 of Table 5, no reactions were observed without catalyst or in the presence of GBI alone. However, GBI is poorly soluble in CH_2Cl_2, and a ruthenium-free system more comparable to $\mathbf{1}-\mathbf{3}^{+}X^{-}$ is described below.

The rates showed strong dependencies on the counteranions of the salts. The chloride salts $\mathbf{1}-\mathbf{3}^{+}Cl^{-}$ (entries 3, 7, 11) did not exhibit any significant activity. The indenyl complex $\mathbf{4}^{+}Cl^{-}$ was not tested due to its reduced stability in CH_2Cl_2 and the possibility of new mechanisms involving η^3/η^1 intermediates. The tetrafluoroborate salts $\mathbf{1}-\mathbf{3}^{+}BF_4^{-}$ (entries 4, 8, 12) gave only poor yields of **7a** (2–6%). More productive were the hexafluorophosphate salts $\mathbf{1}-\mathbf{3}^{+}PF_6^{-}$ (entries 5, 9, 13), which afforded **7a** in yields up to 27%. The best results were obtained with $\mathbf{1}-\mathbf{3}^{+}BAr_f^{-}$, which gave yields of 46–97% (entries 6, 10, 14).

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Table 4. Selected F···H, P···N, and F···N Distances [Å] in $1^+PF_6^-\cdot CH_2Cl_2$

F11···H21A′	2.769	P10···N21A	4.441
F11···H21B′	3.251	P10···N21A′	3.802
F12···H23A	2.789	P10···N23	3.882
F12···H25A	3.801	P10···N25	4.311
F13···H23A	2.545	F11···N21A′	3.262
F13···H25A	2.450	F12···N23	3.284
F15···H21B	2.195	F13···N23	3.018
F15···H23A	2.283	F13···N25	2.939
F15···H21A′	2.863	F15···N23	3.325
F15···H21B′	2.795	F15···N21A	3.215
F16···H21A′	2.286	F15···N21A′	3.158
F16···H21B′	3.324	F16···N21A′	3.068

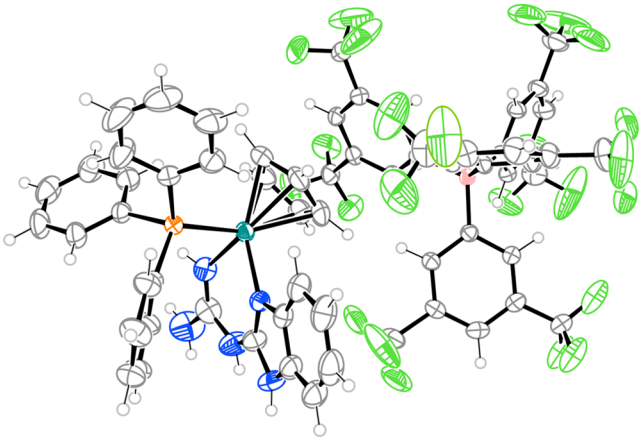


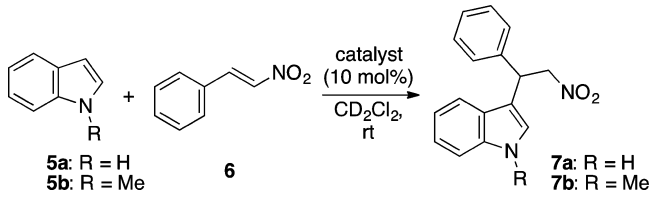
Figure 3. Thermal ellipsoid diagram (50% probability level) of the molecular structure of $1^+BAr_f^-\cdot CH_2Cl_2$ with the solvate molecule omitted.

Within each counteranion series, rates increased as the cations were varied in the order $1^+ < 3^+ < 2^+$. Although these data are further interpreted in the Discussion section, note that the poorer hydrogen bond accepting anions[29] and the less electron rich cations give faster rates.

In order to help analyze the role of the ruthenium and chelate ring in promoting catalysis, an organic cationic GBI derivative was sought. Accordingly, as shown in Scheme 5, GBI was converted to 1-methyl**GBI** by a known deprotonation/methylation sequence[12b] and treated with HCl to give the previously reported hydrochloride salt [1-methyl**GBI**-H]$^+$Cl$^-$.[12b] Subsequent anion exchange using $Na^+BAr_f^-$ gave the new salt [1-methyl**GBI**-H]$^+BAr_f^-$ as a pale pink solid in 58% yield. The compound was soluble in CH_2Cl_2 and other organic solvents of moderate polarity and exhibited a single NH ^{1}H NMR signal. As indicated in entry 15 of Table 5, it showed some catalytic activity with the more reactive indole **5b**, but considerably less than the lead BAr_f^- salts, $2^+BAr_f^-$ (40% yield of **7b** after 3.5 h vs 97% after 1.0 h) and $3^+BAr_f^-$ (97% after 1.5 h).

Finally, possible interactions between *trans*-β-nitrostyrene and 1–3^+X^- (X^- = BF_4^-, PF_6^-, BAr_f^-) were probed by ^{1}H NMR. Spectra of equimolar mixtures of **6** and 1–3^+X^- were recorded in CD_2Cl_2 and compared to those of 1–3^+X^- under identical conditions. The four NH/NH_2 signals of the GBI ligand can be assigned (above), and in each case three shifted downfield. With $2^+BAr_f^-$, which is illustrated in Figure 5, the shifts ranged from 0.09 to 0.02 ppm (top vs bottom spectrum). Similarly, the C**H**=$CHNO_2$ proton of **6** shifted slightly downfield. On the basis of the magnitudes of the NH shifts (Figure 5, box), it is proposed that **6** binds to the cation 2^+ predominantly as shown in **IIIa**. Downfield shifts of NH signals have also been observed when carbonyl compound substrates have been added to urea-based catalysts.[31]

Table 5. Friedel–Crafts Alkylations Catalyzed by 1–3^+X^-



		7a		7b	
entry	catalyst	time	yield[a]	time	yield[a]
1	none	48 h	–[b]	48 h	–[b]
2	GBI	48 h	–[b]	48 h	–[b]
3	1^+Cl^-	48 h	–[b]		–[c]
4	$1^+BF_4^-$	48 h	2%		–[c]
5	$1^+PF_6^-$	48 h	9%	25 h	30%
6	$1^+BAr_f^-$	48 h	46%	8 h	53%
7	2^+Cl^-	48 h	–[b]	60 h	4%
8	$2^+BF_4^-$	48 h	6%	60 h	20%
9	$2^+PF_6^-$	48 h	27%	9.5 h	55%
10	$2^+BAr_f^-$	48 h	94%	1.0 h	97%
11	3^+Cl^-	48 h	–[b]	31 h	–[b]
12	$3^+BF_4^-$	48 h	3%	31 h	14%
13	$3^+PF_6^-$	48 h	22%	7 h	29%
14	$3^+BAr_f^-$	48 h	84%	1.5 h	97%
15	[1-methyl**GBI**-H]$^+BAr_f^-$	–[c]	–[c]	3.5 h	40%[d]

[a]Yields were determined by ^{1}H NMR versus an internal standard (see text). [b]No formation of **7** was observed. [c]This experiment was not conducted. [d]The yield after 1.0 h was 25%.

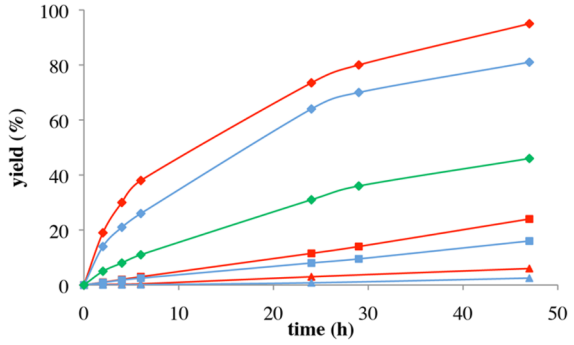


Figure 4. Rate profiles for the condensation of indole (2.0 equiv) and *trans*-β-nitrostyrene (1.0 equiv) with different catalysts (10 mol %, rt, selected reactions from Table 5): (red ◆) $2^+BAr_f^-$, (red ■) $2^+PF_6^-$, (red ▲) $2^+BF_4^-$, (blue ◆) $3^+BAr_f^-$, (blue ■) $3^+PF_6^-$, (blue ▲) $3^+BF_4^-$, (green ◆) $1^+BAr_f^-$.

DISCUSSION

1. Mechanism of Catalysis. The data in Table 5 and Figure 4 validate the underlying hypothesis of this study, namely, that by chelation-induced preorganization of the conformationally flexible GBI ligand by "spectator" transition metal fragments an otherwise unreactive species can be rendered an effective hydrogen bond donor catalyst. The use of a cationic ruthenium chelate was coincidental, simply reflecting the first adduct successfully synthesized. The complexes 1–4^+X^- represent, to

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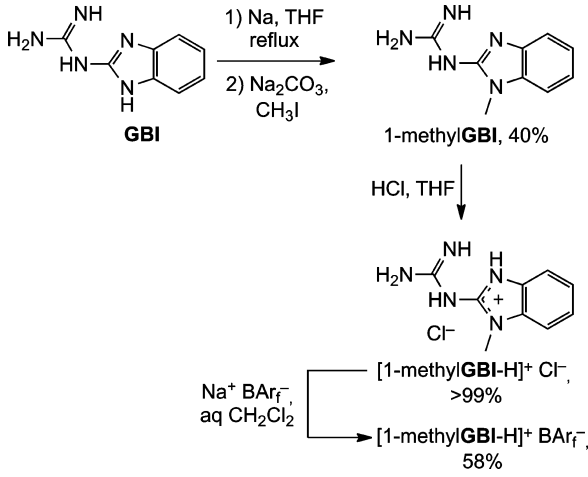
Scheme 5. Synthesis of [1-methylGBI-H]$^+$BAr$_f^-$



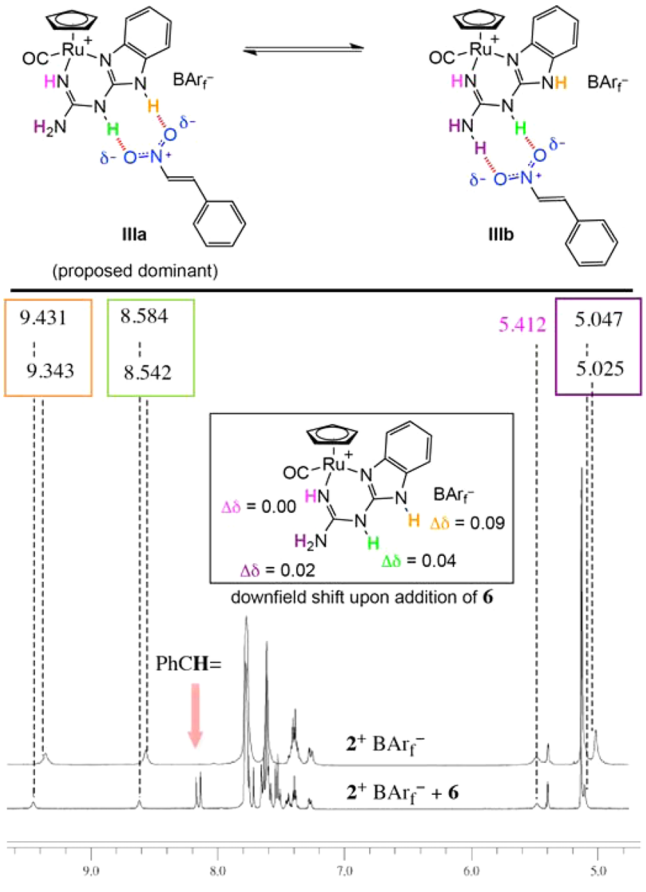


Figure 5. ^{1}H NMR spectra (rt, 300 MHz, CD_2Cl_2) of **2**$^+$BAr$_f^-$ before (above) and after addition of 1 equiv of **6** (below) and some possible structures of **2**$^+$BAr$_f^-$·**6**.

our knowledge, the first organometallic adducts of GBI, which has an extensive inorganic coordination chemistry that has remained largely unexploited.[12]

By analogy to ureas and thioureas (Figure 1), substrate activation would most logically involve two synperiplanar NH units. As illustrated by the crystal structures in Figures 2 and 3, chelation leads to a triad of three synperiplanar NH units and an orthogonal dyad of two synperiplanar NH units. However, there remains a residual conformational degree of freedom about the NH_2 group. The NMR data in Figure 5 suggest that *trans*-β-nitrostyrene preferentially binds to the two synperiplanar NH units *not* associated with the NH_2 group, as depicted in **IIIa**. Note that these two NH groups could adopt any number of conformations in the free ligand, including one in which they would be approximately *anti*.

In any event, preorganization can be an important aspect of second coordination sphere binding to coordinated ligands. However, since the ruthenium fragment is cationic, there remains a question as to the effect of positive charge alone, as this should also enhance NH acidities and hydrogen bond donor strengths. Indeed, the ruthenium-free cationic GBI species [1-methyl**GBI**-H]$^+$BAr$_f^-$ (Scheme 5) proved to be a more effective catalyst than GBI (Table 5, entry 15 vs 2). Nonetheless, activities remain far below those of the lead ruthenium catalysts **2**$^+$BAr$_f^-$ and **3**$^+$BAr$_f^-$ (entries 10 and 14, Table 5), underscoring the role of conformational preorganization.

The counteranion also greatly affects the activities of the ruthenium catalysts **1**−**3**$^+$X$^-$. In each case, the same trend is observed, $Cl^- < BF_4^- < PF_6^- < BAr_f^-$ (Table 5). This parallels the diminishing hydrogen bond accepting properties of the anions.[29] In particular, chloride is an excellent hydrogen bond acceptor,[17d,32] and a single such anion effectively "poisons" the catalyst. Accordingly, we suggest that (1) there is only one productive substrate binding site that leads to turnover and (2) chloride preferentially binds to the same two NH groups as the *trans*-β-nitrostyrene in **IIIa**.

The tetrafluoroborate salts remain very poor catalysts, consistent with the still appreciable coordinating[17] and hydrogen-bonding[29] ability of this formally tetrahedral anion. In this context, the IR data in Table 2 establish that the anion is desymmetrized in the presence of cations **1**−**3**$^+$.[17a] The hexafluorophosphate salts are distinctly more reactive, but the crystal structure of **1**$^+PF_6^-$·CH_2Cl_2 (Figure 2) demonstrates that this formally octahedral anion remains a viable hydrogen bond acceptor. Accordingly, the IR data in Table 2 show that this anion is also desymmetrized by the cations **1**−**3**$^+$. Similar spectra are obtained with the sodium salt, presumably due to hydration.[33]

Finally, there is also a marked dependence of catalyst activities upon the cation (Table 5 and Figure 4). Since CO ligands are weaker donors and stronger π-acceptors than PPh_3 ligands, the ruthenium should be less electron rich in **2**$^+$X$^-$ as compared to **1**$^+$X$^-$, as reflected by the downfield shift of the cyclopentadienyl ^{1}H NMR signals noted above (Table 1).[18] This increases the acidities of the NH units and likewise their hydrogen bond donor strengths, leading to more active catalysts. In the same vein, the pentamethylcyclopentadienyl ligand is more electron releasing than the cyclopentadienyl ligand, as reflected by the decreased ν_{CO} values noted above (Table 1). This decreases hydrogen bond donor strengths, rendering **3**$^+$X$^-$ slightly less active than **2**$^+$X$^-$.

It would be premature to propose a detailed transition state model for the reactions in Table 5 based upon the present data. For example, there are two possible orientations about the *trans*-β-nitrostyrene C═C linkages in **IIIa**,**b** (Figure 5), either of which could react with the nucleophilic indole carbon atom. Adding to the uncertainty, some computational groups have advanced models in which the nucleophilic component preferentially interacts with the hydrogen bond donor.[34] Additional information can often be derived from the absolute configurations of products in enantioselective variants, a subject explored in the following paper.[15]

2. Scope of Catalysis and Future Directions. The new complexes described herein represent a distinct conceptual advance with respect to small-molecule hydrogen bond donor

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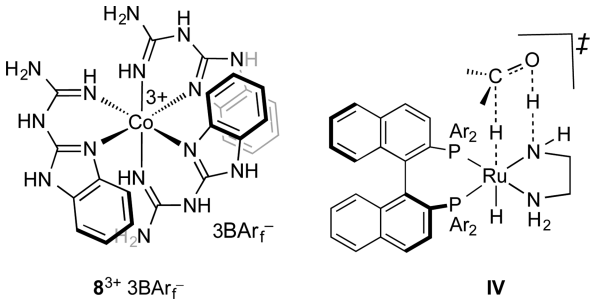
catalysts, which to date have been dominated by organic molecules and therefore have not exploited the diverse types of hydrogen-bonding interactions associated with coordinated ligands. Together with studies involving the chiral cobalt(III) trication $[Co(en)_3]^{3+}$ and substituted derivatives,[9] it is now firmly established that both coordinated and noncoordinated NH units can effectively serve as hydrogen bond donors. In an example highlighted in the following paper, an octahedral iridium(III) cation has been used as a template for a ligand containing a NH(C═X)NH moiety and two ligands containing $ArCH_2OH$ moieties.[35] This has been shown to be an excellent catalyst for other types of additions to nitroalkenes, although in contrast to **1**−**3**$^+$X$^-$ the NH linkages were not conformationally constrained. The hydroxyl groups were proposed to activate the nucleophile by hydrogen bonding.

These new families of catalysts offer a variety of parameters that can be systematically varied, such as the metal, the charge, the counteranion in the case of cations, the non-hydrogen-bonding ancillary ligands, and substituents on the hydrogen-bonding ligand. This represents an impressive number of diversity elements and a high degree of modularity. Although NH hydrogen bond donors dominate in the preceding examples, it is likely—as suggested by the iridium(III) system—that other types of heteroatom−hydrogen bonds (e.g., PH, OH) can also be exploited. Also, in the case of GBI, extensions to main group elements may prove feasible, as chelates are known both with boron and tin.[12c,d] The cobalt tris(GBI) complex **8**$^{3+}$3BAr$_f^-$ shown in Figure 6 has proven to be a particularly effective catalyst



8^{3+} 3BAr$_f^-$

Figure 6. Other relevant catalysts.

for lactide polymerizations,[36] with activities somewhat higher than the monocationic ruthenium complex **2**$^+$BAr$_f^-$.

Some second coordination sphere properties of coordinated NH moieties merit note in passing. First, a variety of ammonia complexes $[L_nMNH_3]^{z+}$ (z = 0, 1) have been found to afford stable adducts with crown ethers.[37,38] Second, M<u>N−H</u> bonds can undergo cleavage in certain metal-catalyzed reactions. The best known examples involve the Noyori ruthenium catalysts for enantioselective hydrogenations of ketones, which proceed via transition-state assemblies such as **IV** in Figure 6.[39] In second coordination sphere catalysis involving **1**−**3**$^+$X$^-$, only supramolecular interactions are involved, whereas in the tandem first/second coordination sphere catalysis embodied in **IV**, covalent bonds are broken and formed.

Although the ruthenium catalysts **1**−**3**$^+$X$^-$ are "chiral at metal" species, they are so far available only in racemic form. For this reason, we have not attempted to expand the scope of the organic reactions studied at this stage. Indeed, with the stereocenter so far removed from the substrate binding site, the prospects for reasonably enantioselective catalysis would seem to be remote, although some strategies with bulky pentasubstituted cyclopentadienyl ligands remain in development.[40] However, the preparation of enantiopure bifunctional analogues, and their successful application as highly enantioselective catalysts, is described in the following paper.[15]

Since ferrocene-containing systems are often included in reviews of "organocatalysis",[41] one could consider expanding this term to accommodate any metal-containing catalyst in which the metal does not directly participate in the any of the bond-breaking or bond-forming steps.[42] Alternatively, perhaps someone more creatively inclined will be able to suggest a catchy new phrase for such systems. However, in our opinion this work highlights the artificiality of such classifications, which can do a disservice by obscuring common underlying mechanistic principles.

In conclusion, the preceding results and related studies[15,36] have established that cationic transition metal chelates of GBI are effective hydrogen bond donors that can catalyze a variety of organic transformations. Chelation removes a conformational degree of freedom, thereby enhancing catalytic activity, and the introduction of positive charge also has a beneficial effect. Complementary data with other types of ligands point to a heretofore unappreciated universe of modular metal-containing hydrogen bond donor catalysts that effect "second coordination sphere promoted catalysis". These encompass but are not limited to the many coordination and organometallic compounds with coordinated and noncoordinated NH moieties.

EXPERIMENTAL SECTION

General Data. All reactions and workups were carried out under nitrogen unless noted. Standard instrumentation and calibration procedures were employed, as detailed in the Supporting Information. Solvents were treated as described in the Supporting Information. The 2-guanidinobenzimidazole (GBI; 95%, Aldrich) and other commercial chemicals were used as received, except for Na$^+$PF$_6^-$ (98.5%, Acros), which was freshly washed with CH_2Cl_2 (5 mL) and dried by oil pump vacuum.

(η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$(Cl).[16,43] A three-necked flask was charged with PPh_3 (14.458 g, 55.182 mmol) and ethanol (100 mL). The mixture was refluxed with stirring. After 15 min, $RuCl_3{\cdot}xH_2O$ (3.581 g, 17.26 mmol for x = 0; 30−40% Ru) in ethanol (40 mL) and then cyclopentadiene (18 mL) were added. The brown solution was refluxed for 16 h, cooled to room temperature, and stored in a freezer. After 24 h, an orange precipitate was collected by filtration and washed with cold ethanol (2 × 5 mL), water (2 × 10 mL), cold ethanol (1 × 5 mL), and hexanes (2 × 15 mL). The residue was dried by oil pump vacuum to give the product as a bright orange solid (8.105 g, 11.16 mmol, ca. 65%).[44] Mp: 131−132 °C (capillary). NMR (δ, $CDCl_3$): ^{1}H (400 MHz) 7.70−6.94 (m, 30H, P(C$_6$**H**$_5$)$_3$), 4.13 (s, 5H, C$_5$**H**$_5$); ^{13}C{^{1}H} (100 MHz) 138.5 (t, $^1J_{CP}$ = 19.6 Hz, *i*-**C**$_6$H$_5$), 133.8 (t, $^2J_{CP}$ = 5.1 Hz, *o*-**C**$_6$H$_5$), 128.7 (s, *p*-**C**$_6$H$_5$), 127.5 (t, $^3J_{CP}$ = 2.7 Hz, *m*-**C**$_6$H$_5$); ^{31}P{^{1}H} (161 MHz) 39.3 (s). IR (cm^{-1}, powder film): 1478 (m), 1432 (s), 1181 (w), 1158 (w), 1085 (s), 995 (m), 829 (w), 806 (m), 745 (m), 690 (s); MS:[45] 726 (23) [M]$^+$, 691 (71) [M − Cl]$^+$, 464 (33) [M − PPh$_3$]$^+$, 429 (100) [M − Cl − PPh$_3$]$^+$.

(η^5-C$_5$Me$_5$)Ru(PPh$_3$)$_2$(Cl).[21] In a new one pot synthesis, a Schlenk flask was charged with $RuCl_3{\cdot}xH_2O$ (0.989 g, 4.82 mmol for x = 0; 30−40% Ru), pentamethylcyclopentadiene (1.5 mL),[46] and ethanol (35 mL). The mixture was refluxed. After 3 h, PPh_3 (3.157 g, 12.05 mmol) was added. After another 16 h, the mixture was cooled to room temperature and stored in a freezer. After 24 h, the precipitate was collected by filtration, washed with cold ethanol (15 mL) and hexanes (3 × 25 mL), and dried by oil pump vacuum to give the product as an orange powder (3.109 g, 3.905 mmol, ca. 81%).[44] Mp: 94−95 °C (capillary). Anal. Calcd (%) for $C_{46}H_{45}ClP_2Ru$ (797.03): C 69.38, H 5.70. Found: C 69.12, H 5.71. NMR (δ, $CDCl_3$): ^{1}H (400 MHz) 7.69−7.03 (m, 30H, P(C$_6$**H**$_5$)$_3$), 1.01 (s, 15H, C$_5$(C**H**$_3$)$_5$); ^{13}C{^{1}H}

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(100 MHz) 137.1 (t, $^1J_{CP}$ = 19.6 Hz, *i*-C_6H_5), 133.7 (t, $^2J_{CP}$ = 5.1 Hz, *o*-C_6H_5), 128.5 (t, $^3J_{CP}$ = 2.7 Hz, *m*-C_6H_5), 126.7 (s, *p*-C_6H_5), 88.9 (s, $C_5(CH_3)_5$), 9.1 (s, $C_5(CH_3)_5$); $^{31}P\{^1H\}$ (161 MHz) 41.5 (s). IR (cm^{-1}, powder film): 3053 (w), 3022 (w), 2988 (w), 2953 (w), 2903 (w), 1568 (m), 1482 (m), 1432 (s), 1185 (w), 1158 (w), 1089 (m), 1023 (w), 999 (w), 741 (m), 698 (m). MS:[45] 796 (13) $[M]^+$, 761 (67) $[M - Cl]^+$, 534 (17) $[M - PPh_3]^+$, 499 (100) $[M - Cl - PPh_3]^+$.

[(η^5-C_5H_5)Ru(CO)($NCCH_3$)$_2$]$^+PF_6^-$.[20] A round-bottom flask was charged with $[(\eta^5\text{-}C_5H_5)Ru(NCCH_3)_3]^+PF_6^-$ (0.504 g, 1.16 mmol)[47] and CH_3CN (25 mL). A stream of CO was passed through the brown-orange solution. After 40 min, the solvent was removed by oil pump vacuum. The residue was chromatographed on a silica gel column (1 × 20 cm, 3:1 v/v CH_2Cl_2/CH_3CN). The solvent was removed from the product-containing fractions to give the product as a golden yellow solid (0.346 g, 0.823 mmol, 71%). ^1H NMR (δ, CD_3CN, 400 MHz):[20] 5.16 (s, 5H, $C_5\mathbf{H}_5$), 2.36 (s, 6H, $C\mathbf{H}_3CN$). IR (cm^{-1}, powder film): 3128 (w), 2949 (w), 2324 (w), 1978 (vs), 1415 (m), 1369 (m), 827 (vs), 556 (vs).

[(η^5-C_5H_5)Ru(PPh_3)(GBI)]$^+Cl^-$ ($\mathbf{1}^+Cl^-$). A Schlenk flask was charged with (η^5-C_5H_5)Ru(PPh_3)$_2$(Cl) (3.326 g, 4.580 mmol), GBI (0.842 g, 4.80 mmol), and toluene (15 mL) and fitted with a condenser. The mixture was refluxed with stirring. After 24 h, the mixture was cooled to room temperature. The solvent was decanted from a precipitate, which was washed with toluene (4 × 5 mL) and hexanes (2 × 15 mL) and dried by oil pump vacuum to give $\mathbf{1}^+Cl^-$ as a yellow powder (2.798 g, 4.378 mmol, 96%). Dec pt: 247 °C (capillary). TGA: onset of the first mass loss regime, T_i 196.07 °C, T_f 264.37 °C; onset of the second mass loss regime, T_i 175.83 °C, T_f 413.65 °C. Anal. Calcd (%) for $C_{31}H_{29}ClN_5PRu$ (639.09): C 58.26, H 4.57, N 10.96. Found: C 58.20, H 4.78, N 11.26. NMR (δ, DMSO-d_6): ^1H (400 MHz)[48] 11.83 (br s, 1H, N**H**), 10.19 (br s, 1H, N**H**), 7.32–7.09 (m, 17H, P($C_6\mathbf{H}_5$)$_3$ and NCC**H**(CH)$_2$C**H**CN), 7.00–6.99 (m, 2H, NCCH(C**H**)$_2$CHCN), 6.28 (s, 2H, $N\mathbf{H}_2$), 6.12 (s, 1H, N**H**), 4.41 (s, 5H, $C_5\mathbf{H}_5$); $^{13}C\{^1H\}$ (100 MHz) 154.1 (s, NH=**C**NH_2), 144.7 (s, N=**C**$(NH)_2$), 142.4 (s, NCCHCHCHCHC**N**), 136.6 (d, $^1J_{CP}$ = 42.9 Hz, *i*-$\mathbf{C}_6H_5$), 132.7 (d, $^2J_{CP}$ = 13.2 Hz, *o*-$\mathbf{C}_6H_5$), 131.6 (s, N**C**CHCHCHCHCN), 129.0 (s, *p*-$\mathbf{C}_6H_5$), 127.8 (d, $^3J_{CP}$ = 9.9 Hz, *m*-$\mathbf{C}_6H_5$), 121.6 (s, NCCHCH-**C**HCHCN), 121.2 (s, NCCH**C**HCHCHCN), 117.2 (s, NCCHC-HCH**C**HCN), 110.5 (s, NC**C**HCHCHCHCN), 74.1 (s, $\mathbf{C}_5H_5$); $^{31}P\{^1H\}$ (161 MHz) 55.9 (s). IR (cm^{-1}, powder film): 3347 (m), 3254 (m), 3200 (w), 3103 (w), 3080 (w), 2798 (m), 2764 (m), 2729 (m), 1679 (s), 1640 (w), 1617 (m), 1590 (m), 1559 (s), 1463 (m), 1436 (m), 1417 (m), 1274 (w), 1251 (m), 1096 (m), 833 (m), 791 (m), 749 (s), 695 (s). MS:[45] 603 (39) $[\mathbf{1}]^+$, 585 (12) $[\mathbf{1} - NH_2]^+$, 341 (100) $[\mathbf{1} - PPh_3]^+$. UV–visible (nm, 0.0010 M in DMSO (ε, $M^{-1}\,cm^{-1}$)): 309 (2760), 324 (2560), 332 (2550), 345 (2380), 384 (1660).

[(η^5-C_5H_5)Ru(PPh_3)(GBI)]$^+BF_4^-$ ($\mathbf{1}^+BF_4^-$). A Schlenk flask was charged with $\mathbf{1}^+Cl^-$ (0.273 g, 0.427 mmol), $Na^+BF_4^-$ (0.051 g, 0.47 mmol), and CH_2Cl_2/water (7.5 mL, 2:1 v/v). The mixture was stirred for 12 h. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic phases were filtered through a plug of Na_2SO_4 (1 × 1 cm), which was rinsed with CH_2Cl_2 (3 × 5 mL). The filtrate was concentrated by oil pump vacuum (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by oil pump vacuum. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by oil pump vacuum. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{1}^+BF_4^-\cdot(H_2O)_{0.5}$ as a yellow powder (0.230 g, 0.329 mmol, 77%).[19] Dec pt: 242 °C (capillary). Anal. Calcd (%) for $C_{31}H_{29}BF_4N_5PRu\cdot(H_2O)_{0.5}$ (700.13): C 53.23, H 4.32, N 10.01. Found: C 53.59, H 4.15, N 9.83. NMR (δ, DMSO-d_6): ^1H (400 MHz) 11.73 (s, 1H, N**H**), 9.71 (s, 1H, N**H**), 7.36–7.10 (m, 17H, P($C_6\mathbf{H}_5$)$_3$ and NCC**H**(CH)$_2$C**H**CN), 7.04–7.01 (m, 2H, NCC**H**(CH)$_2$C**H**CN), 6.10 (s, 1H, N**H**), 6.02 (s, 2H, $N\mathbf{H}_2$), 4.43 (s, 5H, $C_5\mathbf{H}_5$), 3.32 (s, $\mathbf{H}_2O$); $^{13}C\{^1H\}$ (75 MHz) 152.6 (s, NH=**C**NH_2), 145.3 (s, N=**C**$(NH)_2$), 143.9 (s, NCCHCHCHCHC**N**), 137.1 (d, $^1J_{CP}$ = 27.9 Hz, *i*-$\mathbf{C}_6H_5$), 134.9 (s, *o*-$\mathbf{C}_6H_5$), 132.3 (s, N**C**CHCHCHCHCN), 130.1 (s, *p*-$\mathbf{C}_6H_5$), 128.8 (s, *m*-$\mathbf{C}_6H_5$), 123.3 (s, NCCHCH**C**HCHCN), 122.7 (s, NCCH**C**HCHC-HCN), 118.8 (s, NCCHCHCH**C**HCN), 111.5 (s, NC**C**HCHCH-CHCN), 75.2 (s, $\mathbf{C}_5H_5$); $^{31}P\{^1H\}$ (161 MHz) 56.2 (s); $^{19}F\{^1H\}$ (282 MHz) −150.3 (s); $^{11}B\{^1H\}$ (128 MHz) −1.03 (s). IR (cm^{-1}, powder film): 3381 (m), 3354 (m), 1683 (s), 1637 (w), 1586 (m), 1563 (s), 1494 (w), 1463 (m), 1436 (m), 1409 (m), 1239 (w), 1089 (s), 1078 (s), 1011 (s), 845 (w), 741 (s), 694 (s). MS:[45] 603 (51) $[\mathbf{1}]^+$, 341 (100) $[\mathbf{1} - PPh_3]^+$. UV–visible (nm, 0.0011 M in DMSO (ε, $M^{-1}\,cm^{-1}$)): 289 (4650), 310 (5260), 322 (5610), 342 (3360), 390 (1800).

[(η^5-C_5H_5)Ru(PPh_3)(GBI)]$^+PF_6^-$ ($\mathbf{1}^+PF_6^-$). A Schlenk flask was charged with $\mathbf{1}^+Cl^-$ (0.224 g, 0.350 mmol), $Na^+PF_6^-$ (0.295 g, 1.76 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred for 12 h and filtered through a plug of Celite (1 × 1 cm), which was rinsed with CH_2Cl_2 (3 × 5 mL). The filtrate was concentrated by oil pump vacuum (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by oil pump vacuum. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by oil pump vacuum. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{1}^+PF_6^-$ as a yellow powder (0.218 g, 0.291 mmol, 83%).[19] Dec pt: 237 °C (capillary). Anal. Calcd (%) for $C_{31}H_{29}F_6N_5P_2Ru$ (749.09): C 49.74, H 3.90, N 9.36. Found: C 49.39, H 3.85, N 9.10. NMR (δ, DMSO-d_6): ^1H (300 MHz) 12.13 (s, 1H, N**H**), 10.82 (s, 1H, N**H**), 7.53–7.20 (m, 19H, P($C_6\mathbf{H}_5$)$_3$ and NCC**H**(C**H**)$_2$C**H**CN), 6.63 (s, 2H, $N\mathbf{H}_2$), 6.45 (s, 1H, N**H**), 4.61 (s, 5H, $C_5\mathbf{H}_5$); $^{13}C\{^1H\}$ (75 MHz) 152.7 (s, NH=**C**NH_2), 145.3 (s, N=**C**$(NH)_2$), 143.5 (s, NCCHCHCHCHC**N**), 136.8 (d, $^1J_{CP}$ = 39.2 Hz, *i*-$\mathbf{C}_6H_5$), 133.8 (s, *o*-$\mathbf{C}_6H_5$), 132.3 (s, N**C**CHCHCHCHCN), 130.1 (s, *p*-$\mathbf{C}_6H_5$), 128.7 (s, *m*-$\mathbf{C}_6H_5$), 123.4 (s, NCCHCH**C**HCHCN), 122.8 (s, NCCH**C**HCHCHCN), 118.9 (s, NCCHCHCH**C**HCN), 111.4 (s, NC**C**HCHCHCHCN), 75.2 (s, $\mathbf{C}_5H_5$); $^{31}P\{^1H\}$ (161 MHz) 56.3 (s, P(C_6H_5)$_3$), −142.9 (sep, $^1J_{PF}$ = 703.6 Hz, PF_6^-). $^{19}F\{^1H\}$ (282 MHz) −71.6 (d, $^1J_{FP}$ = 707.3 Hz). IR (cm^{-1}, powder film): 3505 (w), 3435 (w), 3412 (w), 3377 (w), 1687 (s), 1637 (w), 1586 (m), 1567 (s), 1478 (w), 1436 (m), 1401 (w), 1254 (m), 1092 (m), 880 (s), 862 (s), 841 (s), 741 (s), 698 (s). MS:[45] 603 (85) $[\mathbf{1}]^+$, 341 (100) $[\mathbf{1} - PPh_3]^+$. UV–visible (nm, 0.0010 M in DMSO (ε, $M^{-1}\,cm^{-1}$)): 296 (5200), 302 (4830), 314 (5340), 328 (5440), 338 (3980), 349 (4020), 400 (1760).

[(η^5-C_5H_5)Ru(PPh_3)(GBI)]$^+BAr_f^-$ ($\mathbf{1}^+BAr_f^-$).[8] A Schlenk flask was charged with $\mathbf{1}^+Cl^-$ (0.273 g, 0.427 mmol), $Na^+BAr_f^-$ (0.415 g, 0.469 mmol),[24] and CH_2Cl_2 (5 mL). The mixture was stirred for 12 h and filtered through a plug of Celite (1 × 2.5 cm), which was rinsed with CH_2Cl_2 (15 mL). The filtrate was concentrated by oil pump vacuum (ca. 5 mL). Hexanes (25 mL) was added, and the solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by oil pump vacuum. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{1}^+BAr_f^-\cdot(H_2O)_2$ as a yellow powder (0.545 g, 0.363 mmol, 85%).[19] Dec pt: 196 °C (capillary). Anal. Calcd (%) for $C_{63}H_{41}BF_{24}N_5PRu\cdot(H_2O)_2$ (1502.88): C 50.96, H 2.92, N 4.72. Found: C 50.65, H 2.61, N 4.64. NMR (δ, DMSO-d_6): ^1H (300 MHz) 11.75 (s, 1H, N**H**), 9.68 (s, 1H, N**H**), 8.31–8.03 (m, 31H, B($C_6\mathbf{H}_3(CF_3)_2$)$_4$, P($C_6\mathbf{H}_5$)$_3$, and NCC**H**(C**H**)$_2$C**H**CN), 6.12 (s, 1H, N**H**), 6.03 (s, 2H, $N\mathbf{H}_2$), 5.02 (s, 5H, $C_5\mathbf{H}_5$), 3.33 (s, $\mathbf{H}_2O$); $^{13}C\{^1H\}$ (75 MHz) 163.1 (q, $^1J_{CB}$ = 49.6 Hz, *i*-$\mathbf{C}_6H_3(CF_3)_2$), 152.6 (s, NH=**C**NH_2), 145.3 (s, N=**C**$(NH)_2$), 143.9 (s, NCCHCHCHCHC**N**), 137.1 (d, $^1J_{CP}$ = 27.9 Hz, *i*-$\mathbf{C}_6H_5$), 135.2 (s, *o*-$\mathbf{C}_6H_3(CF_3)_2$), 134.9 (s, *o*-$\mathbf{C}_6H_5$), 132.3 (s, N**C**CHCHCHCHCN), 130.1 (s, *p*-$\mathbf{C}_6H_5$), 128.8 (s, *m*-$\mathbf{C}_6H_5$), 129.5 (q, $^2J_{CF}$ = 31.2 Hz, *m*-$\mathbf{C}_6H_3(CF_3)_2$), 126.7 (q, $^1J_{CF}$ = 270.7 Hz, $C_6H_3(\mathbf{C}F_3)_2$), 123.3 (s, NCCHCH**C**HCHCN), 122.7 (s, NCCH**C**HCHCHCN), 118.8 (s, NCCHCHCH**C**HCN), 117.9 (s, *p*-$\mathbf{C}_6H_3(CF_3)_2$), 111.5

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(s, NC**C**HCHCHCHCN), 74.7 (s, $\mathbf{C}_5H_5$); $^{31}P\{^1H\}$ (161 MHz) 56.4 (s); $^{19}F\{^1H\}$ (282 MHz) −63.7 (s); $^{11}B\{^1H\}$ (128 MHz) −6.63 (s). IR (cm^{-1}, powder film): 3443 (w), 3405 (w), 1679 (m), 1586 (m), 1563 (m), 1459 (m), 1355 (s), 1274 (s), 1170 (s), 1119 (s), 1011 (w), 887 (m), 837 (m), 810 (m), 737 (m), 714 (m), 683 (m); MS:[45] 603 (49) $[\mathbf{1}]^+$, 341 (100) $[\mathbf{1} - PPh_3]^+$; UV–visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 295 (4170), 306 (5940), 320 (3160), 391 (1160).

[(η^5-C_5H_5)Ru(CO)(GBI)]$^+Cl^-$ ($\mathbf{2}^+Cl^-$).[49] A Schlenk flask was charged with $\mathbf{1}^+Cl^-$ (0.314 g, 0.491 mmol) and $CHCl_3$ (25 mL). The solution was aspirated with CO and monitored by $^{31}P\{^1H\}$ NMR. After 24 h, the solution was concentrated by rotary evaporation (5 mL) and filtered through a plug of Celite (5 × 1 cm), which was rinsed with $CHCl_3$ (30 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 25 mL) and added dropwise to stirred *n*-pentane (150 mL). The solvent was decanted from the precipitate, which was dissolved in $CHCl_3$ (25 mL).[51] The solution was added dropwise to stirred hexanes (100 mL), and the solvent was decanted from the precipitate. This sequence was repeated twice. The residue was triturated with benzene and dried by oil pump vacuum to give $\mathbf{2}^+Cl^-$ as an off-white powder (0.181 g, 0.447 mmol, 91%). Dec pt: 252 °C (capillary). Anal. Calcd (%) for $C_{14}H_{14}ClN_5ORu$ (404.99): C 41.54, H 3.49, N 17.30. Found: C 41.08, H 3.68, N 15.80.[52] NMR (δ): ^1H ($CDCl_3$/MeOH-d_4, 400 MHz)[53] 7.21−7.18 (m, 1H, NCCH(CH)$_2$C**H**CN), 7.09−7.06 (m, 2H, NCCH(C**H**)$_2$CHCN), 6.99−6.96 (m, 1H, NCC**H**(CH)$_2$CHCN), 4.87 (s, 5H, $\mathbf{C}_5H_5$); ^1H (DMSO-d_6, 400 MHz)[48] 11.42 (br s, 2H, N**H**),[54] 7.40−7.38 (m, 1H, NCCH(CH)$_2$C**H**CN), 7.20−7.13 (m, 3H, NCC**H**-(C**H**)$_2$CHCN), 6.72 (br s, 2H, N$\mathbf{H}_2$), 6.39 (s, 1H, N**H**), 5.19 (s, 5H, $\mathbf{C}_5H_5$); $^{13}C\{^1H\}$ ($CDCl_3$, 100 MHz)[48] 204.1 (s, **C**O), 153.6 (s, NH=**C**NH$_2$), 145.4 (s, N=**C**(NH)$_2$), 142.5 (s, NCCHCHCHCH**C**N), 131.6 (s, N**C**CHCHCHCHCN), 123.0 (s, NCCHCH**C**HCHCN), 122.5 (s, NCCH**C**HCHCHCN), 116.9 (s, NCCHCHCH**C**HCN), 111.5 (s, NC**C**HCHCHCHCN), 81.7 (s, $\mathbf{C}_5H_5$). IR (cm^{-1}, powder film): 3331 (w), 3266 (w), 3208 (m), 3138 (m), 3111 (w), 1938 (s, ν_{CO}), 1683 (s), 1652 (w), 1567 (s), 1494 (w), 1463 (m), 1420 (w), 1262 (m), 1220 (w), 1092 (w), 1015 (m), 972 (w), 934 (w), 806 (m), 741 (m), 694 (s), 667 (m). MS:[45] 371 (52) $[\mathbf{2}]^+$, 341 (100) $[\mathbf{2} - CO]^+$, 325 (32) $[\mathbf{2} - CO - NH_2]^+$, 299 (26) $[\mathbf{2} - CO - NHCNH_2]^+$; UV–visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 289 (4180), 294 (3860), 304 (3030), 412 (200).

[(η^5-C_5H_5)Ru(CO)(GBI)]$^+BF_4^-$ ($\mathbf{2}^+BF_4^-$). Route A. A Schlenk flask was charged with $\mathbf{1}^+BF_4^-\cdot(H_2O)_{0.5}$ (0.143 g, 0.204 mmol) and CH_2Cl_2 (5 mL). The sample was saturated with CO, fitted with a balloon filled with CO, and stirred. After 24 h, the mixture was filtered through a plug of Celite (1 × 1 cm), which was rinsed with CH_2Cl_2 (3 × 5 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{2}^+BF_4^-$ as a yellow powder (0.081 g, 0.18 mmol, 87%).[19] **Route B.** A Schlenk flask was charged with $\mathbf{2}^+Cl^-$ (0.161 g, 0.402 mmol), $Na^+BF_4^-$ (0.218 g, 1.99 mmol), and CH_2Cl_2/water (10 mL, 1:1 v/v) with stirring. After 12 h, the organic phase was separated and dried (Na_2SO_4).[50] The mixture was filtered through a plug of Celite (1 × 1 cm), which was rinsed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL). The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{2}^+BF_4^-\cdot(H_2O)_2$ as a yellow powder (0.151 g, 0.306 mmol, 77%). Dec pt: 241 °C (capillary). Anal. Calcd (%) for $C_{14}H_{14}BF_4N_5ORu\cdot(H_2O)_2$ (493.05): C 34.16, H 3.69, N 14.23. Found: C 33.85, H 3.14, N 12.32.[52] NMR (δ): ^1H (DMSO-d_6, 300 MHz) 11.57 (s, 2H, N**H**), 7.41−7.38 (m, 1H, NCCH(CH)$_2$C**H**CN), 7.22−7.14 (m, 3H, NCCH(C**H**)$_2$CHCN), 6.54 (br s, 2H, N$\mathbf{H}_2$), 6.33 (s, 1H, N**H**), 5.19 (s, 5H, $\mathbf{C}_5H_5$), 3.32 (s, $\mathbf{H}_2O$); $^{13}C\{^1H\}$ (CD_2Cl_2, 75 MHz) 204.0 (s, **C**O), 153.3 (s, NH=**C**NH$_2$), 145.1 (s, N=**C**(NH)$_2$), 142.3 (s, NCCHCHCHCH**C**N), 131.3 (s, N**C**CHCHCHCHCN), 122.9 (s, NCCHCH**C**HCHCN), 122.4 (s, NCCH**C**HCHCHCN), 116.9 (s, NC**C**HCHCHCHCN), 111.1 (s, NCCHCHCH**C**HCN), 81.6 (s, $\mathbf{C}_5H_5$); $^{19}F\{^1H\}$ (CD_2Cl_2, 282 MHz) −148.5 (s); $^{11}B\{^1H\}$ (DMSO-d_6, 128 MHz) −1.13 (s). IR (cm^{-1}, powder film): 3331 (w), 3304 (w), 3242 (w), 3212 (w), 3188 (w), 3138 (w), 3100 (w), 3080 (w), 3011 (w), 2922 (w), 2154 (m), 1938 (s, ν_{CO}), 1679 (s), 1637 (m), 1586 (m), 1563 (s), 1463 (m), 1413 (w), 1254 (w), 1220 (w), 1089 (m), 1078 (w), 1011 (m), 829 (w), 802 (m), 741 (s), 690 (s). MS:[45] 371 (67) $[\mathbf{2}]^+$, 341 (100) $[\mathbf{2}–CO]^+$. UV–visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 287 (2650), 300 (2870), 305 (3610), 430 (173).

[(η^5-C_5H_5)Ru(CO)(GBI)]$^+PF_6^-$ ($\mathbf{2}^+PF_6^-$). Route A. A Schlenk flask was charged with $\mathbf{1}^+PF_6^-$ (0.172 g, 0.229 mmol) and CH_2Cl_2 (5 mL). The sample was saturated with CO, fitted with a balloon filled with CO, and stirred. After 12 h, the mixture was filtered through a plug of Celite (1 × 1 cm), which was rinsed with CH_2Cl_2 (3 × 5 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{2}^+PF_6^-$ as a yellow powder (0.105 g, 0.204 mmol, 89%).[19] **Route B.** A Schlenk flask was charged with $\mathbf{2}^+Cl^-$ (0.218 g, 0.538 mmol), $Na^+PF_6^-$ (0.452 g, 2.69 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred for 12 h and filtered through a plug of Celite (1 × 1 cm), which was rinsed with CH_2Cl_2 (3 × 5 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{2}^+PF_6^-$ as a yellow powder (0.241 g, 0.468 mmol, 87%). Dec pt: 221 °C (capillary). Anal. Calcd (%) for $C_{14}H_{14}F_6N_5OPRu$ (514.99): C 32.69, H 2.74, N 13.62. Found: C 32.70, H 3.10, N 11.97.[52] NMR (δ, DMSO-d_6): ^1H (300 MHz) 12.48 (s, 1H, N**H**), 10.43 (s, 1H, N**H**), 7.43−7.39 (m, 1H, NCCH(CH)$_2$C**H**CN), 7.24−7.16 (m, 3H, NCC**H**(C**H**)$_2$CHCN), 6.46 (s, 2H, N$\mathbf{H}_2$), 6.34 (s, 1H, N**H**), 5.20 (s, 5H, $\mathbf{C}_5H_5$); $^{13}C\{^1H\}$ (75 MHz) 203.9 (s, **C**O), 152.9 (s, NH=**C**NH$_2$), 144.7 (s, N=**C**(NH)$_2$), 142.7 (s, NCCHCHCHCH**C**N), 131.2 (s, N**C**CHCHCHCHCN), 124.3 (s, NCCHCH**C**HCHCN), 123.8 (s, NCCH**C**HCHCHCN), 117.9 (s, NCCHCHCH**C**HCN), 111.6 (s, NC**C**HCHCHCHCN), 82.0 (s, $\mathbf{C}_5H_5$); $^{31}P\{^1H\}$ (DMSO-d_6, 121 MHz) −142.7 (sep, $^1J_{PF}$ = 710.3 Hz); $^{19}F\{^1H\}$ (282 MHz) −69.8 (d, $^1J_{FP}$ = 712.3 Hz). IR (cm^{-1}, powder film): 2347 (m), 1942 (s, ν_{CO}), 1683 (m), 1652 (w), 1590 (m), 1567 (m), 1521 (w), 1494 (w), 1463 (m), 1243 (m), 1104 (m), 1061 (w), 1015 (w), 837 (s), 741 (m), 660 (w). MS:[45] 371 (52) $[\mathbf{2}]^+$, 341 (100) $[\mathbf{2} – CO]^+$. UV–visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 291 (2280), 295 (2400), 298 (2650), 305 (4120), 311 (2550), 419 (206).

Route C. A round-bottom flask was charged with $[(\eta^5\text{-}C_5H_5)\text{-}Ru(CO)(NCCH_3)_2]^+PF_6^-$ (0.040 g, 0.095 mmol; see above), GBI (0.016 g, 0.095 mmol), CH_2Cl_2 (2 mL), and MeOH (1 mL) with stirring. After 2 d at room temperature, the solvent was removed by oil pump vacuum and the residue was chromatographed on a silica gel column (0.5 × 15 cm, 3:1 v/v CH_2Cl_2/CH_3CN). The solvent was removed from the product-containing fractions to give a sticky yellow solid. This was dissolved in CH_2Cl_2 (5 mL), and pentane was added until a precipitate formed. The solvent was removed by oil pump vacuum. More pentane (5 mL) was added and removed by oil pump vacuum (2 ×) to give $\mathbf{2}^+PF_6^-$ as a yellow powder (0.039 g, 0.076 mmol, 81%).

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[(η^5-C_5H_5)Ru(CO)(GBI)]$^+BAr_f^-$ ($2^+BAr_f^-$). Route A. A Schlenk flask was charged with $1^+BAr_f^-\cdot(H_2O)_2$ (0.257 g, 0.171 mmol) and CH_2Cl_2 (5 mL). The sample was saturated with CO, fitted with a balloon filled with CO, and stirred. After 24 h, the mixture was filtered through a plug of Celite (1 × 2.5 cm), which was rinsed with CH_2Cl_2 (2 × 10 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $2^+BAr_f^-$ as a yellow powder (0.194 g, 0.157 mmol, 92%).[19] **Route B.** A Schlenk flask was charged with 2^+Cl^- (0.154 g, 0.381 mmol), $Na^+BAr_f^-$ (0.354 g, 0.401 mmol),[24] and CH_2Cl_2 (5 mL). The mixture was stirred for 12 h and filtered through a plug of Celite (1 × 2.5 cm), which was rinsed with CH_2Cl_2 (2 × 25 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $2^+BAr_f^-\cdot(H_2O)_{1.5}$ as a yellow powder (0.420 g, 0.333 mmol, 88%). Dec pt: 187 °C (capillary). Anal. Calcd (%) for $C_{46}H_{26}BF_{24}N_5ORu\cdot(H_2O)_{1.5}$ (1260.11): C 43.86 H 2.32, N 5.56. Found: C 44.06, H 2.77, N 4.94.[52] NMR (δ): ^{1}H (DMSO-d_6, 400 MHz) 12.02 (br s, 2H, N**H**), 7.78 (s 8H, *o*-B(C_6**H**$_3$(CF_3)$_2$)$_4$), 7.71 (s, 4H, *p*-B(C_6**H**$_3$(CF_3)$_2$)$_4$), 7.52−7.49 (m, 1H, NCC**H**(CH)$_2$CHCN), 7.32−7.27 (m, 3H, NCCH(C**H**)$_2$C**H**CN), 6.63 (s, 2H, N**H**$_2$), 6.45 (s, 1H, N**H**), 5.30 (s, 5H, C_5**H**$_5$), 3.31 (s, **H**$_2$O); ^{13}C{^{1}H} (CD_2Cl_2, 75 MHz) 203.3 (s, **C**O), 163.1 (q, $^1J_{CB}$ = 49.6 Hz, *i*-$C_6H_3(CF_3)_2$), 152.4 (s, NH=**C**NH$_2$), 144.1 (s, N=**C**(NH)$_2$), 142.6 (s, NCCHCHCHCH**C**N), 135.2 (s, *o*-$C_6H_3(CF_3)_2$), 130.8 (s, NC**C**HCHCHCHCN), 129.5 (q, $^2J_{CF}$ = 31.2 Hz, *m*-$C_6H_3(CF_3)_2$), 126.7 (q, $^1J_{CF}$ = 270.7 Hz, C_6H_3(**C**F$_3$)$_2$), 124.9 (s, NCCHCH**C**HCHCN), 124.5 (s, NCCH**C**HCHCHCN), 118.4 (s, NCCHCHCH**C**HCN), 117.9 (s, *p*-$C_6H_3(CF_3)_2$), 111.4 (s, NC**C**HCHCHCHCN), 81.9 (s, **C**$_5$H$_5$); ^{19}F{^{1}H} (CD_2Cl_2, 282 MHz) −63.2 (s); ^{11}B{^{1}H} (DMSO-d_6, 128 MHz) −6.63 (s). IR (cm^{-1}, powder film): 3713 (w), 3652 (w), 2362 (w), 2343 (w), 1961 (s, ν_{CO}), 1718 (m), 1687 (m), 1629 (w), 1575 (m), 1355 (s), 1278 (s), 1116 (s), 1061 (m), 934 (w), 887 (w), 837 (w), 745 (m), 710 (m), 671 (m). MS:[45] 603 (51) [**2**]$^+$, 341 (100) [**2** − PPh_3]$^+$. UV−visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 289 (3810), 293 (3130), 305 (2770), 416 (210).

[(η^5-C_5H_5)Ru(CO)(GBI)]$^+$(Δ)-TRISPHAT$^-$ (2^+(Δ)-TRISPHAT$^-$). A Schlenk flask was charged with 2^+Cl^- (0.273 g, 0.427 mmol), (*n*-Bu)$_3$NH$^+$(Δ)-TRISPHAT$^-$ (0.445 g, 0.469 mmol),[26] and CH_2Cl_2 (5 mL) with stirring. After 12 h, the mixture was filtered through a plug of Celite (1 × 2.5 cm), which was rinsed with CH_2Cl_2 (25 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 5 mL). Then CH_2Cl_2/water (15 mL, 1:2 v/v) was added, and the mixture shaken for 5 min. The organic phase was separated, washed with water (5 × 10 mL), dried (Na_2SO_4), and filtered (sintered glass). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give 2^+(Δ)-TRISPHAT$^-$ as a white powder (0.545 g, 0.371 mmol, 81%) of ca. 95% purity by ^{1}H NMR. Dec pt: 187 °C (capillary). NMR (δ): ^{1}H (DMSO-d_6, 300 MHz) 11.55 (br s, 2H, N**H**), 7.39−7.37 (m, 1H, NCCH(CH)$_2$-C**H**CN), 7.18−7.14 (m, 3H, NCC**H**(C**H**)$_2$CHCN), 6.44 (s, 1H, N**H**), 6.30 (s, 2H, N**H**$_2$), 5.18 (s, 5H, C_5**H**$_5$); ^{1}H (C_6D_6, 300 MHz) 10.98 (br s, 2H, N**H**), 7.31−7.12 (m, 4H, NCC**H**(C**H**)$_2$C**H**CN), 6.11 (br s, 1H, N**H**), 5.98 (br s, 2H, N**H**$_2$), 4.61 and 4.60 (2 s, 5H, C_5**H**$_5$); ^{13}C{^{1}H} (DMSO-d_6, 75 MHz) 205.4 (s, **C**O), 153.6 (s, NH=**C**NH$_2$), 145.7 (s, N=**C**(NH)$_2$), 142.5 (s, NCCHCHCHCH**C**N), P($O_2C_6Cl_4$)$_3$ at 141.2 (d, $^2J_{CP}$ = 6.5 Hz), 122.1 (s), 113.2 (d, $^3J_{CP}$ = 19.6 Hz); 131.8 (s, NCCH-CHCHCHCN), 122.7 (s, NCCHCH**C**HCHCN), 122.4 (s, NCCH-**C**HCHCHCN), 117.0 (s, NCCHCHCH**C**HCN), 111.2 (s, NC**C**HC-HCHCHCN), 82.5 (s, C_5H_5); ^{31}P{^{1}H} (DMSO-d_6, 161 MHz) −79.7 (s). IR (cm^{-1}, powder film): 3381 (w), 3354 (m), 3308 (m), 3204 (w), 3184 (w), 3161 (w), 3119 (w), 3038 (w), 2930 (w), 1945 (s, ν_{CO}), 1683 (s), 1637 (w), 1586 (m), 1563 (s), 1494 (s), 1463 (m), 1436 (m), 1409 (w), 1239 (m), 992 (s), 741 (m), 694 (s). MS:[45] 371 (59) [**2**]$^+$, 341 (100) [**2** − CO]$^+$.

[(η^5-C_5Me_5)Ru(CO)(GBI)]$^+Cl^-$ (3^+Cl^-). A Schlenk flask was charged with (η^5-C_5Me_5)Ru(PPh_3)$_2$(Cl) (see above; 2.303 g, 2.893 mmol), GBI (0.760 g, 4.34 mmol), and benzene (15 mL) and fitted with a condenser. The mixture was refluxed with stirring. After 16 h, the yellow-brown precipitate was collected by filtration and washed with toluene (4 × 5 mL) and hexanes (2 × 15 mL). A Schlenk flask was charged with the yellow-brown powder and $CHCl_3$ (25 mL). The suspension was saturated with CO, fitted with a balloon filled with CO, and stirred. After 72 h, the mixture was concentrated by rotary evaporation (ca. 5 mL) and filtered through a plug of Celite (1 × 1 cm), which was rinsed with $CHCl_3$ (40 mL). The filtrate was concentrated by rotary evaporation (ca. 10 mL) and added dropwise to stirred *n*-pentane (35 mL). The solvent was decanted from the precipitate, which was dissolved in $CHCl_3$ (15 mL).[51] The solution was added dropwise to stirred hexanes (100 mL). The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $3^+Cl^-\cdot(CHCl_3)_{0.17}$ as an off-white powder (1.128 g, 2.281 mmol, 77%). Dec pt: 221 °C (capillary). Anal. Calcd (%) for $C_{19}H_{24}ClN_5ORu\cdot(CHCl_3)_{0.17}$ (494.72): C 46.23, H 4.89, N 14.04. Found: C 46.48, H 4.89, N 14.41. NMR[48] (δ): ^{1}H (DMSO-d_6, 400 MHz) 11.53 (br s, 2H, N**H**), 8.32 (s, trace $CHCl_3$), 7.42−7.40 (m, 1H, NCCH(CH)$_2$C**H**CN), 7.27−7.17 (m, 2H, NCCH(C**H**)$_2$CHCN), 7.12−7.10 (m, 1H, NCC**H**(CH)$_2$CHCN), 6.83 (s, 2H, N**H**$_2$), 5.89 (s, 1H, N**H**), 1.58 (s, 15H, C_5(C**H**$_3$)$_5$); ^{13}C{^{1}H} (DMSO-d_6/MeOH-d_4, 100 MHz)[48] 208.5 (s, **C**O), 154.6 (s, NH=**C**NH$_2$), 146.1 (s, N=**C**(NH)$_2$), 141.5 (s, NCCHCHCHCH**C**N), 133.1 (s, NC**C**HCHC-HCHCN), 123.3 (s, NCCHCH**C**HCHCN), 122.8 (s, NCCH**C**HC-HCHCN), 117.5 (s, NCCHCHCH**C**HCN), 111.9 (s, NC**C**HCHCH-CHCN), 93.4 (s, **C**$_5$(CH$_3$)$_5$), 79.4 (s, trace $CHCl_3$), 9.7 (s, C_5(**C**H$_3$)$_5$). IR (cm^{-1}, powder film): 3374 (w), 3289 (m), 3227 (w), 3184 (w), 3146 (w), 3100 (w), 3030 (w), 2972 (w), 2918 (w), 1915 (s, ν_{CO}), 1683 (m), 1637 (w), 1586 (m), 1556 (s), 1490 (w), 1463 (s), 1382 (m), 1251 (m), 810 (m), 741 (s), 690 (m). MS:[45] 440 (49) [**3**]$^+$, 412 (100) [**3** − CO]$^+$. UV−visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 295 (3020), 300 (4850), 302 (4980), 311 (3520), 315 (3140), 405 (253).

[(η^5-C_5Me_5)Ru(CO)(GBI)]$^+BF_4^-$ ($3^+BF_4^-$). A Schlenk flask was charged with 3^+ $Cl^-\cdot(CHCl_3)_{0.17}$ (0.106 g, 0.214 mmol), $Na^+BF_4^-$ (0.117 g, 1.06 mmol), and CH_2Cl_2/water (10 mL, 1:1 v/v) with stirring. After 16 h, the organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 5 mL).[50] The combined organic phases were filtered through a plug of Na_2SO_4 (1 × 1 cm), which was rinsed with CH_2Cl_2 (3 × 10 mL). The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $3^+BF_4^-\cdot(H_2O)_{1.5}$ as a yellow powder (0.072 g, 0.130 mmol, 61%). Dec pt: 219 °C (capillary). Anal. Calcd (%) for $C_{19}H_{24}BF_4N_5ORu\cdot(H_2O)_{1.5}$ (554.13): C 41.17, H 5.09, N 12.63. Found: C 41.46, H 4.89, N 12.21. NMR (δ): ^{1}H (DMSO-d_6, 300 MHz) 11.58 (s, 2H, N**H**), 7.42−7.40 (m, 1H, NCCH(CH)$_2$C**H**CN), 7.26−7.19 (m, 2H, NCC-H(C**H**)$_2$CHCN), 7.12−7.10 (m, 1H, NCC**H**(CH)$_2$CHCN), 6.64 (s, 2H, N**H**$_2$), 5.83 (s, 1H, N**H**), 3.40 (s, **H**$_2$O), 1.58 (s, 15H, C_5(CH$_3$)$_5$);

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$^{13}C\{^1H\}$ ($CDCl_3$, 75 MHz) 206.5 (s, **C**O), 153.1 (s, NH=**C**NH_2), 144.9 (s, N=**C**$(NH)_2$), 140.7 (s, NC**C**HCHCHCHCN), 131.5 (s, NC**C**HCHCHCHCN), 123.5 (s, NCCHCH**C**HCHCN), 122.9 (s, NCCH**C**HCHCHCN), 117.5 (s, NCCHCHCH**C**HCN), 111.3 (s, NC**C**HCHCHCHCN), 92.6 (s, **C**$_5(CH_3)_5$), 9.7 (s, C_5(**C**$H_3)_5$); $^{19}F\{^1H\}$ ($CDCl_3$, 282 MHz) −147.9 (s); $^{11}B\{^1H\}$ (DMSO-d_6, 128 MHz) −1.03 (s). IR (cm^{-1}, powder film): 3375 (w), 3290 (m), 3190 (w), 3144 (w), 3090 (w), 3035 (w), 2966 (w), 2920 (w), 2819 (m), 1915 (s, ν_{CO}), 1684 (m), 1637 (w), 1552 (m), 1468 (m), 1383 (w), 1328 (w), 1259 (m), 1081 (s), 1020 (s), 803 (s), 741 (m), 687 (m). MS:[45] 440 (33) $[\mathbf{3}]^+$, 411 (100) $[\mathbf{3} - CO]^+$. UV–visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 289 (2250), 295 (2140), 308 (3110), 402 (253).

[(η^5-C_5Me_5)Ru(CO)(GBI)]$^+PF_6^-$ ($\mathbf{3}^+PF_6^-$). A Schlenk flask was charged with $\mathbf{3}^+Cl^-\cdot(CHCl_3)_{0.17}$ (0.182 g, 0.368 mmol), $Na^+PF_6^-$ (0.309 g, 1.84 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred for 16 h and filtered through a plug of Celite (1 × 1 cm), which was rinsed with CH_2Cl_2 (3 × 5 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{3}^+PF_6^-$ as a yellow powder (0.182 g, 0.310 mmol, 84%). Dec pt: 211 °C (capillary). Anal. Calcd (%) for $C_{19}H_{24}F_6N_5OPRu$ (585.07): C 39.05, H 4.14, N 11.98. Found: C 39.05, H 4.21, N 11.94. NMR (δ): ^1H (DMSO-d_6, 300 MHz) 11.70 (s, 2H, N**H**),[54] 7.42–7.40 (m, 1H, NCCH-(CH)$_2$C**H**CN), 7.28–7.20 (m, 2H, NCCH(C**H**)$_2$CHCN), 7.13–7.11 (m, 1H, NCC**H**(CH)$_2$CHCN), 6.65 (s, 2H, N**H**$_2$), 5.83 (s, 1H, N**H**), 1.58 (s, 15H, C_5(C**H**$_3)_5$); $^{13}C\{^1H\}$ (CD_2Cl_2, 75 MHz) 206.9 (s, **C**O), 153.4 (s, NH=**C**NH_2), 145.1 (s, N=**C**$(NH)_2$), 141.1 (s, NC**C**HCH-CHCH**C**N), 132.2 (s, NC**C**HCHCHCHCN), 123.9 (s, NCCHCH-**C**HCHCN), 123.5 (s, NCCH**C**HCHCHCN), 118.1 (s, NCCHCH-CH**C**HCN), 111.6 (s, NC**C**HCHCHCHCN), 93.2 (s, **C**$_5(CH_3)_5$), 9.9 (s, C_5(**C**$H_3)_5$); $^{31}P\{^1H\}$ (CD_2Cl_2, 121 MHz) −142.7 (sep, $^1J_{PF}$ = 710.3 Hz); $^{19}F\{^1H\}$ (CD_2Cl_2, 282 MHz) −70.6 (d, $^1J_{FP}$ = 712.1 Hz). IR (cm^{-1}, powder film): 3499 (w), 3406 (m), 2966 (w), 2920 (w), 1922 (s, ν_{CO}), 1684 (m), 1637 (w), 1560 (m), 1460 (m), 1383 (w), 1313 (w), 1259 (w), 1097 (m), 1027 (m), 934 (w), 842 (s), 814 (w), 756 (m). MS:[45] 442 (61) $[\mathbf{3}]^+$, 412 (100) $[\mathbf{3} - CO]^+$. UV–visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 292 (2890), 308 (3260), 403 (258).

[(η^5-C_5Me_5)Ru(CO)(GBI)]$^+BAr_f^-$ ($\mathbf{3}^+BAr_f^-$). A Schlenk flask was charged with $\mathbf{3}^+Cl^-\cdot(CHCl_3)_{0.17}$ (0.187 g, 0.379 mmol), $Na^+BAr_f^-$ (0.352 g, 0.398 mmol),[24] and CH_2Cl_2 (5 mL). The mixture was stirred for 16 h and filtered through a plug of Celite (1 × 2.5 cm), which was rinsed with CH_2Cl_2 (2 × 15 mL).[50] The filtrate was concentrated by rotary evaporation (ca. 5 mL). Hexanes (25 mL) was added, and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dissolved in CH_2Cl_2 (5 mL). The solution was added dropwise to stirred hexanes (25 mL), and the CH_2Cl_2 was removed by rotary evaporation. The solvent was decanted from the precipitate, which was dried by oil pump vacuum to give $\mathbf{3}^+BAr_f^-\cdot H_2O$ as a yellow powder (0.400 g, 0.303 mmol, 80%). Dec pt: 184 °C (capillary). Anal. Calcd (%) for $C_{51}H_{36}BF_{24}N_5ORu\cdot H_2O$ (1321.17): C 46.38, H 2.90, N 5.30. Found: C 46.51, H 2.91, N 5.35. NMR (δ): ^1H (DMSO-d_6, 300 MHz) 11.35 (s, 2H, N**H**),[54] 7.65 (s, 8H, *o*-B(C$_6$**H**$_3$(CF$_3$)$_2$)$_4$), 7.60 (s, 4H, *p*-B(C$_6$**H**$_3$(CF$_3$)$_2$)$_4$), 7.42–7.40 (m, 1H, NCCH(CH)$_2$C**H**CN), 7.26–7.17 (m, 2H, NCCH(C**H**)$_2$CHCN), 7.12–7.10 (m, 1H, NCC**H**(CH)$_2$CHCN), 6.61 (s, 2H, N**H**$_2$), 5.85 (s, 1H, N**H**), 3.34 (s, **H**$_2$O), 1.56 (s, 15H, C_5(C**H**$_3)_5$); $^{13}C\{^1H\}$ (CD_2Cl_2, 75 MHz) 206.2 (s, **C**O), 161.8 (q, $^1J_{CB}$ = 49.6 Hz, *i*-C$_6$H$_3$(CF$_3$)$_2$), 152.5 (s, NH=**C**NH_2), 143.6 (s, N=**C**$(NH)_2$), 141.0 (s, NCCHCHCHCHCN), 135.2 (s, *o*-C$_6$H$_3$(CF$_3$)$_2$), 131.8 (s, NCCHCHCHCHCN), 129.5 (q, $^2J_{CF}$ = 31.2 Hz, *m*-C$_6$H$_3$(**C**F$_3$)$_2$), 126.7 (q, $^1J_{CF}$ = 270.7 Hz, C$_6$H$_3$(**C**F$_3$)$_2$), 125.0 (s, NCCHCH-**C**HCHCN), 124.5 (s, NCCH**C**HCHCHCN), 118.7 (s, NCCHCH-CH**C**HCN), 113.1 (s, NC**C**HCHCHCHCN), 111.5 (s, *p*-C$_6$H$_3$(CF$_3$)$_2$), 93.1 (s, **C**$_5(CH_3)_5$), 9.9 (s, C_5(**C**$H_3)_5$); $^{19}F\{^1H\}$ (CD_2Cl_2, 282 MHz) −63.2 (s); $^{11}B\{^1H\}$ (DMSO-d_6, 128 MHz) −6.64 (s). IR (cm^{-1}, powder film): 3692 (w), 3460 (w), 3391 (w), 3290 (w), 3213 (w), 3097 (w), 2966 (w), 2927 (w), 1931 (s, ν_{CO}), 1676 (m), 1607 (m), 1560 (m), 1460 (m), 1352 (m), 1274 (s), 1120 (s), 888 (m), 834 (m), 741 (m), 672 (m). MS:[45] 441 (51) $[\mathbf{3}]^+$, 411 (100) $[\mathbf{3} - CO]^+$. UV–visible (nm, 0.0011 M in DMSO (ε, M^{-1} cm^{-1})): 290 (3510), 302 (4980), 309 (4000), 317 (2140), 401 (264).

[(η^5-C_9H_7)Ru(PPh$_3$)(GBI)]$^+Cl^-$ ($\mathbf{4}^+Cl^-$). A Schlenk flask was charged with (η^5-C_9H_7)Ru(PPh$_3$)$_2$(Cl) (0.417 g, 0.537 mmol),[23] GBI (0.117 g, 0.671 mmol), and toluene (15 mL). The mixture was refluxed with stirring. After 24 h, the precipitate was collected by filtration, washed with toluene (3 × 15 mL) and hexanes (2 × 15 mL), and dried by oil pump vacuum at 120 °C to give $\mathbf{4}^+Cl^-\cdot(H_2O)_{0.5}$ as an orange powder (0.263 g, 0.377 mmol, 72%). Dec pt: 222 °C. Anal. Calcd (%) for $C_{35}H_{31}ClN_5PRu\cdot(H_2O)_{0.5}$ (699.11): C 60.21, H 4.62, N 10.03. Found: C 59.92, H 5.04, N 10.20. NMR (δ, DMSO-d_6): ^1H (400 MHz)[48] 11.97 (s, 1H, N**H**), 9.96 (s, 1H, N**H**), 7.69 (d, $^3J_{HH}$ = 7.8 Hz, 1H, CC**H**CHCHCHC), 7.47 (d, $^3J_{HH}$ = 8.1 Hz, 1H, CCHCHCHC**H**C), 7.36–7.28 (m, 9H, P(C$_6$**H**$_5)_3$), 7.14–7.08 (m, 8H, P(C$_6$**H**$_5)_3$ and NCCH(C**H**)$_2$CHCN), 7.04–6.98 (m, 2H, NCC**H**(CH)$_2$C**H**CN), 6.77–6.74 (m, 2H, CCHC**H**C**H**CHC), 6.53 (s, 1H, N**H**), 6.13 (s, 2H, N**H**$_2$), 5.08 (br s, 1H, CC**H**CHCHC),[55] 4.86 (br s, 1H, CCHCHC**H**C),[55] 4.30 (dd, 1H, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 2.0 Hz, CCHC-**H**CHC),[55] 3.33 (s, **H**$_2$O); $^{13}C\{^1H\}$ (100 MHz)[48] 151.4 (s, NH=**C**NH_2), 143.9 (s, N=**C**$(NH)_2$), 141.7 (s, NCCHCHCHCH**C**N), 135.3 (d, $^1J_{CP}$ = 42.3 Hz, *i*-C$_6$H$_5$), 132.5 (d, $^2J_{CP}$ = 10.5 Hz, *o*-C$_6$H$_5$), 131.6 (s, NCCHCHCHCHCN), 129.3 (s, *p*-C$_6$H$_5$), 127.7 (d, $^3J_{CP}$ = 9.4 Hz, *m*-C$_6$H$_5$), C_9H_7 at 126.2 (s), 125.6 (s), 121.6 (s), 120.7 (s), 117.1 (s), 106.0 (s), 83.2 (s), 59.2 (s), 55.4 (s); 124.6 (s, NCC-HCH**C**HCHCN), 121.2 (s, NCCH**C**HCHCHCN), 110.5 (s, NCCHCHCH**C**HCN), 110.3 (s, NC**C**HCHCHCHCN); $^{31}P\{^1H\}$ (161 MHz) 70.8 (s). IR (cm^{-1}, powder film): 3428 (m), 3266 (w), 3235 (w), 3192 (w), 3157 (w), 3076 (w), 3034 (m), 2968 (w), 2918 (w), 2826 (w), 2351 (m), 1942 (w), 1675 (s), 1633 (m), 1610 (m), 1559 (s), 1478 (m), 1436 (m), 1413 (m), 1320 (m), 1262 (m), 1185 (m), 1154 (m), 1092 (m), 1027 (w), 972 (w), 926 (w), 856 (w), 806 (w), 737 (m), 694 (m). MS:[45] 653 (82) $[\mathbf{4}]^+$, 391 (100) $[\mathbf{4} - PPh_3]^+$. UV–visible (nm, 0.0010 M in DMSO (ε, M^{-1} cm^{-1})): 289 (3890), 296 (4570), 299 (4360), 311 (5950), 315 (5840), 325 (5260), 329 (5160), 335 (3680), 424 (2440), 445 (3050), 455 (3370).

Friedel–Crafts Alkylations (Table 5).[56] An NMR tube was charged with catalyst (0.010 mmol), *trans*-*β*-nitrostyrene (**6**, 0.015 g, 0.10 mmol), an indole (**5a,b**, 0.20 mmol), an internal standard (mesitylene for **5a**; tridecane for **5b**), and CD_2Cl_2 (0.5 mL). The tube was sealed, and ^1H NMR spectra were periodically recorded. The CH=CH signals of the *trans*-*β*-nitrostyrene and the product CH_2NO_2 signals at ca. 5 ppm were integrated versus those of the standards.

^1H NMR data for **7a** (δ, $CDCl_3$, 300 MHz): 8.08 (br s, 1H, C_8H_5N**H**), 7.55–6.96 (m, 10H, C_8**H**$_5$NH and C$_6$**H**$_5$), 5.19 (t, 1H, $^3J_{HH}$ = 8.2 Hz, C**H**CH$_2$NO$_2$), 5.07 (dd, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 7.2 Hz, CH**H**′NO$_2$), 4.95 (dd, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 8.2 Hz, CH**H**′NO$_2$). Literature chemical shift values ($CDCl_3$)[56a] agree within 0.01 ppm, and data in CD_2Cl_2 are supplied elsewhere.[22]

[2-Guanidinium-1-methyl-3-hydrobenzimidazole] Tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate ([1-methylGBI-H]$^+BAr_f^-$). A round-bottom flask was charged with [1-methylGBI-H]$^+Cl^-$ (0.022 g, 0.100 mmol),[12b] $Na^+BAr_f^-$ (0.089 g, 0.100 mmol), CH_2Cl_2 (2.0 mL), and H_2O (1 mL) with stirring. After 2 h, the organic

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layer was separated and washed with H_2O (3 × 1.0 mL). The solvent was removed by rotary evaporation. The residue was chromatographed on a silica gel column (5 × 1 cm; 98:2 v/v CH_2Cl_2/MeOH). The solvent was removed from the product-containing fractions to give [1-methylGBI-H]$^+BAr_f^-$ as a pale pink powder (0.060 g, 0.058 mmol, 58%). Mp: 110−113 °C (capillary). Anal. Calcd (%) for $C_{41}H_{24}BF_{24}N_5$ (1053.45): C 46.75, H 2.30, N 6.65. Found: C 47.28, H 2.41, N 6.66. NMR (δ, CD_2Cl_2): ^{1}H (500 MHz) 7.71 (s, 8H, *o*-B($C_6\mathbf{H}_3(CF_3)_2)_4$), 7.55 (s, 4H, *p*-B($C_6\mathbf{H}_3(CF_3)_2)_4$), 7.11−7.04 (m, 4H, NC**CH**(**CH**)$_2$**CH**CNCH$_3$), 5.49 (br s, 4H, N**H**),[57] 3.62 (s, 3H, NCCH(CH)$_2$CHCNC**H**$_3$); ^{13}C{^{1}H} (125 MHz) 162.0 (q, $^1J_{CB}$ = 49.8 Hz, *i*-$\mathbf{C}_6H_3(CF_3)_2$), 158.4 (s, NH=**C**NH$_2$), 149.7 (s, N=**C**(NH)$_2$), 135.1 (s, *o*-$\mathbf{C}_6H_3(CF_3)_2$), 130.8 and 128.1 (2 s, NCCHCHCHCH**C**NCH$_3$), 129.1 (q, $^2J_{CF}$ = 31.5 Hz, *m*-$\mathbf{C}_6H_3(CF_3)_2$), 124.9 (q, $^1J_{CF}$ = 272.3 Hz, $C_6H_3(\mathbf{C}F_3)_2$), 125.6 and 125.5 (2 s, NCCH**C**H**C**HCHCNCH$_3$), 117.9 (s, *p*-$\mathbf{C}_6H_3(CF_3)_2$), 112.0 and 111.0 (s, NC**C**HCHCH**C**HCNCH$_3$), 39.6 (s, NCCHCHCHCH-CN**C**H$_3$). IR (cm^{-1}, powder film): 3520 (w), 3444 (w), 3419 (w), 1625 (m), 1585 (s), 1556 (m), 1490 (m), 1456 (w), 1413 (w), 1354 (s), 1315 (w), 1273 (s), 1109 (s), 1097 (s), 931 (w), 885 (s), 835 (s), 746 (s), 709 (s), 680 (s).

Crystallography. A. A CH_2Cl_2 solution of **1**$^+PF_6^-$ was layered with *n*-pentane. After 7 d, yellow prisms of **1**$^+PF_6^-$·CH_2Cl_2 were collected and data were recorded using a Nonius KappaCCD diffractometer as outlined in Table s3. Cell parameters were obtained from 10 reflections using a 10° scan and refined with 7191 reflections. Lorentz, polarization, and absorption corrections were applied.[58] The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by direct methods. The parameters were refined with all data by full-matrix least-squares on F^2 using SHELXL-97.[59] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from the literature.[60] The two cations and anions in the unit cell were related by an inversion center. **B.** A 1:1 v/v CH_2Cl_2/benzene solution of **1**$^+BAr_f^-$ was layered with hexanes. After 21 d at −18 °C, yellow blocks of **1**$^+BAr_f^-$·CH_2Cl_2 were collected and were analyzed as described for **1**$^+PF_6^-$·CH_2Cl_2 (cell parameters from 10 frames using a 10° scan; refined with 4492 reflections). The structure was solved and refined as in A. The fluorine atoms of one CF_3 group showed displacement disorder (F12a:F12a′, F12b:F12b′, F12c:F12c′), which could be refined to a 62:38 occupancy ratio.

■ ASSOCIATED CONTENT

Supporting Information

Additional experimental details and procedures, NMR and UV−visible spectra, tables of ^{1}H and ^{13}C NMR data for GBI complexes, and a table and CIF files with crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997. (b) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48−76; *Angew. Chem.* **2002**, *114*, 50−80. (c) Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. *Pure Appl. Chem.* **2011**, *83*, 1637−1641.

(2) (a) Sinden, R. R. *DNA Structure and Function*; Academic Press: San Diego, CA, 1994. (b) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37−44. (c) Perrin, C. L.; Nielson, J. B. *Annu. Rev. Phys. Chem.* **1997**, *48*, 511−544. (d) Sherrington, D. C.; Taskinen, K. A. *Chem. Soc. Rev.* **2001**, *30*, 83−93. (e) Amendola, V.; Fabbrizzi, L.; Mosca, L. *Chem. Soc. Rev.* **2010**, *39*, 3889−3915.

(3) (a) Reviews: Doyle, A. G.; Jacobsen, E. N. *Chem. Rev.* **2007**, *107*, 5713−5743. (b) Yu, X.; Wang, W. *Chem.—Asian J.* **2008**, *3*, 516−532. (c) Zhang, Z.; Schreiner, P. R. *Chem. Soc. Rev.* **2009**, *38*, 1187−1198.

(4) Representative reports from 2014: (a) Kim, H. J.; Ajitha, M. J.; Lee, Y.; Ryu, J.; Kim, J.; Lee, Y.; Jung, Y.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 1132−1140. (b) Wang, W.; Kumar, M.; Hammond, G. B.; Xu, B. *Org. Lett.* **2014**, *16*, 636−639.

(5) (a) White, A. J.; Wharton, C. W. *Biochem. J.* **1990**, *270*, 627−637. (b) Gerlt, J. A.; Kreevoy, M. M.; Cleland, W. W.; Frey, P. A. *Chem. Biol.* **1997**, *4*, 259−267. (c) Cleland, W. W.; Frey, P. A.; Gerlt, J. A. *J. Biol. Chem.* **1998**, *273*, 25529−25532. (d) Guo, H.; Salahub, D. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 2985−2990; *Angew. Chem.* **1998**, *110*, 3155−3160. (e) Tuchscherer, G.; Lehmann, C.; Mathieu, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 2990−2993; *Angew. Chem.* **1998**, *110*, 3160−3164. (f) Schowen, K. B.; Limbach, H.-H.; Denisov, G. S.; Schowen, R. L. *Biochim. Biophys. Acta* **2000**, *1458*, 43−62. (g) Simón, L.; Goodman, J. M. *J. Org. Chem.* **2010**, *75*, 1831−1840.

(6) (a) Kirby, A. J. *Angew. Chem., Int. Ed.* **1996**, *35*, 707−724; *Angew. Chem.* **1996**, *108*, 770−790. (b) Zhao, Y.; Rodrigo, J.; Hoveyda, A. H.; Snapper, M. L. *Nature* **2006**, *443*, 67−70. (c) Davie, E. A. C.; Mennen, S. M.; Xu, Y.; Miller, S. J. *Chem. Rev.* **2007**, *107*, 5759−5812. (d) Knowles, R. R.; Jacobsen, E. N. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 20678−20685. (e) Wennemers, H. *Chem. Commun.* **2011**, *47*, 12036−12041.

(7) (a) Etter, M. C.; Urbańczyk-Lipkowska, Z.; Zia-Ebrahimi, M.; Panunto, T. W. *J. Am. Chem. Soc.* **1990**, *112*, 8415−8426. (b) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120−126.

(8) Abbreviations: en = 1,2-ethylenediamine; BAr_f = B(3,5-$C_6H_3(CF_3)_2)_4$; TRISPHAT = (tris(tetrachlorobenzenediolato)phosphate(V) or P(*o*-$C_6Cl_4O_2)_3$.

(9) (a) Ganzmann, C.; Gladysz, J. A. *Chem.—Eur. J.* **2008**, *14*, 5397−5400. (b) Lewis, K. G.; Ghosh, S. K.; Bhuvanesh, N.; Gladysz, J. A. Manuscript in preparation. (c) See also: Lewis, K. G.; Ghosh. S. K.; Gladysz, J. A. U.S. Patent WO 2014018978A2; *Chem. Abstr.* **2014**, *160*, 240833.

(10) Representative salts with *y*/*z* = 3/1 from the Cambridge Crystallographic Data Centre (CCDC Refcodes): A07020, A12326, OB6070, A18811, 231235, 645729.

(11) King, F. E.; Acheson, R. M.; Spensley, P. C. *J. Chem. Soc.* **1948**, 1366−1371.

(12) (a) Barba-Behrens, N.; Vázquez-Olmos, A.; Castillo-Blum, S. E.; Höjer, G.; Meza-Höjer, S.; Hernández, R. M.; Rosales-Hoz, M. J.; Vincente, R.; Escuer, A. *Transition Met. Chem.* **1996**, *21*, 31−37. (b) Andrade-López, N.; Ariza-Castolo, A.; Contreras, R.; Vázquez-Olmos, A.; Barba-Behrens, N.; Tlahuext, H. *Heteroat. Chem.* **1997**, *8*, 397−410. (c) Andrade-López, N.; Cartas-Rosado, R.; García-Baéz, E.; Contreras, R.; Tlahuext, H. *Heteroat. Chem.* **1998**, *9*, 399−409. (d) Fialon, M.-P.; Andrade-López, N.; Barba-Behrens, N.; Contreras, R. *Heteroat. Chem.* **1998**, *9*, 637−641. (e) Ceniceros-Gómez, A. E.; Barba-Behrens, N.; Bernès, S.; Nöth, H.; Castillo-Blum, S. E. *Inorg. Chim. Acta* **2000**, *304*, 230−236. (f) Castillo-Blum, S. E.; Barba-Behrens, N. *Coord. Chem. Rev.* **2000**, *196*, 3−30.

(13) (a) Cram, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1039−1057; *Angew. Chem.* **1986**, *98*, 1041−1060. (b) Desper, J. M.; Gellman, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 6732−6734. (c) Wittenberg, J. B; Isaacs, L. Complementarity and Preorganization. In *Supramolecular Chemistry: From Molecules to Nanomaterials*; Gale, P., Steed, J., Eds.; Vol. *1*; Wiley & Sons: Hoboken, NJ, 2012.

(14) Cram, D. J.; Lein, G. M. *J. Am. Chem. Soc.* **1985**, *107*, 3657−3668.

(15) Mukherjee, T.; Ganzmann, C.; Bhuvanesh, N.; Gladysz, J. A. *Organometallics*, doi: 10.1021/om500705s.
(16) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601−1604.
(17) (a) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405−1421. (b) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942. (c) Krossing, I.; Raabe, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066−2090; *Angew. Chem.* **2004**, *116*, 2116−2142. (d) Díaz-Torres, R.; Alvarez, S. *Dalton Trans.* **2011**, *40*, 10742−10750.
(18) King, R. B. *Inorg. Chim. Acta* **1968**, *2*, 454−458 These page numbers correspond to those on the PDF file downloaded from the publisher. However, as of the submission date of this manuscript, the publisher's table of contents on the web indicates the page numbers 449−453.
(19) Specifically, multiple attempts were sometimes required to obtain reasonable yields of $\mathbf{1}^{+}BF_4^{-}$, $\mathbf{1}^{+}PF_6^{-}$, and $\mathbf{1}^{+}BAr_f^{-}$ in the initial step A1.
(20) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485−488.
(21) Previous synthesis of this compound by a two-step procedure: (a) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130−6135. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175.
(22) Scherer, A. Doctoral Thesis, Universität Erlangen-Nürnberg, 2009.
(23) Oro, L. A.; Ciriano, M. A.; Campo, M.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, *289*, 117−131.
(24) Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579−3581.
(25) Complex $\mathbf{2}^{+}Cl^{-}$ is cleanly deprotonated by Na_2CO_3.[22] NMR evidence suggests that the ═CNHC═ proton of the chelate ring is removed. Other salts investigated did not give clean deprotonation with pyridine, NaOMe, or Na_2CO_3, at least under the conditions assayed.
(26) (a) Lacour, J.; Goujon-Ginglinger, C.; Torche-Haldimann, S.; Jodry, J. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3695−3697; *Angew. Chem.* **2000**, *112*, 3830−3832. (b) Favarger, F.; Goujon-Ginglinger, C.; Monchaud, D.; Lacour, J. *J. Org. Chem.* **2004**, *69*, 8521−8524.
(27) Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Méndez, N. Q.; Fernández, J. M.; Patton, A. T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 211−225.
(28) (a) McCrindle, R.; Ferguson, G.; McAlees, A. J.; Massod, P.; Stephenson, D. K. *J. Chem. Soc., Dalton Trans.* **1982**, 1291−1296. (b) Husain, A.; Nami, A. A. A.; Siddiqi, K. S. *Appl. Organomet. Chem.* **2011**, *25*, 761−768.
(29) (a) Lungwitz, R.; Spange, S. *New J. Chem.* **2008**, *32*, 392−394. (b) Cláudio, A. F. M.; Swift, L.; Hallett, J. P.; Welton, T.; Coutinho, J. A. P.; Freire, M. G. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6593−6601.
(30) The following papers describe hydrogen bond donor catalysts for the reaction of indole and *trans*-*β*-nitrostyrene. (a) Dessole, G.; Herrera, R. P.; Ricci, A. *Synlett* **2004**, *13*, 2374−2378. (b) Zhuang, W.; Hazell, R. G.; Jørgensen, K. A. *Org. Biomol. Chem.* **2005**, *3*, 2566−2571. (c) Fleming, E. M.; McCabe, T.; Connon, S. J. *Tetrahedron Lett.* **2006**, *47*, 7037−7042. (d) Akalay, D.; Dürner, G.; Bats, J. W.; Bolte, M.; Göbel, M. W. *J. Org. Chem.* **2007**, *72*, 5618−5624. (e) Takenaka, N.; Sarangthem, R. S.; Seerla, S. K. *Org. Lett.* **2007**, *9*, 2819−2822. (f) Rodriguez, A. A.; Yoo, H.; Ziller, J. W.; Shea, K. J. *Tetrahedron Lett.* **2009**, *50*, 6830−6833. (g) Marqués-López, E.; Alcaine, A.; Tejero, T.; Herrera, R. P. *Eur. J. Org. Chem.* **2011**, 3700−3705. (h) Tran, N. T.; Wilson, S. O.; Franz, A. K. *Org. Lett.* **2012**, *14*, 186−189. (i) Shokri, A.; Wang, X.-B.; Kass, S. R. *J. Am. Chem. Soc.* **2013**, *135*, 9525−9530.
(31) Berkessel, A.; Cleemann, F.; Mukherjee, S.; Müller, T. N.; Lex, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 807−811; *Angew. Chem.* **2005**, *117*, 817−821.
(32) (a) Lam, S. Y.; Louis, C.; Benoit, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 1156−1160. (b) Meshcheryakov, D.; Arnaud-Neu, F.; Böhmer, V.; Bolte, M.; Hubscher-Bruder, V.; Jobin, E.; Thondorf, I.; Werner, S. *Org. Biomol. Chem.* **2008**, *6*, 1004−10014. (c) Amendola, V.; Bergamaschi, G.; Boiocchi, M.; Fabbrizzi, L.; Milani, M. *Chem.—Eur. J.* **2010**, *16*, 4368−4380.
(33) Heyns, A. M. *Spectrochim. Acta, Part A* **1977**, *33*, 315−322.
(34) Hamza, A.; Schubert, G.; Soós, T.; Pápai, I. *J. Am. Chem. Soc.* **2006**, *128*, 13151−13160.
(35) (a) Liang-An, C.; Xu, W.; Huang, B.; Ma, J.; Wang, L.; Xi, J.; Harms, K.; Gong, L.; Meggers, E. *J. Am. Chem. Soc.* **2013**, *135*, 10598−10601. (b) Chen, L.-A.; Tang, X.; Xi, J.; Xu, W.; Gong, L.; Meggers, E. *Angew. Chem., Int. Ed.* **2013**, *52*, 14021−14025; *Angew. Chem.* **2013**, *125*, 14271−14275.
(36) Thomas, C.; Gladysz, J. A. *ACS Catal.* **2014**, *4*, 1134−1138.
(37) (a) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 487−507; *Angew. Chem.* **1986**, *98*, 483−503. (b) Raymo, F. M.; Stoddart, J. F. *Chem. Ber.* **1996**, *129*, 981−990.
(38) Amoroso, A. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1997**, *16*, 6032−6034.
(39) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40−73; *Angew. Chem.* **2001**, *113*, 40−75.
(40) Mukherjee, T. Doctoral Thesis, Texas A&M University, in preparation.
(41) David, O. R. P. Planar Chiral Catalysts In *Comprehensive Enantioselective Organocatalysis: Catalyst, Reactions, and Applications*, 1st ed.; Dalko, P. I., Ed.; Wiley-VCH: Weinheim, Germany, 2013; Vol. *1*, Part II.
(42) For insightful commentary on this issue, see ref 1 in Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138−5175; *Angew. Chem.* **2004**, *116*, 5248−5286.
(43) An alternative microwave procedure is provided in the Supporting Information.
(44) An exact yield cannot be calculated due to the indeterminate hydration level of the $RuCl_3$.
(45) FAB, 3-NBA, *m*/*z* (%); the peaks correspond to the most intense signal of the isotope envelope.
(46) Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 119−121.
(47) This complex was purchased from ACROS or prepared by a literature method: Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544−2546. The commercial material contained up to 10% of the precursor $[(\eta^5\text{-}C_5H_5)Ru(C_6H_6)]^{+}PF_6^{-}$, but gave equally good results.
(48) The ^1H and $^{13}C\{^1H\}$ NMR assignments are supported by $^1H,^1H$ COSY NMR and $^1H,^{13}C$ HETCOR NMR experiments and are consistent with assignments made in previous studies of comparable GBI derivatives; see refs 12c, d.
(49) An alternative procedure using a static CO atmosphere is provided in the Supporting Information.
(50) The workup was carried out under ambient laboratory conditions.
(51) In some cases, the solubility in $CHCl_3$ was poor. When this occurred, a $CHCl_3$/MeOH mixture was employed.
(52) Curiously, the ruthenium cyclopentadienyl carbonyl complexes gave consistently low microanalytical values for nitrogen.
(53) Traces of NH- and NH_2-signals were detectable at δ 8.13, 6.63, and 5.87 ppm.
(54) The very broad signal precluded an accurate integration.
(55) The ^1H and $^{13}C\{^1H\}$ NMR assignments are supported by $^1H,^1H$ COSY NMR and $^1H,^{13}C$ HETCOR NMR experiments and are consistent with assignments made in previous studies of $(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(Cl)$; see ref 23.
(56) (a) Herrera, R. P.; Sgarzani, V.; Bernardi, L.; Ricci, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6576−6579; *Angew. Chem.* **2005**, *117*, 6734−6737. (b) See also ref 30.
(57) Only a single signal was observed for the five NH protons, and it integrated to 4H, suggestive of some H/D exchange.
(58) (a) *Collect* data collection software; Nonius B. V., 1998. (b) *Scalepack* data processing software; Otwinowski, Z.; Minor, W. In *Methods Enzymol.* **1997**, *276* (Macromolecular Crystallography, Part A), 307.
(59) Sheldrick, G. M. *SHELX-97, Program for Refinement of Crystal Structures*; University of Göttingen, 1997.
(60) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A.; Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974.