Reactivity of Tetramethylpyrrole Complexes of Ruthenium and Osmium

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Reaction of [(*p*-cymene)M(OTf)$_2$]$_x$ with tetramethylpyrrole leads to the formation of [(*p*-cymene)M(NC$_4$Me$_4$)]OTf, **1** when M = Ru, **2** when M = Os. Complex **1** crystallized in space group $P2_12_12_1$ with unit cell dimensions a = 8.928(2) Å, b = 13.772(4) Å, c = 17.272(6) Å, V = 2123.7(11) Å^3, and Z = 4. The crystal structure establishes that **1** is a sandwich complex with η^6-cymene and η^5-pyrrolyl ligands. Reaction of **1** or **2** with excess methyl triflate results in alkylation of the pyrrole nitrogen to form [(η^6-*p*-cymene)M(η^5-MeNC$_4$Me$_4$)](OTf)$_2$, **3** when M = Ru and **4** when M = Os. Reactions of **1** or **2** with LiAl(O-*t*-Bu)$_3$H result in nucleophilic attack of hydride on the cymene ligand to form (η^5-cymH)M(η^5-NC$_4$Me$_4$), **5** when M = Ru, **6** when M = Os. Complexes **5** and **6** have been identified by one and two dimensional ^{1}H NMR spectroscopy. Nucleophilic attack on the cymene ligand of **1** and **2** appears to be quite general, and the products of methoxide addition, (η^5-cymOMe)M(η^5-NC$_4$Me$_4$), **7** when M = Ru, **8** when M = Os, have also been characterized by ^{1}H NMR data. In contrast, reactions of the pentamethylpyrrole complexes **3** and **4** with nucleophiles lead to nucleophilic addition to the pentamethylpyrrole ligand. For example, the reaction of **3** with LiAl(O-*t*-Bu)$_3$H resulted in the formation of [η^6-*p*-cymene)Ru(η^4-MeNC$_4$Me$_4$H)OTf, **10**, which was characterized by an X-ray diffraction study. **10** crystallized in space group $P2_1/c$ with a = 8.153(2) Å, b = 17.351(2) Å, c = 16.508(2) Å, β = 104.396(13)°, V = 2261.9(7) Å^3, and Z = 4. The structure established that the hydride nucleophile added to an α carbon of the pentamethylpyrrole ligand in an exo orientation. This α carbon lies out of the plane of the remaining four ring atoms with a dihedral angle of 38°. The modified pentamethylpyrrole ligand coordinates to Ru in a η^4-coordination mode. Further reaction of **10** with protic acid leads to further pyrrole reduction and dissociation from the metal. The reactions of the pyrrole systems are compared to those of related [(arene)Ru(thiophene)]$^{n+}$ derivatives.

Introduction

The coordination chemistry of pyrroles has been quite extensively developed.[1] Many examples of transition metal complexes with η^5-pyrrole[2] (HNC_4H_4 or alkylated analogues) or η^5-pyrrolyl ligands[3] ($NC_4H_4^-$ or alkylated analogues) have been reported. These include the sandwich compounds [CpCo(η^5-MeNC$_4$Me$_4$)]$^{2+}$,[2b] [Fe(η^5-MeNC$_4$Me$_4$)$_2$]$^{2+}$,[2c] Cp*Rh(η^5-MeNC$_4$H$_4$)]$^{2+}$,[2d] CpFe(η^5-NC$_4$H$_4$),[3a] Cp*Ru(η^5-NC$_4$Me$_4$),[3b] and Ru(η^5-NC$_4$Me$_4$)$_2$.[3b] Nitrogen-bonded η^1-pyrrolyl complexes have also been characterized for transition metals throughout the periodic table.[4] In addition, examples of dinuclear pyrrolyl complexes with both η^5 and η^1 metal coordination have been reported.[1,3d,g,5] Much rarer types of pyrrole interactions with transition metals that have been observed include the η^2 and η^4 modes of coordination.[6,7] Despite the many types of pyrrole metal

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(1) For recent reviews of pyrrole complexes, see: (a) Kuhn, N. *Bull. Soc. Chem. Belg.* **1990**, *99*, 707. (b) Zakrzewski, J. *Heterocycles* **1990**, *31*, 383. (c) Kerschner, D. L.; Basolo, F. *Coord. Chem. Rev.* **1987**, *78*, 279. (d) Pannell, K. H.; Kalsotra, B. L.; Parkanyi, C. *J. Heterocycl. Chem.* **1978**, *15*, 1057.

(2) (a) Ofele, K.; Dotzauer, E. *J. Organomet. Chem.* **1971**, *30*, 211. (b) Kuhn, N.; Horn, E. M.; Zauder, E.; Blaser, D.; Boese, R. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 579. (c) Kuhn, N.; Horn, E. M.; Boese, K.; Augart, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 342. (d) Fish, R. H.; Baralt, E.; Kim, H.-S. *Organometallics* **1991**, *10*, 1965. (e) Felkin, H.; Zakrzewski, J. *J. Am. Chem. Soc.* **1985**, *107*, 3374.

(3) (a) Joshi, K. K.; Pauson, P. L.; Oazi, A. R.; Stubbs, W. H. *J. Organomet. Chem.* **1964**, *1*, *471*. (b) Kelly, W. J.; Parthun, W. E. *Organometallics* **1992**, *11*, 4348. (c) Zakrzewski, J. *J. Organomet. Chem.* **1987**, *333*, 71; **1987**, *326*, C17; **1987**, *327*, C41. (d) Kuhn, N.; Schulten, M.; Zauder, E.; Augart, N.; Boese, R. *Chem. Ber.* **1989**, *122*, 1891. (e) Kuhn, N.; Kockerling, M.; Stubenrauch, S.; Blaser, D.; Boese, R. *Chem. Commun.* **1991**, 1368. (f) Kuhn, N.; Jendral, K.; Boese, R.; Blaser, D. *Chem. Ber.* **1991**, *124*, 89. (g) Kuhn, N.; Kuhn, A.; Lampe, E. M. *Chem. Ber.* **1991**, *124*, 997. (h) Maitlis, P. M.; White, C. *J. Chem. Soc.* **1971**, 3322. (i) Kerschner, D. L.; Rheingold, A. L.; Basolo, F. *Organometallics* **1987**, *6*, 196. (j) Chase, K. J.; Bryan, R. F.; Woode, M. K.; Grimes, R. N. *Organometallics* **1991**, *10*, 2631. (k) Sodhi, G. S.; Sharma, A. K.; Kaushik, N. K. *J. Organomet. Chem.* **1982**, *238*, 177.

(4) (a) Bynum, R. V.; Zang, H. M.; Hunter, W. E.; Atwood, J. L. *Can. J. Chem.* **1986**, *64*, 1304, and references within (b) Edema, J. J. H.; Gambarotta, S.; Meetama, A.; Van Bolhuis, F.; Spek, A. L.; Smeets, W. J. J. *Inorg. Chem.* **1990**, *29*, 2147. (c) Ladipo, F. T.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 4172. (d) Efraty, A.; Jubran, N.; Goldman, A. *Inorg. Chem.* **1982**, *21*, 868 and references within. (e) Salifoglou, A.; Simopoulos, A.; Kostikas, A.; Dunham, R. W.; Kanatzidis, M. G.; Coucouvanis, D. *Inorg. Chem.* **1988**, *27*, 3394. (f) Kuhn, N.; Henkel, G.; Kreutzberg, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1143. (g) Carmona, E.; Marin, J. M.; Palma, P.; Paneque, M.; Poveda, M. L. *Inorg. Chem.* **1989**, *28*, 1895. (h) Bradley, D. C.; Chivers, K. J. *J. Chem. Soc. A* **1968**, 1967. (i) Minken, V. I.; Osipov, O. A.; Verkovadova, D. *Russ. J. Inorg. Chem.* **1966**, *11*, 2829.

(5) (a) Pyshnograeva, N. I.; Setkina, V. N.; Andrianov, V. G.; Struchkov, Y. T.; Kursanov, D. N. *J. Organomet. Chem.* **1980**, *186*, 337; **1978**, *157*, 431. (b) Pyshnograeva, N. I.; Batsanov, A. S.; Struchkov, Y. T.; Ginsberg, A. G.; Setkina, V. N. *J. Organomet. Chem.* **1985**, *297*, 69. (c) Reagen, W. K.; Radonovich, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 3881; **1987**, *109*, 2193. (d) Kuhn, N.; Horn, E. M.; Boese, R.; Blaser, D. *Chem. Ber.* **1989**, *122*, 2275. (e) Losilkina, N. I.; Pyshnograeva, N. K.; Baranetskaya, N. K.; Setkina, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 2780.

(6) (a) Cordone, R.; Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 5969. (b) Myers, W. H.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1991**, *113*, 6682. (c) Myers, W. H.; Koontz, J. I.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 5684.

(7) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719.

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complexes, the effect of metal coordination on the reactivity of the pyrrole ligand has not been studied very extensively or systematically.[1b,2e,6] An understanding of how coordinated pyrrole ligands might be activated toward reduction, ring opening, or nucleophilic addition reactions may provide a basis for understanding fundamental mechanistic features of the hydrodenitrogenation catalysts.

Current hydrotreating catalysts based on sulfided molybdenum surfaces permit the removal of nitrogen from both five- and six-membered nitrogen-containing heterocycles, but molybdenum-based catalysts may not be the optimum systems for HDN.[8] A combination of hydrogenation and hydrogenolysis steps has been proposed which ultimately produce ammonia and hydrocarbons.[9,10] The chemistry of the pyrrole derivatives differs significantly from that of pyridines because of the involvement of the nitrogen lone pair in the delocalized π electron density of the five-membered ring. The nonbasic character of the neutral pyrrole ligand suggests that its interaction with the catalyst surface and mechanism for reduction will make use of different catalyst sites and properties than reduction of pyridine and quinoline derivatives.

The tendency of Ru(II) and Os(II) to form stable π-bonded sandwich complexes with aromatic ligands has prompted a study of pyrrole complexes of these metals. The syntheses and reactions of new tetramethylpyrrole derivatives of *p*-cymene-Ru(II) and *p*-cymene–Os(II) are reported here. Our studies have demonstrated that the site of nucleophilic addition in these complexes can be varied and controlled by substitution at the nitrogen atom of the heterocycle.

Results and Discussion

Synthesis of [(η^6-*p*-cymene)M(NC_4Me_4)]OTf (1, M = Ru; 2, M = Os). The reaction of 2,3,4,5-tetramethylpyrrole with [(*p*-cymene)Ru(OSO_2CF_3)$_2$]$_x$ proceeded at room temperature to form a complex with a deprotonated Me_4–pyrrole ligand, [(η^6-*p*-cymene)Ru(η^5-NC_4Me_4)]OTf, 1. Complex 1 was characterized by elemental analyses and ^{1}H and ^{13}C NMR and mass spectroscopy. The data were consistent with a mononuclear product with two π-bonded ligands. Characteristics of the ^{1}H NMR spectrum included two multiplets for the cymene ring protons at 6.06 and 5.99 ppm and two singlets for the pyrrole methyls at 2.19 and 1.97 ppm. Resonances for the cymene substituents were also observed as expected. Complex 1 in acetonitrile solution underwent an irreversible reduction at a platinum electrode at −2.3 V vs the Fc/Fc$^+$ couple (Fc = ferrocene). The reduced product appeared to undergo a rapid chemical reaction even at high scan rates (1000 mV/s). This new reduced product showed a small irreversible oxidation wave at −0.49 V.

[(*p*-cymene)Os(Cl)$_2$]$_2$ was reacted with 4 equiv of AgOTF and tetramethylpyrrole to form the osmium analogue of 1, [(η^6-*p*-cymene)Os(η^5-NC_4Me_4)]OTf, 2. Spectroscopic data for 2 are similar to those identified for 1 and are reported in the Experimental Section. Complex 2 also underwent an irreversible reduction at −2.6 V vs Fc.

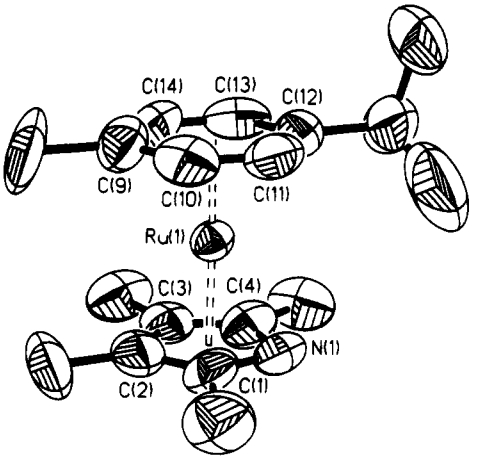


Figure 1. Molecular structure of the cation of [(η^6-*p*-cymene)Ru(η^5-NC_4Me_4)]OTF, 1. Thermal ellipsoids are shown at the 50% probability level.

Table 1. Selected Bond Distances (Å) for [(*p*-cym)Ru(NC_4Me_4)]OTF, 1

Ru(1)–N(1)	2.149(11)	Ru(1)–C(1)	2.115(13)
Ru(1)–C(2)	2.210(16)	Ru(1)–C(3)	2.222(14)
Ru(1)–C(4)	2.131(13)	Ru(1)–C(9)	2.225(16)
N(1)–C(4)	1.357(19)	N(1)–C(1)	1.367(18)
C(1)–C(2)	1.401(23)	C(1)–C(5)	1.468(27)
C(2)–C(3)	1.449(21)	C(3)–C(4)	1.400(24)

The sandwich structure of 1, as well as the deprotonated nature of the pyrrole ligand, were confirmed by an X-ray diffraction study. A perspective drawing of the cation with numbering scheme is shown in Figure 1, and selected bond distances and angles are presented in Table 1. Although the triflate anion in the structure was disordered, the structure of the cation was readily solved. The two planar aromatic ligands in the complex are approximately parallel. The angle between the ruthenium atom and centroid of each ring is 177.7°. The distance between the ruthenium ion and the centroid of the *p*-cymene ligand is 1.698 Å. This value is within the range determined for several other ruthenium–arene ring distances, which average 1.678 Å.[11] The distances between ruthenium and each ring atom in the tetramethylpyrrolyl ligand indicate a slight shift of the ring centroid, with shorter metal distances to C(1), C(4), and N than to C(2) and C(3). Similar shifts have been noted in previous structural studies of metal–η^5-pyrrole complexes.[1f,12] The distance between the metal ion and the pyrrole ring centroid is 1.812 Å.

Reactions of 1 and 2 with Electrophiles. The pyrrolyl ligand in 1 was protonated with excess triflic acid, and the resulting product, [(*p*-cymene)Ru(HNC_5Me_4)](OTf)$_2$, was identified by ^{1}H and ^{13}C NMR and mass spectroscopy. However, this dication was deprotonated on acidic and neutral alumina columns and was not isolated in pure form. Attempted recrystallization of the complex from methanol, for example, also resulted in deprotonation. The η^5-coordination of tetramethylpyrrole to ruthenium(II) significantly diminishes the basicity of the deprotonated heterocycle. A similar effect has been observed for [CpFe(NC_4Me_4)], where the pK_b of the coordinated pyrrolyl ligand was reported to be 6.8 in aqueous solution.[3d]

(8) Ho, T. C. *Catal. Rev.-Sci. Eng.* **1988**, *30*, 117.
(9) (a) Satterfield, C. N.; Yang, S. H. *Ind. Eng. Chem. Process Des. Dev.* **1984**, *23*, 11. (b) Eijsbouts, S.; de Beer, V. H. J.; Prins, R. *J. Catal.* **1990**, *127*, 619. (c) Massoth, F. E.; Balusami, K.; Shabtai, J. *J. Catal.* **1990**, *122*, 256.
(10) (a) Olive, J. L.; Biyoko, S.; Moulinas, C.; Geneste, P. *Appl. Catal.* **1985**, *19*, 165. (b) Odebunmi, E. O.; Ollis, D. F. *J. Catal.* **1983**, *80*, 76.
(11) McCormick, G. B.; Cox, D. D.; Gleason, W. B. *Organometallics* **1993**, *12*, 610 and references within.
(12) Kershner, K. L.; Rheingold, A. C.; Basolo, F. *Organometallics* **1987**, *6*, 196.

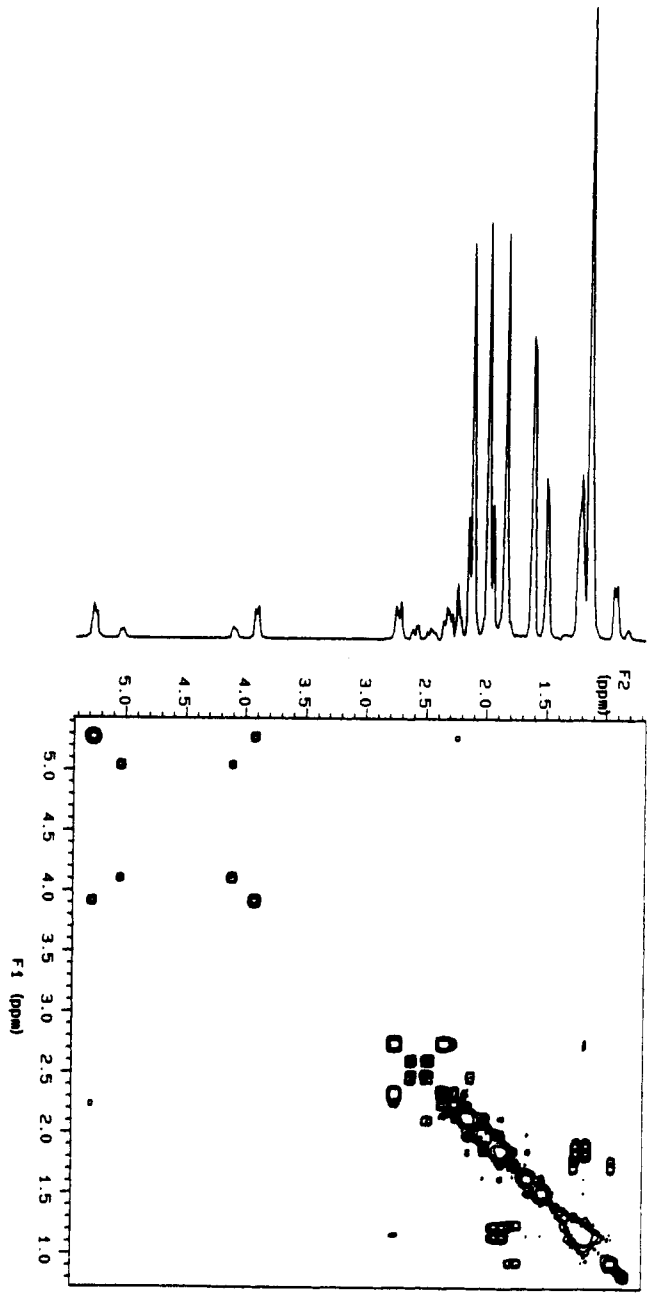
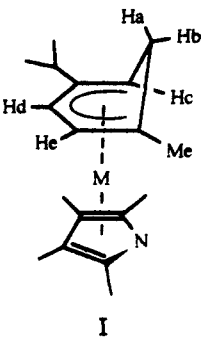


Figure 2. One dimensional and two dimensional ^1H NMR spectra of (η^5-*p*-cymH)Ru(η^5-NC_4Me_4), **5**, in $CDCl_3$. See Table 2 for chemical shift assignments.

The reaction of the ruthenium or osmium complex [(η^6-*p*-cymene)M(η^5-NC_4Me_4)]OTf, **1** or **2**, with excess methyl triflate proceeded slowly to form a new product which was formulated as [(η^6-*p*-cymene)M(η^5-$MeNC_4Me_4$)]$(OTf)_2$, **3**, M = Ru, or **4**, M = Os. The complexes were isolated as white crystalline products and characterized by elemental analyses and by spectroscopic data. The ^1H NMR spectrum suggested that the structure of **3** was similar to that of **1**. The cymene ring protons were assigned to two doublets at 6.37 and 6.32 ppm, and the resonances for the pyrrole methyls were observed as two singlets at 2.47 and 2.10 ppm. A new singlet resonance at 3.54 ppm was assigned to the methyl group on the pyrrole nitrogen. The osmium complex **4** displayed similar spectroscopic characteristics. Cyclic voltammetry of the dicationic complexes **3** and **4** in acetonitrile solution at a platinum electrode showed a quasi-reversible (ΔE_p = 224 mV) reduction wave at −1.24 V vs Fc for each complex, suggesting that the reduction may be ligand-based.

Reactions of [(η^6-*p*-cymene)M(η^5-NC_4Me_4)]OTf, 1 and 2, with Nucleophiles. We have studied the reactions of **1** and **2** with hydride reagents. Nucleophilic addition of hydride to η^6-arene ligands has been well established for many transition metal complexes.[13,14] In most cases these reactions proceed to give the exo addition product. We found that the reaction of 1 equiv of lithium tris(*tert*-butoxide)-aluminum hydride with **1** proceeded in THF to form a new product which was isolated by extraction with pentane and solvent evaporation. The oily, noncrystalline product was identified by ^1H NMR spectroscopy. The ^1H NMR spectrum of this product indicated that the complex no longer contained a molecular plane of symmetry. Four methyl singlets of equal intensity associated with the tetramethylpyrrole ligand were observed at 1.6–2.0 ppm. A fifth methyl singlet was assigned to the cymene methyl group, and two doublets were observed for diastereotopic methyls in the isopropyl group on the cymene ligand. A significant feature of the spectrum was the set of five multiplets (each integating for one hydrogen) with shifts upfield of the aromatic region at 5.27, 3.92, 2.75, 2.34, and 2.25 ppm. On the basis of these data the product was assigned a structure in which hydride addition to the *p*-cymene ring has occurred, (η^5-cymH)-Ru(η^5-NC_4Me_4), **5**. Reaction of **1** with $LiB(Et)_3D$ formed the deutero analogue of **5**. The absence of a multiplet at 2.75 ppm in the ^1H NMR spectrum of the deuterated product led to assignment of this resonance to the external hydride substituent, Ha, structure I.



I

The two dimensional ^1H NMR spectrum of **5** (see Figure 2) showed strong geminal coupling between Ha and Hb (J = 12 Hz) and vicinal coupling between Hb and Hc (J = 6 Hz), with only very weak vicinal coupling between Ha and Hc. The spectrum also identified weak coupling of Ha with the cymene methyl. These data enabled us to assign the position of hydride attack on the cymene ring as ortho to the methyl group and in an axial or exo orientation. Complete chemical shift assignments for **5** are summarized in Table 2. The position of hydride attack was supported by infrared data which showed a strong absorption assigned to the C–H_{exo} stretch at 2774 cm^{-1}.[15] This band shifted to 2052 cm^{-1} in the spectrum of the deuterated analogue.

(13) (a) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, 525. (b) Moriarty, R. M.; Gill, U. S.; Ku, Y, Y. *J. Organomet. Chem.* **1988**, *350*, 157.

(14) (a) Snyder, D. B.; Schauer, S. J.; Eyman, D. P.; Moler, J. L.; Weers, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 6718. (b) Djukir, J. P.; Rose-Munch, F.; Rose, E.; Dromzee, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6434.

(15) Robertson, I. W.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1982**, *228*, 171.

Table 2. 300-MHz ^{1}H NMR Data for Ruthenium and Osmium Complexes

complex (solvent)	*p*-cymene H's	*p*-cymene isopropyl	*p*-cymene Me	NC_4Me_4 Me	other
[(*p*-cym)Ru(NC_4Me_4)]OTf, **1** ($CDCl_3$)	6.07 (m), 5.99 (m)	2.67 (sept), 1.29 (d)	2.22 (s)	2.20 (s), 2.01 (s)	
[(*p*-cym)Os(NC_4Me_4)]OTf, **2** ($CDCl_3$)	6.16 (m)	2.58 (sept), 1.29 (d)	2.27 (s)	2.35 (s), 2.11 (s)	
[(*p*-cym)Ru($MeNC_4Me_4$)]$(OTf)_2$, **3** (CD_3CN)	6.34 (m)	2.86 (sept), 1.28 (d)	2.32 (s)	2.47 (s), 2.10 (s)	3.54 (s, NMe)
[(*p*-cym)Os($MeNC_4Me_4$)]$(OTf)_2$, **4** (CD_3CN)	6.52 (m)	2.78 (sept), 1.28 (d)	2.37 (s)	2.56 (s), 2.22 (s)	3.59 (s, NMe)
[(η^5-p-cym-H)Ru(NC_4Me_4)], **5**, major isomer (C_6D_6)	5.27 (m, Hd)[a] (J_{d-e} = 5 Hz), 3.92 (m, He), 2.75 (m, Ha) (J_{a-b} = 12 Hz), 2.34 (m, Hb), 2.25 (m, Hc) (J_{b-c} = 6 Hz)	1.88 (sept), 1.23 (d), 1.15 (d)	1.17 (s)	2.13 (s), 2.01 (s), 1.86 (s), 1.63 (s)	
minor isomer (C_6D_6)	5.03 (m, Hd)[a] (J_{d-e} = 5 Hz), 4.10 (m, He), 2.61 (m, Ha) (J_{a-b} = 12 Hz), 2.47 (m, Hb), 2.11 (m, Hc) (J_{b-c} = 6 Hz)	1.75 (sept), 1.25 (d), 0.94 (d)	1.51 (s)	2.16 (s), 1.97 (s), 1.65 (s), 1.52 (s)	
(η^5-*p*-cym-H)Os(NC_4Me_4), **6**, major isomer (C_6D_6)	5.66 (m, Hd)[a] (Jd–e = 5 Hz), 4.56 (m, Ha) (J_{a-b} = 11 Hz), 4.17 (m, He), 2.70 (m, Hb), 2.42 (m, Hc) (J_{b-c} = 6 Hz)	1.86 (sept), 1.20 (m)	1.07 (s)	2.31 (s), 2.11 (s), 1.86 (s), 1.72 (s)	
minor isomer (C_6D_6)	5.48 (m, Hd)[a] (J_{d-e} = 5 Hz), 4.36 (m, Ha), 4.35 (m, He), 2.5 (m, H_bH_c)	1.52 (sept), 1.17 (d), 0.96 (d)	1.52 (s)	2.31 (s), 2.10 (s), 1.76 (s), 1.64 (s)	
[(η^5-*p*-cym-OMe)Ru(NC_4Me_4)], **7** ($CDCl_3$)	5.29 (d, Hc), 4.37 (d, Hd) (J_{c-d} = 6 Hz), 3.34 (d, Ha), 2.76 (d, Hb), (J_{a-b} = 6 Hz)	1.92 (sept), 1.14 (app trip)	1.63 (s)[a]	2.06 (s), 2.02 (s), 1.90 (s), 1.89 (s)	3.44 (s, OMe)
[(η^5*p*-cym-OMe)Os(NC_4Me_4)], **8** ($CDCl_3$)	5.73 (d), 4.51 (d), 3.27 (d), 3.13 (d)	1.85 (sept), 1.17 (d), 1.13 (d)	1.48 (s)[a]	2.24 (s), 2.15 (s), 2.00 (s), 1.94 (s)	3.46 (s, OMe)
[(*p*-cym)Ru($MeNC_4Me_4$-OMe)]OTf, **9** (CD_3CN)	5.60 (d), 5.53 (d), 5.46 (d), 5.35 (d)	2.62 (sept), 1.23 (d), 1.25 (d)	2.17[b] (s)	2.44 (s),[b] 2.26 (s), 1.71 (s), 1.52 (s)	2.79 (s, OMe), 1.89[b] (s, NMe)
[(*p*-cym)Ru($MeNC_4Me_4$-OH)]OTf ($CDCl_3$)	5.26 (m), 5.06 (m)	2.46 (sept), 1.19 (d)	1.44 (s)	2.16 (s), 2.10 (s), 1.76 (s), 1.49 (s)	2.35 (s, NMe), 1.37 (s, OH)
[(*p*-cym)Ru(η^4-$MeNC_4Me_4$-H)]OTf, **10** ($CDCl_3$)	5.59 (m), 5.43 (m), 5.34 (m), 5.29 (m)	2.53 (sept), 1.20 (d), 1.19 (d)	2.17 (s)[a]	2.41 (s),[a] 2.24 (s), 1.42 (d), 1.29 (s)	1.91 (s, NMe),[a] 4.07 (q, H on PMP)
[(*p*-cym)Os(η^4-$MeNC_4Me_4$-H)]OTf, **11** ($CDCl_3$)	5.68 (m), 5.49 (m), 5.47 (m), 5.40 (m)	2.52 (sept), 1.23 (m)	2.31 (s)[a]	2.51 (s), 2.36 (s), 1.40 (d), 1.28 (s)	2.05 (s, NMe),[a] 5.63 (q, H on PMP)

[a] Assignments based on COSY experiments. [b] Tentative assignments based on comparison with **10**.

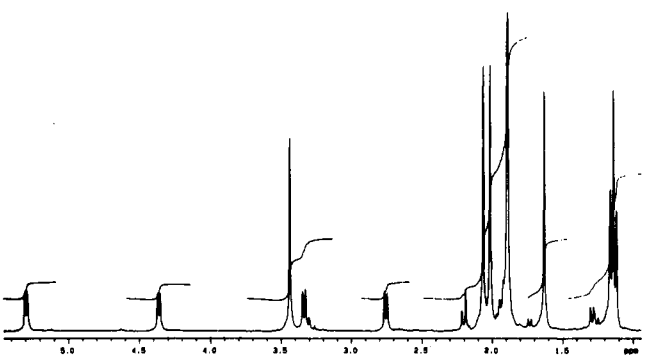
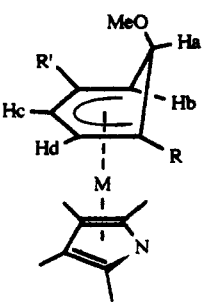


Figure 3. 300-MHz ^{1}H NMR spectrum of [(η^5-*p*-cymOMe)-Ru(η^5-NC_4Me_4)], **7**, in $CDCl_3$. See Table 2 for chemical shift assignments.

The NMR data for a second minor isomer of **5**, which was detected in ca. 30% yield, are also included in Table 2. The data for the minor isomer are consistent with hydride addition at a cymene ring carbon ortho to the isopropyl group. This mixture of isomers may be a factor in our difficulties in obtaining **5** in crystalline form. Attempts to alter the ratio of isomers by changing the steric bulk of the hydride reagent (NaH, $NaBH_4$) were unsuccessful.

The reactivity of **1** with other nucleophiles followed a similar pathway. For example, the reaction of **1** with excess methoxide ion proceeded cleanly at room temperature to form a new product, in which methoxide has added to the cymene ring, (η^5-*p*-cymOMe)Ru(η^5-NC_4Me_4), **7**. The NMR spectrum of **7** (Figure 3) again featured upfield shifts for the resonances of the hydrogens in the *p*-cymene ligand as well as a singlet at 3.4 ppm assigned to coordinated methoxide. The mutually coupled upfield doublets at 3.34 and 2.76 ppm are assigned to Ha and Hb, respectively, in structure II. The two lower field doublets at 5.29 and 4.37



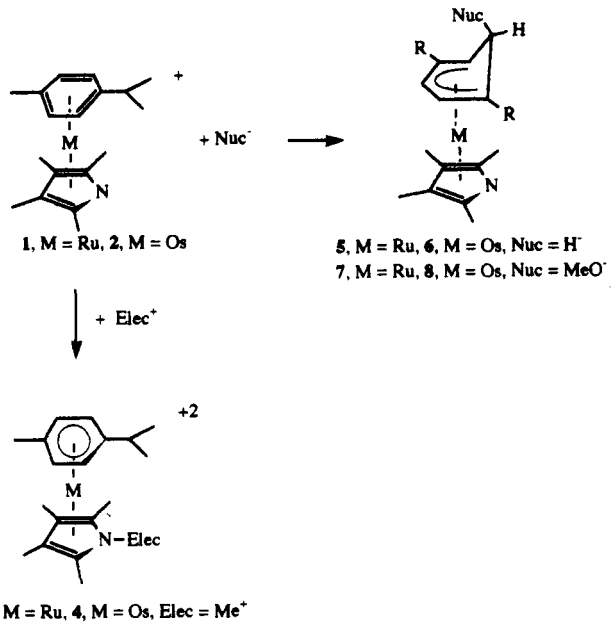
II
R, R' = Me or *i*-Pr

ppm are also coupled and are assigned to Hc and Hd, respectively. The ^{13}C NMR spectrum and DEPT experiments are also consistent with the type of isomer shown. In particular a methine carbon at 32.4 ppm and a quaternary carbon at 45.4 ppm are assigned to the hinge positions of the nonplanar ring, while two methine carbons at 81.6 and 77.0 ppm and a quaternary carbon at 94.1 ppm are assigned to the dienyl portion of the ring. A methine carbon at 63.8 ppm has a characteristic shift for a carbon adjacent to an ether oxygen[16] and is attributed to the out-of-plane ring carbon. A more complete listing of the ^{13}C NMR data is given in the Experimental Section. The absence of a strong C–H_{exo} stretch in the infrared spectrum of **7** is consistent with the structure shown in which methoxide ion has added in an exo position.

The reactions reported here are closely related to nucleophilic additions to [(arene)Ru(Cp)]$^+$ derivatives,

(16) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981; p 249.

Scheme 1



1, M = Ru, 2, M = Os

5, M = Ru, 6, M = Os, Nuc = H⁻
7, M = Ru, 8, M = Os, Nuc = MeO⁻

3, M = Ru, 4, M = Os, Elec = Me⁺

which result in neutral Ru(II) products with η^5-cyclohexadienyl ligands.[13b,17] A comparison of the Cp and TMP (tetramethylpyrrolyl) complexes points out the electronic similarity between these two anionic ligands, which behave as unreactive six electron donors in these nucleophilic addition reactions.

The osmium complex [(η^6-*p*-cymene)Os(η^5-NC_4Me_4)]-OTf, **2**, also underwent nucleophilic addition at the cymene ring, and the products (η^5-*p*-cym-X)Os(η^5-NC_4Me_4), where X = H, **6**, and OMe, **8**, have been characterized by spectroscopic data. Two isomers were observed for **6**, and the ^{1}H NMR data (Table 2) were similar to those discussed above for the ruthenium analogues. The resonance of Ha in **6** at 4.65 ppm is shifted downfield relative to that of Ha in the ruthenium analogue (2.75 ppm). Similar downfield shifts of η^5-cyclohexadienyl resonances for third row vs second row metal complexes have been observed previously.[18] This may be related to the increased basicity of the third row metal ions.[19] The reactions of **1** and **2** with electrophiles and nucleophiles are summarized in Scheme 1.

Reactions of [(η^6-*p*-cymene)M(η^5-$MeNC_4Me_4$)](OTf)$_2$, 3 and 4, with Nucleophiles. Reactions of the dicationic pentamethylpyrrole complexes of ruthenium and osmium have been compared with those of the tetramethylpyrrole derivatives described above. While the reactions of **1** and **2** with nucleophiles led to an addition to and distortion of the arene ring, the reactions of the dications appear to follow a different pathway. The reaction of **3** with excess methoxide, for example, proceeded cleanly to form a single new product, **9**, which was isolated by solvent removal and extraction with chloroform. The ^{1}H NMR spectrum of **9** in CD_3CN was again characteristic of a product of low symmetry. Four multiplets observed at 5.60, 5.53, 5.46, and 5.35 ppm were attributed to inequivalent ring hydrogens in the cymene ligand. Seven methyl singlets of equal intensity were observed between

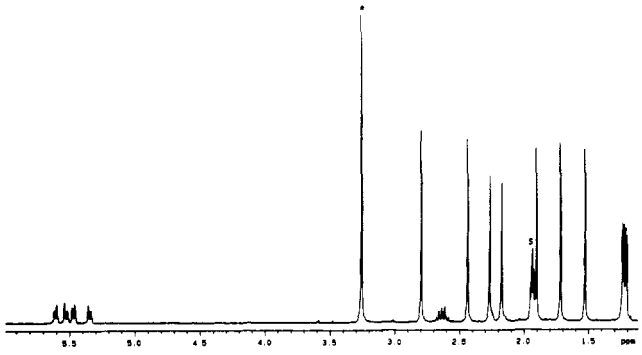


Figure 4. 300-MHz ^{1}H NMR spectrum of [(η^6-*p*-cymene)-Ru(η^4-$MeNC_4Me_4OMe$)OTF, **9**, in CD_3CN. The resonance at 3.25 ppm is assigned to excess methoxide ion. See Table 2 for other chemical shift assignments.

2.8 and 1.5 ppm (see Figure 4). The singlets correspond to five inequivalent pyrrole methyls, to the cymene methyl, and to a methoxide ligand incorporated into the product. Two doublets near 1.2 ppm were assigned to diastereotopic methyls of the isopropyl substituent. The assignment of the resonance at 2.79 ppm to a coordinated methoxide group was confirmed by the disappearance of this singlet when the reaction was carried out with $NaOCD_3$ in CD_3OD. Two other singlets in this spectral region (at 2.34 and 1.77 ppm) underwent slow deuterium incorporation in the basic methanol-d_4, and these are tentatively assigned to the methyls α to the pyrrole nitrogen.

The chemical shifts of the cymene hydrogens of **9** are much less perturbed than those observed for **5** and **7**, in which nucleophilic attack on the cymene ring occurred. The spectroscopic data for **9** seem most consistent with a structure in which nucleophilic addition of methoxide to the pentamethylpyrrole ligand has occurred, and **9** is formulated as [(η^6-*p*-cymene)Ru(η^4-$MeNC_4Me_4$-OMe)]-OTf. Although free pyrrole does not undergo nucleophilic substitution or addition reactions, one previous example of nucleophilic addition to an η^5-pyrrole ligand has been reported for the complex [(η^5-$MeNC_4H_4$)Re(H)$_2$(PR_3)$_2$]$^+$.[2e] Spectroscopic data on the hydride addition product in this ruthenium system led to the assignment of exo hydride addition to an α carbon in the heterocycle.

The reaction of **3** with aqueous potassium hydroxide in THF also led to nucleophilic attack on the pentamethylpyrrole ligand. The product was isolated and identified by spectroscopic data as [(η^6-*p*-cymene)Ru(η^4-$MeNC_4Me_4$-OH)OTF (see Experimental Section). This product appeared to be thermally unstable, and loss of the heterocyclic ligand was observed after mild heating in solution. Although the dissociated ligand was not isolated in pure form, its NMR spectrum showed the symmetry of unsubstituted pentamethylpyrrole.

In order to observe proton–proton coupling in the NMR spectrum and thereby obtain more detailed structural information on the modified pyrrole ligand that results from nucleophilic attack, complex **3** was reacted with LiAl(O-*t*-Bu)$_3$H. The reaction appeared to follow the same pathway as was observed for the reactions of **3** with methoxide and hydroxide ions. The product was isolated and purified by column chromatography and assigned a structure in which nucleophilic hydride addition to the pentamethylpyrrole ligand has occurred to give [(η^6-*p*-cymene)Ru(η^4-$MeNC_4Me_4H$)]OTf, **10**. The ^{1}H NMR spectrum of the product was consistent with this formulation; data are given in Table 2. In particular, a methyl

(17) Volkenau, A.; Bolesova, I. N.; Shulpina, L. S.; Kitaigorodski, A. N. *J. Organomet. Chem.* **1984**, *267*, 318.
(18) Grundy, S. L.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1747.
(19) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267.

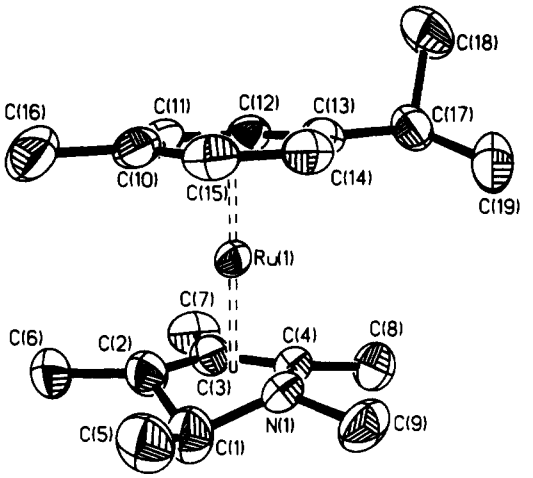
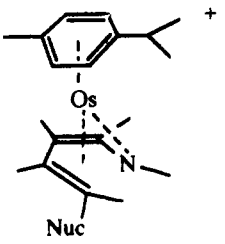


Figure 5. Molecular structure of the cation of [(η^6-*p*-cymene)Ru(η^4-MeNC$_4$Me$_4$H)]OTF, **10**. Thermal ellipsoids are shown at the 50% probability level.

doublet at 1.4 ppm is assigned to a pyrrole methyl split by hydride addition to the ring. The hydrogen on the modified pentamethylpyrrole ligand is observed as a quartet at 4.18 ppm. ^{1}H NMR COSY experiments led to the conclusion that hydride attack has occurred on the carbon α to the pyrrole nitrogen.

The reaction of [(η^6-*p*-cymene)Os(η^5-MeNC$_4$Me$_4$)](OTf)$_2$, **4**, with the same hydride reagent led to the formation of an analogous product [(η^6-*p*-cymene)Os(η^4-MeNC$_4$Me$_4$H)]OTf, **11**. The ^{1}H NMR spectrum of **11** is similar in its features to that of **10**, but the quartet resonance of the added hydride nucleophile is shifted downfield to 5.6 ppm. A similar downfield shift of the hydride nucleophile in the Os complex, relative to the Ru analogue, was discussed above for the cymene addition reaction. The chemical shift of 5.6 ppm could suggest a vinylic hydrogen in an opened ring structure such as III.



III

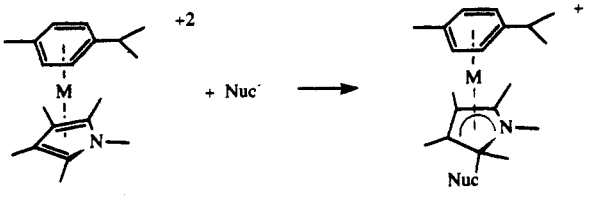
However, the similarity in the ^{13}C chemical shifts of the carbon atom of the pyrrole ring which has added the hydride (determined by C–H coupling) in **10** (81.9 ppm) and **11** (85.6 ppm) suggests that the Ru and Os structures are in fact identical ones which involve an intact, but nonplanar, heterocycle (vide infra).

X-Ray Diffraction Study of 10. In order to establish the stereochemistry of hydride addition in **10** and to determine whether the addition resulted in ring opening, an X-ray diffraction study was carried out. The structure has verified that **10** is composed of discrete mononuclear cations with an η^6-cymene ligand and a cyclic [η^4-MeNC$_4$Me$_4$H]$^-$ ligand. A perspective drawing of the cation of **10** with the numbering scheme is shown in Figure 5. Selected bond distances and angles are given in Table 3. Although the hydride nucleophile was not located directly, it is clear from the distortion of the heterocyclic ligand that the

Table 3. Selected Bond Distances (Å) for [(η^6-*p*-cym)Ru(η^4-MeNC$_4$Me$_4$-H)](OTf), 10

Ru(1)–N(1)	2.112(3)	Ru(1)–C(2)	2.207(3)
Ru(1)–C(3)	2.175(3)	Ru(1)–C(4)	2.106(3)
Ru(1)–C(10)	2.268(4)	N(1)–C(1)	1.502(5)
C(1)–C(2)	1.508(5)	C(2)–C(3)	1.427(3)
C(3)–C(4)	1.420(4)	C(4)–N(1)	1.420(4)
C(1)–C(5)	1.528(7)		

Scheme 2



3, M = Ru, **4**, M = Os

9, M = Ru, Nuc = MeO$^-$
10, M = Ru, Nuc = H$^-$
11, M = Os, Nuc = H$^-$

hydride anion has added to an α carbon of the pyrrole ring in the exo position. Carbon 1 is tetrahedral, and is bent out of the plane of the ring. A rotational disorder of the heterocycle was suggested by the observation of a difference peak in the plane of the ring above C1. As a result of the disorder, C_1 was refined with an occupancy of 0.75 (see Experimental Section). The remaining four atoms of the ring lie in a plane.[20] The plane of N–Cl–C2 intersects that of the ring with a dihedral angle of 37.8°. The Ru–C(2), –C(3), –C(4) and Ru–N distances are similar within experimental error to those in [(C^6-cymene)Ru(η^5-NC$_4$Me$_4$)]OTf, **1**, discussed above. The similarity in spectroscopic data for the products of hydride addition and methoxide addition to **3** leads us to propose analogous structures for **9** and **10**. These reactions are summarized in Scheme 2.

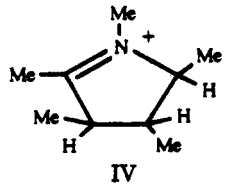
Reactivity of [(η^6-*p*-cymene)M(η^4-MeNC$_4$Me$_4$H)]OTf. Further reactivity of the modified pyrrole ligand in complexes **10** and **11** was investigated. We wished to determine whether a stepwise reduction of the ring could be effected. Such a process might lead to the identification of novel modified ring complexes of lower hapticity. Alternatively, partial displacement of the η^4-ligand by other donor ligands might lead to further reduction or ring opening reactions of the coordinated heterocycle.

No reaction was observed when **10** was reacted with 5 equiv of MeI for 10 h, or with excess trimethylphosphine in refluxing acetonitrile for 15 h. Similarly, carbon monoxide failed to displace the methoxide-modified η^4-pentamethylpyrrole ligand in **9**. The very stable η^4-ligand in **10** was, however, reactive toward protic acid. For example, the reaction of **10** with 1 equiv triflic acid in acetonitrile for 24 h proceeded to give a mixture of ruthenium complexes which were identified as [(η^6-*p*-cymene)Ru(η^5-MeNC$_4$Me$_4$)](OTf)$_2$, **3**, [(η^6-*p*-cymene)Ru(CH$_3$CN)$_3$](OTf)$_2$, and starting reagent **10** in a ratio of 1:2:2. No evidence was observed for a new ruthenium complex containing a reduced pyrrole ligand. A similar reaction of **10** was observed for an acid with a potential coordinating anion, HCl, in CH_2Cl_2. In this case, [(*p*-cymene)RuCl$_2$]$_2$[21] was observed in addition to **3** and **10**.

(20) The least squares plane for these atoms is $7.284x + 7.796y + 3.674z - 3.1086 = 0$, with a mean deviation of 0.0042 Å.

(21) Bennett, M. A.; Smith, A. K. *J. Chem. Soc. Dalton Trans.* **1974**, *233*.

The protonated ligand which was displaced in the formation of the acetonitrile or chloride complex was isolated by chromatography from a reaction of **10** with excess triflic acid. The spectroscopic data for the displaced ligand suggest structure IV. In particular, three methyl



IV

doublets and two singlets in the ^{1}H NMR spectrum confirm the reduced nature of the heterocycle. A single low field resonance for a quaternary carbon in the ^{13}C spectrum (193 ppm) is consistent with the iminum structure. An infrared band at 1676 cm^{-1} was assigned as a C=N stretch.

Similar reactions were studied with the osmium analogue ([η^6-*p*-cymene)Os(η^4-MeNC$_4$Me$_4$H)]OTf, **11**, and HCl to determine whether a greater kinetic stability of the osmium complex might permit identification of intermediate Os products with partially reduced heterocyclic ligands. However we again observed displacement of the heterocycle as [MeNC$_4$Me$_4$H$_3$]$^+$, IV, and formation of [(*p*-cymene)OsCl$_2$]$_2$.[22]

Conclusions. Tetramethylpyrrolyl and pentamethylpyrrole form stable η^5-sandwich complexes with arene–ruthenium and arene–osmium fragments. The complexes of the two metals appear to be analogous in both structure and reactivity. Nucleophiles add to the *p*-cymene ligand in [(η^6-*p*-cymene)M(η^5-NC$_4$Me$_4$)]OTf, **1** or **2**, to form a product with an anionic [η^5-cymNuc]$^-$ ligand. The site of hydride addition was established by COSY ^{1}H NMR spectroscopy.

Methylation of the nitrogen heteroatom of the coordinated tetramethylpyrrolyl ligand has led to the formation of complexes [(η^6-cymene)M(η^5-MeNC$_4$Me$_4$)](OTf)$_2$, **3** and **4**. Alkylation of the tetramethylpyrrolyl ligand alters the site of nucleophilic attack in these complexes compared to the pyrrolyl derivatives discussed above. Reactions of **3** and **4** with methoxide or hydride nucleophiles result in nucleophilic addition to the coordinated nitrogen heterocycle. An X-ray diffraction study has confirmed that hydride addition occurs in an exo position on an α carbon atom of the ring. Further reactions of [(η^6-*p*-cymene)M(η^4-MeNC$_4$Me$_4$H)]OTf, **10** and **11**, with protic acids result in the dissociation of a reduced heterocycle.

In mechanistic studies of hydrodenitrogenation reactions of nitrogen heterocycles on heterogeneous catalysts, the general pattern of ring hydrogenation prior to ring opening has been indicated.[9,10] The synthetic complexes studied here appear to follow the same pattern. No evidence for ring opening of the unsaturated heterocycle has been observed in the reactions discussed here. This characteristic of the tetramethylpyrrole derivatives shows a marked contrast to related ruthenium thiophene complexes, which have been studied extensively. For example, reaction of the ruthenium(II) complex [(Cp)Ru(SC$_4$H$_4$)]$^+$ with hydride ion resulted in cleavage of the C–S bond of the thiophene ring.[23] The reaction of [(*p*-cymene)Ru(SC$_4$Me$_4$)]$^{2+}$ with aqueous hydroxide also led to a ring opening reaction of thiophene through initial nucleophilic attack on the thiophene sulfur.[24] The differences in reactivity for the thiophene and pyrrole derivatives appear to reflect the higher C---N bond energies relative to C---S bonds,[25] as well as the greater electron richness of the pyrrole heterocycle.

(22) Kiel, W. A.; Ball, R. G.; Graham, W. A. G. *J. Organomet. Chem.* **1990**, *383*, 481.
(23) Angelici, R. J.; Hachgenei, J. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 909.

Experimental Section

Materials. [(*p*-cymene)Ru(OTf)$_2$]$_x$,[26] [(*p*-cymene)OsCl$_2$]$_2$,[22] and tetramethylpyrrole[27] were synthesized by literature procedures. [(*p*-cymene)OsCl$_2$]$_2$ was converted to the triflate derivative in a procedure similar to that reported for the ruthenium analogue. Dichloromethane and acetonitrile were distilled from CaH$_2$; tetrahydrofuran was distilled from Na/benzophenone. Reactions were carried out under nitrogen using standard Schlenk techniques, but unless mentioned otherwise, purification steps were carried out in air.

Instrumentation. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C spectra at 75.4 MHz on a Varian VXR-300 NMR spectrometer. Chemical shifts were referenced to tetramethylsilane by using the deuterated solvent as the secondary reference. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer. 3-Nitrobenzyl alcohol was used as a matrix for the FAB spectra. Elemental analyses were performed by Desert Analytical Laboratory, Tucson, AZ. Electrochemical measurements were made on a Cypress Systems CYSY-1 electroanalysis system. A platinum disk and platinum wire were used as working and auxiliary electrodes, and a copper wire was used for a reference electrode. Cyclic voltammograms were run in acetonitrile solutions of 0.1 M tetra-*n*-butylammonium hexafluorophosphate at scan rates of 100 mV/s. Ferrocene was used as an internal reference for potentials.

The COSY spectra were collected by use of 1024 points in t_2 that were collected over the bandwidth necessary to include the desired resonances with 512 t_1 blocks and 1024 scans per block. These were zero filled to 1024 t_2 × 1024 t_1.

[(η^6-*p*-cymene)Ru(η^5-NC$_4$Me$_4$)]OTf, 1. A solution of [(*p*-cymene)Ru(OTf)$_2$]$_x$ (1.00 g, 1.86 mmol) and tetramethylpyrrole (0.230 g, 1.88 mmol) in 50 mL of CH$_2$Cl$_2$ was stirred with protection from light. After 14 h the solvent was evaporated, leaving a yellow/brown oily residue. The crude product was chromatographed on a neutral alumina column. Eluting with CH$_2$Cl$_2$ gave two slow moving bands. Elution with CH$_3$CN broadened the bands, but moved them down the column quickly. The solvent from the first band was evaporated. The resulting tan solid was dried under vacuum. Yield: 0.531 g, 58%. Crystals suitable for a X-ray diffraction study were grown from EtOH/hexanes. Addition of NH$_4$PF$_6$ to **1** in EtOH permitted crystallization of the same cation as the PF$_6$ salt. ^{13}C NMR (CD$_2$Cl$_2$): δ 121.0 (q, OTf); δ 113.6 (2 pyr C), 111.6 (1 cym C), 100.9 (2 pyr C), 99.6 (1 cym C), 88.7 (2 cym C), 86.1 (2 cym C), 31.4 (1 *i*-Pr C), 22.8 (2 Me), 17.9 (1 Me), 13.4 (2 Me), 9.3 (2 Me). Mass Spec for the PF$_6$ salt, FAB$^+$; *m/e* 358 (M – PF$_6$). Mass Spec, FAB$^-$: *m/e* 648 (M + PF$_6$). Anal. Calcd for C$_{19}$H$_{26}$NF$_3$O$_3$SRu: C, 45.05; H, 5.17, N, 2.77. Found: C, 45.67; H, 5.19; N, 2.80.

[(η^6-*p*-cymene)Os(η^5-NC$_4$Me$_4$)]OTf, 2. The procedure was similar to that described above for **1**. Yield: 49%. Mass spec, FAB$^+$: *m/e* 448 (M – OTf). Mass Spec, FAB$^-$: *m/e* 746 (M + OTf). Anal. Calcd for C$_{19}$H$_{26}$NF$_3$O$_3$SOs: C, 38.31; H, 4.40; N, 2.35. Found: C, 38.26; H, 4.20; N, 2.45.

[(η^6-*p*-cymene)Ru)η^5-HNC$_4$Me$_4$)](OTf)$_2$. To a solution of **1** (0.106 g, 0.209 mmol) in 10 mL of CH$_2$Cl$_2$ was added HOTf (20 μL, 0.226 mmol). A dark brown residue precipitated within 5

(24) Krautscheid, H.; Feng, Q.; Rauchfuss, T. B. *Organometallics* **1993**, *12*, 3273.
(25) Katzer, J. R.; Siva-Subramanian, R. *Catal. Rev. Sci. Eng.* **1979**, *20*, 155.
(26) Ganja, E. A.; Rauchfuss, T. B.; Stern, C. L. *Organometallics* **1991**, *10*, 270.
(27) Johnson, A. W.; Markham, E.; Price, R.; Shaw, K. B. *J. Chem. Soc.* **1958**, 4254.

min. The solvent was evaporated and the brown solid was dried under vacuum. ^{1}H NMR spectroscopy indicated the only impurity to be residual HOTf. Attempts to chromatograph or recrystallize the product from EtOH/hexane or MeOH/hexane led to deprotonation. Attempts to recrystallize from CH_3CN/hexane or CH_3CN/Et_2O were also unsuccessful. ^{1}H NMR (CD_3CN): δ 6.18 (m, 4, CH); δ 2.80 (sept, 1, CH); δ 2.24 (s, 3, CH_3); δ 1.28 (d, 6 CH_3); δ 2.30, 2.01 (s, 6, pyrrole Me's). ^{13}C NMR (CD_3CN): δ 120.7 (q, OTf), δ 117.3, 107.2, 106.9, δ 102.2, 92.1, 89.6, 31.8, 22.7, 18.3, 11.1, 9.2. Mass Spec, FAB$^+$: *m/e* 358 (M − H − 2OTf). Mass Spec, FAB$^-$: *m/e* 806 (M + OTf), 656 (M − H).

[(η^6-*p*-cymene)Ru(η^5-MeNC$_4$Me$_4$)](OTf)$_2$, 3. To a solution of **1** (0.274 g, 0.541 mmol) in 50 mL of CH_2Cl_2 was added MeOTf (400 μL, 3.5 mmol). The solution was stirred for 12 h and the solvent was then evaporated, leaving a brown solid. The crude product was washed with 50 mL of $CHCl_3$ and 5 mL of EtOH, leaving an off-white solid which was dried under vacuum. Yield: 0.331 g, 91%. ^{13}C NMR (CD_3CN): δ 122.1 (q, OTf); δ 117.4 (1 cym C), 110.2 (2 pyr C), 107.8 (1 cym C), 101.3 (2 pyr C), 92.4 (2 cym C), 89.8 (2 cym C), 38.7 (NCH_3), 31.4 (*i*-Pr C), 22.5 (2 Me), 18.1 (1 Me), 10.7 (2 Me), 9.8 (2 Me). Mass Spec, FAB$^+$: *m/e* 370 (373 calcd for M − 2OTf). Mass Spec, FAB$^-$: *m/e* 820 (M + OTf). Anal. Calcd for $C_{21}H_{29}NF_6O_6S_2Ru$: C, 37.61; H, 4.36; N, 2.09. Found: C, 37.31; H, 4.30; N, 1.95.

[(η^6-*p*-cymene)Os(η^5-MeNC$_4$Me$_4$)](OTf)$_2$, 4. The procedure was similar to that described above for **3**. Yield: 72%. Mass Spec, FAB$^+$: *m/e* 612 (M − OTf), 462 (463 calcd for M − 2OTf), 448 (M − 2OTf − CH_3). Mass Spec, FAB$^-$: *m/e* 910 (M + OTf), 761 (M). Anal. Calcd for $C_{12}H_{29}NS_2O_6F_6O_5$: C, 33.20; H, 3.85; N, 1.84. Found: C, 33.12; H, 3.95; N, 1.92.

[(η^5-*p*-cymene-H)Ru(η^5-NC$_4$Me$_4$)], 5. A solution of **1** (0.364 g, 0.718 mmol) and LiAl(O-*t*-Bu)$_3$H (0.183 g, 0.720 mmol) in 40 mL of THF was stirred for 3 h before solvent was evaporated. The resulting brown/orange residue was extracted with 50 mL of pentane. The yellow solution was filtered away from white/tan solids and evaporated, leaving a yellow-green oil. The crude product was purified on a neutral alumina column eluted with CH_2Cl_2/C_6H_6 (1:1). The first and only band (yellow) was collected and evaporated yielding the yellow/green oil. The product was stable in air for short periods of time but was stored under nitrogen or vacuum. ^{13}C NMR (C_6D_6) for the major isomer: (quart C) δ 110.2, 108.8, 93.4, and 92.4 (pyr), 104.1 and 35.7 (cym); (CH) δ 81.0, 76.6, 33.2, and 27.9 (cym); (CH_2) δ 36.5 (cym); (CH_3) 24.4, 23.0, and 22.5 (cym), 14.6, 14.2, 10.2, and 9.9 (pyr). ^{13}C NMR for the minor isomer: (quart C) δ 109.6, 108.2, 94.0, and 93.2 (pyr), 91.2 and 49.1 (cym); (CH) δ 80.5, 78.9, 33.8, and 29.3 (cym); (CH_2) δ 30.2 δ (cym); (CH_3) δ 21.2, 20.6, and 20.5 (cym), 14.00, 13.97, 10.1, and 9.7 (pyr). IR ($CDCl_3$), cm^{-1}: 2774 ($\nu_{C-H\ exo}$), 2052 ($\nu_{C-D\ exo}$). Mass Spec, EI: *m/e* 358 (M − H). Mass Spec, FAB$^+$: *m/e* 358 (M − H). (Mass Spec for the deuterated analogue: *m/e* 359 (M − H).) Exact mass: calcd 358.1109; found 258.1114.

(η^5-*p*-cymene-H)Os(η^5-NC$_4$Me$_4$), 6. The procedure was similar to that described above for **7**. The product was extracted with pentane and the solvent was evaporated to give a yellow oil. See Table 2 for ^{1}H NMR data.

(η^5-*p*-cymene-OMe)Ru(η^5-NC$_4$Me$_4$), 7. A solution of sodium methoxide prepared from sodium (0.053 g, 2.3 mmol) in 25 mL of MeOH was added to **1** (0.23 g, 0.46 mmol) in methanol. The solution gradually turned from tan to yellow. After stirring for 12 h, the solvent was evaporated, leaving a pale yellow solid. Extraction with $CDCl_3$ and filtering under nitrogen yielded a yellow solution which displayed ^{1}H NMR signals consistent with the single Ru product indicated above and, in most cases, residual NaOMe. Attempts to recrystallize the product from CH_3CN/Et_2O, CH_3CN/hexanes, or CH_2Cl_2/Et_2O were unsuccessful. NMR ($CDCl_3$), carbon types established by DEPT experiments: (quart C) δ 109.6, 108.6, 105.7, and 101.8 (pyrrole), 94.3 and 94.1 (cym); (CH) δ 81.6, 77.0, 63.8, 32.4, and 32.3 (cym); (CH_3) δ 24.2, 23.4, and 21.3 (cym), 13.9, 13.4, 10.1, and 9.5 (pyr), 50.3 (NaOMe), 51.2 (MeOH), 45.4 (impurity). Mass Spec, FAB$^+$: *m/e* 358 (M − OCH_3).

(η^5-*p*-cymene-OMe)Os(η^5-NC$_4$Me$_4$), 8. The procedure was similar to that described above for **7**. See Table 2 for ^{1}H NMR data.

[(η^6-*p*-cymene)(Ru(η^4-MeNC$_4$Me$_4$-OMe)]OTf, 9. A solution of sodium methoxide prepared from sodium (0.024 g, 1.0 mmol) in 25 mL of MeOH was added to **3** (0.415 g, 0.618 mmol) in methanol. The solution was stirred for 2 h; then the solvent was evaporated to give a pale yellow, air sensitive solid. The solid was extracted with $CDCl_3$ and filtered under nitrogen to give a pale yellow solution which exhibited ^{1}H NMR resonances for a single Ru product and residual NaOMe. Attempts to crystallize the product from CH_2Cl_2/hexane, CH_3CN/hexane, and CH_3CN/Et_2O were unsuccessful. ^{13}C NMR (CD_3CN): δ 122.2 (q, OTf); δ 112.9, 107.2, 102.8, 92.8, 90.3, 87.9, 85.8, 84.3, 83.9, 66.6 (quart C), 52.0 (OCH_3, free or coord); δ 49.7 (OCH_3, free or coord); δ 32.3, 31.5, 24.3, 23.3, 22.8, 18.4, 11.1, 10.6, 10.3. Mass Spec, FAB$^+$: 525, 404 (M − OTf); 390 (M − OTf − CH_3).

[(η^6-*p*-cymene)Ru(η^4-MeNC$_4$Me$_4$OH)]OTf. A degassed solution of aqueous KOH (0.096 g, 1.7 mmol of KOH in ~4.5 mL of H_2O) in 20 mL of THF was added to 0.317 g of **3** (0.472 mmol). After stirring for 2 h, the solvents were evaporated. The crude product was extracted with 40 mL of CH_2Cl_2 under N_2. A light brown solution was filtered away from a pale solid. Solvent evaloration of the filtrate at room temperature afforded the product as a light brown solid. Yield: 0.054 g (21%). The product decomposed slowly in air or in the presence of acid. Furthermore, heating the compound (~50 °C) in CH_2Cl_2 labilized the modified pyrrole ligand and led to an unidentified Ru product which showed no evidence of coordinated PMP in the ^{1}H NMR spectrum. The free ligand was not isolated in pure form, but ^{1}H NMR spectroscopy suggests that the hydroxide ion is no longer incorporated into the pyrrole ring because the mirror plane of symmetry has been restored. ^{13}C NMR ($CDCl_3$): δ 124.1 (q, OTf); δ 118.6, 110.0, 99.6, 91.7, 89.2, 85.5, 83.7, 82.0, 81.2, 73.9, 31.0, 30.8, 30.1, 23.0, 22.5, 18.3, 12.1, 11.4, 10.3. Mass Spec, FAB$^+$: 539 (M − e), 525 (M − OTf + 135), 390 (M − OTf), 136. MASS Spec, FAB$^-$: *m/e* 823 (M + OTf + 135). IR (KBr), cm^{-1}: 3240 (ν_{O-H}).

[(η^6-*p*-cymene)Ru(η^4-MeNC$_4$Me$_4$-H)]OTf, 10. A solution of **3** (1.52 g, 2.26 mmol) and LiAl(O-*t*-Bu)$_3$H (0.57 g, 2.26 mmol) in 80 mL of CH_3CN/THF (1:1) was stirred for 1 h before the solvent was evaporated. The resulting brown/orange residue was extracted with 50 mL of CH_2Cl_2 and filtered. The solvent volume was reduced and the solution was loaded onto a neutral alumina column. Eluting with CH_2Cl_2 followed by CH_2Cl_2/CH_3CN (1:1) moved a yellow band off the column. Evaporation of the solvent from this fraction resulted in a yellow/tan crystalline solid which was dried under vacuum. Yield: 0.44 g, 37%. Crystals suitable for an X-ray diffraction study were grown by slow evaporation of a CH_2Cl_2 solution. ^{13}C NMR ($CDCl_3$): (quart C) δ 120.9 (q, OTf), 111.6, 101.0, 94.3, 90.7, and 62.2; (CH) δ 86.1, 84.8, 83.0, 82.2, and 81.9 (CHMe in pyr), 30.9 (*i*-Pr in cym); (CH_3) δ 35.5 (N–Me), 23.1, 22.5, 18.6, 17.0, 11.7, 11.6, and 11.0. Mass Spec, FAB$^+$: *m/e* 374 (M − OTf). Mass Spec, FAB$^-$: *m/e* 672 (M + OTf). Anal. Calcd for $C_{20}H_{30}NF_3O_3SRu$: C, 45.97; H, 5.79; N, 2.68. Found: C, 45.13; H, 5.72; N, 2.65.

[(η^6-*p*-cymene)Os(η^4-MeNC$_4$Me$_4$-H)OTf, 11. The procedure was similar to that described above for **10**. ^{13}C NMR (CD_2Cl_2): δ 121.4 (q, OTf): δ 106.3, 96.0, 88.0, 87.1, 85.6 (CHMe in pyr), 77.2, 75.9, 74.3, 73.6, 49.5 (quart C), 37.7, 31.5, 23.3, 22.7, 18.9, 17.2, 12.2, 11.8, 11.4. Mass Spec, FAB$^+$: *m/e* 464 (M − OTf). Mass Spec, FAB$^-$: *m/e* 762 (M + OTf). Anal. Calcd for $C_{20}H_{30}NSO_3F_3Os$: C, 39.27; H, 4.94; N, 2.29. Found: C, 39.24; H, 4.98; N, 2.36.

Reaction of 10 with Triflic Acid. To a solution of **10** (0.13 g, 0.25 mmol) in 15 mL of CH_3CN was added $HOSO_2CF_3$ (1 equiv) via syringe. After 18 h the crude product was extracted with C_6D_6 to give a dilute solution which gave a complicated ^{1}H NMR spectrum. The solvent was evaporated, and the solid was extracted with CD_3CN. ^{1}H NMR spectroscopy showed a 1:2:2 ratio of the following three ruthenium complexes: **3**, **10**, and [(*p*-cymene)Ru(CH_3CN)$_3$](OTf)$_2$. The displaced pentameth-

ylpyrrole ligand was not isolated when the crude material was chromatographed on neutral alumina.

The above reaction was repeated with 4 equiv of triflic acid. After 12 h the solvent was evaporated, leaving a brown/orange oily residue. This crude product was chromatographed on an acidic alumina column with CH_2Cl_2/CH_3CN (1:1). A purple band was eluted and the solvent was evaporated to give $[MeNC_4H_3Me_4]^+$, structure IV. ^1H NMR ($CDCl_3$): δ 4.02 (1, m, CHMe), 3.39 (3, s, NMe), 2.97 (1, m, CHMe), 2.40 (3, s, N=CMe), 1.73 (1, m, CHMe), 1.45 (3, d, Me), 1.30 (3, d, Me), 1.18 (3 d, Me). Very weak coupling between adjacent ring hydrogens observed in the COSY spectrum suggests the stereochemistry shown in structure IV. ^{13}C NMR ($CDCl_3$): δ 120.6 (q, OTf); (quart c) δ 193.9; (CH) δ 73.3, 51.4, 44.8; (CH_3) δ 35.2 (NMe), 16.6, 16.4, 14.6, and 14.3. IR ($CDCl_3$), cm^{-1}: 2940, 2890 (ν_{C-H}), 1676 ($\nu_{C=N}$). Mass Spec, FAB^+: m/e 140 (M - OTf). Mass Spec, FAB^-: m/e 438 (M + OTf).

Reaction of 10 or 11 with HCl. A soluton of **10** (0.042 g, 0.080 mmol) in 10 mL of CH_2Cl_2 was degassed via three freeze/pump/thaw cycles. The Schlenk tube was then charged with 1.6 equiv of HCl and the solution was stirred for 9 h. The solution was evaporated and the NMR spectrum of the products showed resonances for unreacted **10**, $[(p\text{-cymene})RuCl_2)_2$,[21] and $[MeNC_4H_3Me_4]^+$, structure IV.

A solution of **11** (0.020 g, 0.033 mmol) in 5 mL of CH_2Cl_2 was degassed as described above and ca. 10 equiv of HCl was added. The solution was stirred at room temperature for 16 h, and the solution gradually changed from orange/yellow to lemon yellow. The solvent was evaporated. The NMR spectrum of the crude product showed resonances for **11** and $[(p\text{-cymene})OsCl_2]_2$[22] in a ratio of 5:1. Resonances for $[MeNC_4H_3Me_4]^+$ were also observed.

X-ray Diffraction Studies. Complex **1** crystallized from EtOH/hexanes with one cation and one counterion per asymmetric unit. The ruthenium atom was located by using direct methods. Other atoms were located with the use of structure factors and Fourier calculations. The disordered CF_3SO_3 anion was refined with bond distance constraints.[28] The occupancies of the fluorines located summed to <1. Hydrogens were included in fixed, ideal positions. All atoms of the cation and the sulfur of the triflate were refined anisotropically during the final cycles of full-matrix, least-squares refinement. The largest shift/error in the final refinement was for the y/b position coordinate of O(1) of the triflate. The largest difference peak was 0.83 Å from the ruthenium. Details of the crystal data, experimental conditions, and a summary of solution and refinement information are given in Table IV.

Complex **10** was crystallized by slow evaporation of a dichloromethane solution. Crystals formed in the centrosymmetric space group $P2_1/c$, and both enantiomers were equally present in the unit cell. The asymmetric unit contained one cation and one counterion. The ruthenium position was determined by direct methods, and other atoms were located using difference Fourier calculations in SHELX. The CF_3SO_3 anion was not disordered as in **1**, although the temperature factors of the counterion atoms were higher than any of the atoms in the cation. All hydrogens were observed as difference peaks and were refined in fixed ideal positions. All non-hydrogen atoms were refined anisotropically during the final cycles of full-matrix least squares refinement. The largest difference peak was 0.86 e/Å^3 and was 0.81 Å from the ruthenium. On the opposite side of the ruthenium, there was another peak with a height of ~0.75 e/Å^3, 0.87 Å from the metal.

Another difference peak (0.7 e/Å^3) was present in the plane of the pyrrole ring above C1 and has been attributed to rotational disorder of the ring. Sterically, other orientations of the pyrrole ligand are quite similar. C_5 is only 0.038 Å out of the plane defined by C_6, C_7, C_8, and C_9. The positions of the planar methyl groups and the four planar pyrrole ring atoms are occupied in the other comformations. As a result of this disorder, C_1 was refined with an occupancy of 0.75. Details of the crystal data, experimental conditions, and a summary of the solution refinement information are given in Table 4.

Table 4. Experimental Data for X-ray Diffraction Studies on 1 and 10

	1	10
chemical formula	$C_{19}H_{25}NO_3F_3SRu$	$C_{20}H_{30}NO_3F_3SRu$
fw	505.5	523.4
T, °C	22–24	23
space group	$P2_12_12_1$	$P2_1/c$
a, Å	8.928(2)	8.153(2)
b, Å	13.772(4)	17.351(2)
c, Å	17.272(6)	16.508(2)
β, deg	90	104.396(13)
V, Å^3	2123.7(11)	2261.9(7)
Z	4	4
d_{calcd}, g cm^{-3}	1.581	1.537
μ, mm^{-1}	0.861	0.811
$F(000)$	1028	1075.0
diffractometer	Siemens P3/F	Siemens P3/F
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
$2\theta_{max}$, deg	55.0	55.0
scan type	θ–2θ	θ–2θ
scan width	from 1.00° below 2θ for Kα_1 to 1.00° above 2θ for Kα_2	
h range	$-11 \le h \le 11$	$-10 \le h \le 6$
k range	$-17 \le k \le 17$	$0 \le k \le 22$
l range	$0 \le l \le 22$	$-20 \le l \le 20$
total no. of data collcd	5443	9591
no. of unique data collcd	3836	5226
no. of data with $I > 3\sigma(I)$	2146	4362 ($I > 4\sigma I$)
weight scheme	$w = 1.0/[\sigma^2(F) + 0.0500F^2]$	$w = 1.0/\sigma^2(F) + 0.0013F^2]$
R	6.44	3.34
R_w	8.71	4.90
data to param ratio	8.6:1	16.1:1

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Supplementary Material Available: Tables of bond distances and angles and positional and thermal parameters for **1** and **10** (15 pages). Ordering information is given on any current masthead page.

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(28) The bond distance constraints, given as distances in angstroms (esd's), are as follows: $CF_3SO_3^-$, S–O = 1.43 (20), S–C = 1.80 (12), C–F = 1.33 (19), F···F = 2.17 (14).