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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ments.[4] However, in spite of progress made in this direction,[5] so far no other ligand system has been able to display the same variety of reactivity as discovered with decamethylsamarocene.

Attempts to isolate a Sm^{II} complex of a calix-pyrrole ligand[6] led to the isolation of a compound in which dinitrogen was encapsulated into a Sm_2Li_4 cage.[7] The rarity of this transformation and the considerable extent of reduction of N_2 indicated that this ligand system is perhaps a valid alternative to the Cp systems. Herein we report the isolation and characterization of Sm^{II} complexes of two calix-pyrrole ligands and their reaction with ethylene which provides the first example of reversible ethylene fixation in lanthanide chemistry.[8]

Reduction of $[(R_8\text{-calix-pyrrole})ClSm\{Li(thf)\}_2\{Li(thf)_2\}(\mu_3\text{-Cl})]$ ($R = Et$ (**1a**), $-(CH_2)_5-\}_{0.5}$ (**1b**))[7] with lithium under argon in THF formed dark green solutions (Scheme 1). The result of the reduction depended on the aliphatic chains attached to the macrocycle. Two compounds formulated as $[(R_8\text{-calix-pyrrole})(L)Sm\{Li(thf)\}_2\{Li(thf)_2\}(\mu_3\text{-X})(Et_2O)_{1.5}]$ ($R = \{-(CH_2)_5-\}_{0.5}$, $X = Cl$, $L = thf$ (**2b**); $R = Et$, $X = OCHCH_2$, $L = Et_2O$ (**3a**)) were isolated in good yield and characterized. In the case of the octaethyl derivative the enolate group, probably arising from a THF cleavage process,[9] replaced the Cl^- ion. Reaction of the tetralithium salts of both ligands[9g, 10] with $[SmI_2(thf)_2]$ afforded low yields of the two isomorphous enolate derivatives **3a** and **3b**. Both complexes are paramagnetic, and informative NMR spectra were obtained only in the case of **3a**.

The crystal structure of **3a** consists of a samarium atom surrounded by a calix-pyrrole ligand arranged in a basketlike conformation (Figure 1). The coordination geometry of the samarium atom is distorted pseudo-trigonal bipyramidal and is defined by two nitrogen atoms of two pyrrole rings (σ-bonded), two centroids of the other two pyrrole rings (π-bonded), and the oxygen atom of one molecule of coordinated solvent (diethyl ether or THF). On the opposite side of the macrocycle, three lithium atoms are bonded to the pyrrole rings, and adopt either σ- or π-bonding modes and are also connected to the oxygen atom of the enolate group (or a chlorine atom as in the case of **2b**).[11]

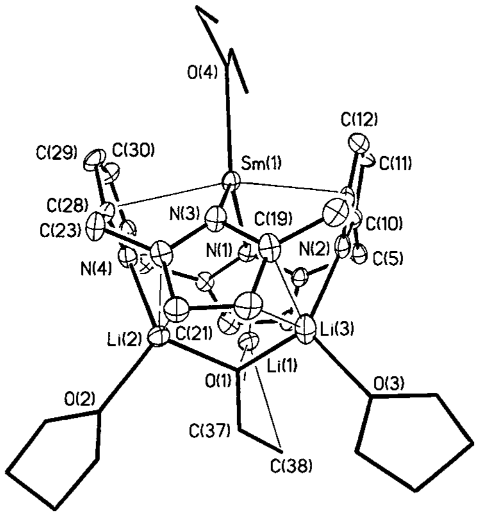
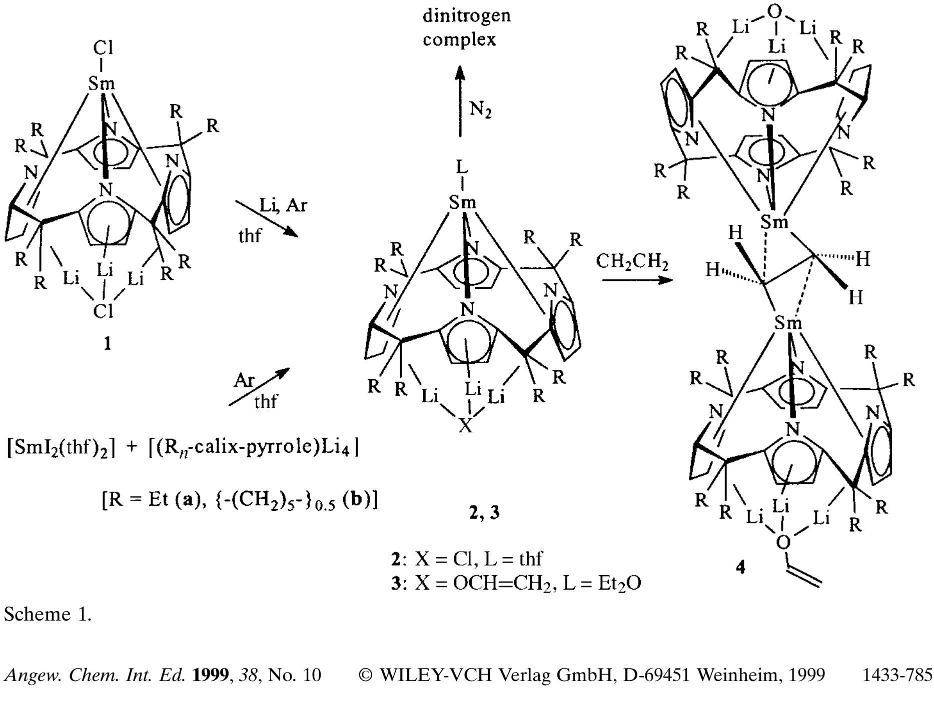


Figure 1. ORTEP drawing of **3a**. Thermal ellipsoids are drawn at the 30% probability level. Bond lengths [Å] and angles [°]: Sm(1)–N(1) 2.597(7), Sm(1)–N(3) 2.602(7), Sm(1)–N(2) 2.853(6), Sm1–C(10) 2.913(8), Sm(1)–C(11) 2.986(8), Sm(1)–C(12) 2.976(9), Sm(1)–C(13) 2.901(8), Li(2)–N(4) 2.09(2), Li(1)–N(1) 2.16(2), Li(1)–C(1) 2.18(2), Li(1)–C(2) 2.22(2), Li(1)–C(3) 2.24(2), Li(1)–C(4) 2.17(2), Li(1)–O(1) 1.84(2), Li(2)–O(1) 1.93(2), Li(3)–O(1) 1.90(2), O(1)–C(37) 1.330(11), C(37–C(38) 1.303(13), Li(1)–C(37) 2.37(2), Li(1)–C(38) 2.67(2); N(1)-Sm(1)-N(3) 123.2(2), N(1)-Sm(1)-O(4) 114.6(3), N(3)-Sm(1)-O(4) 122.2(3), centroid-Sm(1)-centroid 161.6(3), O(1)-C(37)-C(38) 125.1(10), Li(1)-O(1)-Li(2) 104.5(7), Li(1)-O(1)-Li(3) 102.1(7), Li(2)-O(1)-Li(3) 110.0(8).



1

[SmI$_2$(thf)$_2$] + [(R$_n$-calix-pyrrole)Li$_4$]

[R = Et (**a**), {-(CH$_2$)$_5$-}$_{0.5}$ (**b**)]

2, 3

2: X = Cl, L = thf
3: X = OCH=CH$_2$, L = Et$_2$O

4

Scheme 1.

The enolate Sm^{II} derivatives **3a** and **3b** react reversibly with ethylene in a fast reaction, the extent of which depends on the nature of the R group. Upon exposure to ethylene, the initially dark green color of the solution persists in the case of **3a** but turns light green in the case of **3b.** Light green paramagnetic crystals of $[\{(R_8\text{-calix-pyrrole})[(CH_2{=}CHO)Li][Li(thf)]_2Sm\}_2(\mu\text{-}CH_2CH_2)]$ (**4a, b**) may be isolated in good yield. The magnetic moment measured at room temperature for **4b** ($\mu_{eff} = 1.40\,\mu_B$ per metal center) supports the premise of complete oxidation to Sm^{III}. In each case crystals suitable for X-ray analysis were obtained.

The structure of **4a** consists of a dimer lying on an inversion center where each samarium atom is surrounded by the calix-pyrrole ligand (Figure 2). One C_2 unit is located between the two metal centers in a distorted side-on fashion (Sm–C(37) 2.427(5), Sm–C(37A) 2.711(5) Å), but still forms a planar Sm-C-C-Sm core. On the opposite side of the

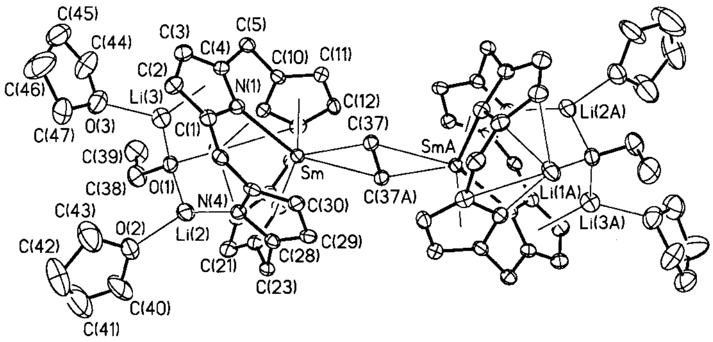


Figure 2. ORTEP drawing of **4a**. Thermal ellipsoids are drawn at the 30% probability level. Bond lengths [Å] and angles [°]: C(37)–C(37A) 1.493(15), Sm–C(37) 2.427(5), Sm–C(37A) 2.711(5), Sm–N(2) 2.738(4), Sm–N(4) 2.720(3), Sm–N(1) 2.549(4), Sm–C(10) 2.855(4), Sm–C(11) 2.899(9), Sm–C(12) 2.892(9), Sm–C(13) 2.853(4), N(2)–Li(1) 2.014(9), N(4)–Li(2) 2.024(9), Li(3)–N(1) 2.512(10), Li(3)–C(1) 2.434(10), Li(3)–C(2) 2.318(10), Li(3)–C(3) 2.312(10), Li(3)–C(4) 2.433(10), O(1)–Li(1) 1.860(9), O(1)–Li(2) 1.886(9), O(1)–Li(3) 1.859(9), O(1)–C(38) 1.399(6), C(38)–C(39) 1.427(8); C(37)-Sm-C(37A) 33.0(2), centroid-Sm-centroid 165.1(3), N(2)-Sm-N(4) 122.4(2), O(1)-C(38)-C(39) 114.6(5).

cavities defined by each of the calix-pyrroles, three lithium atoms are bonded to the pyrrolyl rings. The C–C bond length of the coordinated ethylene group is rather long (C(37)–C(37A) 1.487(10) Å) and indicative of the presence of a C–C single bond. Thus, in combination with the light color, this suggests the complete reduction of ethylene and oxidation of the two metal centers. The crystal structure was of sufficient quality to locate and refine the hydrogen atoms attached to the coordinated ethylene group. According to the positions of the hydrogen atoms, the ethylene molecule is perpendicular to the Sm_2 vector. The hydrogen atoms attached to each carbon atom deviate from the ethylene plane and point in the opposite direction with respect to the neighboring samarium atom, thus conferring to the carbon center a distorted tetrahedral geometry (Sm-C(37)-H(37A) 112.9, Sm-C(37)-H(37B) 115.4, H(37A)-C(37)-H(37B) 107.2°). This indicates that ethylene predominantly adopted a σ- rather than π-bonding mode which is also consistent with the remarkable elongation of the C–C bond and the zigzag conformation of the Sm_2C_2 core. In spite of the presence of significant $Sm{-}C_{ethylene}$ σ-bond character, the fixation of ethylene is a reversible process as indicated by the behavior of solutions of both **4a** and **4b**. Addition of pale green crystals of **4** to C_6D_6 gave dark green solutions for which the peak for free ethylene was clearly visible at $\delta = 5.23$ in the ^1H NMR spectrum. In addition, the resonances characteristic of **2** were also clearly identified in the NMR spectrum, although these partly overlapped with the resonance of **4**. Conversely, subsequent saturation of the same sample in the NMR tube with ethylene conferred the characteristic pale green color to the solution in the case of **4a**, while the resonances of the enolate starting complex disappeared. In the case of **4b**, however, the solutions always remained dark green and the peaks of the starting **3b** were invariably present in the NMR spectra. The peaks for coordinated ethylene in complex **4a** were clearly identified by using C_2D_4 and are present as two resonances of equal intensity at $\delta = 19.08$ and 18.97 in the ^2H NMR spectrum.

In spite of the dominant σ character of the $Sm{-}C_{ethylene}$ bond, this complex does not insert further ethylene under normal reaction conditions and does not perform polymerization, which strikingly contrasts with the fact that decamethylsamarocene is an ethylene polymerization initiator.[12]

Experimental Section

2b: A suspension of $[SmCl_3(thf)_3]$(3.20 g, 6.80 mmol) in THF (150 mL) was treated with colorless $[(R_8\text{-calix-pyrrole})\{Li(thf)\}_4]$ $(R = \{-(CH_2)_5-\}_{0.5})$ (6.80 mmol). The resulting golden-yellow suspension was heated gently for about 10 min and then stirred at room temperature for 2 h. Lithium foil (70 mg, 10 mmol) was added to the reaction mixture under argon, and the color changed from yellow to deep green over 30 min. After stirring the mixture for 18 h, the solvent was removed in vacuo and the resulting deep green solid residue was extracted with diethyl ether (75 mL). The extract was concentrated to 50 mL and left to stand at −30°C overnight, which afforded large dark green crystals of **2b** (75%). Crystals suitable for X-ray structural analysis[10] were grown at room temperature upon cooling a concentrated solution of **2b** in THF. IR (Nujol mull): $\tilde{\nu} = 3090$(w), 2730(w), 2662(w), 1550(w), 1355(m), 1315(w), 1286(s), 1270(s), 1256(s), 1191(s), 1140(m), 1074(s), 970(m), 845(m), 780(s) cm^{-1}; elemental analysis calcd for $SmLi_3ClC_{56}H_{80}N_4$ (%): C 62.28, H 7.47, N 5.19; found: C 63.22, H 8.31, N 5.88; $\mu_{eff} = 3.70\,\mu_B$.

3a: The procedure was analogous to that for **2b**. Yield 79%. IR (Nujol mull): $\tilde{\nu} = 3090$(w), 2723(w), 1625(m), 1585(m), 1322(s), 1260(s), 1195(s), 1156(w), 1104(w), 1046(s), 975(s), 925(w), 888(s), 799(s), 756(s) cm^{-1}; elemental analysis calcd for $Sm_2Li_6C_{104}H_{166}N_8O_9$ (%): C 62.06, H 8.21, N 5.56; found: C 61.94, H 7.91, N 5.57; $\mu_{eff} = 3.62\,\mu_B$; ^1H NMR (500 MHz, C_6D_6, 23°C): $\delta = 14.53$ (s, 4H, CH pyrrole), 14.22 (br. s, 4H, CH_2 ether), 8.73 (s, 4H, CH pyrrole), 5.35 (t, 6H, CH_3 ether), 3.85 (br. s, 8H, THF), 3.75 (s, 4H, CH_2 ethyl), 1.20 (s, 4H, CH_2 ethyl), 0.97(s, 8H, THF), −2.98 (s, 12H, CH_3 ethyl), −4.67 (br. s, 1H, enolate), −5.01 (s, 12H, CH_3 ethyl), −6.95 (br. s, 1H, enolate), −7.03 (s, 8H, CH_2 ethyl), −15.62 (br. s, 1H, enolate).

4b. A stirred solution of $[SmI_2(thf)_2]$ (2.0 g, 3.65 mmol) in THF (75 mL) was treated with $[(R_8\text{-calix-pyrrole})Li_4]$ (2.23 g, 3.66 mmol). The resulting red-brown solution was refluxed for 2 h then stirred at room temperature overnight. The solvent was removed in vacuo to yield a deep green solid residue which was extracted with hexane (100 mL). Upon exposure of the deep green hexane solution to ethylene (1 atm), the color changed to a lighter green. After the solution had been left to stand at room temperature for two days, light green crystals separated (1.5 g, 0.78 mmol, 43%). IR (Nujol mull): $\tilde{\nu} = 3088$(w), 2731(w), 2664(w), 1564(w), 1350(m), 1309(s), 1267(s), 1240(s), 1185(s), 1140(m), 1070(s), 1040(s), 978(m), 898(s), 877(s), 830(m), 777(s), 740(s), 690(m) cm^{-1}; elemental analysis calcd for $Sm_2Li_6C_{102}H_{138}O_6N_8$ (%): C 62.08, H 7.65, N 6.16; found: C 61.30, H 7.00, N 5.45; $\mu_{eff} = 1.40\,\mu_B$. A similar procedure was followed for the preparation of **4a.** Yield (39%). The extreme air-sensitivity and spontaneous loss of ethylene prevented satisfactory analytical data from being obtained. ^1H NMR (500 MHz, C_6D_6, 23°C): $\delta = 19.08$ (br. s, 2H, ethylene), 18.97 (br. s, 2H, ethylene), 8.60 (br. s, 8H, THF), 7.17 (s, 16H, CH pyrrole), 4.01 (br. s, 8H, CH_2 ethyl), 3.47 (br. s, 8H, THF), 2.13 (br. s, 8H, CH_2 ethyl), 1.25 (br. s, 8H, CH_2 ethyl), 1.22 (br. s, 8H, CH_2 ethyl), −0.66 (br. s, 24H, CH_3 ethyl), −2.68 (br. s, 24H, CH_3 ethyl), −4.53 (br. s, 2H, enolate), −6.75 (br. s, 2H, enolate), −15.60 (br. s, 2H, enolate).

Crystal data **3a**: $C_{104}H_{166}Li_6N_8O_9Sm_2$, $M_r = 2014.79$, triclinic $P\bar{1}$, $a = 13.6634(2)$, $b = 15.7346(2)$, $c = 27.7960(5)$ Å, $\alpha = 100.779(1)$, $\beta = 91.537(1)$, $\gamma = 91.893(1)°$, $V = 5863.9(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.141$ Mg m^{-3}, absorption coefficient 10.42 cm^{-1}, $F(000) = 2120$, 38577 reflections collected, 16227 independent reflections, GOF = 1.011, $R = 0.0715$, $wR2 = 0.1560$. All non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms were introduced at their idealized positions and refined with a riding mode. Absorption corrections (SADABS) were applied to the data. Two crystallographically independent but chemically equivalent molecules and one molecule of diethyl ether were found in the unit cell.

4a: $C_{94}H_{138}Li_6N_8O_6Sm_2$, $M_r = 1818.46$, orthorhombic, $Pbca$, $a = 20.926(2)$, $b = 20.614(2)$, $c = 21.577(2)$ Å, $V = 9308(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.298$ Mg m^{-3}, absorption coefficient 13.04 cm^{-1}, $F(000) = 3792$, 73045 reflections collected, 6089 independent reflections, GOF = 1.024, $R = 0.0318$, $wR2 = 0.0869$.

All non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms were located from different Fourier maps and refined with a riding mode. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101917 and CCDC-101918. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Directed Metalation Linked to Transition Metal Catalyzed Cascade Reactions: Two Total Syntheses of Plicadin, the Alleged Coumestan from *Psoralea plicata*[**]

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Plicadin, isolated in 1991 from the herb *Psoralea plicata*[1] and assigned structure **1** (see Scheme 1),[2] has a compact, oxygen-rich heterocyclic structure that poses a synthetic challenge from the perspective of combined directed *ortho* metalation/directed remote metalation (D*o*M/DreM) and transition metal catalyzed coupling strategies, a current theme in our laboratories.[3] Herein we report two syntheses of plicadin (**1**) which incorporate effective use of the following sequences: a) D*o*M/DreM, Sonogashira, and Castro–Stephens reactions (Scheme 1, retrosynthesis A), and b) D*o*M, Negishi, and carbamoyl Baker–Venkataraman reactions[4] (retrosynthesis B). We also demonstrate inconsistencies between physical and spectral data of the synthetic material and those reported for the natural product isolated from *Psoralea*

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