both in its contributions to the understanding of the chemistry of organocobaloximes and other organocobalt complexes and in its ability to predict the properties of such complexes. Attempts to extend these concepts to organocobalt corrins are currently in progress.

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Supplementary Material Available: Tables SI, SII, and SIII listing the ^{13}C spectral data for the $YCH_2Co(D_2H_2)OH_2$, $YCH_2Co(D_2H_2)CN^-$, and $YCH_2Co(D_2H_2)CNCo(D_2H_2)CH_2Y^-$ complexes (3 pages). Ordering information is given on any current masthead page.

Tautomerizations, Protonations, and Electrophilic Additions of η^2-Coordinated Pyrroles

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Abstract: A series of complexes is synthesized of the form $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-pyrrole})]^{2+}$, with pyrrole and various alkylated pyrroles. In contrast to the free ligands, these complexes can be protonated chemo- and stereoselectively at the β carbon, away from the metal, to produce pyrrolium species whose acidities range in pK_a from 4.2 to 7.5. In the presence of a weak base, two of these 3*H*-pyrrolium species can be converted to the corresponding 2*H*-pyrrolium tautomer, $[Os(NH_3)_5(3,4\text{-}\eta^2\text{-}2H\text{-pyrrolium})]^{3+}$. In the case of L = 2,5-dimethylpyrrole, the 2*H*-pyrrolium species can be deprotonated at nitrogen (pK_a = 7.9), rendering a neutral 2*H*-pyrrole ligand. When L = 1-methylpyrrole, the 2*H*-pyrrolium species can be deprotonated at the α carbon, generating an unstable azomethine ylide complex bound through C3 and C4. Rapid rearrangement of this species yields the neutral 1*H*-pyrrole complex, $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-1-methylpyrrole})]^{2+}$ (pK_{ep} = 7.8 (overall process)). Through consideration of pK_a and electrochemical data, the pyrrole/pyrrolenine isomerization energy ($\Delta G°$) is found to decrease by about 16 kcal on osmium(II), to the point where these tautomers become virtually isoergic. In contrast, the pyrrole/pyrrolenine equilibrium is largely unaffected by coordination to Os(III), in comparison to the free ligand.

Pyrroles are widely distributed in nature, serving as a subunit or precursor to chlorophylls, bile pigments, porphyrins, and corrins, as well as assorted antibiotics. They also represent an important class of synthons for alkaloids and other N-heterocyclic systems, potentially providing up to four activated carbons. However, the pronounced nature of pyrrole to undergo electrophilic attack at the α position often preempts reactivity at the biologically more significant β positions, and its tendency to rearomatize or polymerize in the presence of electrophiles limits the scope of useful addition reactions. Recently, three examples of η^2-coordinated pyrrole complexes have been reported in which an $[Os(NH_3)_5]^{2+}$ moiety engages C2 and C3.[1] Such coordination renders the uncoordinated portion of the pyrrolic ligand an enamine, an action that is expected to enhance the nucleophilic nature of the β carbon, C4, and to inhibit activity at the α positions.

As we embarked on an investigation into the ligand activation and the stereocontrol offered by the osmium in these pyrrolic systems, it became apparent that many neutral and cationic tautomers of pyrrole are made possible by metal coordination (Figure 1) and that a firm understanding was needed of their relative stabilities and properties. This paper summarizes those findings.

Experimental Section

Routine ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer and are reported in parts per million shift from tetramethylsilane. Nonroutine spectra (e.g., low temperature, COSY, HETCOR, NOESY, or DEPT) were recorded on a General Electric GN-300 or Omega-500 spectrometer. Electrochemical experiments were performed under nitrogen by using a PAR Model 362 potentiostat driven by a PAR Model 175 univeral programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell[2] from +1.5 to −1.5 V with a glassy carbon or platinum disk working electrode. All potentials are reported vs NHE and, unless otherwise noted, were determined in acetonitrile (~0.5 M tetrabutylammonium hexafluorophosphate (TBAH)) with ferrocene ($E_{1/2}$ = 0.55 V), decamethylferrocene ($E_{1/2}$ = 0.04 V), or cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) in situ as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 70 and 100 mV for all reversible couples reported unless otherwise noted. This work was carried out under nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox, separate boxes being used for aqueous and nonaqueous reactions.

Solvents. All distillations were performed under nitrogen, and all solvents were deoxygenated by purging with nitrogen for at least 20 min; deuterated solvents were deoxygenated by repeated freeze–pump–thaw cycles. Methylene chloride was refluxed for at least 8 h over P_2O_5 and distilled. Diethyl ether was refluxed for at least 8 h over Na/benzophenone and distilled. Methanol was refluxed over $Mg(OMe)_2$, prepared in situ from Mg^0 activated by I_2, and distilled.[3] 1,2-Dimethoxyethane was refluxed over Na and distilled. Acetonitrile was refluxed over CaH_2 and distilled. *N*,*N*-Dimethylacetamide (DMA) was refluxed over CaH_2 for 24 h and distilled. Acetone was used as received (Burdick and Johnston), except that it was deoxygenated prior to use.

Reagents. $[Os(NH_3)_5(OTf)](OTf)_2$ ($OTf^- = CF_3SO_3^-$) was synthesized as described by Lay et al.[4] Magnesium powder (Aldrich, 50 mesh) was activated by treating with iodine in DME (1,2-dimethoxyethane) under nitrogen, stirring for several hours, and washing with

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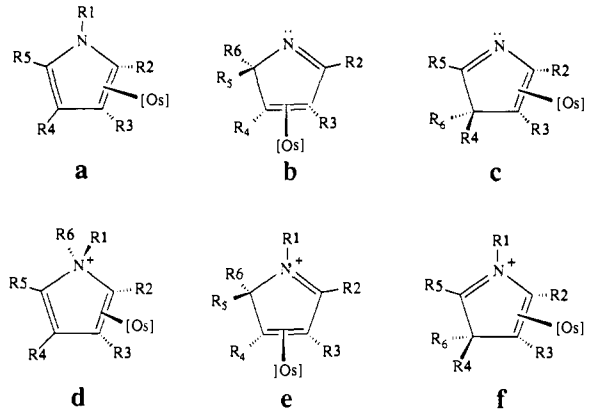


Figure 1. Hypothetical isomers for C,C-η^2-coordinated pyrrole (**a**–**c**) and pyrrolium (**d**–**f**) species.

DMA, acetone, and ether. Pyrrole ligands and other liquid reagents (aniline, pyridine, etc.) were used as received (Aldrich), except that they were deoxygenated by repeated freeze–pump–thaw cycles prior to use. Methyl triflate and triflic acid were used as received (Aldrich). Anilinium triflate, diphenylammonium triflate, and pyridinium triflate were prepared by treating a solution of 2 g of the appropriate base in 7.5 mL of CH_2Cl_2 with 1.5 mL of cold triflic acid (CAUTION!), filtering off the precipitated salt, and washing with additional CH_2Cl_2.

Preparations. (Characterization data are summarized in Table I.) **[Os(NH$_3$)$_5$(2,3-η^2-pyrrole)](OTf)$_2$ [[1a](OTf)$_2$].** The synthesis and characterization of this compound have been previously reported.[1a] In our hands, Mg^0 (2.62 g, 108 mmol) was added to a solution of Os(NH$_3$)$_5$(OTf)$_3$ (0.87 g, 1.21 mmol) and pyrrole (1.98 g, 29.6 mmol) dissolved in DME (7.11 g) and DMA (3.10 g), and the slurry was stirred. After 1 h, the slurry was filtered through a fine-porosity frit into CH_2Cl_2 (140 mL), producing a yellow precipitate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried in vacuo, yielding a pale yellow powder (0.66 g, 1.02 mmol, 85%).

[Os(NH$_3$)$_5$(2,3-η^2-1-methylpyrrole)](OTf)$_2$ [[2a](OTf)$_2$]. The preparation of this compound has been reported,[1a] though its yield and characterization were not. In our hands, Mg^0 (1.35 g, 55.6 mmol) was added to a solution of Os(NH$_3$)$_5$(OTf)$_3$ (0.86 g, 1.19 mmol) and 1-methylpyrrole (2.19 g, 27.0 mmol) dissolved in DME (5.29 g) and DMA (2.07 g), and the slurry was stirred. After 1 h, the slurry was filtered through a fine-porosity frit into CH_2Cl_2 (125 mL), producing a yellow precipitate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried in vacuo, yielding a yellow powder (0.67 g, 1.02 mmol, 86%). ^{13}C NMR (20 °C, acetone-d_6): 129.3 (C5), 103.8 (C4), 80.1 (C2), 57.7 (C3), 35.8 (CH_3) ppm.

[Os(NH$_3$)$_5$(2,3-η^2-2,5-dimethylpyrrole)](OTf)$_2$ [[3a](OTf)$_2$]. As reported earlier,[1b] a solution of 2,5-dimethylpyrrole (2.90 g, 30 mmol), Os(NH$_3$)$_5$(OTf)$_3$ (0.90 g, 1.25 mmol), 1,2-dimethoxyethane (7.0 g), and *N*,*N*-dimethylacetamide (3.0 g) was treated with activated Mg^0 powder (2.9 g). After 100 min, addition of CH_2Cl_2 (150 mL) to the filtered reaction mixture resulted in a light yellow precipitate (0.60 g, 0.90 mmol, 72% yield). A sample of [**3a**](OTf)$_2$ (0.35 g) was purified by ion-exchange chromatography and precipitated as a tetraphenylborate salt.

[Os(NH$_3$)$_5$(2,3-η^2-1,2,5-trimethylpyrrole)](OTf)$_2$ [[4a](OTf)$_2$]. Mg^0 (1.65 g, 67.9 mmol) was added to a solution of Os(NH$_3$)$_5$(OTf)$_3$ (0.24 g, 0.34 mmol) and 1,2,5-trimethylpyrrole (0.93 g, 8.52 mmol) dissolved in DME (4.45 g) and DMA (0.99 g), and the slurry was stirred. After 1 h, the slurry was filtered through a fine-porosity frit into CH_2Cl_2 (125 mL), producing a yellow precipitate, which was filtered, washed with CH_2Cl_2 and Et_2O, and dried in vacuo, yielding a yellow powder (0.15 g, 0.23 mmol, 67%). ^{13}C NMR (proton decoupled, 20 °C, acetone-d_6): 102 (C(2,5), br); 60 (C(3,4), br); 15 (CH_3, br) ppm.

[Os(NH$_3$)$_5$(2,3-η^2-5-ethylpyrrole)](OTf)$_2$ [[5a](OTf)$_2$]. Mg^0 (0.60 g, 24.6 mmol) was added to a solution of Os(NH$_3$)$_5$(OTf)$_3$ (0.20 g, 0.27 mmol) and 2-ethylpyrrole (0.40 g, 4.19 mmol) dissolved in DME (1.69 g) and DMA (0.87 g), and the slurry was stirred. After 1 h, the slurry was filtered through a fine-porosity frit into CH_2Cl_2 (50 mL), producing a yellow precipitate, which was filtered, washed with Et_2O, and dried in vacuo, yielding a light tan powder (0.15 g, 0.23 mmol, 83%). ^{13}C NMR (20 °C, acetone-d_6): 144.2 (C5), 100.8 (C4), 75.2 (C2), 57.8 (C3), 21.1 (CH2), 13.5 (CH_3) ppm.

[Os(NH$_3$)$_5$(2,3-η^2-1,4-dimethylpyrrole)](BPh$_4$)$_2$ [[6a](BPh$_4$)$_2$]. A slurry of [**2a**]OTf$_2$ (248 mg, 378 μmol) in DME (0.38 g) was treated with a solution of CH_3OTf (196 mg, 1190 μmol, 3.2 equiv) in DME (0.82 g) and the resulting orange slurry stirred. After 1 h, a solution of *i*-Pr_2EtN (81 mg, 626 μmol, 1.7 equiv) in DME (0.91 g) was added. After 3 h, a DME solution of *n*-$PrNH_2$ (36 mg, 615 μmol, 1.6 equiv) was added, with the result that the slurry turned yellow, and most of the solid dissolved. After 15 min of additional stirring, CH_2Cl_2 (5 mL) was added, precipitating an orange-yellow solid, which was filtered, washed with CH_2Cl_2, and dried in vacuo. The bright yellow solid appeared by ^1H NMR to be a mixture of [**6a**](OTf)$_2$ and [**2d**](OTf)$_3$ in 4:1 ratio. A sample of this solid (100 mg) was purified by ion-exchange chromatography and precipitated as a BPh_4^- salt. Yield: 74.3 mg, 61%. ^{13}C NMR (20 °C, acetone-d_6): 125.9 (C5), 117.3 (C4), 83.9 (C2), 59.7 (C3), 37.67 (NCH_3), 13.5 (CCH_3) ppm.

[Os(NH$_3$)$_5$(2,3-η^2-4*H*-pyrrolium)](OTf)$_3$ [[1f](OTf)$_3$]. Treatment of a red-brown solution of [**1a**](OTf)$_2$ (44.0 mg, 69 μmol) in CH_3OH (255 mg) with a solution of HOTf (20.4 mg, 136 μmol, 2 equiv) in CH_3OH (91 mg) gave a dark red solution, which, on treatment with Et_2O, followed by filtration, washing with Et_2O, and drying, yielded a light pink-brown powder (45.9 mg, 58 μmol, 85%).

[Os(NH$_3$)$_5$(2,3-η^2-1-methyl-4*H*-pyrrolium)](OTf)$_3$ [[2f](OTf)$_3$]. Treatment of a yellow solution of [**2a**](OTf)$_2$ (57 mg, 86 μmol) in CH_3OH (336 mg) with a solution of HOTf (13 mg, 87 μmol, 1 equiv) in CH_3OH (142 mg) gave an orange solution, which, on treatment with Et_2O, followed by filtration, washing with Et_2O, and drying, yielded an orange powder (41 mg, 51 μmol, 60%). ^{13}C NMR (20 °C, acetone-d_6): 173.9 (C5), 76.2 (C2), 43.0 (C3), 42.8 (C4), 42.0 (CH_3) ppm.

[Os(NH$_3$)$_5$(2,3-η^2-2,5-dimethyl-4*H*-pyrrolium)](OTf)$_3$ [[3f](OTf)$_3$]. This compound was prepared in a manner similar to [**2f**](OTf)$_3$ and has been previously characterized.[1b] ^{13}C NMR (20 °C, acetone-d_6): 187.1 (C5), 74.3 (C2), 46.2 (C4), 42.1 (C3), 17.8 (CH_3), 16.1 (CH_3) ppm.

[Os(NH$_3$)$_5$(2,3-η^2-1,2,5-trimethyl-4*H*-pyrrolium)](OTf)$_3$ [[4f](OTf)$_3$]. To a sample of [**4a**](OTf)$_2$ (66.7 mg, 97.8 μmol) dissolved in CH_3OH (362 mg) was added a solution of HOTf (18.3 mg, 122 μmol, 1.2 equiv) in CH_3OH (119 mg). After 3 min, Et_2O was added, precipitating a yellow solid, which was filtered, washed with Et_2O, and dried in vacuo. Yield of light yellow powder: 64.0 mg, 76.9 μmol, 79%.

[Os(NH$_3$)$_5$(2,3-η^2-5-ethyl-4*H*-pyrrolium)](OTf)$_3$ [[5f](OTf)$_3$]. To a sample of [**5a**](OTf)$_2$ (57.3 mg, 85.6 μmol) dissolved in CH_3OH (475 mg) was added a solution of HOTf (13.8 mg, 92.0 μmol, 1.1 equiv) in CH_3OH (162 mg). After 3 min, Et_2O was added, precipitating light yellow crystals, which were filtered, washed with Et_2O, and dried in vacuo. Yield of bright yellow crystals: 59.3 mg, 72.4 μmol, 85%. ^{13}C NMR (20 °C, acetone-d_6): 193.3 (C5), 71.2 (C2), 44.3 (C4), 41.6 (C3), 26.3 (CH_2), 9.9 (CH_3) ppm.

[Os(NH$_3$)$_5$(2,3-η^2-1,4-dimethyl-4*H*-pyrrolium)](OTf)$_3$ [[6f](OTf)$_3$] and [Os(NH$_3$)$_5$(2,3-η^2-1,1-dimethylpyrrolium)](OTf)$_3$ [[2d](OTf)$_3$]. A slurry of [**2a**](OTf)$_2$ (93.1 mg, 142 μmol) in DME (1.40 g) was treated with a solution of CH_3OTf (69.7 mg, 425 μmol, 3.0 equiv) in DME (0.26 g), and the resulting orange slurry was stirred. After 1 h, a solution of *i*-Pr_2EtN (25.5 mg, 197 μmol, 1.4 equiv) in DME (0.44 g) was added, and the slurry was stirred an additional 20 min. CH_2Cl_2 (2 mL) was added, precipitating an orange-yellow solid, which was filtered, washed with CH_2Cl_2, and dried in vacuo. Yield of light orange solid: 112 mg, 137 μmol, 96%. This solid appeared by ^1H NMR to be a mixture of [**6f**](OTf)$_3$ and [**2d**](OTf)$_3$ in 4:1 ratio.[5]

[Os(NH$_3$)$_5$(3,4-η^2-1-methyl-5*H*-pyrrolium)](OTf)$_3$ [2e](OTf)$_3$. A yellow solution of [**2a**](OTf)$_2$ (38 mg, 58 μmol) in CH_3OH (50 mg) was treated with a solution of $PhNH_3OTf$ (14 mg, 59 μmol, 1 equiv) and $PhNH_2$ (27 mg, 293 μmol, 5 equiv) in CH_3OH (150 mg), and the resulting red solution was allowed to stand. After 24 h, addition of Et_2O precipitated a dark red solid, which was filtered, washed with Et_2O, and dried in vacuo. Yield of light red solid: 29 mg, 36 μmol, 62%.

[Os(NH$_3$)$_5$(3,4-η^2-2,5-dimethyl-5*H*-pyrrolium)](OTf)$_3$ [3e](OTf)$_3$. A yellow solution of [**3a**](OTf)$_2$ (200 mg, 299 μmol) in CH_3OH (375 mg) was treated with a solution of $PhNH_3OTf$ (74 mg, 305 μmol, 1 equiv) and $PhNH_2$ (162 mg, 1742 μmol, 5.8 equiv) in CH_3OH (161 mg), and the resulting red-brown solution was allowed to stand. Within a few hours, a reddish solid formed in the solution. After 96 h the slurry was treated with Et_2O, and the red precipitate was filtered, washed with more Et_2O, and dried in vacuo. Yield of pink-orange solid: 226 mg, 276 μmol, 92%. ^{13}C NMR (20 °C, acetone-d_6): 201.4 (C2), 65.9 (C5), 56.2 (C3), 52.7 (C4), 17.9 (CH_3), 12.4 (CH_3) ppm.

[Os(NH$_3$)$_5$(3,4-η^2-2,5-dimethyl-5*H*-pyrrole)](OTf)$_2$ [3b](OTf)$_2$. A slurry of [**3e**](OTf)$_3$ (62 mg, 75 μmol) in CH_3CN (285 mg) was treated with a solution of proton sponge [1,8-bis(dimethylamino)naphthalene] (73 mg, 383 μmol, 5.1 equiv) in CH_3CN (160 mg). The solid in the slurry dissolved as the mixture was stirred, and the mixture turned from red to yellow. Adding CH_2Cl_2 precipitated a yellow-orange solid, which was filtered, washed with CH_2Cl_2, and dried in vacuo. Yield of pale

(5) Note that these two complexes have the same molar mass and the same elemental analysis.

Table I

							^{1}H NMR Data,[a] ppm							
compd	R1	R2	R3	R4	R5	R6	R1	R2	R3	R4	R5	R6	*c*-NH_3	*t*-NH_3
1a[b]	H	H	H	H	H		7.45	6.59	5.28	5.60	6.76		3.32	4.53
2a[c]	Me	H	H	H	H		3.52	6.52	5.34	5.51	6.63		3.34	4.47
3a[d]	H	Me	H	H	Me		7.05	1.53	4.88	5.32	1.98		3.30	4.41
4a[e]	Me	Me	H	H	Me		3.44	1.65	4.99	5.37	2.03		3.31	4.38
5a	H	Et	H	H	H		7.31	6.54	5.23	5.42	Et[f]		3.31	4.45
6a	Me	H	Me	H	H		3.49	6.51	5.29	2.17	6.31		3.43	4.51
3b		Me	H	H	Me	H		2.05	5.15	4.87	1.16	4.10	3.71	4.85
2d	Me	H	H	H	H	Me	3.28	6.90	5.43	6.58	7.08	3.79	4.05	5.15
6d	Me	H	H	Me	H	Me	3.17	6.57	5.32	2.01	6.57	3.73	4.07	5.11
2e	Me	H	H	H	H	H	3.71	9.58	5.70	5.70	~3.5	~3.5	4.06	5.31
3e	H	Me	H	H	Me	H	11.6	2.57	5.70	5.54	1.46	4.10	4.11	5.23
5e	H	Et	H	H	H	H	11.3	Et[f]	5.70	5.70	~3.5	~3.5	4.01	5.29
1f	H	H	H	H	H	H	*e*	6.78	5.01	3.81	9.24	3.27	3.85	5.12
2f	Me	H	H	H	H	H	4.07	6.74	5.10	3.23	9.07	2.90	3.91	5.13
3f	H	Me	H	H	Me	H	*e*	1.85	4.66	3.28	2.55	3.05	3.83	5.07
4f	Me	Me	H	H	Me	H	3.82	1.97	4.71	3.82	2.53	3.29	3.83	5.04
5f	H	H	H	H	Et	H	*e*	6.63	4.97	3.36	Et[f]	3.02	3.84	5.10
6f	Me	H	H	Me	H	H	4.05	6.69	4.96	3.30	9.03	1.67	3.92	5.14

	elemental analysis[g]							
	C		H		N		cyclic voltammetry[i]	
compd	calcd	found	calcd	found	calcd	found	$E_{p,a}$, V	$E_{1/2}$, V
1a			previously reported[1a]					+0.11
2a	12.84	13.07	3.39	3.68	12.84	12.90		+0.14
3a			previously reported[1b]					+0.05
4a	15.84	15.24	3.84	3.58	12.31	12.01		−0.03
5a	14.37	14.52	3.62	3.54	12.57	12.62	+0.13	
6a[h]	64.38	64.64	6.40	6.44	8.34	8.45		+0.11
3b	14.37	14.07	3.62	3.42	12.57	11.73	+0.84	
2e	11.94	12.55	2.88	2.91	10.44	10.21	+1.33	
3e	13.20	13.15	3.08	2.95	10.27	10.21	+1.34	
1f	10.65	11.15	2.68	2.69	10.63	10.23	+1.24	
2f	11.94	13.02	2.88	3.00	10.44	10.17	+1.29	
3f			previously reported[1b]				+1.09	
4f	14.42	13.98	3.31	3.27	10.09	11.58		
5f	13.20	13.02	3.08	3.12	10.27	10.25	+1.23	
6f	13.20	13.02	3.08	2.97	10.27	9.76	+1.35	

[a] Recorded in acetone-d_6 solution as a triflate salt (OTf^-), at 20 °C unless otherwise noted. [b] At −20 °C. [c] At −40 °C. [d] At −50 °C. [e] Signal not observed in acetone-d_6. [f] Ethyl group: **5a**, 2.38 (2 H), 1.12 (3 H); **5e**, 3.00 (2 H), 1.37 (3 H); **5f**, 2.92 (2 H), 1.33 (3 H). [g] Analysis of triflate salts ($F_3CSO_3^-$) unless otherwise noted. [h] Tetraphenylborate salt ($(C_6H_5)_4B^-$). [i] Recorded in acetonitrile/~0.5 M TBAH; NHE.

tan-yellow solid: 43 mg, 65 μmol, 86%.

Results

2,3-η^2-Pyrrole Complexes. In order to facilitate the assignment of the various pyrrole tautomers from ^{1}H NMR data, a series of alkylated pyrrole complexes, $[\mathbf{1a}–\mathbf{5a}]^{2+}$, was generated by reducing $Os(NH_3)_5(OTf)_3$ in a DME/DMA mixture containing an excess of the desired pyrrole, where L = pyrrole (**1**), 1-methylpyrrole (**2**), 2,5-dimethylpyrrole (**3**), 1,2,5-trimethylpyrrole (**4**), and 5-ethylpyrrole (i.e., 2-ethylpyrrole) (**5**) (Table I). Judging from the ^{1}H NMR data shown in Table I,[6] the osmium is located across C2 and C3 in all cases, even where C2 is alkylated. A ORTEP drawing for the cation of the 2,5-dimethylpyrrole species ($[\mathbf{3a}]^{2+}$) is shown in Figure 2.[1b] Despite the methyl substituent, Os–C2 (2.218 (8) Å) and Os–C3 (2.219 (8) Å) distances are identical. Analogous to structures of other η^2-aromatic species,[7] the metal forms a plane with C2 and C3, which lies roughly perpendicular to that of the ligand (dihedral angle = 112.9°). The methyl carbon attached at C2 is displaced by 0.87 Å from the ring plane, approximating sp^3 geometry. The C3–C4 bond length has increased 0.05 Å and the C4–C5 bond shortened 0.06 Å, compared to free pyrrole,[8] an observation that indicates a significant localization of pyrrole π electron density.

With the exception of the asymmetric 5-ethylpyrrole complex, $[\mathbf{5a}]^{2+}$, all pyrrole complexes appear fluctional in the ^{1}H NMR at ambient temperature (~20 °C). As earlier reported,[1a] the ^{1}H NMR for the parent pyrrole species ($[\mathbf{1a}]^{2+}$) shows four broadened but resolved resonances at 20 °C in the range 5–7 ppm. Irradiation of the proton H2 results in spin saturation of the H5 signal, an observation which indicates that the osmium undergoes a η^2-2,3

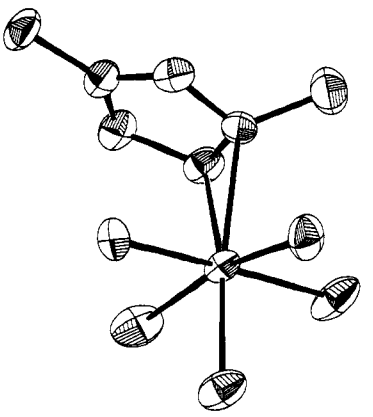


Figure 2. ORTEP drawing of [(2,3-η^2-2,5-dimethylpyrrole)$Os(NH_3)_5]^{2+}$ ($[\mathbf{3a}]^{2+}$). Selected bond distances (Å) and angles (deg) are Os–C2 = 2.218 (8), Os–C3 = 2.219 (7), N1–C2 = 1.41 (1), C2–C3 = 1.41 (1), C3–C4 = 1.47 (1), C4–C5 = 1.32 (1), C5–N1 = 1.388 (9), C2–C6 = 1.51 (1), Os–N2 = 2.13 (1), Os–N3 = 2.15 (1), Os–N6 = 2.171 (8), C2–Os–C3 = 37.1 (3), N1–C2–C3 = 106.4 (7), C2–C3–C4 = 105.8 (7), C3–C4–C5 = 109.1 (6), C4–C5–N1 = 109.5 (5), C5–N1–C2 = 109.3 (6), N1–C2–C6 = 113.0 (7), N1–C5–C7 = 120.4 (7), C3–C2–C6 = 126.3 (9), C4–C5–C7 = 130.1 (7), N2–Os–N6 = 86.1 (3), N2–Os–N3 = 176.7 (5), N2–Os–N4 = 89.9 (3).

(6) Assignments made on the basis of homonuclear decoupling and spin saturation exchange.

(7) Harman, W. D.; Gebhard, M.; Taube, H. *Inorg. Chem.* **1990**, *29*, 567.

(8) Chadwick, D. J. In *Pyrroles: Part One*; Jones, R. A., Ed.; Wiley: New York, 1990. See also: Baird, M. D.; Ammon, H. L. *J. Org. Chem.* **1979**, *44*, 444.

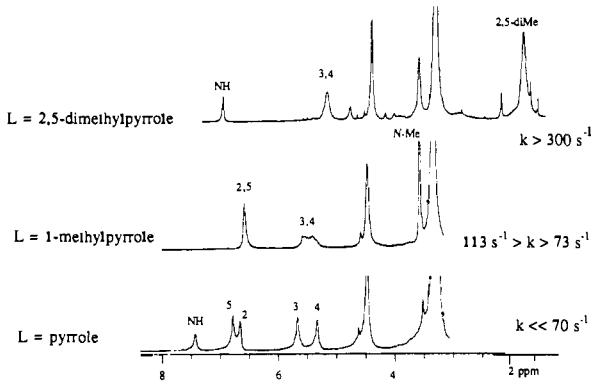


Figure 3. ^{1}H NMR spectra recorded at 20 ± 2 °C for η^2-pyrrole complexes of the form $[Os(NH_3)_5(L)]^{2+}$.

↔ η^2-4,5 shift at this temperature. ^{1}H NMR spectra recorded at subambient temperatures for compounds **2a–4a** show that a similar process occurs for these materials. Comparison of these data establishes a quantitative increase in the rate of 2,3 ↔ 4,5 tautomerization for the ligands pyrrole < 1-methylpyrrole < 2,5-dimethylpyrrole < 1,2,5-trimethylpyrrole.[9] The NMR spectra for compounds $[\mathbf{1a}]^{2+}$–$[\mathbf{3a}]^{2+}$ are shown at room temperature (Figure 3) for comparison. Although the 5-ethyl derivative ($[\mathbf{5a}]^{2+}$) appears static in the ^{1}H NMR, the possibility of an analogous 2,3 ↔ 4,5 ring shift cannot be ruled out as the two tautomers are no longer isoergic.[10]

The ^{1}H NMR spectrum for the 1-methylpyrrole complex $[\mathbf{2a}]^{2+}$ shows at 20 °C a single, broad peak corresponding to the α protons ($\delta\nu$ = 33 ± 3 Hz); at this same temperature, the β protons, separated by a greater frequency ($\delta\nu$ = 51 ± 3 Hz), are not coalesced. For this case, the specific rate of 2,3-η^2 to 4,5-η^2 tautomerization can be bracketed from the coalescence expression as $73 < k < 113 \pm 6$ s^{-1}.[11]

β-Protonations. When the pyrrolic complexes $[\mathbf{2a–5a}]^{2+}$ are treated with 1 equiv of triflic acid in methanol, the dominant reaction is protonation at C4 ($[\mathbf{2f–5f}]^{3+}$) (Figure 1). In all these cases this reaction is quantitative and reversible; application of proton sponge fully restores the original materials to their pyrrolic forms $[\mathbf{2a–5a}]^{2+}$. For the parent pyrrole species $[\mathbf{1a}]^{2+}$, protonation must be carried out in acetonitrile in order to generate $[\mathbf{1f}]^{3+}$ free of contaminants. ^{1}H NMR data for compounds **1f–5f** appear in Table I. Significant here is the large downfield shift of the α proton (H5) resonance for $[\mathbf{1f}]^{3+}$ and $[\mathbf{2f}]^{3+}$; this iminium-like hydrogen is located near 9 ppm in acetone-d_6, a position close to that expected for an aldehyde proton. Also diastereotopic methylene protons are observed (H4, H6) for **1f–5f** with geminal coupling constants of ~25 Hz. The ^{13}C NMR data for $[\mathbf{3f}]^{3+}$ include a resonance at 187.1 ppm, assigned to the iminium carbon, and DEPT spectra reveal a methylene carbon at 46.2 ppm, consistent with our assignment of $[\mathbf{3f}]^{3+}$ as a β-protonated pyrrole. These β-protonated pyrrolium complexes show no fluctionality in their NMR spectra, consistent with the osmium moiety being restricted to the 2,3 position in the ring. Mixtures of the 2,5-dimethylpyrrole complex $[\mathbf{3a}]^{2+}$ with its β-protonated derivative $[\mathbf{3f}]^{3+}$ ($[[\mathbf{3a}]^{2+}] \sim [[\mathbf{3f}]^{3+}] \sim 15$ mM) show no merging of signals at 20 °C.

When the synthesis of $[\mathbf{3f}]^{3+}$ is repeated in CD_3OD, the product, $[\mathbf{3f}]^{3+}$-d_1 shows an ^{1}H NMR signal for H6 that is greatly diminished, while that of H4 appears fully intact. The residual signal for H6 (~20% of original) remains a crisp doublet-of-doublets suggesting that the minor component responsible for this resonance is probably the *nondeuterated* $[\mathbf{3f}]^{3+}$, rather than a diastereomer of $[\mathbf{3f}]^{3+}$-d_1 in which the deuterium occupies the position R4 (Figure 1). Subsequent deprotonation using a hindered base such as proton sponge returns $[\mathbf{3a}]^{2+}$ with proton H4 intact. When a freshly prepared sample of $[\mathbf{3f}]^{3+}$ is allowed to stand in CD_3OD for a period of hours, complete exchange of H6 occurs, but H4 remains at full intensity. The latter proton (H4) shows no coupling to H3 (J < 1 Hz), which has been pushed out of the pyrrole plane by the osmium. By consideration of molecular models, H4 is best assigned to the proton syn to the osmium (Figure 1), a scenario that requires an H3–C3–C4–H4 dihedral angle of 70–90°, consistent with NMR data.[12] Together, these observations indicate that protonation and deprotonation at C4 occur stereoselectively, on the ring face opposite metal coordination.

3,4-η^2-2*H*-Pyrrole Complexes (b, e). The 2,5-dimethylpyrrole complex ($[\mathbf{3a}]^{2+}$) is readily protonated, even by mild acids such as anilinium triflate (pK_a = 4.6) to give the β-protonated product, $[\mathbf{3f}]^{3+}$. In contrast to what is observed with triflic acid, this product slowly degrades in the presence of the conjugate base aniline to give a new material, $[\mathbf{3e}]^{3+}$. The ^{1}H NMR of this species shows cis and trans ammine resonances and four ring proton and two methyl signals, like its precursor ($[\mathbf{3f}]^{3+}$), but both methyl groups are now doublets (J = 7.2, 2,4 Hz). On the basis of ^{1}H and ^{13}C NMR, ^{1}H COSY, and ^{13}C DEPT data, we have assigned $[\mathbf{3e}]^{3+}$ as an α-protonated pyrrole coordinated by osmium at C3 and C4 as shown in Figure 1. Given that there is a significant spin/spin coupling between H4 and H6 (J = 4.8 Hz), inspection of a Karplus plot suggests that the H4–C4–C5–H6 dihedral angle is near 40°.[12] Consideration of molecular models indicates that H6 must be anti to osmium to be consistent with the coupling data and that Me5 must be syn to the metal, despite the apparent steric disadvantage.

Treatment of $[\mathbf{3e}]^{3+}$ with base (5 equiv of proton sponge) in acetonitrile yields a new product, $[\mathbf{3b}]^{2+}$, whose ^{1}H NMR spectrum in acetone-d_6 is virtually identical in pattern with that of $[\mathbf{3e}]^{3+}$, except that most peak positions have shifted upfield. Over the course of 24 h these signals diminish and are replaced by those corresponding to the pyrrolic tautomer $[\mathbf{3a}]^{2+}$, 2,5-dimethylpyrrole, and the acetone complex $[Os(NH_3)_5(\eta^2\text{-acetone})]^{2+}$. Given that the acetone species is highly substitution inert,[13] the formation of $[\mathbf{3a}]^{2+}$ must result from the isomerization of $[\mathbf{3b}]^{2+}$. In a separate experiment, a ^{1}H NMR spectrum of a 1:1 mixture of $[\mathbf{3a}]^{3+}$ and $[\mathbf{3b}]^{2+}$ in acetone-d_6 gave a single set of ammine and ring resonances, intermediate in position between the corresponding resonances of the isolated species. This coalescence of the proton signals for $[\mathbf{3e}]^{3+}$ and $[\mathbf{3b}]^{2+}$, together with the observation of $[\mathbf{3b}]^{2+}$ partially decomposing to give $[\mathbf{3a}]^{2+}$, leave little doubt as to the assignment of $[\mathbf{3b}]^{2+}$ as a 2*H*-pyrrole complex stabilized by osmium coordination (Figure 1).

Hydration and Titration Experiments in Aqueous Solution. Proton NMR spectra in D_2O for both the η^2-pyrrole ($[\mathbf{1a}]^{2+}$) and η^2-1-methylpyrrole ($[\mathbf{2a}]^{2+}$) complexes are virtually identical with those recorded in acetone-d_6. However, when a sample of the 2,5-dimethyl species ($[\mathbf{3a}]^{2+}$) is examined in D_2O, the ^{1}H NMR spectrum indicates ~90% conversion to a new compound. The new material, $[\mathbf{3a}\cdot D_2O]^{2+}$, shows two methyl singlets and two other slightly broadened ring proton resonances at 3.81 (H3) and 2.22 ppm (H4), which integrate to one proton each. No exchange is observed for these protons after 1 h. When the spectrum of $[\mathbf{3a}\cdot H_2O]^{2+}$ is recorded in H_2O,[14] an additional resonance is observed at 2.78 ppm, which strongly couples (J = 24 Hz) with the upfield ring proton and weakly couples with the downfield proton (J = 7.5 Hz). Treatment of an aqueous solution of $[\mathbf{3a}\cdot H_2O]^{2+}$ with an aqueous solution of sodium tetraphenylborate produces a precipitate, which, after isolation and drying in vacuo, appears to be the pyrrole complex $[\mathbf{3a}]^{2+}$ in acetone-d_6 solution.

(9) A qualitative assignment of tautomerization rates can be made through consideration of the extent of coalescence of the β ring protons (H3, H4), since the frequency difference ($\delta\nu$) for H3 and H4 for complexes $[\mathbf{1a–3a}]^{2+}$ is comparable. See ref 11.

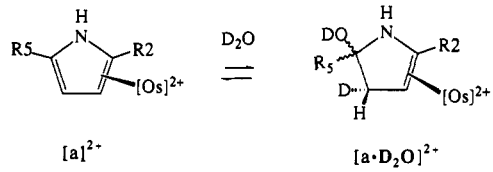
(10) It remains entirely possible that the 4,5-η^2 form of **5a** is kinetically accessible but in low enough population that the ^{1}H NMR for this species under equilibrium conditions is not observed.

(11) Sandström, J. In *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; p 79.

(12) Jackman, L. M.; Sternhell, S. *Applications of NMR Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon: New York, 1969.

(13) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223.

(14) 10% of D_2O is added in order to obtain an instrument lock signal. ^{1}H NMR spectrum of $[\mathbf{3a}\cdot H_2O]^{2+}$: 4.40 (b, 3 H), 3.81 (d, 1 H), 2.78 (dd, 1 H), 2.22 (d, 1 H), 2.08 (s, 3 H), 1.54 (s, 3 H) ppm.



3a: R2 = R5 = CH_3: $K_1 = 9 \pm 1$

5a: R2 = H; R5 = CH_2CH_3: $K_2 = 4.5 \pm 0.5$

Figure 4. Hydration equilibria for various η^2-pyrrole complexes of pentaammineosmium(II).

Table II

compd	ligand	pK_a	deprotonation
$[\mathbf{1f}]^{3+}$	3*H*-pyrrolium	4.2	C4
$[\mathbf{2f}]^{3+}$	1-methyl-3*H*-pyrrolium	5.6	C4
$[\mathbf{3f}]^{3+}$	2,5-dimethyl-3*H*-pyrrolium	7.5[a] (6.6)	C4
$[\mathbf{2e}]^{3+}$	1-methyl-2*H*-pyrrolium	>8.8[b] (7.8)	C5
$[\mathbf{3e}]^{3+}$	2,5-dimethyl-2*H*-pyrrolium	7.9	N
pyrrolium ion		-3.8	C5
pyrrolium ion		-5.9	C4
pyrrolium ion		~-10	N
1-methylpyrrolium		-2.9	C5
2,5-dimethylpyrrolium		-0.71	C5

[a] Value adjusted for coupled hydrolysis reaction. [b] Value adjusted for coupled linkage isomerization. The pK of equilibrium product is shown in parentheses.

When an acetone-d_6 (285 mg) solution of $[\mathbf{3a}](OTf)_2$ (11.4 mg) is treated with 60 mg of D_2O (7.3 M), an equilibrium mixture of 1:1 is established for $[\mathbf{3a}]^{2+}$ and $[\mathbf{3a}\cdot D_2O]^{2+}$. Neglecting solvent differences, this would correspond to an equilibrium constant of $K_{1'} = 7.6$ in pure water, in reasonable agreement with that directly observed in water, where $K_1 = 9 \pm 1$. Given that the hydrolysis product $[\mathbf{3a}\cdot D_2O]^{2+}$ does not show a ν(C=O) in the range 1650–1800 cm^{-1}, we conclude that the pyrrole ring is not opened to a ketone but rather is hydrolyzed to an amino alcohol as shown in Figure 4. A comparison of the ^1H NMR spectra for $[\mathbf{3a}]^{2+}$ recorded in D_2O and H_2O indicates that both hydration and dehydration must occur stereospecifically; the signal corresponding to H4 in $[\mathbf{3a}\cdot H_2O]^{2+}$ remains at full intensity for several hours at 20 °C, whereas the hydration and dehydration reactions occur on the order of seconds to minutes in aqueous solution. Given that *H*4 shows a vanishingly small coupling with *H*3, these observations suggest that deuteration occurs on the ring face opposite to osmium coordination, consistent with the stereochemistry of protonation by strong acids discussed earlier. The stereochemistry about C5 has not been determined, but, since only one set of methyl resonances can be seen in the ^1H NMR, there appears to be only one diastereomer present in solution.

A similar equilibrium is observed for the 5-ethylpyrrole species $[\mathbf{5a}]^{2+}$ in which the equilibrium ratio of amino alcohol to pyrrole is $K_2 = 4.5$.[15] On the basis of ^1H NMR data, the water adds across C4 and C5, the hydroxyl group bonding to the latter. The complexes $[\mathbf{1a}]^{2+}$ and $[\mathbf{2a}]^{2+}$ show no reactivity in D_2O, but the trimethylated derivative $[\mathbf{4a}]^{2+}$ undergoes decomposition in a matter of minutes, yielding paramagnetic products.

Conventional titrations of $[\mathbf{1–3a}]^{2+}$ were carried out with HCl(aq) since both the pyrrolic complexes $[\mathbf{a}]^{2+}$ and their β-protonated counterparts $[\mathbf{f}]^{3+}$ are either stable in water or form reversible hydrolysis products. The titration curve for $[\mathbf{3a}]^{2+}$ is shown in Figure 5 as an example. Each final solution was treated with excess $NaBPh_4$ to precipitate the osmium products. ^1H NMR spectra of these materials showed in all cases essentially quantitative formation of the β-protonated tautomer. The pK_a values for $[\mathbf{1–3f}]^{2+}$ are shown in Table II along with the corresponding data for several free ligands. In the case of $[\mathbf{3a}]^{2+}$, the pK_a values reported have been adjusted, taking into account the hydrolysis

(15) ^1H NMR for $[\mathbf{5a}\cdot H_2O]^{2+}$ (H_2O, presaturation): 5.96 (d, 1 H); 4.08 (dd, 1 H), 2.69 (dd, 1 H), 2.38 (m, 2 H), 2.26 (d, 1 H), 1.09 (~t, 3 H); ammine protons obscured.

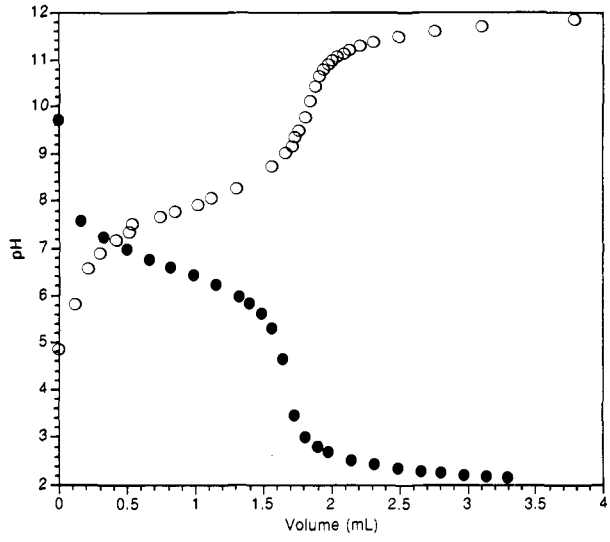


Figure 5. Titration curves for the protonation of the 2,5-dimethylpyrrole complex $[\mathbf{3a}]^{2+}$ (●; HCl(aq)) and the deprotonation of the 2,5-dimethylpyrrole 2*H*-pyrrolium complex $[\mathbf{3e}]^{3+}$ (○; NaOH(aq)).

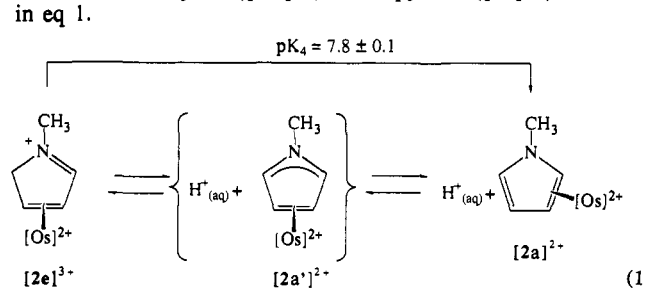
equilibrium for the pyrrolic species. The experimentally derived pK_a for the equilibrium product of deprotonation and hydrolysis is 6.6 When the hydrolysis is factored out of this product, the adjusted pK_a becomes 7.5.

For comparison, a pK_a for the 2*H*-pyrrolium complex, $[\mathbf{3e}]^{3+}$, was determined by titration with NaOH(aq) (Figure 5). As before, the end product was precipitated as a BPh_4^- salt and analyzed by ^1H NMR, which shows this material to be $[\mathbf{3b}]^{2+}$. Combining the two pK_a equations for the 2,5-dimethylpyrrole ligand describes an equilibrium, K_4, among species $[\mathbf{3a}]^{2+}$, $[\mathbf{3b}]^{2+}$, $[\mathbf{3e}]^{3+}$, and $[\mathbf{3f}]^{3+}$, as shown in Figure 6.

The ^1H NMR for $[\mathbf{3e}]^{3+}$ is consistent with the formation of a single diastereomer, even after this compound has been equilibrated with $[\mathbf{3b}]^{2+}$ for 3 days. Deprotonation of the nitrogen in $[\mathbf{3e}]^{3+}$ does not alter the splitting pattern for H4 or H6 in compound $[\mathbf{3b}]^{2+}$, as the coupling between H4 and H6 remains substantial ($J = 4.5$ Hz). These observations suggest that this stereochemical relationship at C5 has been maintained.

In the presence of a weak base, a rearrangement of the β-protonated species occurs for the N-methylated complex $[\mathbf{2f}]^{3+}$, producing $[\mathbf{2e}]^{3+}$, a process parallel to the rearrangement of $[\mathbf{3f}]^{3+}$ to $[\mathbf{3e}]^{3+}$. Upon treatment with NaOH(aq), $[\mathbf{2e}]^{3+}$ is slowly converted to its pyrrolic form $[\mathbf{2a}]^{2+}$. Because the nitrogen is alkylated for this species, deprotonation cannot occur at the heteroatom. For the 2*H*-pyrrolium ligand $[\mathbf{2e}]^{3+}$, loss of the C5 hydrogen (H6) is required to restore the aromatic system. The resulting azomethine ylide generated by removal of the proton H6 is unstable with respect to the metal, reverting back to 2,3-η^2 coordination, and is not detected at ambient temperatures.

Because of its significance in determining the free energy of isomerization for a 1*H*- to a 2*H*-pyrrolic ligand (see Discussion), it was of interest to determine the equilibrium product that combines the pK_a of $[\mathbf{2b}]^{2+}$ and the subsequent isomerization of the azomethane ylide ($[\mathbf{2a'}]^{2+}$) to the pyrrole ($[\mathbf{2a}]^{2+}$) as shown in eq 1.



(1)

This was accomplished by titrating a sample of $[\mathbf{2e}]^{3+}$ with NaOH as described earlier for $[\mathbf{3e}]^{3+}$ and determining pK_4 cor-

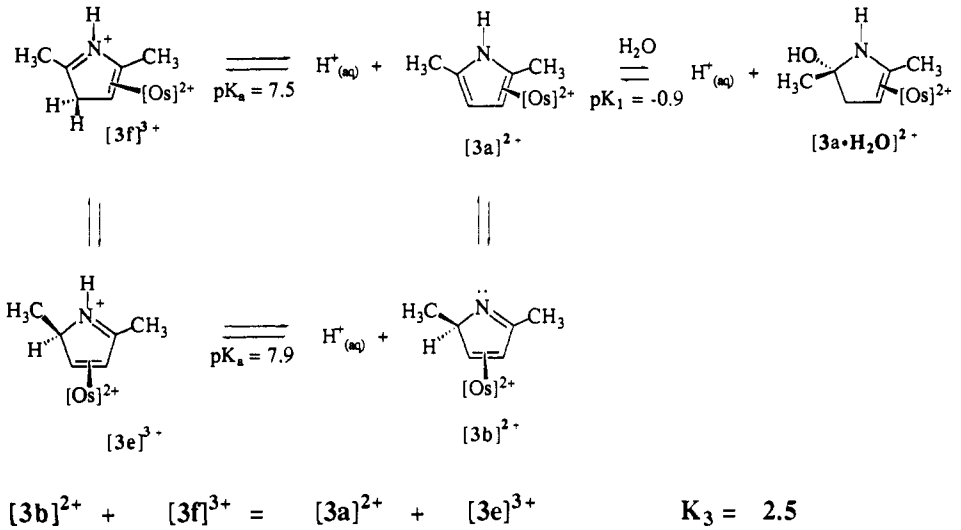


Figure 6. Summary of acid/base and hydration equilibria for the 2,5-dimethylpyrrole system.

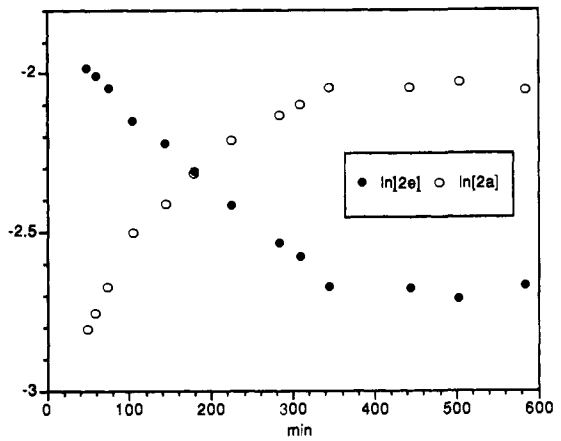
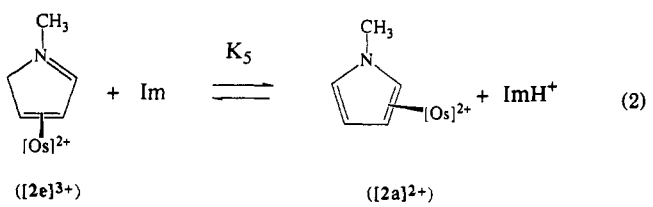


Figure 7. Approaching an equilibrium between *N*-methylpyrrole/*N*-methylpyrrolium ligands on pentaammineosmium(II) and imidazole/imidazolium.

responding to eq 1 from the buffer region of the titration curve. Complicating this measurement is the slow rate of deprotonation at C5, which required an equilibration period of at least 20 min for each data point recorded. From the titration curve, pK_4 was estimated as 8.5, which value serves as an upper limit for the true value.[16] In order better to determine pK_4, we sought to measure directly an equilibrium of $[\mathbf{2e}]^{3+}$ and $[\mathbf{2a}]^{2+}$ with an organic acid/conjugate base pair whose pK_a was known. The imidazole/imidazolium ion couple was chosen because of the proximity of the pK_a of imidazolium to that value expected for the $[\mathbf{2e}]^{3+}/[\mathbf{2a}]^{2+}$ equilibrium (≤8.5).

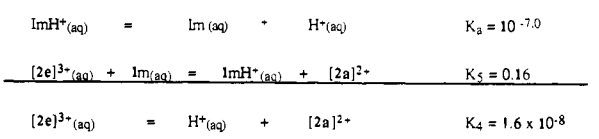
An NMR tube was charged with the 2*H*-pyrrolium complex $[\mathbf{2e}]^{3+}$ (66 mg, 101 μmol), imidazole (830 μmol), and D_2O (0.51 g). Within 1 h, distinctive methyl signals appear at 3.31 and 3.35 ppm for $[\mathbf{2a}]^{2+}$ and $[\mathbf{2e}]^{3+}$, respectively. These peaks were monitored over a 10-h period, the results of which appear in Figure 7. By t = 350 min, an equilibrium was established as shown in eq 2.



(2)

(16) Given that the consumption of base by $[\mathbf{2e}]^{3+}$ is slow, the recorded pH of solution is anticipated to be slightly higher than the equilibrium value.

Equilibrium concentrations for $[\mathbf{2e}]^{3+}$, Im, $[\mathbf{2a}]^{2+}$, and ImH^+ are 0.075, 1.66, 0.14, and 0.14 M, respectively, which determine an equilibrium constant K_5 = 0.164. Taking the pK_a of imidazolium ion (ImH^+) as 7.0,[17] a value for the equilibrium product K_4 can be determined according to eq 3.



(3)

Thus, an equilibrium product of $K_4 = 1.6 \times 10^{-8}$ is determined for $[\mathbf{2a}]^{2+}$ and $[\mathbf{2e}]^{3+}$ in acidic aqueous solution. For comparison with the earlier results of the titration of $[\mathbf{2e}]^{3+}$, this would correspond to a pK_4 = 7.8 ± 0.1, in good agreement with that found through titration.

Cyclic Voltammetry. Electrochemical data for all complexes reported are shown in Table I. In many cases, oxidations are chemically irreversible and, correspondingly, only peak potentials for the first anodic wave ($E_{p,a}$) are reported. In all cases, the reported value is assumed to correspond to an Os(II/III) oxidation, as is so for numerous other π complexes of pentaammineosmium(II).[18] The neutral pyrrole complexes show oxidation waves in the range −0.03 to 0.14 V (NHE), with the more negative values corresponding to those compounds with ring alkylation at C2 and C5 ($[\mathbf{3a}]^{2+}$, $[\mathbf{4a}]^{2+}$). These reduction potentials are similar to those reported for other complexes of electron-rich aromatic ligands on pentaammineosmium(II), such as $[Os(NH_3)_5(\eta^2$-aniline$)]^{2+}$, which has a III/II couple with $E_{1/2}$ = 0.16 V.[19] In contrast, the III/II reduction potential for the neutral 3,4-η^2-2*H*-pyrrole species $[\mathbf{3b}]^{2+}$ occurs at 0.84 V, over 0.5 V positive of that of its 1*H*-pyrrole tautomer. Here, a comparison can be made with $[Os(NH_3)_5(2,3$-η^2-2-cyclohexen-1-one$)]^{2+}$,[20] whose $E_{1/2}$ = 0.88 V. With the exception of the pyrrole complex ($[\mathbf{1a}]^{2+}$), all the neutral 2,3-η^2-pyrrole complexes investigated show reversible or pseudoreversible electrochemistry at 100 mV/s in CH_3CN.

Not surprisingly, when the pyrrole ligand is protonated, the III/II reduction potential becomes substantially more positive, as these ligands become more powerful π-acids and weaker σ-donors. Both the 2,3-η^2- and the 3,4-η^2-pyrrolium species (type e and f) are oxidized at potentials well over 1 V ($E_{p,a}$ = 1.09–1.41 V), with the 3,4-η^2-pyrrolium complexes being more difficult to

(17) Hofmann, K. In *Imidazole and its Derivatives*; Interscience Publishers: New York, 1953; p 15.
(18) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5725.
(19) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 5403.
(20) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682.

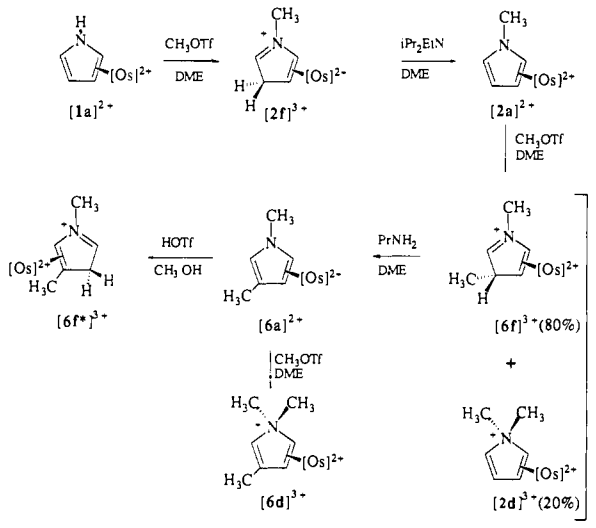


Figure 8. Summary of methylation experiments on η^2-pyrrole ligand and alkylated η^2-pyrrole ligands.

oxidize. For comparison, the pentaammineosmium(II) complex of *N*-methylpyridinium ion shows an irreversible oxidation wave at 0.90 V,[21] but, unlike the pyrrole systems, this cationic ligand remains aromatic and, therefore, is less effective as a π-acid.

Methylations. When the 2,3-η^2-pyrrole complex $[\mathbf{1a}]^{2+}$ is treated with 1 equiv of methyl triflate, alkylation of the nitrogen occurs and the β-protonated 1-methylpyrrole product, $[\mathbf{2f}]^{3+}$, is recovered in quantitative yield. However, when the N-methylated pyrrole species $[\mathbf{2a}]^{2+}$ is treated with this alkylating agent, a new species, $[\mathbf{6f}]^{3+}$, is recovered, which gives a ^{1}H NMR spectrum similar to that of $[\mathbf{2f}]^{3+}$ but with an additional methyl signal, split into a doublet, in place of one of the methylene protons. Deprotonation of $[\mathbf{6f}]^{3+}$ with $PrNH_2$ returns a pyrrolic species in which C4 and N are methylated.

The major product, $[\mathbf{6f}]^{3+}$ (80%), recovered from the methylation of $[\mathbf{2a}]^{2+}$ occurs as a single diastereomer. The absence of significant coupling between H4 and H3 indicates that alkylation occurs on the ring face opposite to metal coordination as shown in Figure 8. Treatment of $[\mathbf{2a}]^{2+}$ with methyl triflate generated as a minor product 20% of an Os(II)–pyrrolium species, $[\mathbf{2d}]^{3+}$, thought to be dimethylated at nitrogen (Table I). In an effort to generate the diastereomer in which the methyl group at C4 is syn to osmium, the pyrrolic species $[\mathbf{6a}]^{2+}$ was treated with 1 equiv of HOTf in methanol and the resulting product isolated by precipitation with ether. The product, $[\mathbf{6f^*}]^{3+}$ (70% yield), appears to be a 2,3-η^2-pyrrolium complex, judging from the NMR data,[22] but shows two methyl singlets. On the basis of homonuclear decoupling experiments and comparison to other spectra, we assign $[\mathbf{6f^*}]^{3+}$ as a C3 protonated species with the osmium coordinating to C4 and C5, as shown in Figure 8. When the 1,3-dimethylated pyrrole species $[\mathbf{6a}]^{2+}$ is treated with an additional equivalent of CH_3OTf, a product, $[\mathbf{6d}]^{3+}$, is isolated in which the nitrogen is doubly methylated as in the case of $[\mathbf{2d}]^{3+}$ (Table I).

Protonation Experiments with Pyrrole. When the parent pyrrole complex $[\mathbf{1a}]^{2+}$ is treated with triflic acid in acetonitrile (pK_a = −10.1) or in ether, the yield of the 2,3-η^2-pyrrolium species, $[\mathbf{1f}]^{3+}$, is essentially quantitative. If weaker acids are used, however, such as triflic acid in methanol (pK_a = −2.2), pyridinium triflate (pK_a = 5.3), or diphenylammonium triflate (pK_a = 0.8), at least three other species are identified in varying amounts. For many of these impurities, subsequent treatment with base fails to restore the original complex, $[\mathbf{1a}]^{2+}$. Despite repeated attempts to resolve and characterize these impurities, all but $[\mathbf{1f}]^{3+}$ remain uncharacterized, although ^{1}H NMR spectra reveal signals consistent with the formation of 3,4-η^2 species of type **d** and **e**.

Other Electrophilic Additions. Preliminary results indicate that electrophilic addition at the β position of pyrrole (C4) is a general reaction for 2,3-η^2-pyrroles. In one example, a solution of $[\mathbf{1a}]^{2+}$ is treated with 1 equiv of methylacetonitrilium triflate in acetonitrile. The product is then precipitated by the addition of ether. ^{1}H NMR and cyclic voltammetric data[23] are consistent with the *N*-methylacetylpyrrole iminium complex, $[\mathbf{7}]^{3+}$, shown in Figure 9. In contrast, certain α,β-unsaturated carbonyls are found to undergo a 1,3-dipolar cycloaddition with the azomethine ylide intermediate (type **a'**).[24] The resulting cycloadducts, such as $[\mathbf{8}]^{2+}$, can be ring opened under acidic conditions and neutralized to yield 2*H*-pyrroles such as $[\mathbf{8b}]^{2+}$, also shown in Figure 9.[25]

Discussion

The pentaammineosmium(II) system has been widely studied,[26] with interest stemming largely from the tendency of this metal to form π complexes with unsaturated ligands. A variety of ligands have been reported to form dihaptocoordinate complexes with osmium(II) including alkenes and alkynes,[27] arenes[18] and pyridines,[28] aldehydes and ketones,[29] pyrrole, furan, and thiophene.[1a] The strong interaction of metal d_π orbitals with ligand π^* orbitals has been considered the primary source of stabilization for these species, as is the case in the current study. Although η^5-pyrrole and pyrrolyl complexes are known,[30] to date, pentaammineosmium(II) is the only metal center reported to form a dihaptocoordinate complex with pyrrole. Although transition-metal complexes of unsaturated hydrocarbons have been widely investigated for their applications to organic synthesis, remarkably little has been reported about the synthetic potential of heterocyclic complexes.[31]

Both structural and chemical evidence indicates that complexation of pyrrole at C2 and C3 results in the uncoordinated portion of the ring resembling an enamine. In deuterated solvents such as CD_3OD, exchange of the nitrogen ring proton (H1) of $[\mathbf{1a}]^{2+}$ occurs in less than 10 min, indicating that this process is kinetically accessible, yet treatment of $[\mathbf{1a}]^{2+}$ with acid results in protonation at C4. Thus, protonation of the β carbon of pyrrole (C4) is thermodynamically favored over that at nitrogen or C5, provided that osmium remains coordinated at C2 and C3. Although nitrogen protonation is most likely kinetically favored for complexes **1a–5a**, the stereospecific nature of their protonation prevents drawing such conclusions on the basis of relative H/D exchange rates.

Comparison of the pK_a values reported in Table II with those reported for various enamines demonstrates the extent to which the osmium modifies the pyrrolic ligand. Thermodynamic protonation of simple enamines occurs at the β carbon,[32] analogous to compounds **1a–5a**. Typically, the conjugate iminium ions have pK_a's ranging from 9 to 12. For comparison, the iminium ion derived from 2,3-dihydro-1,3,4-trimethylpyrrole has a reported pK_a of 9.6,[32] a value similar to that of the 2,5-dimethylpyrrolium complex $[\mathbf{3f}]^{3+}$, where pK_a = 7.5. As the extent of alkylation is reduced, the pK_a for the pyrrolium complexes decreases and the parent pyrrolium species ($[\mathbf{1f}]^{3+}$) exhibits a pK_a of just over 4.

(21) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 2896.

(22) ^{1}H NMR data for $[\mathbf{6f^*}]^{3+}$ (acetone-d_6): 8.93 (1 H, s), 6.77 (1 H, s), 5.10 (3 H, br), 3.93 (12 H, br), 4.05 (3 H, s), 1.74 (3 H, s), 3.2–3.5 (2 H) ppm.

(23) ^{1}H NMR for $[\mathbf{7}]^{3+}$ (acetone-d_6): 9.5 (NH, br 1 H), 8.20 (C5, s, 1 H), 6.77 (C2, d, 1 H), 5.67 (C3, d, 1 H), 4.88 (*t*-NH_3, br, 3 H), 3.60 (*c*-NH_3, br, 12 H). $E_{p,a}$ = 0.58 V, NHE.

(24) For the case of maleic anhydride, see: Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969.

(25) (a) Reference 1b. (b) Koontz, J. I.; Myers, W. H.; Harman, W. D., manuscript in preparation.

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(29) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.

(30) (a) Felkin, H.; Zakrzewski, J. *J. Am. Chem. Soc.* **1985**, *107*, 3374. (b) Chase, K. J.; Grimes, R. N. *Organometallics* **1989**, *8*, 2492 and references therein.

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(32) Cook, A. G. In *Enamines, Synthesis, Structure and Reactions*; Marcel Dekker, Inc.: New York, 1988; p 77.

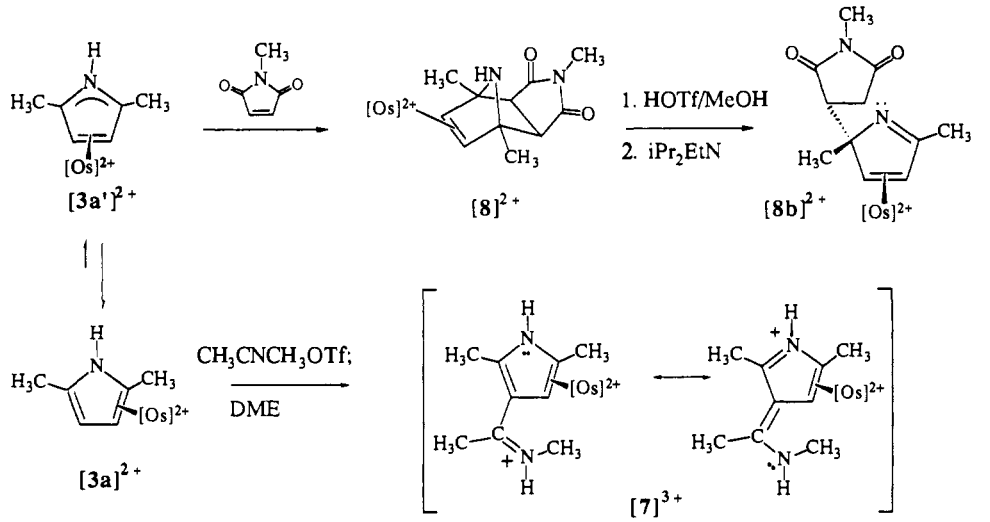


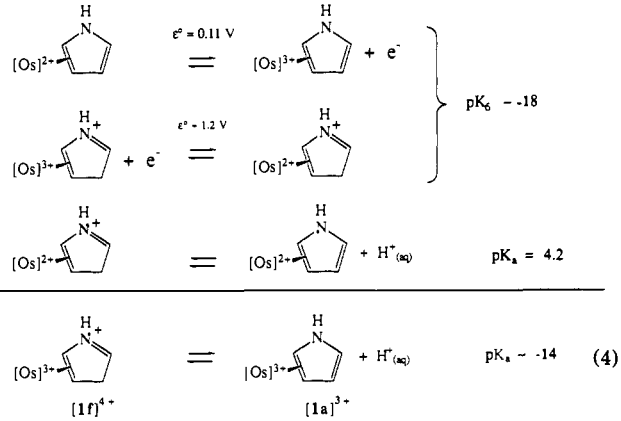
Figure 9. Two modes of electrophilic addition to η^2-pyrrole: 2,5-dipolar cycloadditions and β-electrophilic addition.

This is in dramatic contrast to uncoordinated pyrrolium ion which is over *10 orders of magnitude more acidic* ($pK_a \sim -5.9$).

pK_a measurements for the 3,4-η^2 tautomers also reveal striking differences in their acidities relative to that of the free ligand. For the 3,4-η^2-coordinated 2*H*-pyrrolium tautomer $[\mathbf{3e}]^{3+}$, deprotonation occurs at nitrogen without subsequent shift in the coordination site of the metal. For this process, the pK_a is determined in water to be 7.9. The N-protonated conjugate acid of pyrrole has an estimated pK_a of -10.[8]

In the case of $[\mathbf{2e}]^{3+}$, the nitrogen is alkylated and, thus, deprotonation must occur at the α carbon, C5. Note that the value reported in Table II is actually the product of this deprotonation and the subsequent rearrangement of the resulting azomethine ylide (eq 1). Given that only one species is detectable in a ^1H NMR spectrum recorded at -40 °C, where ring slippage is static on the NMR time scale, we assume that the 2,3-η^2-tautomer $[\mathbf{2a}]^{2+}$ is at least 10 times more abundant than the hypothetical azomethine ylide intermediate, $[\mathbf{2a'}]^{2+}$. Taking the equilibrium constant of $[[\mathbf{2a'}]^{2+}]/[[\mathbf{2a}]^{2+}] \leq 0.1$ at 20 °C, the pK_a of $[\mathbf{2e}]^{3+}$ of 8.8 reported in Table II represents a lower limit for deprotonation of the α carbon, when the metal coordination site is conserved.

The oxidation waves recorded for the pyrrole species $[\mathbf{1a}]^{2+}$ and its β-protonated analogue $[\mathbf{1f}]^{3+}$ differ by more than a volt, the protonated form being more difficult to oxidize. Although the irreversible nature of these waves prevents the exact determination of the formal reduction potentials, a crude approximation for the acidity of the osmium(III)–pyrrolium species $[\mathbf{1f}]^{4+}$ can be obtained by equating the reduction potentials for $[\mathbf{1a}]^{2+}$ and $[\mathbf{1f}]^{3+}$ with their anodic peak potentials. Combining the two half-reactions corresponding to these redox processes (K_6) with the pK_a for $[\mathbf{1f}]^{3+}$ gives an estimate of -14.3 for the pK_a of a β-protonated pyrrole coordinated to osmium(III) (eq 4):



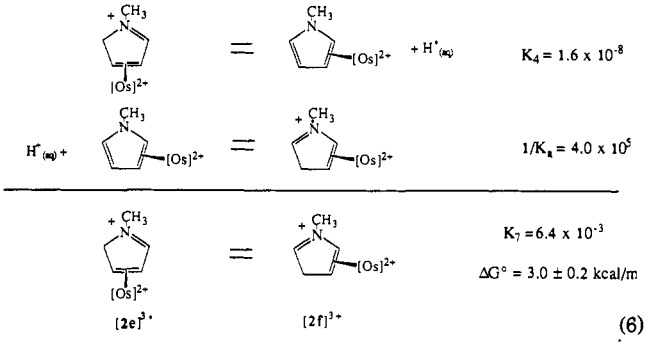
(4)

Rigorously, the reduction potentials for $[\mathbf{1f}]^{3+}$ and $[\mathbf{1a}]^{2+}$ utilized in eq 4 should be those obtained in aqueous media, but the highly oxidizing conditions required to generate $[\mathbf{1f}]^{4+}$ make such a measurement difficult.

An analogous calculation can be made by using the electrochemical data reported for the 2*H*-pyrrolium species $[\mathbf{3e}]^{3+}$ and $[\mathbf{3b}]^{2+}$, which differ by a proton on the nitrogen. Taking the pK_a for $[\mathbf{3e}]^{3+}$ as 7.9, and again approximating the III/II reduction potentials for $[\mathbf{3e}]^{3+}$ and $[\mathbf{3b}]^{2+}$ as their anodic peak currents, $[\mathbf{3e}]^{4+}$ is estimated to have a $pK_a \sim -1$, as shown in eq 5.

(5)

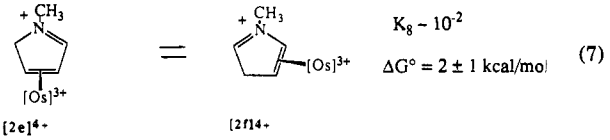
Isomerization Energies. As previously described, the 2*H*-pyrrolium complex derived from 1-methylpyrrole $[\mathbf{2e}]^{3+}$ cannot deprotonate at nitrogen and consequently undergoes deprotonation at the α carbon, C5. The direct product from this deprotonation is the azomethine ylide $[\mathbf{2a'}]^{2+}$, which rapidly undergoes a rearrangement to the pyrrolic form $[\mathbf{2a}]^{2+}$. The equilibrium product ($K_4 = 1.6 \times 10^{-8}$), which describes deprotonation and linkage isomerization, can be used in conjunction with the K_a for the 3*H*-pyrrolium species, $[\mathbf{2e}]^{3+}$, to provide an accurate equilibrium constant and corresponding free energy of isomerization for the 2*H*- to the 3*H*-pyrrolium complex of $\Delta G° = 3.0$ kcal/mol (eq 6).



(6)

As before, an estimate of this isomerization energy for osmium(III) may be obtained if one assumes that the reduction potentials for the osmium(III) species $[\mathbf{2e}]^{4+}$ and $[\mathbf{2f}]^{4+}$ are approximated by the corresponding $E_{p,a}$ values reported in Table I. Using the Nernst equation and the equilibrium constant obtained in eq 6, an equilibrium constant $K_{eq} \sim 10^{-2}$ for the pyrrolium species on osmium(III) is obtained (eq 7).[33]

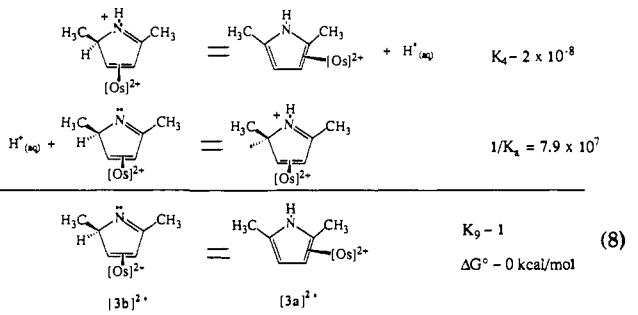
(33) An estimated error of 100 mV in the difference between the formal reduction potentials for $[\mathbf{2e}]^{3+}$ and $[\mathbf{2f}]^{3+}$ would alter K_8 by as much as an order of magnitude.



(7)

Interestingly, the equilibrium between α-protonated (C5) and β-protonated (C4) pyrrolium ion is almost the same as that of the free pyrrole (7.7×10^{-3}), regardless of the oxidation state of the metal. Thus the α-protonated species is still the thermodynamically favored product on osmium(II). This observation suggests that the preference shown by these η^2-pyrrole complexes for electrophilic attack at the β-carbon is purely a kinetic phenomenon: substitution at the α carbon is only possible when preceded by an endothermic linkage isomerization. Such is indeed the case for reactions of $[\mathbf{1a}]^{2+}$–$[\mathbf{3a}]^{2+}$ with various α,β-unsaturated carbonyls:[34] here the predicted Michael additions at the β carbon (C4) are preempted by a dipolar cycloaddition with the azomethine ylide, $[\mathbf{1a'}]^{2+}$–$[\mathbf{3a'}]^{2+}$.[35] Preliminary evidence suggests that these cycloaddition reactions are concerted and not initiated by a conjugate addition at C5 (Figure 9).

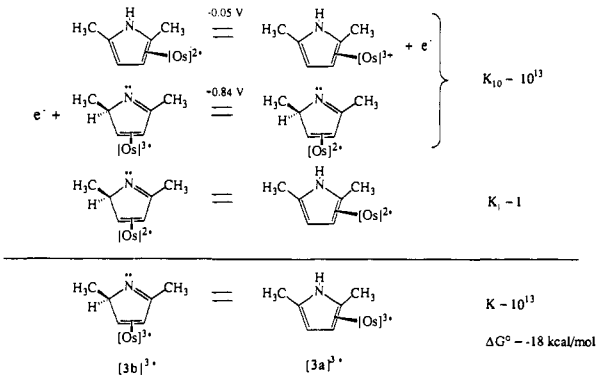
Finally, one can calculate the isomerization energy for the 1*H*-pyrrole and the corresponding 2*H*-pyrrole species $[\mathbf{3a}]^{2+}$ and $[\mathbf{3b}]^{2+}$, by utilizing the pK_a for the 2*H*-pyrrolium species $[\mathbf{3e}]^{3+}$ and an equilibrium product analogous to that produced in eq 3. Since deprotonation of $[\mathbf{3e}]^{3+}$ leaves the α proton (H5) intact, this equilibrium product must be estimated. If one assumes that the equilibrium product derived in eq 3 is unchanged for the 2,5-dimethylpyrrole system, then the equilibrium constant for 1*H*-pyrrole to 2*H*-pyrrole on osmium(II) can be determined to approach unity (eq 8).



(8)

The isomerization energy in eq 8 can also be estimated by combining the 2,5-dimethylpyrrole equilibrium constant K_3 with K_7 of the 1-methylpyrrolium system shown in eq 6. Here the approximation must be made that the latter equilibrium constant is equal to that for the analogous process of the 2,5-dimethylpyrrole system. By combination of these two equilibria, a value of $K_9 = 1 \times 10^{-2}$ is obtained, which corresponds to a $\Delta G \sim 2$ kcal/mol. By either method, the greatest error lies in the assumption that the 3*H*/2*H*-pyrrolium equilibrium determined in eq 7 for the 1-methylpyrrole system is the same as for the 2,5-dimethylpyrrole case, where such a value is not readily obtained. The most significant error in this assumption is most likely the steric repulsion of the C2 methyl group with osmium, which would destabilize the 1*H*-pyrrole isomer $[\mathbf{3b}]^{2+}$. Such an interaction is confirmed by the X-ray structure determination mentioned earlier, though the magnitude of such an interaction is difficult to assess. Our attempts to experimentally measure the 1*H*/2*H*-pyrrole equilibrium (eq 8) were hampered by slow rates of isomerization relative to substitution and oxidation.

In contrast to the pyrrolium tautomers, the neutral ligand types 2,3-η^2-1*H*-pyrrole and 3,4-η^2-2*H*-pyrrole show widely different oxidation potentials for the 2,5-dimethylpyrrole system: the 1*H*-pyrrole has a reduction potential at $\mathcal{E}° \sim E_{1/2} = -0.14$ V, whereas the pyrrolinene tautomer, $[\mathbf{3b}]^{2+}$, gives an anodic peak in its voltammogram at +0.84 V (100 mV/s). If one assumes this to represent an approximate value for $\mathcal{E}°$ for this process, one can derive the 1*H*-pyrrole/2*H*-pyrrole isomerization energy for osmium(III) given the difference in redox potentials (0.70 V) and the equilibrium constant K_9 derived in eq 8 for osmium(II) (eq 9).



(9)

The corresponding (pyrrole → pyrrolenine) isomerization energy has not been experimentally determined, but INDO[36] and MINDO/3[37] calculations put this value at 14 and 19 kcal/mol, respectively (average ~16 kcal). Thus, the trivalent metal is completely ineffective in stabilizing the 2*H*-pyrrole tautomer over the 1*H*-pyrrole form. In contrast, however, the highly π-basic osmium(II) metal center causes a dramatic shift in the pyrrole/pyrrolenine equilibrium, erasing 16 of the estimated 20 kcal of resonance stabilization in the 1*H*-pyrrole.[38] In a related system, we have recently investigated the effect of pentaammineosmium(II/III) on the phenol–dienone equilibrium.[39] In this study we find that osmium(II), which coordinates the arene 2,3-η^2, decreases the phenol → 2,5-cyclohexadienone isomerization energy by about 10 kcal/mol, bringing the two tautomers within 1 kcal of each other. Osmium(III) coordination for this system, as in the present study, has little effect on this equilibrium.

Conclusions

Dihapto-coordination dramatically perturbs the π-electron system in pyrrole, lowering the pyrrole/pyrrolenine isomerization energy ($\Delta G°$) by approximately 16 kcal/mol. The acidities of various pyrrolium species investigated are decreased by 10 orders of magnitude or more upon their coordination to osmium.

In contrast to the free ligand, electrophilic additions occur preferentially at the β carbon. The stereochemistry of the resulting pyrrolium species is controlled by the bulky pentaammineosmium(II) moiety, which eclipses one face of the pyrrole ring and thereby directs attack to the opposite face. Given this powerful combination of chemical activation, chemoselectivity, and stereoselectivity achieved by the dihapto-coordination of pyrrole, such a strategy may ultimately lead to new synthetic methodologies for pyrroles.

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(34) These reactions are currently under investigation in our laboratories.
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