Synthesis and Structures of Dinuclear 3,5-Bis(trifluoromethyl)pyrazolate Complexes of Ruthenium

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Reaction of 3,5-$(CF_3)_2$PzLi with $[Cp^*RuCl_2]_n$ (2:1) in diethyl ether at −78 °C gives $[(Cp^*RuLi)_2(\mu_4\text{-}O)(\mu_2\text{-}Cl)(\mu\text{-}3,5\text{-}(CF_3)_2Pz)_3]$ (**1**) in 75% yield [3,5-$(CF_3)_2$Pz = 3,5-bis(trifluoromethyl)pyrazolate]. With a 1:1 ratio of $[Cp^*RuCl_2]_n$ to 3,5-$(CF_3)_2$PzLi, dark-green crystalline $[Cp^*Ru(\mu\text{-}Cl)]_2(\mu\text{-}3,5\text{-}(CF_3)_2Pz)$ (**2**) is produced in ca. 50% yield. The reaction of 3,5-$(CF_3)_2$PzLi with $[RuCl_2(1,4\text{-}Me,iPrC_6H_4)]_2$ in diethyl ether at −78 °C gives the chloride-bridged dimer $[RuCl(\eta^6\text{-}1,4\text{-}Me,iPrC_6H_4)(\mu\text{-}3,5\text{-}(CF_3)_2Pz)]_2$ (**3**) in 65% yield. The reaction of $Cp^*Ru(OSO_2CF_3)_2$ with 3,5-$(CF_3)_2$PzLi (2:1) in diethyl ether at −78 °C produced the unusual dinuclear $Ru^{III}-Ru^{III}$ complex $[Cp^*Ru(\mu\text{-}O)(\mu\text{-}\eta^5,\eta^1\text{-}C_5Me_4CH_2)Ru(\eta^1\text{-}3,5\text{-}(CF_3)_2Pz)]\cdot 0.25Et_2O$ (**4**) in 75% yield. Complexes **1–4** have been characterized spectroscopically and by single-crystal X-ray diffraction studies.

Introduction

Pyrazolylate complexes of ruthenium are known with a variety of ancilliary ligands.[1] They include oxo-bridged dinuclear nitrosyls,[2] dinuclear carbonyls,[3] and trinuclear derivatives.[4] As part of a project aimed at the development of new volatile precursors for the chemical vapor deposition (CVD) of Pt group metals, we recently described a series of 3,5-bis(trifluoromethyl)pyrazolate [3,5-$(CF_3)_2$Pz] derivatives of Rh, Ir, Pd, and Pt.[5] While these studies were in progress, Carty and co-workers reported the synthesis and structure of $[(CO)_3Ru(3,5\text{-}(CF_3)_2Pz)]_2$ and its use for the CVD of ruthenium metal.[6] We were therefore curious to see if other 3,5-$(CF_3)_2$Pz derivations of ruthenium might prove useful for the CVD or atomic layer deposition of ruthenium. Our studies have resulted in the discovery of a number of interesting new ruthenium 3,5-$(CF_3)_2$Pz complexes, **1**−**4**, which are described in this paper (Scheme 1). These include the unusual odd electron Ru_2^{5+} complex $[Cp^*Ru(\mu\text{-}Cl)]_2(\mu\text{-}3,5\text{-}(CF_3)_2Pz)$ (**2**) and the unsymmetrical dinuclear complex $[Cp^*Ru(\mu\text{-}O)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)Ru(\eta^1\text{-}3,5\text{-}(CF_3)_2Pz)]\cdot 0.25Et_2O$ (**4**), which is formed via loss of H from a Me group on Cp*.

Results and Discussion

Pentamethylcyclopentadienyl (Cp*) Derivatives 1 and 2. The reaction of 3,5-$(CF_3)_2$PzLi with $[Cp^*RuCl_2]_n$ in diethyl ether in a 2:1 mol ratio at −78 °C gave good yields of the unusual tetrametallic Ru_2Li_2 complex $[(Cp^*RuLi)_2(\mu_4\text{-}O)(\mu_2\text{-}Cl)(\mu\text{-}3,5\text{-}(CF_3)_2Pz)_3]$ (**1**). Interestingly, higher ratios of 3,5-$(CF_3)_2$PzLi to $[Cp^*RuCl_2]_n$ do not affect the yield of **1** (ca. 75%), while a lower ratio (1:1) gives the dark-green paramagnetic complex **2** described below. Despite careful exclusion of oxygen and moisture from the system, the source of adventitious oxygen in **1** has not been determined. X-ray-quality crystals of the dark-brown complex were grown from hexane solutions at −60 °C. The compound crystallizes in the monoclinic space group *C*2/*c* with four molecules per unit cell. Crystallographic details are given in Table 1 and key bond lengths and angles in Table 2. A view of the complex is shown in Figure 1. The central core of **1** (Figure 2) contains two Cp*Ru units (Ru−Ru = 2.794 Å), bridged by a single Cl atom and coordinated to two μ-3,5-$(CF_3)_2$Pz groups and a unique central μ_4-O atom. The Cl and O atoms bridge the two Ru atoms in a planar arrangement. Two Li atoms are bound to the O atom (O1−Li1 = 1.869 Å) and to the outer N atoms of the μ-3,5-$(CF_3)_2$Pz groups (Li1−N2 = 2.039 Å). A third μ-3,5-$(CF_3)_2$Pz group spans the two Li atoms (Li1−N1′ = 2.001 Å). There is a crystallographic C_2 axis that runs through Cl1−O1−C18. Each Li has a virtually planar three-coordinate environment. Methyl H atoms from the Cp* groups lie in axial positions close to the Li atoms, but the C−H···Li distances of 2.072 and 2.237 Å are too long to be considered bonding interactions. Complex **1** appears to be stable both in solution ($CDCl_3$) and in the gas phase. In solution, the ^{1}H NMR spectrum is consistent with the structure found in the solid state. The fast atom bombardment (FAB) mass spectrum also shows the molecular ions *m*/*e* = 1146 as the highest mass peak.

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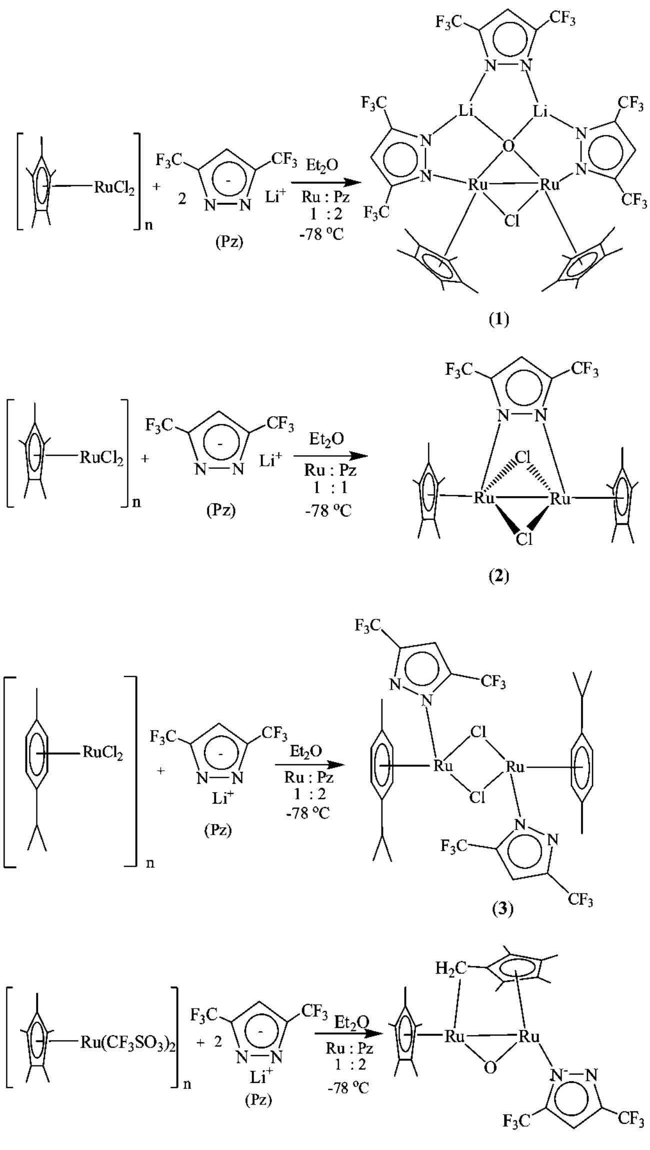
Scheme 1. Synthesis of 3,5-(CF_3)$_2$Pz derivatives



[Cp*Ru(μ-Cl)]$_2$(μ-3,5-(CF_3)$_2$Pz) (2). Under reaction conditions similar to those used for the formation of **1** but with a 1:1 ratio of [Cp*RuCl$_2$]$_n$ to 3,5-(CF_3)$_2$PzLi, a dark-green solution is formed from which dark-green crystals of **2** can be isolated in ca. 50% yield. Despite the fact that the compound is weakly paramagnetic in solution ($\mu_{eff} = 0.72\ \mu_B$ per Ru atom; 0.055 M in C_6H_6), reasonably sharp ^{1}H NMR signals were observed in $CDCl_3$. The structure of **2** in the solid state was determined by X-ray crystallography. Molecules of **2** crystallize in the monoclinic space group *C*2/*c* with four per unit cell. A view of **2** is shown in Figure 3. The central Ru_2 core is bridged by two μ-Cl atoms and a single μ-3,5-(CF_3)$_2$Pz group. Each end of the molecule is capped by an η^5-C_5Me_5 group. There is a C_2 axis that bisects the Ru−Ru vector and passes through C11 of the 3,5-(CF_3)$_2$Pz ligand. Formal oxidation state considerations are consistent with **2** being an example of a Ru_2^{5+} complex.[7] The compound is extremely air-sensitive in the solid state and in solution, and we have been unable to obtain reliable magnetic measurements over a variable-temperature range. The relatively low value for one unpaired electron, obtained by Evans' method (above), may be due to partial decomposition in solution. The symmetrical structure and room temperature magnetic moment are consistent with the presence of one unpaired electron, which is delocalized over both Ru centers. In order to gain more insight into the electronic structure of **2**, we performed density functional theory (DFT) calculations on the model complex [CpRuCl]$_2$(μ-3,5-(CF_3)$_2$Pz). Key calculated bond lengths and angles for the energy-optimized structure are provided in Table 3 along with the experimentally determined (crystallographic) parameters for **2**. Bearing in mind that the calculated values are based on the nonmethylated Cp analogue and are "gas phase", the data show a relatively good level of agreement. Thus, the calculated Ru−Ru distance is slightly overestimated at 3.132 vs 2.941 Å in **2**. The more important result of these calculations is that the most stable electronic configuration of the molecule is one that has a single unpaired electron (doublet; Table 3). This is calculated to be 94.30 kJ/mol more stable than the configuration with three unpaired electrons (quartet). This result is consistent with the experimentally determined magnetic data for **2** ($\mu_{eff} = 0.72\ \mu_B$ per Ru). In view of the symmetrical structure found for **2**, it seems reasonable to assume that the single unpaired electron is delocalized over both Ru atoms. Thus, the Mulliken population analysis of the model complex places a negative charge on both Ru atoms evenly. The spin-density plot (Figure 4) also shows a charge distribution with the electron density evenly divided between the two Ru atoms. The highest occupied molecular orbital (HOMO; Figures 5−7) appears to be constructed primarily from d orbitals and reveals an orbital that is delocalized over both Ru atoms.

[RuCl(η^6-1,4-Me,iPrC_6H_4)(μ-3,5-(CF_3)$_2$Pz)]$_2$ (3). Another possible starting material for volatile Ru CVD precursors is the well-known derivative [$RuCl_2$(1,4-Me,iPrC_6H_4)]$_2$. However, as for **1** and **2**, we were unable to isolate a complex that was not free of chloride. The reaction of 3,5-(CF_3)$_2$PzLi with [$RuCl_2$(1,4-Me,iPrC_6H_4)]$_2$ in diethyl ether at −78 °C gave the chloride-bridged dimer **3** in 65% yield. Red-brown crystals of **3** may be grown from hexane solutions at −60 °C. The compound crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules per unit cell. Each dimeric unit sits on an inversion center, and the metric parameters of both molecules are very similar (Figure 4). Crystallographic details for **3** are given in Table 1, and key bond lengths and angles for one independent dimer are given in Table 4. The electron count for each Ru atom is 18, and there is no need for the presence of a Ru−Ru bond (the Ru···Ru distances are 3.277 and 3.273 Å). The Cl atoms bridge in a symmetrical fashion, and each arene group is η^6-bound to the metal and tilted slightly away from the central Ru_2Cl_2 plane. The 1,3-(CF_3)$_2$Pz groups are simply bound via one N atom in a trans configuration and are essentially parallel with each other. The metrical values of the complex all fall within normal parameters. The compound has a straightforward ^{1}H NMR spectrum in $CDCl_3$ that is similar to those of other ruthenium (*p*-cymene)pyrazolate derivatives.[8]

[Cp*Ru(μ-O)(μ-η^1,η^5-$CH_2C_5Me_4$)Ru(η^1-3,5-(CF_3)$_2$Pz)]·0.25(Et_2O) (4). In order to avoid the presence of chlorine in the product, we explored reactions of Ru starting materials containing the triflate (OSO_2CF_3) anion. The reaction of $RuCl_3\cdot 3H_2O$ with triflic acid ($HOSO_2CF_3$) at room temperature produces a very dark-red-brown insoluble solid. Further reaction of this solid with Cp*H in refluxing EtOH produces a slightly lighter-red-brown solid. Full characterization of this material

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Table 1. Crystal Data and Structure Refinement for Complexes 1−4

	1	2	3	4
formula	$C_{35}H_{33}N_6OClF_{18}Li_2Ru_2$	$C_{25}H_{31}N_2Cl_2F_6Ru_2$	$C_{30}H_{30}N_4Cl_2F_{12}Ru_2$	$C_{52}H_{67}N_4O_{2.5}F_{12}Ru_4$
fw	1147.14	746.56	947.62	1420.38
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	*C*2/*c*	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
a, Å	20.3642	13.463(3)	11.934(2)	9.4914(19)
b, Å	12.9183	11.055(2)	12.222(2)	11.171(2)
c, Å	16.3695	19.130(4)	14.088(3)	13.850(3)
α, deg	90	90	66.09(3)	90.60(3)
β, deg	104.436	108.32(3)	66.11(3)	97.65(3)
γ, deg	90	90	67.46(3)	92.15(3)
V, $Å^3$	4170.4	2702.9(9)	1657.3(6)	1454.2(5)
Z	4	4	2	2
D_{calc}, g cm^{-3}	1.827	1.835	1.899	1.622
temp, K	153(1)	153(1)	153(1)	153(1)
F(000)	2264	1484	936	711
μ, mm^{-1}	0.908	1.375	1.170	1.099
θ range, deg	2.97–27.51	2.95–25.00	2.98–25.00	2.97–25.00
reflns measd	8333	4411	9914	9621
reflns used	4732	2383	5812	5120
params	300	169	453	361
R^a [$I > 2\sigma(I)$]	R1 = 0.0541	R1 = 0.0718	R1 = 0.0568	R1 = 0.0366
	wR2 = 0.1059	wR2 = 0.1895	wR2 = 0.1574	wR2 = 0.1014
R^a (all data)	R1 = 0.1251	R1 = 0.0895	R1 = 0.0801	R1 = 0.0523
	wR2 = 0.1388	wR2 = 0.2128	wR2 = 0.1777	wR2 = 0.1156
S	0.981	1.104	1.024	1.130

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

Ru1−O1	2.019(4)	Li1−N3	2.005(11)
Ru1−N1	2.144(4)	Li1−N2A	2.032(11)
Ru1−Cl1	2.3832(16)	Li1−Li1A	2.97(2)
Ru1−Ru1A	2.7940(8)	O1−Ru1−N1	88.25(12)
Ru1−Li1A	3.011(10)	O1−Ru1−Cl1	100.34(10)
Li1−O1	1.871(11)	N1−Ru1−Cl1	88.17(12)

was not possible because it was virtually insoluble in all solvents. The reaction product of the red solid with 3,5-$(CF_3)_2$PzLi in diethyl ether at −78 °C produced the unusual dinuclear Ru^{III}−Ru^{III} complex **4** in 75% yield. The dark-brown complex may be crystallized from a hexane solution at −60 °C. The asymmetric complex bears an η^1-3,5-$(CF_3)_2$Pz group plus a μ-O atom. The interesting feature here is the presence of a Cp* metalated at one CH_3 group. ^{1}H and ^{19}F NMR spectroscopic data in solution are in accordance with the solid-state structure as determined by X-ray crystallography. A view of the molecular structure of **4** is shown in Figure 5. Crystallographic details are given in Table 1, and key bond lengths and angles are given in Table 5. The compound crystallizes in the monoclinic space group $P\bar{1}$ with two molecules per unit cell. There are a number of other examples of dinuclear complexes that feature similar metalated Cp* groups. The structural parameters of **4** can be compared to those of (η^1,η^5-$CH_2C_5Me_4$)$Ru_2(CO)_6$, which contains the same metalated ligand.[9] Thus, the C−C bond distances in the Cp* ring in **4** range from 1.427 to 1.456 Å compared to from 1.422 to 1.445 Å in (η^1,η^5-$CH_2C_5Me_4$)$Ru_2(CO)_6$. The ring C to *exo*-methylene bond distance (C9′−C14′) is 1.452(1) Å compared to 1.462(5) Å in (η^1,η^5-$CH_2C_5Me_4$)$Ru_2(CO)_6$. The data are consistent with an η^1,η^5 coordination mode for the metalated Cp* ligand versus η^2,η^4 or η^3,η^3. The C9′−C14′ distance suggests that there is some remaining double-bond character because it is shorter than typical C−C single-bond distances. The angle subtended at the *exo*-methylene C (C9′−C14′−Ru1) is 95.36° compared to 100.3 (2)° in (η^1,η^5-$CH_2C_5Me_4$)$Ru_2(CO)_6$. This may be due to the much shorter Ru−Ru distance of 2.601 Å in **4** versus 2.813 (1)

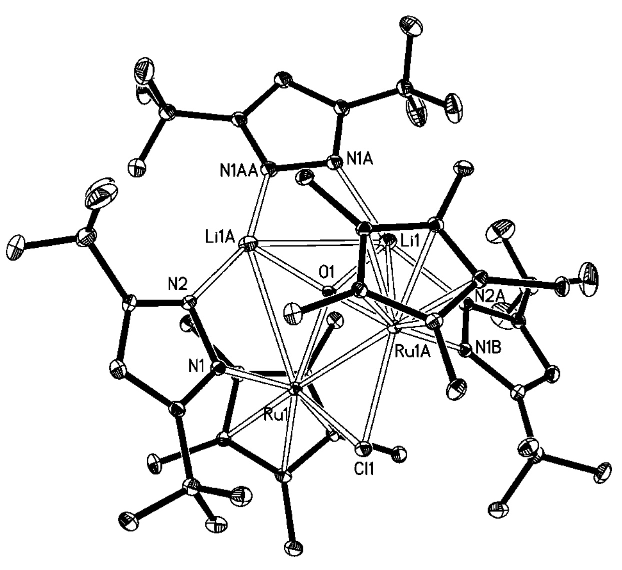

Figure 1. X-ray crystal structure of **1**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.

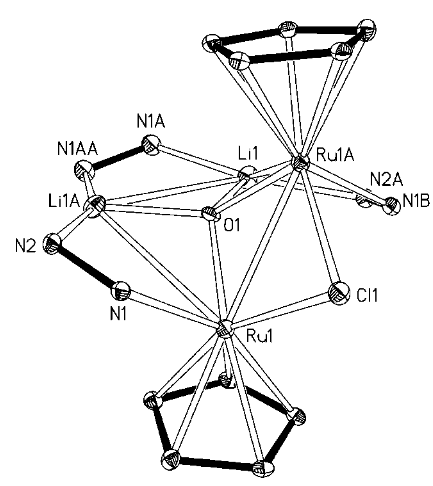

Figure 2. View of the central core of **1**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.

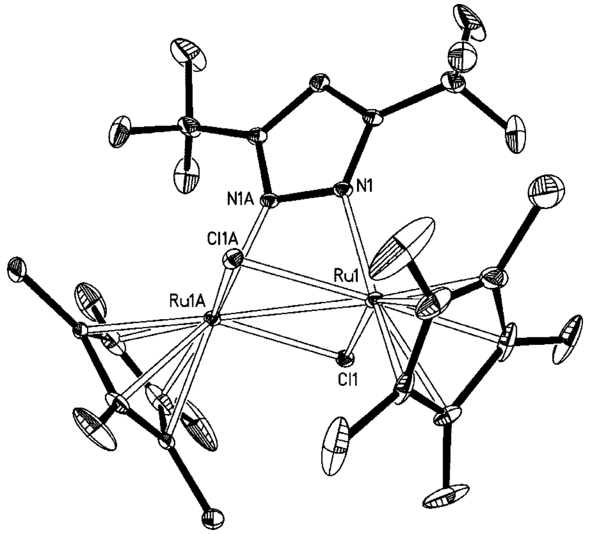

Figure 3. X-ray crystal structure of **2**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.

Table 3. DFT-Calculated Bond Lengths (Å) and Angles (deg) for $[CpRuCl]_2(\mu\text{-}3,5\text{-}(CF_3)_2Pz)$ and Experimentally Determined Values for 2 from X-ray Crystallography

	crystallography	calculated
Ru1−Ru1A	2.9416(17)	3.132
Ru1−Cl1	2.432(2)	2.538
Ru1−N1	2.206(6)	2.164
Ru1−ring$_{ave}$	2.172(15)	2.186
Ru1−Cl1−Ru1A	74.37(7)	76.70
Cl1−Ru1−Cl1A	105.61(7)	102.11
Ru1−C3	2.155(9)	
Ru1−C4	2.155(9)	
Ru1−C5	2.156(9)	
Ru1−C2	2.183(12)	
Ru1−C1	2.191(14)	
N1−Ru1−Cl1	78.35(19)	
N1−Ru1−Cl1A	78.05(18)	

Å in $(\eta^1,\eta^5\text{-}CH_2C_5Me_4)Ru_2(CO)_6$. The difference may be due to the differences in the oxidation states and electron counts for the Ru atoms in these compounds. In **4**, the two Ru atoms have formal oxidation states of 3+ and electron counts of 16, while $(\eta^1,\eta^5\text{-}CH_2C_5Me_4)Ru_2(CO)_6$ has two 18-electron Ru (1+) atoms. The 3,5-$(CF_3)_2$Pz ligand binds in a monodentate fashion with Ru2−N1 = 2.120(4) Å. This is similar to the analogous Ru−N single bond lengths found in **3** [2.122(5) and 2.132(5) Å].

Conclusion

We have shown that reactions of 3,5-$(CF_3)_2$PzLi with a variety of Ru-based starting materials give unusual complexes of the 3,5-$(CF_3)_2$Pz ligand. Further studies are in progress.

Experimental Section

All reactions were performed under dry oxygen-free nitrogen or under vacuum. The solvents diethyl ether and hexane were dried over sodium and freshly distilled from a sodium benzophenone ketyl anion under nitrogen before use. The compounds 3,5-bis(trifluoromethyl)pyrazole,[10] $[Cp^*RuCl_2]_n$,[11] and $[RuCl_2(\eta^6\text{-}1,4\text{-}Me,iPrC_6H_4)]_2$[12] were prepared as previously

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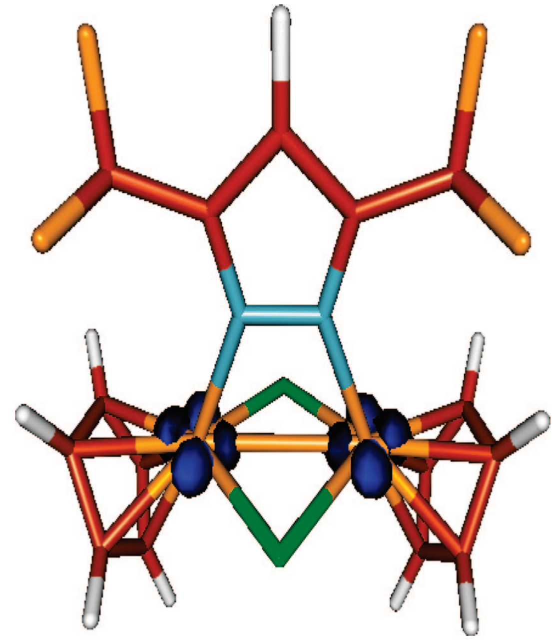

Figure 4. DFT-calculated spin density for $[CpRu(\mu\text{-}Cl)]_2(\mu\text{-}3,5\text{-}(CF_3)_2Pz)$.

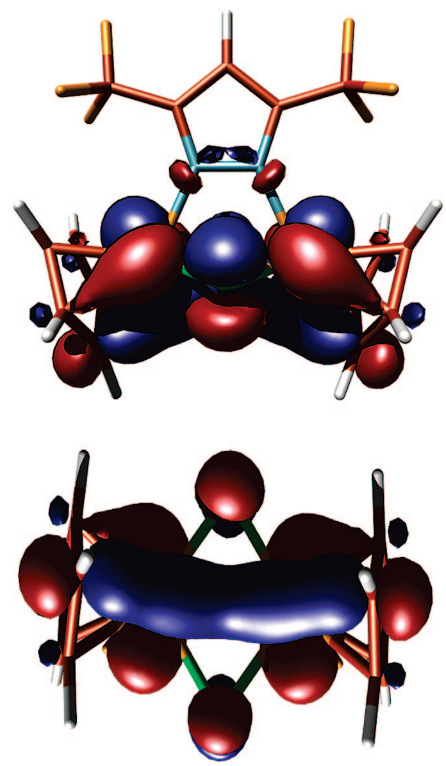

Figure 5. Two views of the DFT-calculated HOMO for $[CpRu(\mu\text{-}Cl)]_2(\mu\text{-}3,5\text{-}(CF_3)_2Pz)$.

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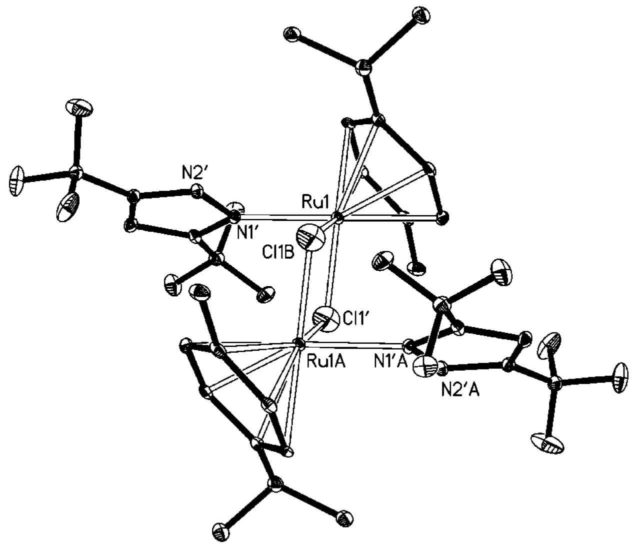

Figure 6. X-ray crystal structure of **3**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.

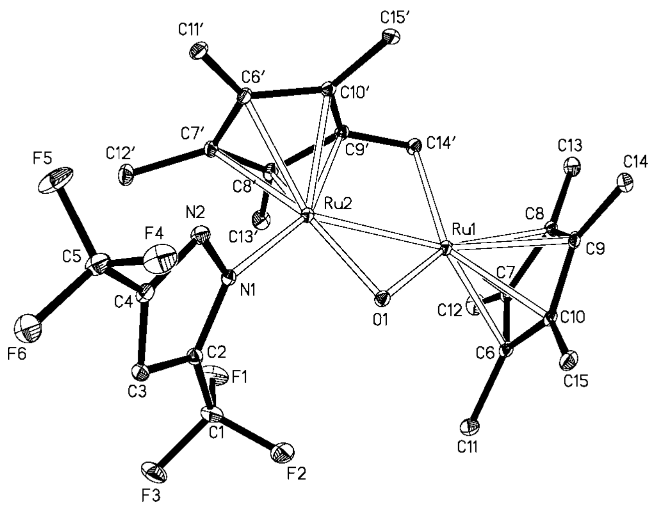

Figure 7. X-ray crystal structure of **4**. H atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 25% probability level.

described. Physical measurements: ESIMS and FABMS, Finnigan MAT TSQ 700; NMR, Varian 300 Unity Plus spectrometer (^{1}H, 300 MHz) at 298 K (chemical shifts referenced to the deuterated solvent); IR, Nicolet IR 200 FTIR spectrometer; UV–visible, Beckman DU 640 spectrophotometer. Microanalytical data (C, H, and N) on all compounds fell within expected limits. Melting points were obtained in sealed glass capillaries under dinitrogen and are uncorrected.

Synthesis of [(Cp*RuLi)$_2$(μ_4-O)(μ_2-Cl)(μ-3,5-(CF$_3$)$_2$Pz)$_3$] (1). A solution of *n*-butyllithium (5.5 mL, 1.6 M in hexane) was added dropwise to a solution of 3,5-(CF$_3$)$_2$PzH (1.6 g, 7.84 mmol) in diethyl ether (30 mL) at −78 °C, giving a light-yellow solution. The solution was stirred (30 min) and then added dropwise to a solution of [RuCl$_2$(η^5-C$_5$Me$_5$)]$_n$ (1.0 g, 3.3 mmol) in diethyl ether (15 mL) at −78 °C. The resulting mixture was allowed to warm to room temperature (30 min) and stirred overnight (10 h). The reaction mixture was then filtered through a short bed of Celite and the filtrate evaporated to dryness under vacuum. The solid residue was extracted with hexane (2 × 20 mL), and the filtrates were combined. The volume of the filtrate was reduced under vacuum (5 mL). Cooling for 5 days (−60 °C) gave dark-brown crystals, which were collected and dried under vacuum. Yield: 75%. Mp: 147–150 °C. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.2 (s, 30H, −C*H*$_3$), 1.62–1.66 (br m, 3H, 3,5-(CF$_3$)$_2$*Pz*). ^{19}F NMR (CDCl$_3$, δ, ppm): −54.52, −56.36, −63.70, −63.14. FT-IR (Nujol, cm^{-1}): 2431 s, 2065 b, 1865 s, 1506 b. FABMS: *m/e* M$^+$ [1146], 977 [M$^+$ − (C$_5$Me$_5$ + Cl)], 775 [(M$^+$ − 2Ru)], 573 [M$^+$ − 3,5-(CF$_3$)$_2$Pz]. Calcd for C$_{35}$H$_{33}$N$_6$OClF$_{18}$Li$_2$Ru$_2$: C, 36.65; H, 2.90; N, 7.33. Found: C, 36.17; H, 2.78; N, 6.99.

Synthesis of [Cp*Ru(μ-Cl)]$_2$(μ-3,5-(CF$_3$)$_2$Pz) (2). A solution of *n*-butyllithium (2.3 mL, 1.6 M in hexane) was added dropwise to a solution of 3,5-(CF$_3$)$_2$PzH (0.67 g, 3.3 mmol) in diethyl ether (10 mL) at −78 °C. The solution was stirred (30 min) and added dropwise to a solution of [RuCl$_2$(η^5-C$_5$Me$_5$)]$_n$ (1.0 g, 3.3 mmol) in diethyl ether (15 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred (10 h). The solution was then filtered through a short bed of Celite and the filtrate evaporated to dryness under vacuum. The solid was extracted with hexane (2 × 10 mL), the filtrates were combined, and the volume was reduced (5 mL). Cooling (−60 °C) gave dark-green crystals of **2** after 1 week. They were collected and dried under vacuum. Yield: 57%. Mp: 92–102 °C. ^{1}H NMR (CDCl$_3$, δ, ppm): 1.10 (t, 30H, −C*H*$_3$), 6.40 (br s, 1H, 3,5-(CF$_3$)$_2$*Pz*). ^{19}F NMR (CDCl$_3$, δ, ppm): −57.70, −56.06, −58.43, −59.82, −60.71, 60.88. FT-IR (Nujol, cm^{-1}): 2231 s, 2156 b, 1735 s, 1356 b. FABMS: *m/e* 948 [M$^+$], 877 [M$^+$ − Cl$_2$], 775 [M$^+$ − Ru], 745 [M$^+$ − CF], 641 [M$^+$ − Ru]. Calcd for C$_{25}$H$_{31}$N$_2$Cl$_2$F$_6$Ru$_2$: C, 40.22; H, 4.19; N, 3.75. Found: C, 40.20; H, 4.33; N, 3.87.

Synthesis of [RuCl(η^6-1,4-Me,iPrC$_6$H$_4$)(μ-3,5-(CF$_3$)$_2$Pz)]$_2$ (3). A solution of *n*-butyllithium (0.5 mL, 1.6 M in hexane) was added dropwise to a solution of 3,5-(CF$_3$)$_2$PzH (0.1 g, 0.5 mmol) in diethyl

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3

Ru1−Cl1′	2.072(4)
Ru1−N1′	2.122(5)
Ru1−Cl1′A	2.128(4)
Ru1−C6′	2.154(6)
Ru1−C4′	2.157(6)
Ru1−C5′	2.161(6)
Ru1−C7′	2.172(5)
Ru1−C3′	2.174(6)
Ru1−C2′	2.175(6)
Ru2−Cl1	2.084(4)
Ru2−Cl1A	2.117(4)
Ru2−N1	2.132(5)
Ru2−C4	2.164(6)
Ru2−C6	2.171(5)
Ru2−C3	2.173(6)
Ru2−C7	2.174(5)
Ru2−C5	2.176(6)
Ru2−C2	2.203(6)
Cl1′−Ru1−N1′	84.36(18)
Cl1′−Ru1−Cl1′A	77.43(18)
N1′−Ru1−Cl1′A	82.30(17)
Cl1−Ru2−Cl1A	77.66(17)
Cl1−Ru2−N1	83.50(17)
Cl1A−Ru2−N1	82.43(18)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 4

Ru2−N1	2.120(4)
Ru2−C8′	2.134(5)
Ru2−C10′	2.150(5)
Ru2−C9′	2.177(5)
Ru2−C7′	2.188(5)
Ru2−C6′	2.218(5)
Ru2−Ru1	2.6008(8)
Ru1−O1	1.914(3)
Ru1−C6	2.131(5)
Ru1−C7	2.167(5)
Ru1−C10	2.170(5)
Ru1−C14′	2.184(5)
Ru1−C9	2.185(5)
Ru1−C8	2.262(5)
O1−Ru2−Ru1	47.27(9)
N1−Ru2−Ru1	132.18(11)

ether (10 mL) at −78 °C. The solution was stirred (30 min) and added dropwise to a solution of $[RuCl_2(\eta^6\text{-}1,4\text{-Me,iPrC}_6H_4)]_2$ (0.15 g, 0.25 mmol) in diethyl ether (10 mL) at −78 °C. The solution was allowed to warm to room temperature and stirred (10 h). The solution was then filtered through a short bed of Celite and the filtrate evaporated to dryness under vacuum. The solid was extracted with hexane (2 × 10 mL), the filtrates were combined, and the volume was reduced under vacuum (5 mL). Cooling (−60 °C) gave red-brown crystals of **3** after 1 week. Yield: 65%. Mp: 165–173 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.22 (d, 6H, J = 7.5 Hz, iPr), 2.15 (s, 3H, $-CH_3$), 2.90 (septet, 1H, J = 7.5 Hz, iPr), 5.49, 5.36 (dd, 4H, $H_{AA'}/H_{BB'}$, J = 5.5 Hz), 7.05 (s, 1H, 3,5-$(CF_3)_2$*Pz*). ^{19}F NMR ($CDCl_3$, δ, ppm): −56.34, −58.33, −61.11. FT-IR (Nujol, cm^{-1}): 2231 s, 2156 b, 1735 s, 1356 b. FABMS: *m/e* 726 [M^+], 707 [M^+ − F]. Calcd for $C_{30}H_{30}N_4Cl_2F_{12}Ru_2$: C, 38.02; H, 3.19; N, 5.91. Found: C, 37.79; H, 2.78; N, 5.54.

Synthesis of [Cp*Ru(μ-O)(μ-η^5,η^1-$C_5Me_4CH_2$)Ru(η^1-3,5-$(CF_3)_2$Pz)]·0.25Et_2O (4). $RuCl_3\cdot 3H_2O$ (0.5 g, 1.9 mmol) was placed under vacuum in a 100 mL Schlenk flask (6 h). The vacuum was replaced with a nitrogen atmosphere, and triflic acid (0.5 mL, 5.7 mmol) was added slowly. The flask was then placed in an oil bath and the temperature raised to 60 °C. A steady stream of nitrogen was passed over the reaction mixture (1 h). The flask was then cooled in an ice bath and the precipitated material washed with small quantities of cold dry diethyl ether (2 × 5 mL) and dried under vacuum. Ethanol (25 mL) and Cp*H (0.3 g, 2.3 mmol) were then added, and the reaction mixture was heated under reflux (3 h). The reaction was then allowed to cool to room temperature and the red-brown solid washed with ethanol (2 × 5 mL) and dried under vacuum. In a separate flask, a solution of *n*-butyllithium (0.5 mL, 1.6 M in hexane) was added dropwise to a solution of 3,5-$(CF_3)_2$PzH (0.12 g, 0.59 mmol) in diethyl ether (10 mL) at −78 °C. The solution was stirred (30 min) and added dropwise to a suspension of the red-brown solid in diethyl ether (10 mL) at −78 °C. The resulting mixture was allowed to warm to room temperature and stirred (10 h). The solution was filtered through a short bed of Celite. The filtrate was evaporated to dryness under vacuum and the residue extracted with hexane (2 × 20 mL). The filtrates were combined, and the volume was reduced (5 mL) under vacuum. Cooling (−60 °C) gave dark-brown crystals of **4** after 5 days. They were collected and dried under vacuum. Yield: 0.33 g, 50%, based on $RuCl_3\cdot 3H_2O$. Mp: 109–111 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.95 (s, 15H, C_5*Me*$_5$), 1.3–1.9 (br m., 14H, C_5*Me*$_4CH_2$), 6.80 (s, 1H, 3,5-$(CF_3)_2$*Pz*). ^{19}F NMR ($CDCl_3$, δ, ppm): −59.43, −61.21. FT-IR (Nujol, cm^{-1}): 2371 s, 2156 b, 1945 b, 1627 s, 1405 b, 1165 s. FABMS: *m/e* 691 [M^+], 675 [M^+ − O]. Calcd for $C_{25}H_{30}N_2OF_6Ru_2$: C, 43.48; H, 4.38; N, 4.06. Found: C, 43.86; H, 4.36; N, 3.85.

X-ray Crystallography. Details of crystallographic parameters, data collection, and refinements are listed in Table 1. Selected bond lengths (Å) and angles (deg) for **1**–**4** are listed in Tables 2−5, respectively. Data were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 153 K. Absorption corrections were applied using *Gaussian*. The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the *SHELX 97* program package.[13] The coordinates of the non-H atoms were refined anisotropically, while H atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[14]

Computational Details. All calculations were performed at the UB3LYP level of theory using the *Gaussian 03* suite of programs.[15] For the geometry optimizations, the 3-21G* basis set was used for C, N, F, and H and the Stuttgart/Dresden (SDD) ECP basis set was employed for Cl and Ru.[16] Single-point calculations were carried out at the optimized geometries using the 6-311++G(d,p) basis set for C, N, F, and H and the SDD basis set for Cl and Ru. Stationary points were identified by calculation of the vibrational frequencies on the optimized geometry. Graphical representations of the calculated molecular orbitals were produced using the *Molden* program[17] and the *POV-ray* windows program.

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Supporting Information Available: Crystallographic data in CIF format for compounds **1**–**4**, tables of atomic coordinates and vibrational analysis, and a figure depicting the atom-labeling scheme used for the DFT calculations on $[CpRuCl]_2(\mu\text{-}3,5\text{-}(CF_3)_2Pz)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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