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Thiophene Carbon–Sulfur Bond Cleavage by Cobalt. Synthesis, Structure, and Dynamics of $[(C_5Me_5)Co]_2(C_4H_4S)$

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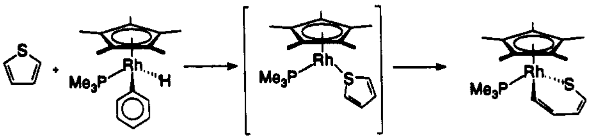
Summary: The reaction of $(C_5Me_5)Co(C_2H_4)_2$ with thiophene proceeds thermally to give the unusual dimer $[(C_5Me_5)Co]_2(C_4H_4S)$. An X-ray structure shows that a carbon–sulfur bond has been cleaved and the sulfur and α-carbon bridge the two metal centers. The compound crystallizes in monoclinic space group $P2_1/n$ with a = 8.512 (2) Å, b = 14.566 (4) Å, c = 18.954 (4) Å, β = 100.15 (2)°, Z = 4, and V = 2313.2 (2.0) Å^3. In solution, the complex shows dynamic behavior in which the μ_2-C_4H_4S group flip-flops from one metal center to the other. Modeling of this behavior gives activation parameters $\Delta H^\ddagger$ = 8.6 (3) kcal/mol and $\Delta S^\ddagger$ = −13.8 (1.3) eu.

There has been substantial interest in the interactions of homogeneous transition-metal complexes with thiophene derivatives as models for hydrodesulfurization (HDS) catalysis. The latter process is carried out industrially in the hydroprocessing of oil over a cobalt-containing molybdenum sulfide catalyst.[1] Recent reviews have covered a variety of coordination geometries and reaction pathways found in homogeneous thiophene complexes.[2] One of the more intriguing of these pathways involves the reaction in which the aromatic thiophene ring is broken open by oxidative addition to a transition metal.

Earlier work in our lab has provided an example of this type of C–S bond cleavage, and the oxidative addition has been shown to occur by way of initial coordination of the thiophene sulfur, followed by migration of the α-carbon to the metal center, thereby producing a six-membered metallathiahexadiene ring (eq 1).[3] Angelici has seen this same type of reaction in a related iridium complex, although the immediate precursor was an η^4-thiophene ligand.[4] Other complexes in which the C–S bond of a thiophene derivative are cleaved are also known, although the polynuclear binding of the ligand masks the initial C–S cleavage adduct.[5-7]



(1)

In this paper we report the first example of a cobalt complex that cleaves the C–S bond of thiophene. The work stems from the discovery that the rhodium complex $(C_5Me_5)Rh(C_2H_4)_2$ reacts with thiophene to give a ring-opened C–C coupled product, $[(C_5Me_5)Rh]_2[\mu_2\text{-}1,2,3,4\text{-}\eta^4\text{-}5,6,7,10\text{-}\eta^4\text{-}S(CH)_8S]$, by way of an initial C–S insertion.[8]

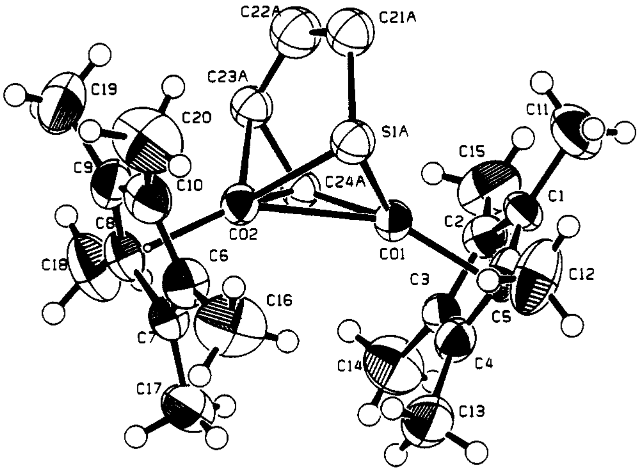
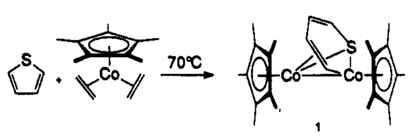


Figure 1. ORTEP drawing of $[(C_5Me_5)Co]_2(C_4H_4S)$. Ellipsoids are shown at the 50% level, and hydrogen atoms have been omitted for clarity.

Results and Discussion

The cobalt complex $(C_5Me_5)Co(C_2H_4)_2$ reacts with excess thiophene in benzene solution at 70 °C. Reaction is apparent after heating for only a few minutes, as the red-orange solution becomes dark black. Ethylene was removed periodically by freeze–pump–thaw degassing, ultimately leading to the isolation of a black solid following solvent removal. This solid was examined by ^1H NMR spectroscopy, showing a large broad singlet at δ 1.892 and four multiplets at 3.249, 4.542, 5.581, and 9.145 in a 30:1:1:1:1 ratio. The ^{13}C JMOD NMR spectrum (recorded at −50 °C to decrease quadrupolar broadening by the cobalt) shows four downfield singlet resonances at δ 187.91, 139.24, 120.85, and 85.08 and two distinct sets of C_5Me_5 resonances. These observations led to the formulation of the product as $[(C_5Me_5)Co]_2(C_4H_4S)$ (1) (eq 2), in which the cobalt has inserted into the thiophene C–S bond to form a six-membered ring that is chelated to a second $(C_5Me_5)Co$ moiety.



(2)

A single-crystal X-ray determination of the structure of 1 confirms the above assignment. The complex crystallizes in a monoclinic space group $P2_1/n$ with Z = 4, and routine solution of the structure showed evidence for disorder of the bridging ligand, in which the bridging ring had interchanged the locations of the sulfur and the coordinated double bond, and in which the η^2-coordinated double bond

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[1] Schuman, S. C.; Shalit, H. *Catal. Rev.* **1970**, *4*, 245–313.

[2] Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387–394. Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259–329. Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61–76. Friend, C. M.; Roberts, J. T. *Acc. Chem. Res.* **1988**, *21*, 394–400.

[3] Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1991**, *113*, 559–564. Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151–160.

[4] Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199–204.

[5] King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600–3604.

[6] Hübener, P.; Weiss, E. *J. Organomet. Chem.* **1977**, *129*, 105–115.

[7] Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B. *Organometallics* **1988**, *7*, 1171–1177.

[8] Jones, W. D.; Chin, R. M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 357–358.

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Table I. Selected Distances (Å) and Angles (deg) for $[(C_5Me_5)Co]_2(C_4H_4S)$[a]

Comparative Bond Lengths			
Co(1)–S(1A)	2.120 (4)	Co(1)–S(1B)	2.19 (1)
Co(2)–S(1A)	2.204 (4)	Co(2)–S(1B)	2.028 (7)
Co(1)–C(24A)	1.90 (1)	Co(2)–C(24B)	2.05 (2)
S(1A)–C(21A)	1.94 (2)	S(1B)–C(21B)	2.08 (4)
C(21A)–C(22A)	1.36 (2)	C(21B)–C(22B)	1.30 (5)
C(22A)–C(23A)	1.40 (2)	C(22B)–C(23B)	1.19 (4)
C(23A)–C(24A)	1.53 (2)	C(23B)–C(24B)	1.41 (4)
Co(2)–C(23A)	2.12 (1)	Co(1)–C(23B)	2.21 (3)
Co(2)–C(24A)	2.07 (1)	Co(1)–C(24B)	2.18 (2)
CEN(1)–Co(1)	1.67	CEN(2)–Co(2)	1.67
Co(1)–Co(2)	2.484 (2)		
Comparative Bond Angles			
Co(2)–Co(1)–S(1A)	56.5 (1)	Co(1)–Co(2)–S(1B)	56.9 (3)
Co(2)–Co(1)–C(24A)	54.4 (3)	Co(1)–Co(2)–C(24B)	56.5 (7)
S(1A)–Co(1)–C(24A)	94.7 (4)	S(1B)–Co(2)–C(24B)	96.4 (8)
Co(1)–Co(2)–S(1A)	53.4 (1)	Co(2)–Co(1)–S(1B)	51.0 (2)
Co(1)–Co(2)–C(23A)	78.8 (4)	Co(2)–Co(1)–C(23B)	72.3 (7)
Co(1)–Co(2)–C(24A)	48.4 (3)	Co(2)–Co(1)–C(24B)	51.7 (6)
S(1A)–Co(2)–C(23A)	84.6 (3)	S(1B)–Co(1)–C(23B)	79.2 (7)
S(1A)–Co(2)–C(24A)	87.7 (3)	S(1B)–Co(1)–C(24B)	88.2 (7)
C(23A)–Co(2)–C(24A)	42.9 (5)	C(23B)–Co(1)–C(24B)	37 (1)
Co(1)–S(1A)–Co(2)	70.1 (1)	Co(1)–S(1B)–Co(2)	72.1 (3)
Co(1)–S(1A)–C(21A)	99.1 (5)	Co(2)–S(1B)–C(21B)	89 (1)
Co(2)–S(1A)–C(21A)	100.0 (5)	Co(1)–S(1B)–C(21B)	101 (1)
S(1A)–C(21A)–C(22A)	113 (1)	S(1B)–C(21B)–C(22B)	108 (3)
C(21A)–C(22A)–C(23A)	122 (1)	C(21B)–C(22B)–C(23B)	125 (3)
Co(2)–C(23A)–C(22A)	116.0 (9)	Co(1)–C(23B)–C(22B)	126 (2)
Co(2)–C(23A)–C(24A)	67.0 (6)	Co(1)–C(23B)–C(24B)	70 (1)
C(22A)–C(23A)–C(24A)	121 (1)	C(22B)–C(23B)–C(24B)	119 (3)
Co(1)–C(24A)–Co(2)	77.2 (4)	Co(1)–C(24B)–Co(2)	71.9 (8)
Co(1)–C(24A)–C(23A)	116.6 (8)	Co(2)–C(24B)–C(23B)	105 (2)
Co(2)–C(24A)–C(23A)	70.0 (6)	Co(1)–C(24B)–C(23B)	73 (1)
Co(2)–Co(1)–CEN(1)	155.3	Co(1)–Co(2)–CEN(2)	149.7

[a] Data for the disordered molecules A and B are in opposing columns. CEN(1) is the centroid of the C_5Me_5 ligand attached to Co(1), and CEN(2) is the centroid of the C_5Me_5 ligand attached to Co(2).

Table II. Positional Parameters and B_{eq} Values for $[(C_5Me_5)Co]_2(C_4H_4S)$

Atom	x	y	z	B_{eq}, Å^2
Co(1)	0.3756 (1)	0.35724 (7)	0.70670 (5)	3.21 (5)
Co(2)	0.3166 (1)	0.25371 (8)	0.60119 (5)	3.28 (5)
S(1A)	0.5448 (4)	0.3233 (2)	0.6411 (2)	3.91 (7)
S(1B)	0.356 (1)	0.2075 (6)	0.7037 (4)	3.9
C(1)	0.4790 (9)	0.4405 (6)	0.7883 (4)	3.5 (4)
C(2)	0.349 (1)	0.3939 (5)	0.8076 (4)	3.7 (4)
C(3)	0.2126 (9)	0.4173 (5)	0.7582 (4)	3.3 (4)
C(4)	0.254 (1)	0.4828 (5)	0.7095 (4)	3.9 (4)
C(5)	0.420 (1)	0.4950 (5)	0.7280 (4)	4.0 (4)
C(6)	0.232 (1)	0.3053 (6)	0.4999 (4)	4.2 (4)
C(7)	0.100 (1)	0.2782 (6)	0.5317 (4)	3.6 (4)
C(8)	0.119 (1)	0.1843 (6)	0.5498 (4)	4.0 (4)
C(9)	0.258 (1)	0.1521 (6)	0.5272 (4)	4.4 (4)
C(10)	0.329 (1)	0.2237 (7)	0.4971 (4)	4.7 (5)
C(11)	0.651 (1)	0.4352 (8)	0.8258 (5)	7.3 (6)
C(12)	0.515 (1)	0.5600 (6)	0.6904 (5)	7.4 (6)
C(13)	0.145 (1)	0.5324 (6)	0.6517 (5)	6.8 (5)
C(14)	0.044 (1)	0.3845 (7)	0.7615 (5)	7.0 (6)
C(15)	0.356 (1)	0.3290 (7)	0.8706 (4)	6.5 (5)
C(16)	0.263 (1)	0.3974 (7)	0.4715 (5)	7.7 (6)
C(17)	−0.042 (1)	0.3365 (7)	0.5392 (4)	5.9 (5)
C(18)	0.006 (1)	0.1289 (7)	0.5838 (5)	7.1 (5)
C(19)	0.319 (1)	0.0534 (7)	0.5332 (6)	8.3 (6)
C(20)	0.478 (1)	0.2208 (9)	0.4645 (5)	8.5 (7)
C(21A)	0.657 (2)	0.226 (1)	0.6987 (8)	4.6 (4)
C(21B)	0.586 (4)	0.170 (3)	0.691 (2)	4.6
C(22A)	0.559 (2)	0.155 (1)	0.7099 (8)	5.2 (4)
C(22B)	0.659 (4)	0.244 (3)	0.676 (2)	5.2
C(23A)	0.394 (1)	0.159 (1)	0.6844 (6)	3.6 (2)
C(23B)	0.605 (3)	0.320 (2)	0.675 (2)	3.6
C(24A)	0.292 (2)	0.2361 (9)	0.7071 (6)	3.1 (2)
C(24B)	0.496 (3)	0.349 (2)	0.615 (1)	3.1

had changed cobalt atoms (effectively a C_2 rotation of the SC_4H_4 group perpendicular to the Co–Co axis). The solution proceeded to model this type of disorder, with 69/31 refined populations for the two sites. An ORTEP drawing is shown in Figure 1. Unfortunately, the effect of the disorder renders discussion of the bond lengths unreliable, and it is difficult to ascertain if the noncoordinated double bond is localized. The σ-vinylic double bond that π-coordinates to the second cobalt does appear to be lengthened slightly. The opened thiophene ligand is puckered in such a fashion that the cobalt, sulfur, C(23), and C(24) are nearly planar, but with the C(21)–C(22) double bond lying above this plane. The cobalt–cobalt distance of 2.484 Å is in the range seen for other dicobalt species with bridging ligands, such as $[(C_5Me_5)Co]_2(\mu\text{-}CH_2)(CO)_2$ (2.502 Å),[9] but is longer than that of the multiply bonded dimers such as $[(C_5Me_5)Co]_2(\mu\text{-}CO)_2$ (2.338 Å)[10] and $[(C_5H_5)Co]_2(\mu\text{-}NO)_2$ (2.372 Å).[11] Other bond distances are given in Table I, and coordinates are listed in Table II.

The observation of a broad resonance in the ^1H NMR spectrum at room temperature suggests that a fluxional process equilibrates the two C_5Me_5 rings (eq 3). When the temperature is lowered to −50 °C (THF-d_8 solvent), the broad resonance is observed to separate into two distinct resonances at δ 1.900 and 1.568. Spectra were recorded at intermediate temperatures, and computer modeling of the coalescence behavior by complete band shape analysis[12] allowed the determination of the rate as a function of temperature. An Eyring plot of this data (Figure 2) gives the activation parameters $\Delta H^{\ddagger}$ = 8.6 (3) kcal/mol and $\Delta S^{\ddagger}$ = −13.8 (1.3) eu. During the coalescence of the two C_5Me_5 rings, the four olefin resonances remain sharp.

(3)

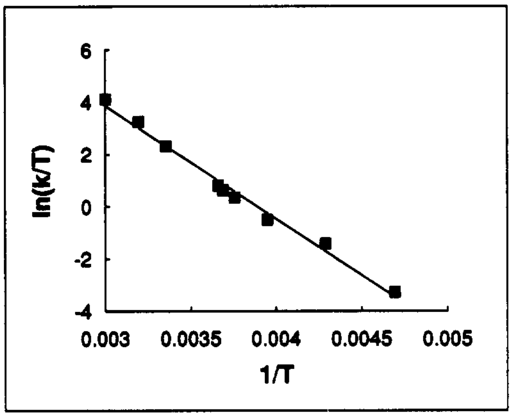

Figure 2. Eyring plot for the "flip-flop" of the thiophene ligand in 1.

The formation of this dimeric complex is believed to occur by way of initial loss of ethylene, followed by thiophene coordination and insertion into the C–S bond. Loss of the second ethylene most likely occurs in this Co^{III} intermediate, which then reacts with another $[(C_5Me_5)Co]$ fragment to produce the dimer. It is interesting to compare

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[9] Herrmann, W. A.; Huggins, J. M.; Bauer, C.; Ziegler, M. L.; Pfisterer, H. *J. Organomet. Chem.* **1984**, *262*, 253–262.

[10] Cirjak, L. M.; Ginsberg, R. E.; Dahl, L. F. *Inorg. Chem.* **1982**, *21*, 940–957.

[11] Bernal, I.; Korp, J. D.; Reisner, G. M.; Herrmann, W. A. *J. Organomet. Chem.* **1977**, *139*, 321–336.

[12] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

Table III. Summary of Crystallographic Data for $[(C_5Me_5)Co]_2(C_4H_4S)$

Crystal Parameters	
chem formula	$Co_2SC_{24}H_{34}$
fw	472.46
cryst syst	monoclinic
space group (No.)	$P2_1/n$ (14)
Z	4
a, Å	8.512 (2)
b, Å	14.566 (4)
c, Å	18.954 (4)
β, deg	100.15 (2)
vol, Å^3	2313.2 (2.0)
ρ_{calc}, g cm^{-3}	1.356
cryst dimens, mm	0.22 × 0.26 × 0.30
temp, °C	−20
Measurement of Intensity Data	
λ (Mo radiation, graphite monochromated), Å	0.710 73
2θ range, deg	4–50
no. of data collcd	$+h,+k,\pm l$
no. of unique data $F^2 > 3\sigma(F^2)$	1849
no. of params varied	235
μ, cm^{-1}	15.25
systematic absences	$0k0$, k odd; $h0l$, $h + l$ odd
abs cor (range of transm factors)	differential (0.81–1.19)
$R(F_o)$	0.0467
$R_w(F_o)$	0.0522
goodness of fit	1.71
largest residual peak in difference map, e Å^{-3}	0.45

this reaction with the rhodium analog, in which the 16-electron intermediate $[(C_5Me_5)\overline{Rh(SCH{=}CHCH{=}C}H)]$ dimerizes to give a product with a $-S(CH)_8S-$ chain.[8] Also of interest is comparison with the tetramethylthiophene complexes studied by Rauchfuss and co-workers.[13] Thermal decomposition of $(C_5Me_5)Rh(\eta^4\text{-}C_4Me_4S)$ initially gives the bis(thiophenyl) adduct $((C_5Me_5)Rh)[(C_5Me_5)Rh(C_4Me_4S)]_2$, which then goes on to give small amounts of a complex assigned as the rhodium–tetramethylthiophene analog of 1. Of substantial interest are the iron complexes studied by Hübener and Weiss[6] and Rauchfuss.[7] The former workers have found that reaction of 2-methylthiophene with $Fe_3(CO)_{12}$ gives a diiron product (0.7% yield) containing a similar ring-opened bridging thiophene unit that was crystallographically characterized. No mention was made as to the rigidity of this species, but Rauchfuss has reported similar diiron derivatives in which a ring-opened benzothiophene bridges the two metal centers, and has confirmed the presence of a "flip-flop" of the organic ligand by dynamic ^{13}C NMR spectroscopy. This thiaferrole complex was also shown to undergo further desulfurization to give a ferrole derivative and FeS.

Conclusions

In summary, this paper reports the first example of a cobalt complex that is capable of activating thiophene via C–S bond cleavage. As cobalt is an integral part of commercial HDS catalysts, this work may serve to model species that are actively involved in HDS.

Experimental Section

General Comments. All manipulations were done under nitrogen, either in a glovebox or on a high-vacuum line. All solvents were distilled from benzophenone ketyl under nitrogen. All materials were of reagent grade quality and were used without further purification. $(C_5Me_5)Co(C_2H_4)_2$ was prepared as previously described.[14] NMR spectra were recorded on a Bruker AMX-400 spectrometer. X-ray data were collected using an Enraf-Nonius Cad4 diffractometer.

Synthesis of $[(C_5Me_5)Co]_2(C_4H_4S)$. $(C_5Me_5)Co(C_2H_4)_2$ (97 mg, 0.39 mmol) was dissolved in 8 mL of C_6H_6 and thiophene (0.65 mL, 8.12 mmol) added to the dark red-orange solution. The solution was placed in a Teflon stopcock sealed ampule, freeze–pump–thaw degassed three times, and heated in an oil bath at 70 °C for 1 h. The sample was then freeze–pump–thaw degassed and heated for another 1 h. This cycle was repeated a third time, after which the solvent was removed under vacuum (10^{-4} mm, 25 °C) and the black solid that remained washed with hexane, yielding pure product (74 mg, 80%). Anal. Calcd for $Co_2SC_{24}H_{34}$: C, 61.10; H, 7.25. Found: C, 61.24; H, 7.18. ^1H NMR (−60 °C, toluene-d_8): δ 9.371 (d, J = 7.0 Hz, 1 H), 5.927 (t, J = 5.1 Hz, 1 H), 5.031 (d, J = 5.8 Hz, 1 H), 3.540 (t, J = 5.0 Hz, 1 H), 2.023 (s, 15 H), 1.544 (s, 15 H). $^{13}C\{^1H\}$ NMR (−50 °C, THF-d_8): δ 187.91 (s), 139.24 (s), 120.85 (s), 89.97 (s), 87.88 (s), 85.08 (s), 11.49 (s), 10.46 (s).

X-ray Structure of $[(C_5Me_5)Co]_2(C_4H_4S)$. A single crystal of the complex was mounted, and cell constants were obtained from 25 centered reflections with values of χ between 0 and 70°. Routine data collection of one quadrant of data was undertaken on the primitive monoclinic cell, as indicated in Table III. Axial photos were used to confirm the chosen axes and showed no evidence for "super lattice" effects. The Molecular Structure Corp. TEXSAN analysis software package was used for data reduction and solution.[15] A Patterson map solution of the structure to locate the two cobalt atoms, followed by expansion of the structure with the program DIRDIF, revealed all non-hydrogen atoms. After isotropic refinement, the initial model showed residual electron peaks on either side of the sulfur and in the center of the C(23)–C(24) double bond. These were modeled as a disordered SCH═CHCH═CH ligand with the opposite orientation, in which the sulfur and C═C double bond had exchanged sites and in which the double bond had changed cobalt atoms to which it was η^2-bound. There was no evidence for disordered atoms corresponding to the C_5Me_5 rings, suggesting that these atoms lies in virtually the same locations in the disordered partners. In the final model used, the pairs of S(1A/B), C(21A/B), C(22A/B), C(23A/B), and C(24A/B) atoms were refined with pairwise equivalent isotropic thermal parameters while constraining the populations to vary together. Following isotropic refinement, an absorption correction was applied using the program DIFABS. Full matrix least squares anisotropic refinement of the nondisordered non-hydrogen atoms (with hydrogens attached to nondisordered carbons in idealized positions) was carried out to convergence. In the final model, the populations of the disordered atoms refined to 68.6 (5)–31.4 (5). Fractional coordinates are given in Table I and selected distances and angles in Table II.

Acknowledgment is made to the National Science Foundation (Grant CHE-9102318) for their support of this work.

Supplementary Material Available: PLUTO drawing of the disordered model and tables of crystal data, bond distances and angles, and positional and thermal parameters (12 pages). Ordering information is given on any current masthead page.

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(13) Luo, S.; Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 1732–1735.

(14) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1985**, *23*, 15–21.

(15) $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\{\sum wF_o^2\}$, where $w = [\sigma^2(F_o) + (pF_o^2)^2]^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV, Tables 2.2B and 2.3.1.