Notes

Cleavage of the Carbon−Sulfur Bonds in Thiophenes by a Binuclear Ruthenium Complex

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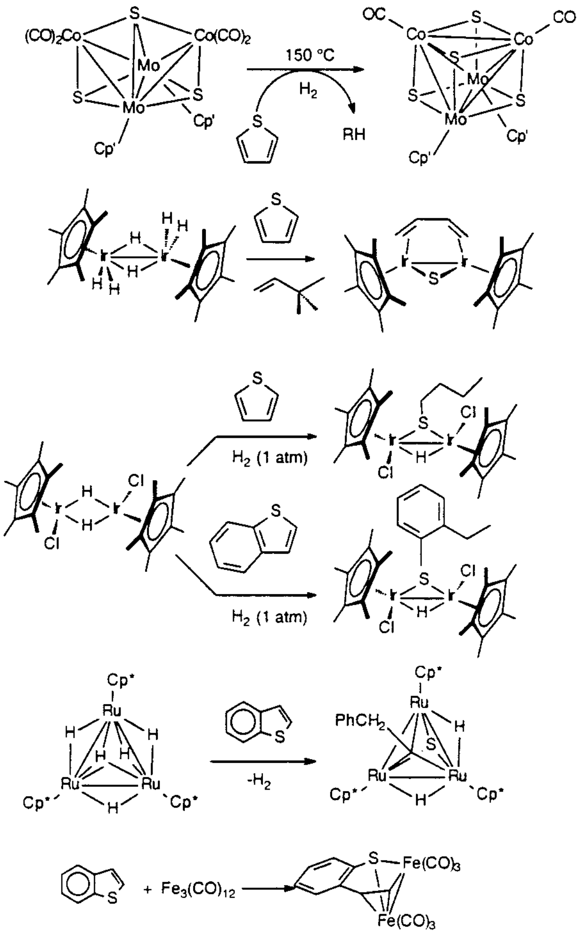
Received December 10, 1998

*Summary: The dinuclear polyhydride [Cp*RuH$_2$]$_2$ (Cp* = C$_5$Me$_5$) reacts with thiophene at ambient temperature to give a C−S ring-opened "flyover" complex in which all atoms are bound to the metal centers. A similar reaction with 2-methylthiophene also gives a related product. The products were characterized by single-crystal X-ray diffraction.*

Introduction

Hydrodesulfurization is the industrial process in which sulfur is removed from organosulfur compounds found in petroleum feedstocks. The process is conducted by treating the fuel with H_2 at approximately 350 °C over a cobalt- or nickel-doped molybdenum sulfide catalyst supported on alumina. Other metals, such as Ru, Os, Rh, and Ir, are known to produce better catalysts, but are not used due to their increased expense.[1] While many homogeneous systems have been explored to model the HDS process, few of these have focused on the use of ruthenium as the active species.[2−4]

Scheme 1



As the commercial catalyst is believed to involve reactions at the edge of a cobalt-containing molydenum sulfide sheet,[1] polynuclear transition metal complexes serve as particularly appropriate models for studying the binding modes of sulfur-containing hydrocarbons to a metal−sulfide surface. Several polynuclear systems have been studied in some detail, such as those shown in Scheme 1. Extensive work has been done by Curtis and co-workers with Mo_2Co_2 sulfido clusters. The species $Cp'_2Mo_2Co_2S_3(CO)_4$ can react with thiophene in the presence of H_2 at 150 °C to give the cluster $Cp'_2Mo_2Co_2(CO)_2S_4$ and a mixture of C_2−C_4 hydrocarbons.[5,6] Adams has used osmium carbonyl clusters to cleave C−S bonds in thietanes.[7,8] The iridium dimer [Cp*IrH$_3$]$_2$ reacts with thiophene in the presence of a hydrogen acceptor to give a product in which *both* C−S bonds have been cleaved.[9] The less reactive chloro dimer [Cp*IrH(μ-Cl)]$_2$ cleaves only one bond in thiophene and benzothiophene, but also hydrogenates the hydrocarbon portion of the fragment.[10] Recently, a trinuclear ruthenium cluster has been reported that cleaves both C−S bonds in benzothiophene.[11] Perhaps the oldest example

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10.1021/om981007g CCC: $18.00 © 1999 American Chemical Society
Publication on Web 03/31/1999

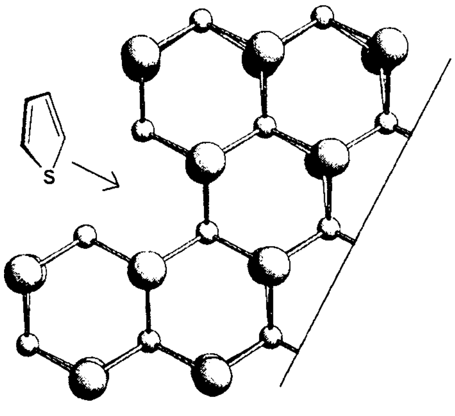


Figure 1. Representation of an edge site on a molybdenum/cobalt sulfide particle containing two sulfur vacancies.

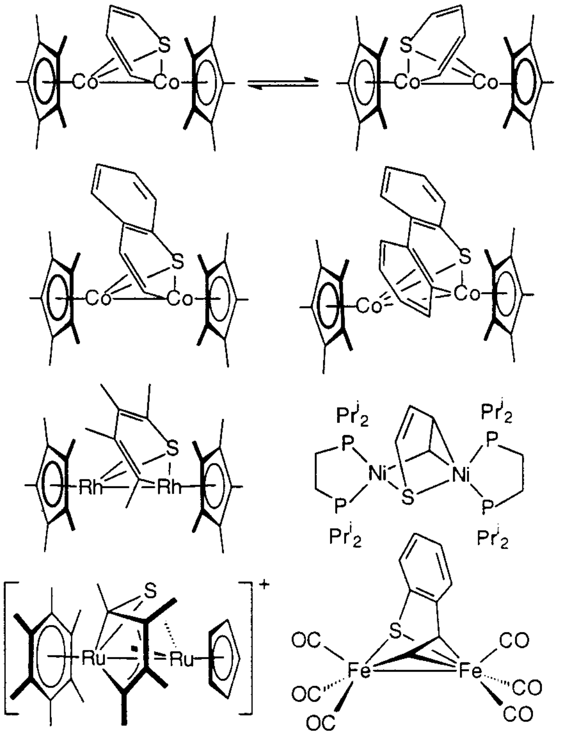


Figure 2. Examples of bridging thiophene complexes.

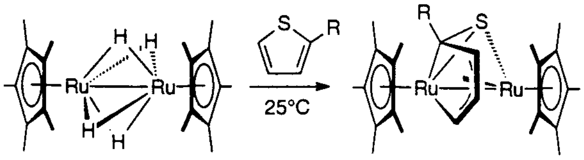
of thiophene C−S cleavage by a cluster is that of $Fe_3(CO)_{12}$ reacting with benzothiophene.[12,13]

Several examples of mononuclear metal complexes that activate thiophene (or benzothiophene) and then go on to produce a dinuclear product in which the thiophene bridges the metal center are known. These compounds serve as particularly good models for intermediates in the HDS reaction in which two adjacent edge sites on molybdenum/cobalt sulfide particle have been made available for thiophene activation, as indicated in Figure 1.[1] One family of complexes that have been structurally characterized include $Cp^*_2Co_2(\mu$-thiophene$)$,[14] $Cp^*_2Co_2(\mu$-benzothiophene$)$,[15] and $Cp^*_2Co_2(\mu$-dibenzothiophene$)$,[16] as shown in Figure 2. The bridging thiophene moieties in these complexes are fluxional, with one carbon (γ to sulfur) undergoing a "flip-flop" from one metal center to the other. Rauchfuss has prepared an analogous dinuclear rhodium complex formed from tetramethylthiophene (Figure 2), although the product was not structurally characterized.[17] The iron compound $Fe_2(CO)_6(\mu$-benzothiophene$)$ displays a similar structure and is also fluxional. Bis(phosphine)nickel complexes are also known with the μ-S,μ-C structure for the ring-opened thiophene. The complexes are fluxional, and structural characterization of the benzothiophene complex shows that there is no nickel−nickel bond,[18] unlike the cobalt and iron complexes. Finally, a $CpRu(\eta^3,\eta^4\text{-}SC_4Me_4)Ru(C_6Me_6)$ system has also been characterized by Rauchfuss that is closely related to the complexes to be described here.[19]

This note continues our studies of the reactivity of thiophene with binuclear metal polyhydric systems. Examples of thiophene activation by ruthenium to give similar bridging μ-S,μ-C structures are presented. The products are compared and contrasted with the other members of this class of compounds.

Results and Discussion

Reaction of $[(C_5Me_5)RuH_2]_2$ with Thiophene. The polyhydride $[(C_5Me_5)RuH_2]_2$ (**1**) was prepared as a red crystalline solid by the reaction of $[(C_5Me_5)RuCl_2]_2$ with $LiAlH_4$ as described in the literature.[20] **1** was then reacted with excess thiophene at room temperature for a period of 48−60 h. A dark brown product, formulated as $[(C_5Me_5)Ru]_2(\eta^3,\eta^4\text{-}C_4H_4S)$ (**2**), was obtained in quantitative NMR yield (eq 1).



1

2, R = H
3, R = Me (1)

The ^1H NMR spectrum of the complex showed four inequivalent proton resonances at δ 9.08, 4.42, 4.15, and 3.15 for the coordinated thiabutadienyl ligand and two distinct Cp* resonances at δ 1.96 and 1.66. High-temperature ^1H NMR spectroscopy of **2** up to 358 K showed no change in the two Cp* resonances, indicating that the two Cp* ligands do not exchange on the time scale of a few milliseconds, unlike the previously mentioned cobalt complex $[Cp^*Co]_2(\eta^2,\eta^3\text{-}C_4H_4S)$. A COSY spectrum of **2** is shown in Figure 3. The downfield resonance at δ 9.08 is assigned as being attached to C4, coupling to H3 (δ 3.15) and H2 (δ 4.15), rather than thioaldehyde carbon C1, by comparison to NMR data

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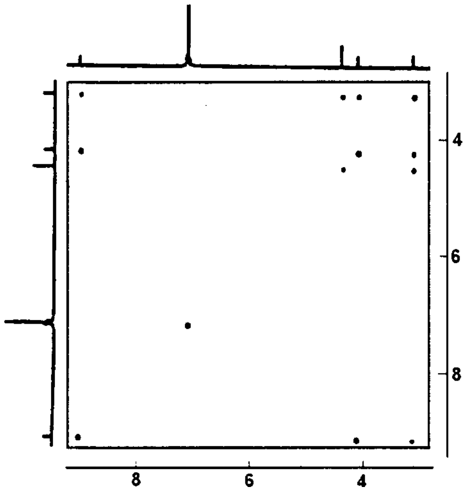

Figure 3. COSY spectrum of **2**.

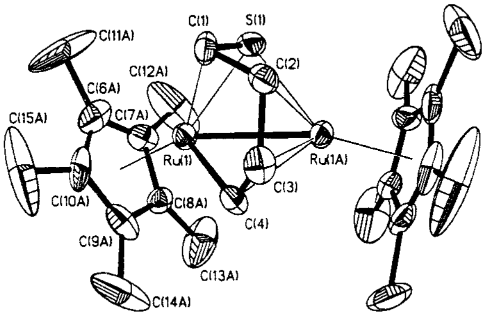

Figure 4. ORTEP drawing of **2**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Distances (Å) for 2 and 3

	distance, Å	
bond	**2**	**3**
Ru1−Ru1A	2.764(1)	2.754(2)
Ru1−S1	2.234(4)	2.254(10)
Ru1−C1	2.18(3)	2.06(2)
Ru1−C4	2.04(2)	2.04(3)
Ru1A−S1	2.336(5)	2.333(9)
Ru1A−C2	2.12(3)	2.27(2)
Ru1A−C3	2.222(14)	2.22(2)
Ru1A−C4	2.17(2)	2.13(4)
S1−C1	1.63(3)	1.72(2)
C1−C2	1.48(2)	1.51(3)
C2−C3	1.57(3)	1.47(3)
C3−C4	1.42(2)	1.43(4)

for the methylthiophene analogue (vide infra). The resonance at δ 4.42 is assigned to H1, coupling only to H3 via a w-coupling.

A single-crystal X-ray structure of **2** was determined with some difficulty, as the Cp* ring was disordered over two sites and the molecule sits on a crystallographic 2-fold axis, inducing a disorder in the thiabutadienyl ligand. These disorders were successfully modeled and refined to R1 = 0.0332, wR2 = 0.0885. Figure 4 shows an ORTEP drawing of the molecule, confirming the cleavage of the C−S bond and the η^3,η^4-coordination geometry of the ligand. Selected distances are given in Table 1. The two ruthenium atoms are 2.764 Å apart, indicating the presence of a ruthenium−ruthenium single bond as seen in $(C_6Me_6)CpRu_2(\eta^3,\eta^4\text{-}SC_4Me_4)$ (d_{Ru-Ru} = 2.728 Å). The dihedral angle S1−C1−C2−C3 is 104°, permitting little π-overlap between C1 and C2. Rather, the molecule adopts an η^2-thioaldehyde/η^3-allyl bonding motif, unlike most of the previously characterized systems shown in Figure 2 but similar to the diruthenium system synthesized by Rauchfuss.[19] This "flyover" binding of a thiabutadienyl ligand was also seen in $Co_2(CO)_4[\eta^3,\eta^4\text{-}SC_4(CF_3)_4]$.[21] The presence of the disorder renders further discussion of the bond distances unreliable.

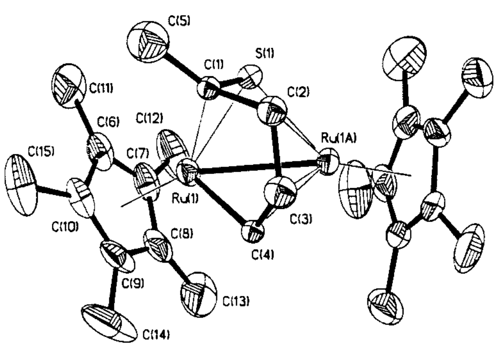

Figure 5. ORTEP drawing of **3**. Ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Reaction of $[(C_5Me_5)RuH_2]_2$ with 2-Methylthiophene. The reaction of $[(C_5Me_5)RuH_2]_2$ with 2-methylthiophene over 5 days at 22 °C yielded a C−S cleaved compound (**3**) similar to **2** (eq 1). A single-crystal X-ray structure determination showed the same 2-fold disorder of the thiabutadienyl ligand as in **2**, but the Cp* groups were now ordered. Refinement was carried to convergence, with R1 = 0.0578, wR2 = 0.1223. An ORTEP drawing is shown in Figure 5. Once again, η^3,η^4-coordination geometry of thiabutadienyl ligand is observed. The methyl group appears at C1, indicating that cleavage of the less hindered C−S bond has occurred as seen previously with $[Cp^*Rh(PMe_3)]$.[22] Selected distances are given in Table 1.

The ^1H NMR spectrum of **3** shows two distinct Cp* resonances (δ 1.92, 1.67) and three vinylic resonances at δ 9.00, 4.32, and 3.00. The upfield resonance at δ 9.00 is assigned to H4 (cf. 9.08 in **2**), with the resonances at 4.32 and 3.00 being assigned to H2 and H3 by analogy with **2**. No reaction of either **2** or **3** with 1 atm hydrogen occurred after 1 day at 65 °C.

Conclusions

Both thiophene and 2-methylthiophene undergo C−S cleavage upon reaction with $(Cp^*RuH_2)_2$. No incorporation of hydrogen is observed. C−S cleavage occurs away from the methyl group in 2-methylthiophene. An unusual η^3,η^4-coordination is seen in which each atom of the thiophene is bound to one of the metal centers. In comparing these dinuclear ruthenium compounds with the dicobalt and dirhodium analogues (Figure 2), the obvious difference is the absence of a free double bond in the thiabutadienyl ligand. The ruthenium compounds achieve an 18-electron configuration by inclusion of the second double bond of the thiabutadienyl ligand in bonding to the metals. To formally add one electron to each ruthenium center, the butadiene coordination is

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split in an η^3/η^1 fashion. The dinuclear nickel complexes, on the other hand, have one extra electron compared to the dicobalt and dirhodium complexes (Figure 2) and reduce their electron count by cleaving the nickel−nickel bond.

Experimental Section

General Comments. All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corporation dri-lab. Diethyl ether, benzene, and toluene were distilled from dark purple solutions of benzophenone ketyl. $[(C_5Me_5)RuCl_2]_2$[23]and $[(C_5Me_5)RuH_2]_2$[24] were prepared as described in the literature. Thiophene and 2-methylthiophene were purchased from Aldrich Chemical Co. and purified as previously reported.[25]

All NMR spectra were recorded on a Bruker AMX400 NMR spectrometer. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced to the chemical shifts of residual solvent resonances (C_6H_6, δ 7.15). Data were typically recorded with a digital resolution of 0.3 Hz. All temperatures for variable-temperature NMR spectroscopy were calibrated relative to the chemical shift differences in the NMR spectra of known standards (298−386 K, 80% ethylene glycol in DMSO-d_6; 298−228 K, 4% methanol in methanol-d_4). Analyses were obtained from Desert Analytics.

Reaction of $[(C_5Me_5)RuH_2]_2$ with Thiophene. $[(C_5Me_5)RuH_2]_2$ (294 mg, 0.617 mmol) and thiophene (0.873 mg, 10.4 mmol) were added to 16 mL of benzene. The dark red solution was stirred for 72 h at 22 °C. The solvent was removed under reduced pressure and the residue recrystallized from a toluene/hexanes mixture (3 mL:5 mL) at −30 °C for 48 h. The black-red powder was collected on a frit to yield 22 mg of pure product (6%). The mother liquor was allowed to sit at 22 °C until all of the solvent had evaporated. The large black-red crystals were washed 3 × 2 mL with hexanes and gave another 106 mg of product (37% total). For **2**, ^1H NMR (C_6D_6): δ 9.08 (dd, $J = 5.5$, 2 Hz, 1 H), 4.42 (d, $J = 2$ Hz, 1 H), 4.15 (dd, $J = 4.4$, 3 Hz, 1 H), 3.15 (q, $J = 2$ Hz, 1 H), 1.96 (s, 15 H), 1.66 (s, 15 H). ^{13}C NMR (C_6D_6): δ 174.2 (s, C_4H_4S), 102.4 (s, C_4H_4S), 70.9 (s, C_4H_4S), 52.9 (s, C_4H_4S), 92.8 (s, C_5Me_5), 90.6 (s, C_5Me_5), 12.5 (s, C_5Me_5), 11.1 (s, C_5Me_5). Anal. Calcd (found) for $Ru_2SC_{24}H_{34}$: C, 51.78 (51.73); H, 6.16 (6.14).

Reaction of $[(C_5Me_5)RuH_2]_2$ with 2-Methylthiophene. $[(C_5Me_5)RuH_2]_2$ (84 mg, 0.176 mmol) and 2-methylthiophene (259 mg, 2.64 mmol) were added to 8 mL of benzene. The solution was stirred for 5 days at 22 °C. The solvent was removed under reduced pressure and the residue recrystallized from 2 mL of hexanes at −30 °C to give 22 mg of pure product (22%). Additional less pure product was obtained by evaporation of solvent. ^1H NMR (C_6D_6): δ 9.00 (dd, $J = 4.3$, 1.8 Hz, 1 H), 4.32 (dd, $J = 4.5$, 2.7 Hz, 1 H), 3.00 (t, $J = 2.3$ Hz, 1 H), 1.92 (s, 15 H), 1.67 (s, 15 H), 1.38 (s, 3 H). Anal. Calcd (found) for $Ru_2SC_{25}H_{36}$: C, 52.61 (52.13); H, 6.36 (6.34).

Structural Determination of 2 and 3. Crystals of **2** were grown from a concentrated solution of toluene. A red-brown crystal was mounted on a glass fiber using epoxy. The unit cell parameters were determined from the least-squares refinement of 25 reflections with θ between 4° and 15° on an Enraf-Nonius CAD4. One quadrant of intensity data was collected on a c-centered monoclinic lattice according to the parameters given in Table 2. The space group was assigned as *C*2/*c* on the basis of systematic absences and intensity distribution statistics. For a *Z* value of 4, there is only half of a molecule in the asymmetric unit. The structure was solved by using the Patterson method to locate the Ru atom. Subsequent difference Fourier maps located the Cp* ligand and the thiabutadiene ligand, which was disordered due to the molecule lying on a crystallographic 2-fold axis. The molecule was refined isotropically employing full-matrix least-squares on F^2 (Siemens, SHELXTL, version 5.04). Anisotropic refinement showed severe elongation of the thermal ellipsoids of the Cp* ligand, so a model was imposed in which two isotropic rigid Cp* groups (0.5 occupancy each) were allowed to refine independently. In the final model, hydrogen atoms were included in idealized positions and all non-hydrogen atoms were refined anisotropically. The structure refined with final residuals[26] of R1 = 0.0332% ($I > 2\sigma(I)$), wR2 = 0.0885% ($I > 2\sigma(I)$).

Table 2. X-ray Structural Parameters for 2 and 3

	2	**3**
Crystal Parameters		
chemical formula	$Ru_2SC_{24}H_{34}$	$Ru_2SC_{25}H_{36}$
fw	556.71	570.74
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
Z	4	4
a, Å	11.311(2)	11.708(3)
b, Å	13.485(3)	13.206(6)
c, Å	15.682(5)	16.289(6)
β, deg	103.26(2)	106.56(3)
vol., Å^3	2328.2(9)	2414(2)
ρ_{calc}, g cm^{-3}	1.588	1.570
cryst dimens, mm^3	0.34 × 0.26 × 0.22	0.22 × 0.20 × 0.16
temp, K	233	293
Measurement of Intensity Data		
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	Mo, 0.71073 Å	Mo, 0.71073 Å
scan range/time, deg/s	$0.8 + 0.35 \tan \theta/3 - 30$	$0.8 + 0.35 \tan \theta/3 - 30$
2θ range, deg	2.4−25.0	2.4−25.0
data collected	$0 \leq h \leq 13$, $0 \leq k \leq 16$, $-18 \leq l \leq 18$	$0 \leq h \leq 13$, $0 \leq k \leq 15$, $-19 \leq l \leq 18$
no. of data collected	2155	2232
no. of unique data	2048	2123
no. of obs data ($I > 2\sigma(I)$)	1682	1234
agreement between equivalent data (R_{int})	0.0220	0.0715
no. of params varied	255	138
μ, mm^{-1}	1.393	1.346
systematic absences	*hkl*, *h*+*k* odd, *h*0*l*, *l* odd	*hkl*, *h*+*k* odd, *h*0*l*, *l* odd
abs cor	none	none
R1(F_o), wR2(F_o^2) ($I > 2\sigma$)	0.0332, 0.0885	0.0578, 0.1223
R1(F_o), wR2(F_o^2) (all data)	0.0488, 0.1060	0.1541, 0.1515
goodness of fit	0.686	1.041

The structural determination of **3** was carried out similarly to that of **2**, except that no disorder of the Cp* ligand was noted and the thiabutadienyl ligand was refined isotropically, as anisotropic refinement led to nonpositive definite values for these ellipsoids. The structure refined with final residuals of R1 = 0.0578, wR2 = 0.1223.

Acknowledgment is made to the National Science Foundation (Grant CHE-9421727) for their support of this work.

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[26] Using the SHELX95 package, $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$, $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [f^0(\text{max of 0 or } F_o^2) + (1 - f)F_c^2]$. Source of scattering factors f_o, f', and f'': Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Supporting Information Available: A summary of crystallographic data, bond distances and angles, thermal parameters, and calculated hydrogen coordinates for the structures of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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