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Synthesis and Structural Characterization of Ruthenium π-Arene and π-Cyclodienyl Complexes Containing 1,4,7-Trimethyl-1,4,7-triazacyclononane

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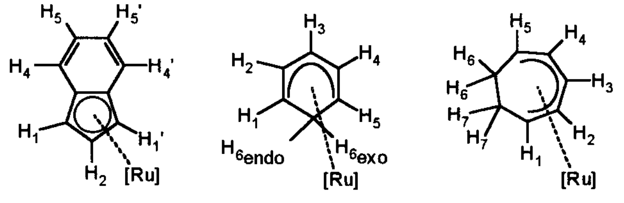
The reaction between $Ru(Me_3tacn)Cl_3$ (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) and silver trifluoromethanesulfonate in ethanol affords a green species: treatment with cyclohexa-1,3-diene gives $[Ru(Me_3tacn)(\eta^6\text{-}C_6H_6)]^{2+}$ (**1**), while in the presence of zinc dust, reactions with 1-(trimethylsilyl)cyclopentadiene, 1-(trimethylsilyl)indene, cyclohexa-1,3-diene, and cycloheptatriene yield $[Ru(Me_3tacn)(\eta^5\text{-}C_5H_5)]^+$ (**2**), $[Ru(Me_3tacn)(\eta^5\text{-}C_9H_7)]^+$ (**3**), $[Ru(Me_3tacn)((1{-}5\text{-}\eta)\text{-}C_6H_7)]^+$ (**4**), and $[Ru(Me_3tacn)((1{-}5\text{-}\eta)\text{-}C_7H_9)]^+$ (**5**), respectively. X-ray diffraction studies of the $[PF_6]^-$ salts of complexes **3**−**5** show that in each case the η^5-bonded unsaturated hydrocarbon moiety is virtually planar.

(π-Polyenyl)ruthenium complexes occupy an increasingly important role in organometallic chemistry, and the reactivity of the (η^6-arene)ruthenium fragment has been extensively investigated.[1] Substituted arenes with appropriate leaving groups are activated toward nucleophilic substitution, and this has found important applications in peptide labeling and synthesis.[2] Accounts describing the formation of (η^5-cyclohexadienyl)ruthenium complexes from η^6-benzene derivatives have appeared.[3] It has been suggested that the incorporation of ancillary ligands such as benzene,[1] cyclopentadienyl anion,[4] 1,4,7-trithiacyclononane,[5] tris(2-pyrazolyl)borate,[6] and (2-pyridylethyl)(2-pyridylmethyl)methylamine[7] can affect the electrophilicity of the coordinated arene, which decreases as the electron-donating ability of the ligand increases. The syntheses of (η^6-benzene)ruthenium complexes containing 1,4,7-triazacyclononane[5] (tacn) and ammonia[8] ligands respectively have been reported, but their reactivities toward nucleophiles have not been investigated because the amine hydrogens in each case display low tolerance toward basic substrates. We therefore focused on the formation of congeners containing tertiary amine ligands and now describe the preparation of (η^6-arene)- and (η^5-cyclodienyl)ruthenium complexes containing 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) and their reactivities toward nucleophiles. The molecular structures of three new derivatives are presented. The syntheses of cyclooctadienylruthenium species containing Me_3tacn have been reported.[9]



3 **4** **5**

Figure 1. Numbering of hydrogens in complexes **3**−**5** ([Ru] = $Ru(Me_3tacn)$).

Experimental Section

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. $Ru(Me_3tacn)Cl_3$,[10] 1-(trimethylsilyl)cyclopentadiene, and 1-(trimethylsilyl)indene[11] were prepared according to literature procedures. Cycloheptatriene (Aldrich) was distilled before use. Silver trifluoromethanesulfonate (AgOTf) was obtained from Aldrich. All solvents were reagent grade and were used without further purification. ^{13}C (67.5 MHz) and ^1H (270 MHz) NMR spectra were recorded on a JEOL 270 FT-NMR spectrometer with Me_4Si as internal reference. The numbering of hydrogens in **3**−**5** is given in Figure 1. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan MAT 95 mass spectrometer with a 3-nitrobenzyl alcohol matrix. Elemental analyses were performed by Butterworth Laboratory Ltd, Teddington, U.K.

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(1) Albers, M. O.; Robinson, D. J.; Singleton, E. *Coord. Chem. Rev.* **1987**, *79*, 1.

(2) Krämer, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1197.

(3) (a) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458. (b) Grundy, S. L.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 379.

(4) Moriarty, R. M.; Gill, U. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157.

(5) Schröder, M. *Pure Appl. Chem.* **1988**, *60*, 517.

(6) Bhambri, S.; Tocher, D. A. *Polyhedron* **1996**, *15*, 2763.

(7) Shirin, Z.; Mukherjee, R.; Richardson, J. F.; Buchanan, R. M. *J. Chem. Soc., Dalton Trans.* **1994**, 465.

(8) Hung, Y.; Kung, W. J.; Taube, H. *Inorg. Chem.* **1981**, *20*, 457.

(9) Yang, S. M.; Cheng, W. C.; Cheung, K. K.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1995**, 227.

(10) Neubold, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 459.

(11) Kraihanzel, C. S.; Losee, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 4701.

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Table 1. Crystallographic Data for Complexes 3−5

	3	**4**	**5**
formula	$C_{18}H_{28}N_3RuPF_6$	$C_{15}H_{28}N_3RuPF_6$	$C_{16}H_{30}N_3RuPF_6$
mol wt	532.47	496.44	510.46
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$Pnma$	$Pca2_1$
cryst dimens/mm^3	$0.20 \times 0.35 \times 0.50$	$0.25 \times 0.25 \times 0.40$	$0.25 \times 0.25 \times 0.30$
a/Å	7.9977(12)	16.2680(15)	16.5735(20)
b/Å	23.072(3)	14.8099(18)	8.1781(11)
c/Å	11.9401(16)	8.0606(16)	14.6570(18)
β/deg	106.856(12)	−	−
U/Å^3	2108.6(5)	1942.0(5)	1986.6(4)
F(000)	1075	1003	1035
Z	4	4	4
D_c/g cm^{-3}	1.677	1.698	1.707
μ/cm^{-1}	8.724	9.325	9.115
$2\theta_{max}$/deg	50	55	55
no. of rflns used	3022 ($I \geq 2\sigma(I)$)	1863 ($I \geq 2\sigma(I)$)	1795 ($I \geq 2\sigma(I)$)
no. of variables	263	128	244
R, R_w	0.046, 0.052	0.050, 0.054	0.034, 0.035
GOF	1.48	1.13	2.02
residual ρ/e Å^{-3}	+0.96 to −0.85	+1.45 to −0.72	+0.41 to −0.47
$(\Delta/\sigma)_{max}$	0.01	0.01	0.05

Synthesis. [Ru(Me$_3$tacn)(η^6-C_6H_6)](OTf)$_2$ (1). A mixture of Ru(Me$_3$tacn)Cl$_3$ (0.1 g, 0.26 mmol) and AgOTf (0.23 g, 0.87 mmol) in absolute ethanol (30 cm^3) was refluxed for 2 h. After filtration, 1,3-cyclohexadiene (0.50 g, 6.25 mmol) was added to the green solution, which was refluxed for 18 h. The resultant yellow microcrystalline solid was collected, washed with diethyl ether, and air-dried (yield 0.1 g, 58%). Anal. Found: C, 31.60; H, 4.17; N, 6.43. Calcd for $C_{17}H_{27}N_3O_6F_6RuS_2$: C, 31.48; H, 4.17; N, 6.48. ^{1}H NMR (CD_3OD): δ 6.04 (6H, s, C_6H_6), 3.62 (9H, s, NCH_3), 2.94−3.06, 3.12−3.34 (12H, m, NCH_2−). ^{13}C NMR (CD_3OD): δ 59.9 (NCH$_3$), 62.5 (NCH$_2$−), 88.3 (C_6H_6). FAB MS (^{102}Ru): m/z 500 [M$^+$ − OTf], 351 [M$^+$ − 2OTf].

[Ru(Me$_3$tacn)(η^5-C_5H_5)]PF$_6$ (2). A mixture of Ru(Me$_3$tacn)Cl$_3$ (0.1 g, 0.26 mmol) and AgOTf (0.23 g, 0.87 mmol) in absolute ethanol (30 cm^3) was refluxed for 2 h. After filtration, zinc powder (1 g) and 1-(trimethylsilyl)cyclopentadiene (0.5 g, 3.5 mmol) were added to the green solution. The resultant mixture was refluxed for 12 h and then filtered and concentrated to *ca.* 5 cm^3. Addition of NH_4PF_6 resulted in the precipitation of a yellow-orange solid, which was recrystallized by diffusion of diethyl ether into an acetone solution (yield 0.11 g, 86%). Anal. Found: C, 34.95; H, 5.31; N, 8.80. Calcd for $C_{14}H_{26}N_3F_6PRu$: C, 34.86; H, 5.43; N, 8.71. ^{1}H NMR ($(CD_3)_2CO$): δ 3.92 (5H, s, C_5H_5), 3.57 (9H, s, NCH_3), 3.18−3.07, 2.95−2.86 (12H, m, NCH_2−). ^{13}C NMR ($(CD_3)_2CO$): δ 57.5 (NCH$_3$), 59.4 (NCH$_2$−), 65.4 (C_5H_5). FAB MS (^{102}Ru): m/z 338 [M$^+$ − PF$_6$].

[Ru(Me$_3$tacn)(η^5-C_9H_7)]PF$_6$ (3). The procedure is similar to that for complex **2**, except 1-(trimethylsilyl)indene (1 g, 5.3 mmol) was used. The mixture was refluxed for 3 days to give an orange solution. Removal of zinc followed by addition of NH_4PF_6 afforded **3** as red-brown microcrystals (yield 0.05 g, 36%). Anal. Found: C, 40.43; H, 5.07; N, 7.80. Calcd for $C_{18}H_{28}N_3F_6PRu$: C, 40.60; H, 5.30; N, 7.89. ^{1}H NMR ($(CD_3)_2CO$): δ 7.56−7.52, 7.10−7.16 (4H, two dd, $H_{4/4'}$ and $H_{5/5'}$, $J_{4,5}$ = 6.59 Hz, $J_{4,5'}$ = 3.17 Hz), 4.64−4.62 (1H, t, H$_2$, $J_{1,2}$ = 2.34 Hz), 4.57−4.55 (2H, d, $H_{1/1'}$, $J_{1,2}$ = 2.34 Hz), 3.52 (9H, s, NCH_3), 2.87−2.73 (12H, m, NCH_2−). ^{13}C NMR ($(CD_3)_2CO$): δ 128.9, 126.0 (C$_4$ and C$_5$), 92.9 (C$_3$), 86.8 (C$_2$), 61.0 (NCH$_2$−), 59.1 (NCH$_3$), 51.7 (C$_1$). FAB MS (^{102}Ru): m/z 388 [M$^+$ − PF$_6$].

[Ru(Me$_3$tacn)((1−5-η)-C_6H_7)]PF$_6$ (4). Method A. Complex **1** (0.1 g, 0.14 mmol) was dissolved in absolute methanol (10 cm^3) and $NaBH_4$ (0.1 g, 2.6 mmol) was added slowly over 0.5 h. The mixture was stirred for 2 h and then concentrated. Addition of NH_4PF_6 yielded **4** as a yellow solid (yield 0.06 g, 78%).

Method B. In contrast to the procedure used for **2**, 1,3-cyclohexadiene (0.5 g, 6.25 mmol) was added instead and the mixture was refluxed for 18 h. Removal of zinc followed by addition of NH_4PF_6 afforded a yellow microcrystalline solid (yield 0.03 g, 23%). Anal. Found: C, 36.37; H, 5.78; N, 8.66. Calcd for $C_{15}H_{28}N_3F_6PRu$: C, 36.29; H, 5.68; N, 8.46. ^{1}H NMR (CD_2Cl_2): δ 5.37 (1H, t, J = 4.5 Hz, H$_3$), 4.11 (3H, s, NCH_3), 4.03 (2H, t, H$_2$ and H$_4$), 3.28−3.23, 3.13−3.08 (4H, m, NCH_2−), 2.69−2.57 (14H, m, two NCH_3 and NCH_2−), 2.38−2.33 (1H, dt, H_{6endo}, ^2J = 13.1 Hz, ^3J = 6.0 Hz), 1.69−1.67 (2H, t, H$_1$ and H$_5$), 1.46−1.43 (1H, d, H_{6exo}, ^2J = 13.1 Hz). ^{13}C NMR (CD_3CN): δ 89.9 (C$_3$), 64.2 (C$_2$ and C$_4$), 61.1 (C$_1$ and C$_5$), 61−56 (NCH$_3$ and NCH$_2$−), 25.4 (C$_6$). FAB MS (^{102}Ru): m/z 352 [M$^+$ − PF$_6$].

[Ru(Me$_3$tacn)((1−5-η)-C_7H_9)]PF$_6$ (5). In contrast to the procedure used for **2**, cycloheptatriene (0.5 g, 5.5 mmol) was added instead and the mixture was refluxed for 7 days. Removal of zinc followed by addition of NH_4PF_6 gave light yellow microcrystals (yield 0.03 g, 22%). Anal. Found: C, 37.36; H, 5.89; N, 8.55. Calcd for $C_{16}H_{30}N_3F_6PRu$: C, 37.65; H, 5.92; N, 8.23. ^{1}H NMR ($(CD_3)_2CO$): δ 5.42 (1H, t, J = 5.6 Hz, H$_3$), 4.28 (2H, dd, J = 5.6 and 8.5 Hz, H$_2$ and H$_4$), 3.97 (3H, s, NCH_3), 3.22−3.42 (14H, m, NCH_2−, H$_1$ and H$_5$), 2.83 (6H, s, NCH_3), 1.95, 0.82 (4H, m, H$_6$ and H$_7$). ^{13}C NMR ($(CD_3)_2CO$): δ 90.8 (C$_3$), 77.8 (C$_2$ and C$_4$), 61.4 (C$_1$ and C$_5$), 60.5, 59.8, 59.3, 54.3, 53.6 (NCH$_3$ and NCH$_2$−), 28.8 (C$_6$ and C$_7$). FAB MS (^{102}Ru): m/z 366 [M$^+$ − PF$_6$].

Structural Determinations. Crystallographic data for compounds **3**−**5** are listed in Table 1 (see Supporting Information for details). Diffraction data were collected at 298 K on an Enraf-Nonius diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.7107 Å) using the θ−2θ scan mode (three standard reflections every 3600 s, <2% decay). The structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques and refinement by full-matrix least squares using the NRCVAX programs.[12] All non-H atoms in each structure were refined anisotropically. For complex **4**, the space group is *Pnma* and the atoms ending in "a" have coordinates at x, $^1/_2 - y$, z.

Results and Discussion

A series of η^6-arene and η^5-cyclodienyl complexes have been prepared using the ruthenium(III) precursor Ru(Me$_3$tacn)Cl$_3$, as summarized in Scheme 1. Interaction between Ru(Me$_3$tacn)Cl$_3$ and 3 equiv of AgOTf in absolute ethanol yielded a green solution (labeled **X**),

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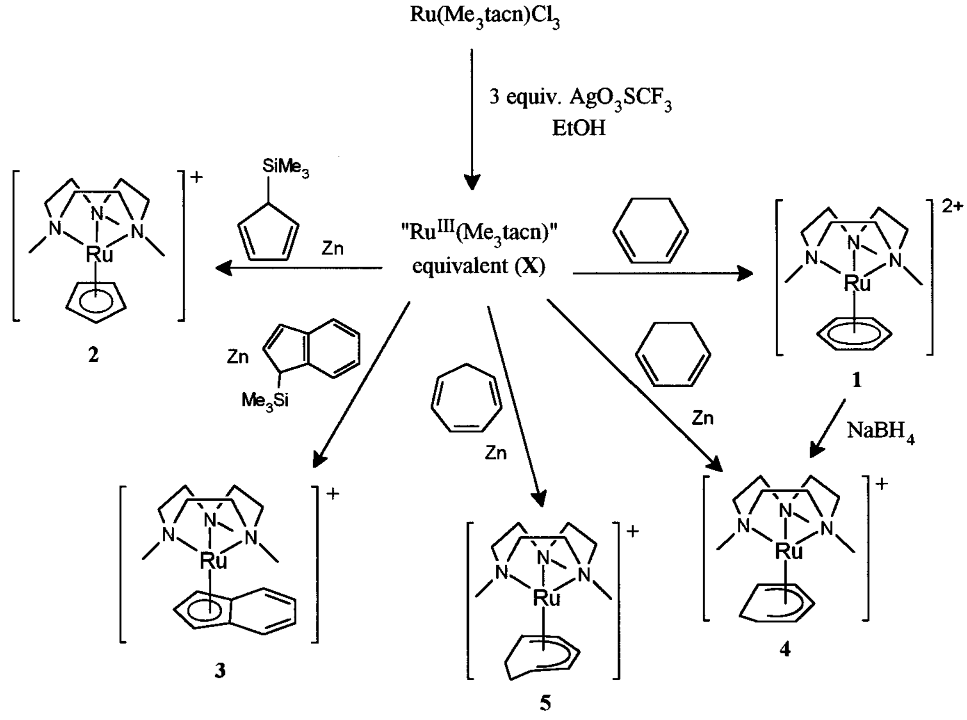
[12] Cable, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

Scheme 1



and results of gravimetric analysis revealed the formation of 3 molar equiv of AgCl. Attempts to characterize the resultant green species were unsuccessful, but its reactivity suggests that it is effectively a "$Ru^{III}(Me_3$-tacn)" equivalent.

Reports on (η^6-arene)ruthenium complexes containing nitrogen donor ligands have appeared.[5-8] Schröder and co-workers prepared $[(tacn)Ru(\eta^6\text{-arene})]^{2+}$ (arene = C_6H_6, *p*-cymene) by reacting $\{Ru(\eta^6\text{-arene})Cl_2\}_n$ with tacn in ethanol, but the corresponding reaction with Me_3tacn gave intractable products.[5] In addition, the reaction of $[(\eta^6\text{-}C_6H_6)Ru(NCMe)_3]^{2+}$ with Me_3tacn in ethanol did not yield the desired complex. A general method for the preparation of $[Cp^*Ru(polyarene)]^+$ complexes is by treatment of $[Cp^*Ru(NCMe)_3]^+$ with the aromatic substrate.[13] However, no reaction was observed between $[Ru(Me_3tacn)(NCMe)_3]^{2+}$ and benzene. In this study, addition of 1,3-cyclohexadiene to the generated green solution **X** afforded $[Ru(Me_3tacn)(\eta^6\text{-}C_6H_6)](OTf)_2$ (**1**) in moderate yield. Complex **1** is soluble in acetone and methanol but insoluble in acetonitrile and dichloromethane. Metathesis of **1** with other anions (e.g. ClO_4^-, PF_6^-) in methanol yielded an insoluble solid which hampered further characterization. The mechanism for the formation of **1** presumably involves coordination of 1,3-cyclohexadiene to the ruthenium(III) center followed by dehydrogenation to yield the $[(\eta^6\text{-}C_6H_6)Ru^{II}]$ moiety; this pathway is related to the preparation of $\{(\eta^6\text{-}C_6H_6)RuCl_2\}_2$.[14] The green solution **X** did not react with benzene in the presence of zinc, which is in accordance with the unsuccessful synthesis of $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ from $[Ru(H_2O)_6]^{2+}$ and C_6H_6.[15] These observations reflect the importance in the coordination of 1,3-cyclohexadiene to the metal center. Attempts to synthesize $[Ru(Me_3tacn)(\eta^6\text{-anisole})]^{2+}$ and $[Ru(Me_3tacn)(\eta^6\text{-}p\text{-cymene})]^{2+}$ by reacting the solution **X** with 1-methoxycyclohexa-1,3-diene and α-phellandrene respectively were unsuccessful. We suggest that the steric repulsion between the methyl groups of Me_3-tacn and the bulky substituents on each 1,3-diene hinders their interaction with the ruthenium center, a prerequisite for the dehydrogenation process.

In the presence of zinc powder, the aforementioned solution **X** reacted with 1-(trimethylsilyl)cyclopentadiene and 1-(trimethylsilyl)indene to afford $[Ru(Me_3tacn)(\eta^5\text{-}C_5H_5)]PF_6$ (**2**) and $[Ru(Me_3tacn)(\eta^5\text{-}C_9H_7)]PF_6$ (**3**), respectively. However, no reaction was observed with cyclopentadiene, indene, or 2,4-dimethylpenta-2,4-diene in the presence of zinc. Cyclopentadienylsilicon and -tin reagents have been extensively used as precursors to η^5-cyclopentadienyl complexes,[16] e.g., $CpSiMe_3$ reacts with ethanolic $RuCl_3$ to give ruthenocene in 96% yield.[17] Cp^*SiMe_3 did not react with the solution **X** to give $[Ru(Me_3tacn)(Cp^*)]^+$ even after prolonged reflux in the presence of zinc.

$[Ru(Me_3tacn)((1-5\text{-}\eta)\text{-}C_6H_7)]PF_6$ (**4**) was prepared in moderate yield by the reduction of **1** in methanol using $NaBH_4$. The enhanced electrophilicity of the coordinated benzene ring in **1** facilitates nucleophilic attack by borohydride anions to afford the cyclohexadienyl group. However, complex **1** did not react with sodium methoxide or sodium dimethyl malonate in methanol. These observations are in contrast to those for $[RuL'(\eta^6\text{-}C_6H_6)]^{2+}$ (L′ = (2-pyridylethyl)(2-pyridylmethyl)-methylamine), which reacts with OH^- and CN^- species.[18] Since nucleophilic attack occurs at the *exo* face

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[13] Koelle, U.; Wang, M. H. *Organometallics* **1990**, *9*, 195.

[14] Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

[15] Koelle, U.; Weissschadel, C.; Englert, U. *J. Organomet. Chem.* **1995**, *490*, 101.

[16] (a) Abel, E. W.; Dunster, M. O.; Waters, A. *J. Organomet. Chem.* **1973**, *49*, 287. (b) Llinás, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37.

[17] Winter, C. H.; Pirzad, S.; Cao, D. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1026.

Table 2. ^{1}H NMR Chemical Shifts of η^5-C_5H_5 Ligands in Ruthenium Mixed-Sandwich-Type Complexes

complexes	δ	ref
[Ru(η^5-C_5H_5)(Me$_3$tacn)]PF_6 (**2**)	3.77,[a] 3.92[b]	this work
[Ru(η^5-C_5H_5)(η^6-C_6H_6)]BF_4	5.37[a]	23
Ru(η^5-C_5H_5)$_2$	4.58[a]	24
[Ru(η^5-C_5H_5)(η^6-C_6Me_6)]BF_4	5.30[b]	25
[Ru(η^5-C_5H_5)(η^6-1,3,5-$C_6H_3Me_3$)]BF_4	5.31[b]	25
Ru(η^5-C_5H_5)(η^5-C_5Me_5)	4.18[a]	25
Ru(η^5-C_5H_5)(η^5-$C_5(CO_2Me)_5$)	4.93[a]	26
[Ru(η^5-C_5H_5)(P(OMe)$_3$)$_3$]PF_6	5.23[a]	27
[Ru(η^5-C_5H_5)(CO)$_3$]PF_6	6.30[b]	28
Ru(η^5-C_5H_5)(BHPz$_3$)	4.27[b]	29
Ru(η^5-C_5H_5)(BH(3,5-Me$_2$Pz)$_3$)	4.57[b]	29
Ru(η^5-C_5H_5)(BPz$_4$)	4.35[b]	29

[a] In $CDCl_3$. [b] In $(CD_3)_2CO$; Pz = 2-pyrazolyl.

of the arene ligand, it is improbable that the steric bulk of the incoming base can account for the lack of reactivity. This is more likely to arise from the strongly electron-donating nature of Me$_3$tacn, which would lower the electrophilicity of the arene ring relative to [RuL′(η^6-C_6H_6)]$^{2+}$ so that **1** reacts with the highly nucleophilic hydride anion only. Reaction of the solution **X** with 1,3-cyclohexadiene and cycloheptatriene in the presence of zinc afforded **4** and [Ru(Me$_3$tacn)((1−5-η)-C_7H_9)]PF_6 (**5**), respectively. In this method, **4** is presumably formed via **1** and then reduced by hydride anions generated from the combination of zinc and refluxing ethanol. For complex **5**, the role of the zinc/ethanol mixture is to reduce the metal center ($Ru^{III} \rightarrow Ru^{II}$) as well as to generate hydride anions *in situ*, which subsequently attack the cycloheptatriene ring.

Spectroscopy and Molecular Structures. The ^{1}H chemical shifts of the cyclopentadienyl ring in a series of related mixed-sandwich type ruthenium complexes are listed in Table 2. The Cp protons in **2** appear as a singlet at δ 3.77 ($CDCl_3$)/δ 3.92 ($(CD_3)_2CO$), which is significantly upfield from the other examples. This can be attributed to the enhancement of π-basicity at the ruthenium center by the σ-donating strength of Me$_3$tacn. The ^{1}H NMR spectra for **4** and **5** each reveal a characteristic triplet at *ca.* δ 5.5 for the H_3 proton in η^5-dienyl complexes.[19] For complex **4**, the doublet of triplets centered at δ 2.35 for H_{6endo} shows a large geminal (^2J) coupling of 13.1 Hz to H_{6exo} (at δ 1.45) and smaller vicinal (^3J) coupling of 6.0 Hz to H_1 and H_5. No vicinal coupling is observed between H_{6exo} and H_1 or H_5 because the respective dihedral angles are approximately 90°.

Complexes **3**−**5** have been studied by X-ray crystallography. Perspective views of the cations and selected bond lengths and angles are presented in Figure 2 and Tables 3−5, respectively. All three complexes display a mixed-sandwich-type structure, and the η^5-arene and -cyclodienyl moieties are virtually planar (deviation from mean planes within 0.1 Å). In **3**, the C−C distances of the C_5 ring range from 1.409(12) to 1.447(11) Å and the Ru−C distances vary slightly between 2.147(7) and 2.264(4) Å. Distortion of the C_5 moiety is therefore small and is probably due to the influence of the adjacent ring. The average Ru−C distance of **3** is 2.195 Å, which is similar to those in

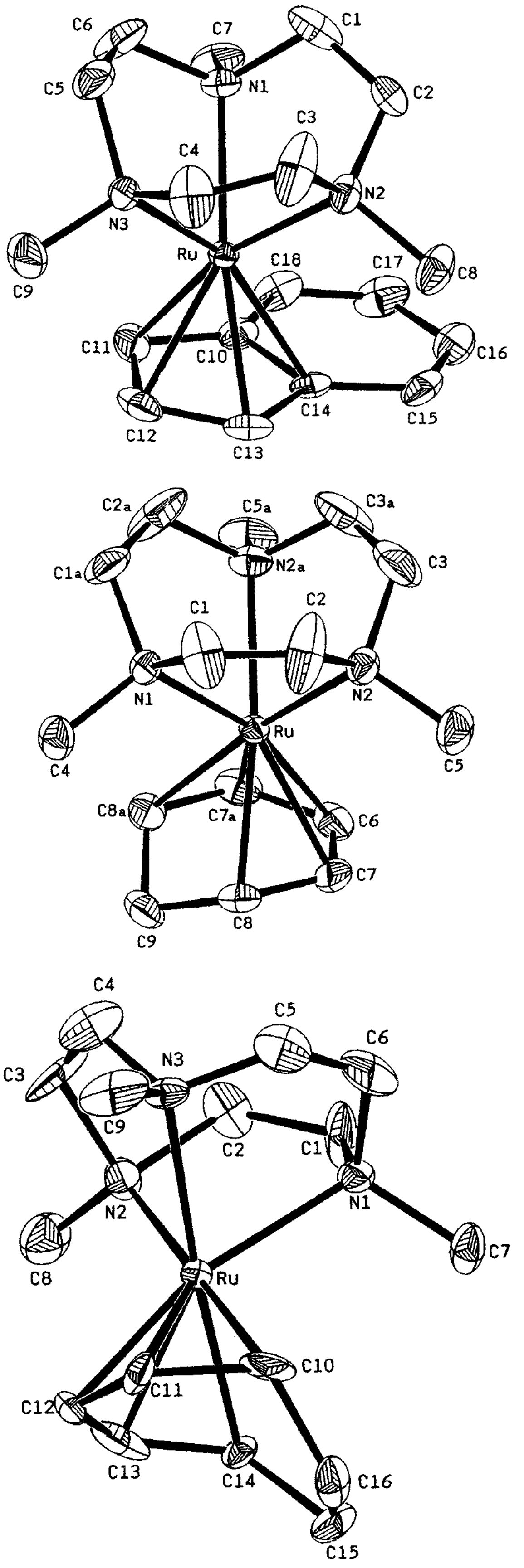

Figure 2. Perspective views of the cation in (top) [Ru(Me$_3$tacn)(η^5-C_9H_7)]PF_6 (**3**), (middle) [Ru(Me$_3$tacn)((1−5-η)-C_6H_7)]PF_6 (**4**), and (bottom) [Ru(Me$_3$tacn)((1−5-η)-C_7H_9)]PF_6 (**5**).

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(18) Shirin, Z.; Pramanik, A.; Ghosh, P.; Mukherjee, R. *Inorg. Chem.* **1996**, *35*, 3431.

(19) Pertici, P.; Vitulli, G.; Paci, M.; Porri, L. *J. Chem. Soc., Dalton Trans.* **1980**, 1961.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Ru(Me$_3$tacn)(η^5-C$_9$H$_7$)]PF$_6$ (3)

Ru−N1	2.177(5)	Ru−N2	2.177(5)
Ru−N3	2.159(5)	Ru−C10	2.264(6)
Ru−C11	2.167(6)	Ru−C12	2.147(7)
Ru−C13	2.152(6)	Ru−C4	2.244(6)
C10−C11	1.447(11)	C10−C14	1.440(9)
C10−C18	1.413(11)	C11−C12	1.419(12)
C12−C13	1.409(12)	C13−C14	1.446(10)
C14−C15	1.431(11)	C15−C16	1.340(12)
C16−C17	1.406(13)	C17−C18	1.330(13)
C11−C10−C14	107.9(6)	C11−C10−C18	133.1(7)
C14−C10−C18	119.0(7)	C10−C11−C12	107.3(6)
C11−C12−C13	109.4(7)	C12−C13−C14	108.1(6)
C10−C14−C13	107.1(6)	C10−C14−C15	118.5(6)
C13−C14−C15	134.4(7)	C14−C15−C16	119.2(7)
C15−C16−C17	121.7(8)	C16−C17−C18	121.5(7)
C10−C18−C17	120.1(7)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for [Ru(Me$_3$tacn)((1−5-η)-C$_6$H$_7$)]PF$_6$ (4)

Ru−N1	2.194(6)	C1−C2	1.327(12)
Ru−N2	2.205(5)	C3−C3a	1.344(19)
Ru−C6	2.153(9)	C6−C7	1.402(9)
Ru−C7	2.140(6)	C7−C8	1.400(10)
Ru−C8	2.187(6)	C8−C9	1.501(9)
C7−C6−C7a	118.1(8)	C6−C7−C8	119.6(7)
C7−C8−C9	118.6(7)	C8−C9−C8a	102.5(6)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Ru(Me$_3$tacn)((1−5-η)-C$_7$H$_9$)]PF$_6$ (5)

Ru−N1	2.185(5)	Ru−N2	2.247(6)
Ru−N3	2.218(5)	Ru−C10	2.164(10)
Ru−C11	2.099(7)	Ru−C12	2.141(6)
Ru−C13	2.143(8)	Ru−C14	2.186(6)
C10−C16	1.525(13)	C10−C11	1.456(12)
C11−C12	1.41(3)	C12−C13	1.41(3)
C13−C14	1.361(13)	C14−C15	1.497(10)
C15−C16	1.525(13)		
C11−C10−C16	115.1(7)	C10−C11−C12	127.0(9)
C11−C12−C13	122.4(6)	C12−C13−C14	121.2(9)
C13−C14−C15	134.7(7)	C14−C15−C16	106.3(6)
C10−C16−C15	120.6(7)		

Ru(η^5-C$_9$H$_7$)$_2$[20] and Cp*Ru(η^5-C$_9$H$_7$)[21] (2.189 and 2.202 Å, respectively). Comparison of complex **4** with the related complexes [Ru((1−5-η)-C$_6$H$_6$CN)(HBPz$_3$)][22] and [Ru((1−5-η)-C$_6$H$_6$CN)L′]$^+$ (L′ = (2-pyridylethyl)(2-pyridylmethyl)methylamine)[18] show that the structure of the η^5-cyclodienyl ligand in **4** is unremarkable. The average Ru−C distances at the η^5-bonded moieties in **4** and **5** (2.161 and 2.147 Å, respectively) are similar to that in [Ru(Me$_3$tacn)((1−5-η)-C$_8$H$_{11}$)]$^+$ (2.159 Å).[9] However, it is apparent that the ruthenium−nitrogen contact *trans* to the central carbon of the η^5 fragment (Ru−N1 in **4** and **5**) is shorter than the remaining two. This is presumably a consequence of the alleviation of steric repulsion between Me$_3$tacn and the respective cyclodienyl ligand.

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Supporting Information Available: Tables of crystal data and refinement details, final positional parameters, calculated coordinates (for hydrogen), anisotropic displacement parameters, and bond lengths and angles for **3**−**5** (19 pages). Ordering information is given on any current masthead page.

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(20) Webb, N. C.; Marsh, R. E. *Acta Crystallogr.* **1967**, *22*, 382.

(21) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130.

(22) Bhambri, S.; Tocher, D. A. *J. Organomet. Chem.* **1996**, *507*, 291.

(23) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Inorg. Chem.* **1986**, *25*, 3407.

(24) Fischer, E. O.; Von Foerster, M.; Kreiter, C. G.; Schwarzhans, K. E. *J. Organomet. Chem.* **1967**, *7*, 113.

(25) Roman, E.; Astruc, D. *Inorg. Chim. Acta* **1979**, *37*, L465.

(26) Bruce, M. I.; Wallis, R. C.; Williams, M. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2183.

(27) Ashby, G. S.; Bruce, M. I.; Tomkins, B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003.

(28) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710.

(29) McNair, A. M.; Boyd, D. C.; Mann, K. R. *Organometallics* **1986**, *5*, 303.