8.1 Hz, 4F), −162.35 (dt, ^1J = 23.03, ^2J = 6.9 Hz, 2F); HR-MS: *m/z*: 797.0854 (calcd for $C_{37}H_{12}N_4F_{15}$: 797.0822).

2: UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$): 406 (118.6), 562 (20.3), 602 nm (11.9); ^{1}H NMR ($CDCl_3$): δ = 8.99 (d, J = 4.3 Hz, 2H), 8.71 (d, J = 4.3 Hz, 2H), 8.52 (t, J = 4.3 Hz, 4H), 7.72 (m, 3H), 7.33 (m, 6H), −2.1 (br s, 3H); ^{19}F NMR ($CDCl_3$): δ = −109.32 (t, J = 6.4 Hz, 2F), −109.75 (t, J = 6.4 Hz, 4F); HR-MS: *m/z*: 635.1660 (calcd for $C_{37}H_{21}N_4F_6$: 635.1670).

3: UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$): 408 (106.1), 422 (86.6), 560 (16.7), 604 nm (9.3); ^{1}H NMR ($CDCl_3$): δ = 8.91 (d, J = 4.2 Hz, 2H), 8.49 (d, J = 4.8 Hz, 2H), 8.35 (d J = 4.6 Hz, 4H), 7.72 (m, 3H), 7.33 (m, 6H), −1.7 (br s, 3H); HR-MS: *m/z*: 729.9810 (calcd for $C_{37}H_{20}N_4Cl_6$: 729.9819).

4: A 1.6 M *n*BuLi solution (0.42 mL, 0.7 mmol) was added to a stirred solution of 2-bromopyridine (0.054 mL, 0.56 mmol) in dry THF (6 mL) under an argon atmosphere at −78 °C, at such a rate that the temperature of the reaction mixture did not exceed −70 °C. After the addition was complete, the reaction mixture was stirred for 1 h at −78 °C, resulting an a clear yellow solution. Next, a solution of **1** (0.03 g, 0.038 mmol) in dry THF (6 mL) was added dropwise. The mixture was stirred for 1 h at −78 °C and then hydrolyzed with saturated aqueous bicarbonate solution. The layers were separated, the aqueous layer was washed with diethyl ether, and the combined diethyl ether extracts were dried and evaporated to yield a solid residue. The product was purified by column chromatography on silica gel (EtOAc/hexane 1/1) and recrystallized from CH_2Cl_2/hexane to provide 13 mg (35 % yield) of pure **4** as a violet solid. UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$): 414 (111.6), 564 (18.4), 606 nm (sh); ^{1}H NMR ($CDCl_3$): δ = 9.12 (d, J = 3.9 Hz, 2H), 8.93 (m, 5H), 8.73 (d, J = 4.88 Hz, 2H), 8.66 (d, J = 3.91 Hz, 2H), 8.00 (dt, ^1J = 7.81, ^2J = 1.95 Hz, 3H), 7.84 (br d, J = 7.81 Hz, 3H), 7.51 (dt, ^1J = 6.84, ^2J = 1.95 Hz, 3H), −2.02 (br s, 3H); ^{19}F NMR ($CDCl_3$): δ = −138.19 (q, J = 23.79 Hz, 2F), −138.81 (q, J = 23.79 Hz, 4F), −144.11 (q, J = 23.79 Hz, 4F), −144.57 (q, J = 23.79 Hz, 2F); HR-MS: *m/z*: 973.1910 (calcd for $C_{52}H_{23}N_7F_{12}$: 973.1823).

5: A mixture of **4** (11 mg, 11 μmol) and CH_3I (0.8 mL, 13 mmol) in freshly distilled DMF (2 mL) was heated to 70 °C for 3 h. After evaporation of the solvent, the product was recrystallized from MeOH/diethyl ether to provide 15.5 mg (98 % yield) of **5** as a green solid. UV/Vis (MeOH): λ_{max} ($\varepsilon \times 10^{-3}$): 430 (76.2), 576 (10.9), 622 nm (17.8); ^{1}H NMR ([D$_6$]DMSO): δ = 9.49 (d, J = 5.98 Hz, 3H), 9.16 (br m, 8H), 9.00 (t, J = 8.54 Hz, 3H), 8.75 (t, J = 7.68 Hz, 3H), 8.51 (t, J = 7.68 Hz, 3H), 4.68 (s, 3H), 4.65 (s, 6H); ^{19}F NMR ([D$_6$]DMSO): δ = −137.26 (br m, 4F), −138.04 (br m, 6F), −138.60 (br m, 2F); electron spray MS: *m/z*: 339.9 ([M^+ − 3I]/3, 100 %).

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Regioselective Reduction of NAD$^+$ Models with [Cp*Rh(bpy)H]$^+$: Structure – Activity Relationships and Mechanistic Aspects in the Formation of the 1,4-NADH Derivatives**

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The interest in practical methods for the regeneration of the co-enzyme 1,4-NADH, the reduced form of nicotinamide adenine dinucleotide (NAD$^+$), has continued to be high in the field of biocatalysis, where enzymatic reduction reactions are important for the synthesis of chiral organic compounds.[1a, b] Conversion of NAD$^+$ into 1,4-NADH by enzymatic, chemical, photochemical, and electrochemical methods has been studied extensively in order to increase the rate of the regeneration, while maintaining the necessary high regioselectivity. The regeneration is frequently the limiting step in the eventual use of 1,4-NADH in enzymatic synthesis, particularly for higher volume and more energy intensive processes.[1a, b]

In the search for higher rates and a more economical regeneration process various transition metal hydrides have been studied as catalysts for the regioselective reduction of NAD$^+$ and NAD$^+$ models to their corresponding 1,4-NADH derivatives.[2a–g] In the most successful example, Steckhan and co-workers have described the use of [Cp*Rh(bpy)(H)]$^+$ (Cp* = pentamethylcyclopentadienyl, bpy = 2,2′-bipyridyl), generated in situ, for the regiospecific reduction of NAD$^+$ to 1,4-NADH,[2b] and then demonstrated the cofactor regeneration process in enzymatic, chiral reduction reactions.[3, 4]

While the above mentioned reduction of NAD$^+$ by [Cp*Rh(bpy)H]$^+$ was shown to be regiospecific for 1,4-NADH,[2b, 5a] the full mechanistic details of this important

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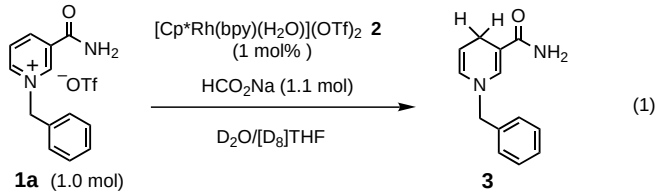
cofactor conversion and the role of the substituents on the nicotinamide moiety have not been elucidated. Thus, we have initiated a program to determine the source of this high regioselectivity and other mechanistic aspects with the model NAD^+ compound 1-benzylnicotinamide triflate (**1a**)[6] by using $[Cp^*Rh(bpy)(H_2O)](OTf)_2$ (**2**) as the catalyst precursor and sodium formate as the hydride source.[2b] Furthermore, a variety of 3-substituted derivatives of 1-benzylpyridinium triflate (**1b–i**) were synthesized and studied along with **1a** to ascertain how other substitutents in position 3 would influence the regioselectivity. We were also interested in examining any electronic and steric effects that these substituents in the 3 position might impart on the rate of hydride transfer.

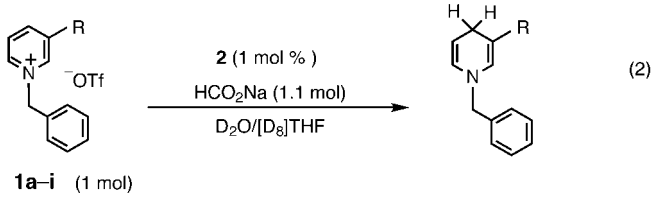
Initial ^1H NMR experiments in $D_2O/[D_8]THF$ of **1a** and **2** in the presence of the hydride source HCO_2Na showed that both 1-benzyl-1,4-dihydronicotinamide (**3**, >95%) and its 1,6-isomer (<5%) were formed [Eq. (1)]. However, the 1,4-dihydro product **3** was separately found to be converted,



(1)

under similar reaction conditions, into less than 5% (2 h) of the 1,6-dihydro isomer by a rearrangement catalyzed by complex **2**. Thus, as with NAD^+ itself, the model compound **1a** also provides high regioselectivity for the 1,4-dihydro product with $[Cp^*Rh(bpy)H]^+$, but is mitigated, to a very minor extent, by a rearrangement catalyzed by complex **2** of the kinetic 1,4-dihydro product to the 1,6-dihydro isomer; the overall ratio of **3** to its 1,6-isomer in Equation (1) was found to be about 20:1. More importantly, when we used DCO_2Na (98% D) as the hydride source, the deuterium was found to be incorporated at the C4 position (>95%, ^1H NMR spectroscopy) rather than the C6 position. This observation, therefore, further defined the initial kinetic product as being the 1,4-isomer, **3**.

Table 1 shows the relative rates and turnover frequencies of **1a** and other *N*-benzylpyridinium compounds substituted in position 3 (**1b** and **1d–g**) that also provide regioselective 1,4-dihydro products under the same conditions [Eq. (2)]. Additionally, complex **2** also catalyzed the rearrangement of the



(2)

1,4-dihydro derivatives of **1b**, and **1d–g** to the corresponding 1,6-dihydro derivative (ca. 5–15%). It is interesting to note that the $C(S)NH_2$ group in **1d** increased the relative rate by approximately 30% relative to the $C(O)NH_2$ group in **1a**, and this suggests that the more polarizable, soft S atom, which is a

Table 1. Relative rates and turnover frequencies of the regioselective reductions of NAD^+ models [see Equation (2)].[a]

Substrate	R	Relative reaction rate[b]	TOF [h][c]
1a		1.0	8
1b		0.9	8
1c		0.0	0
1d		1.3	11
1e		1.1	9
1f		1.3	11
1g	CN	0.9	8
1h	CH_3	0.0	0
1i	H	0.0	0

[a] The reactions were conducted in presilylated NMR tubes (J. Young) and were followed by ^1H NMR spectroscopy. [b] The relative reaction rates were determined by observing the disappearance of the pyridinium signals versus an internal standard, $[(CH_3)_4N]OTf$, during the first 2 h, with the relative rate of **1a** set to 1.0. [c] The turnover frequencies (TOFs) were calculated by the amount of product [mmol] per amount of the catalyst [mmol] per hour.

better σ donor, coordinates more readily to the Cp*Rh metal center and, thereby, facilitates hydride transfer to C4. Moreover, the $C(O)OCH_3$ group in the 3 position in **1f** also increased the relative rate by about 30%, presumably for reasons associated with both coordination and the favorable electron-withdrawing effect. In contrast, replacement of the substituent in position 3 with a noncoordinating, electron-donating CH_3 group (**1h**) or a hydrogen atom (**1i**) leads to decomposition of the $[Cp^*Rh(bpy)H]^+$ complex[5b] rather than formation of the corresponding 1,4-dihydro compound.

We observed no 1,4-dihydro product and only $[Cp^*Rh(bpy)H]^+$ decomposition when the $C(O)NH_2$ group in **1a** ($E_p = -1.23$ V versus Ag/AgCl) was replaced with a $-C(O)NEt_2$ group (**1c**; $E_p = -1.26$ V versus Ag/AgCl), even though both substituents would be of equal σ-donating ability and equal overall electronic effect. A plausible explanation would entail that steric interactions between the methyl groups of the Cp* ligand and the ethyl groups in position 3 (NEt_2) inhibit coordination of the substrate to the Cp*Rh metal center, thereby limiting the hydride-transfer process. More interestingly, this result occurs even when the most electrophilic and sterically unencumbered C6 position of **1c** is readily available, which further strengthens the concept of the coordination of the carbonyl unit of the $C(O)NH_2$ group in **1a**, as well as of those substituents in substrates **1b** and **1d–g**, to the Cp*Rh metal center.[7]

Several competitive substrate reduction experiments were performed to establish whether the σ-donating ability or the electron-withdrawing effect of the substitutent in the 3 position was the more important parameter. We found that when we reduced **1a** in the presence of either **1e** (competitive rate = 0.9; $E_p = -1.08$ V versus Ag/AgCl) or **1g** (competitive rate = 0.8; $E_p = -0.97$ V versus Ag/AgCl) substrate **1a** with a $-C(O)NH_2$ group was more reactive than either the

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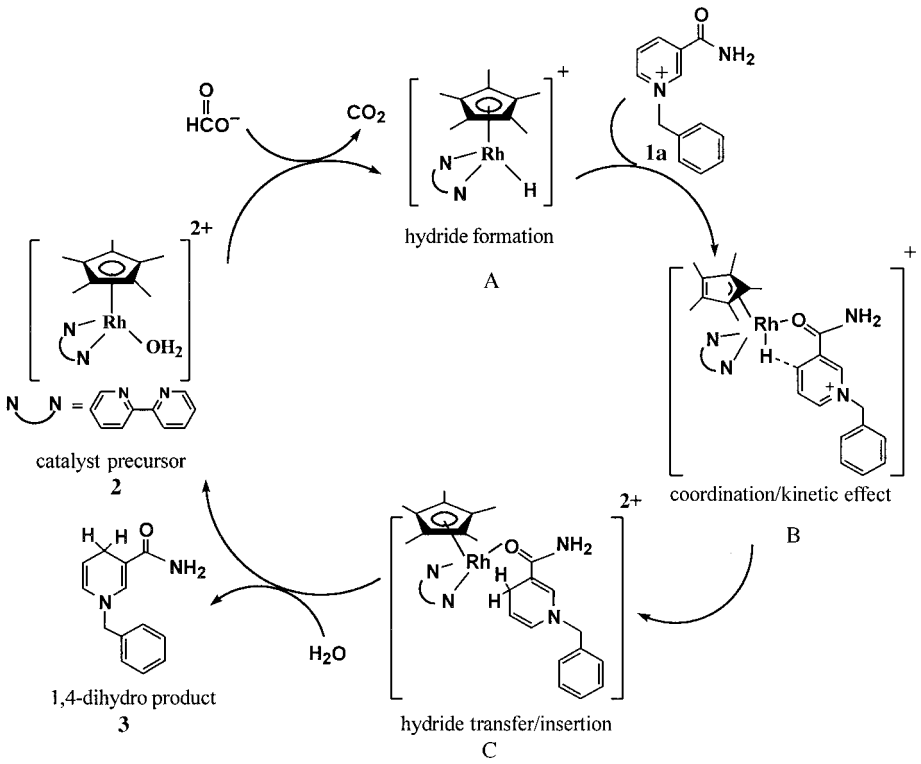
$-C(O)CH_3$ or $-CN$ analogues (1.1 and 1.3 times faster, respectively), and if we reduced **1a** in the presence of **1d** or **1f** the $-C(S)NH_2$ and $-C(O)OCH_3$ derivatives were both found to be more reactive (1.3 and 1.2 times faster, respectively). Thus, we tentatively conclude that the σ-donating ability of the substitutent in the 3 position (for example, in **1a**, **d**, and **f**) is a more important parameter than the electron-withdrawing effect of this group (for example, in **1e**, and **g**) in the overall reduction reaction.

We also examined the possible electronic effect of substituents bound to the nitrogen atom of the nicotinamide nucleus. Thus, we replaced the 1-benzyl group in **1a** with a 1-methyl group (**4**; $E_p = -1.31$ V versus Ag/AgCl), and found that this change in substituent reduced the relative rate to 0.5, and provided a ratio of the relative rate of the 1-benzyl/1-methyl derivatives of 2.0. The implication of this latter result is that the 1-benzyl group is a better electron-withdrawing substituent than the electron-donating 1-methyl group, and this further facilitates hydride attack at C4. The electron reorganization upon hydride transfer to C4 would benefit from a through-bond electron-withdrawing substituent on the nitrogen atom of the nicotinamide nucleus.

Therefore, our initial results allow us to propose a catalytic cycle for the regioselective reduction of the NAD^+ model compound **1a** with **2** as the catalyst precursor, and sodium formate as the hydride source (Scheme 1). The reaction of **2** with HCO_2Na provides the $[Cp^*Rh(bpy)(H)]^+$ complex through a β-hydrogen elimination reaction to produce CO_2 (A in Scheme 1).[2b, 5a] The critical role of the amide functionality is to coordinate to the Cp*Rh metal center through an open coordination site on the metal center. We suggest that this open site occurs by the well documented ring-slippage mechanism[8] of the Cp* ring by a change in the coordination mode of this ligand from η^5 to η^3. This mechanism includes a kinetically favorable six-membered ring transition state (B in Scheme 1), which further provides a driving force for regioselective hydride transfer at C4 (C in Scheme 1; this step also includes a reversion of the η^3 to η^5 coordination of the Cp* ligand). During this coordination process, the induced electronic effect of the bound carbonyl group may also cause the C4 position to be a more electrophilic site towards hydride transfer. We also suggest that the other pyridinium NAD^+ models substituted at position 3 (**1b**, **d**–**g**) can coordinate to the Cp*Rh metal center and exert an electron-withdrawing effect at C4 by a similar mechanism as shown for the NAD^+ model compound **1a** in Scheme 1.

It is also interesting to note that the reduced forms of both complexes $[Rh\{tris(2,2'\text{-bpy})\}]^{3+}$ and $[Rh\{bis(terpy)\}]^{3+}$ (terpy = 2,2′:6′,2″-terpyridine) provide similar regioselectivities in NAD^+ reductions;[2f–h] however, the rate of reduction of NAD^+ with **2** was reported to be 20 times faster[4a] than that by $[Rh\{tris(2,2'\text{-bpy})\}]^{3+}$. Since this latter inorganic complex cannot undergo a ring-slippage mechanism this reaction rate data may provide further support for the participation of this process.

Thus, we have provided evidence, for the first time, that regioselective hydride transfer from $[Cp^*Rh(bpy)H]^+$ to NAD^+ to give 1,4-NADH is a consequence of the crucial role of the ability of the amide to coordinate to the ring-slipped Cp*Rh metal center. The overall rate of this regioselective hydride transfer process is further affected by the induced electron-withdrawing effect of the bound amide group on C4, as well as by the substituent in position 1; that is, the 1-ribose group of the nicotinamide moiety of NAD^+. More importantly, the role of the amide carbonyl or other coordinating groups at the 3 position may also be prevalent in other regioselective transition metal hydride reactions[2c] with NAD^+ models that provide the 1,4-dihydro isomer. It is worthwhile to note that a sterically encumbered porphyrin-Ru-H complex provided the 1,6-dihydro isomer regioselectively as the sole kinetic product with substrate **1c**, with no evidence for the 1,4-dihydro isomer.[2d] To reiterate, we see no reduction product with **1c**, even though C6 is fully accessible and, therefore, coordination appears to be a mandatory step in the pathway to the 1,4-dihydro isomer with $[Cp^*Rh(bpy)H]^+$. In addition, the non-coordinating, direct hydride reducing agent $NaBH_4$ only provides a mixture of 1,2- and 1,6-dihydro isomers with substrates **1f** and **1g**, with no 1,4-dihydro isomer evident.[9] Thus, BH_4^- appears to attack the most electrophilic carbon



Scheme 1. Proposed mechanism for the regioselective, catalytic reduction of an NAD^+ model substrate in H_2O/THF (1/1).

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atoms, which again is exactly opposite to our findings.

We will continue these regioselective cofactor regeneration studies using electrochemical techniques to form the $[Cp^*Rh(bpy)H]^+$ complex, attempt to synthesize the indenyl analogue[8] of **2** for further evidence of the ring-slippage mechanism, and also synthesize a new, water soluble NAD^+ model to fully comprehend the effect of pH on the rates, the turnover frequency, and if enzymes recognize the 1,4-dihydro derivative in chiral reduction reactions.

Experimental Section

General procedure for the synthesis of NAD^+ model substrates: The chloride or bromide salts of the NAD^+ model substrates were prepared by related published methods;[6] however, THF was used as the reaction solvent so as to simplify the purification process. Anion exchange was conducted either by utilizing AgOTf (1.0 equiv in MeOH) or NaOTf (1.05 equiv in acetone). After solvent removal from the filtrate the crude products were further purified by recrystallization from acetone/CH_2Cl_2 (1/1) and Et_2O, followed by refrigeration at $-15\,^\circ C$. The resulting crystals were collected on a glass-fritted funnel and washed with acetone ($0\,^\circ C$), then dried in vacuo over P_2O_5 (yield 86–97%).

1-Benzyl-*N*-methylnicotinamide (triflate salt, **1b**): ^1H NMR (D_2O): $\delta =$ 9.20 (s, 1H, H2 on Py), 8.96 (d, $J = 5.8$ Hz, 1H, H6 on Py), 8.75 (d, $J =$ 8.0 Hz, 1H), 8.08 (app. t, $J = 7.2$ Hz, 1H), 7.43 (app. s, 5H), 5.81 (s, 2H, -CH_2Ph), 2.88 (s, 3H); elemental analysis calcd for $C_{15}H_{15}F_3N_2O_4S$ (376.39): C 47.86, H 4.03, N 7.44; found: C 47.66, H 4.35, N 7.08.

1-Benzylthionicotinamide (triflate salt, **1d**): ^1H NMR (D_2O): $\delta = 9.31$ (s, 1H, H2 on Py), 8.88 (d, $J = 6.4$ Hz, 1H, H6 on Py), 8.71 (d, $J = 8.4$ Hz, 1H), 8.00 (dd, $J = 6.0$, 8.1 Hz, 1H), 7.41 (app. s, 5H), 5.77 (s, 2H, -CH_2Ph); elemental analysis calcd for $C_{14}H_{13}F_3N_2O_3S_2$ (378.43): C 44.43, H 3.47, N 7.40; found: C 44.36, H 3.56, N 7.65.

1-Benzyl-3-acetylpyridinium triflate (**1e**): ^1H NMR (D_2O): $\delta = 9.35$ (s, 1H, H2 on Py), 8.97 (d, $J = 6.6$ Hz, 1H, H6 on Py), 8.93 (d, $J = 8.0$ Hz, 1H), 8.11 (app. t, $J = 7.2$ Hz, 1H), 7.40 (app. s, 5H), 5.81 (s, 2H, -CH_2Ph), 2.65 (s, 3H); elemental analysis calcd for $C_{15}H_{14}F_3NO_4S$ (361.37): C 49.85, H 3.91, N 3.88; found: C 50.12, H 3.57, N 3.89.

1-Benzyl-3-methylpyridinium triflate (**1h**): ^1H NMR (D_2O): $\delta = 8.62$ (s, 1H, H2 on Py), 8.61 (d, $J = 5.0$ Hz, 1H, H6 on Py), 8.25 (d, $J = 7.8$ Hz, 1H), 7.81 (app. t, $J = 7.2$ Hz, 1H), 7.37 (app. s, 5H), 5.64 (s, 2H, -CH_2Ph), 2.40 (s, 3H); elemental analysis calcd for $C_{14}H_{14}F_3NO_3S$ (333.36): C 50.44, H 4.24, N 4.20; found: C 50.01, H 4.56, N 4.64.

1-Benzylpyridinium triflate (**1i**): ^1H NMR (D_2O): $\delta = 8.82$ (d, $J = 5.9$ Hz, 2H), 8.48 (app. t, $J = 7.8$ Hz, 1H), 7.98 (t, $J = 6.5$ Hz, 2H), 7.42 (app. s, 5H), 5.73 (s, 2H, -CH_2Ph); elemental analysis calcd for $C_{13}H_{12}F_3NO_3S$ (319.33): C 48.89, H 3.80, N 4.39; found: C 49.01, H 3.78, N 4.55.

1-Methylnicotinamide (triflate salt, **4**): ^1H NMR (D_2O): $\delta = 9.19$ (s, 1H, H2 on Py), 8.88 (d, $J = 6.0$ Hz, 1H, H6 on Py), 8.80 (d, $J = 8.7$ Hz, 1H), 8.10 (app. t, $J = 7.1$ Hz, 1H), 4.39 (s, 3H, CH_3); elemental analysis calcd for $C_8H_9F_3N_2O_4S$ (286.26): C 33.56, H 3.18, N 9.79; found: C 33.80, H 3.23, N 10.02.

Electrochemical measurements: These were carried out by means of cyclic voltammetry using a standard three electrode cell with a glassy carbon electrode and a Ag/AgCl reference electrode. The solutions were generally a water/THF mixture with an appropriate buffer salt. All of the electrochemical responses of the compounds **1a–i** exhibited a chemically irreversible peak in the voltammetric experiments when a 20–50 $mV\,s^{-1}$ sweep rate was used.

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Reversible Fixation of Ethylene on a Sm^{II} Calix-Pyrrole Complex**

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The chemistry of lanthanides has become a very important field of inorganic chemistry since the 1980s when a series of reports describing the unique richness and variety of reactivity of Sm^{II}[1] rejuvenated the interest in this field.[2] Cyclopentadienyl (Cp) and related ligands have been used to develop the major part of the chemistry of Sm^{II}.[3] Given the caliber of transformations afforded by $[Cp^*_2Sm]$ ($Cp^* = C_5Me_5$), it is not surprising that several attempts have been made to prepare complexes of divalent samarium in different ligand environ-

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