dissociation of its thioether–Pd bonds and that these bonds are on average 0.041 Å shorter than the corresponding bonds in $[Pd(\eta^3\text{-}C_3H_5)(L)]^+$, probably as a result of the differing trans effects of Br and allyl.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Dr. P. D. Golding for helpful discussions.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen coordinates and thermal parameters, complete bond lengths and angles, and crystal data for $[Pd(\eta^3\text{-}C_3H_5)(L)][CF_3SO_3]$ (4 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Thiometalate Complexes Containing Arene, Thiophene, and Cyclobutadiene Coligands. Are Thiometalate Clusters Good Models for Desulfurization Catalysts?

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Reaction of $[(p\text{-cymene})RuCl_2]_2$ and $(PPh_4)_2WS_4$ gives $[(p\text{-cymene})RuCl]_2WS_4$; the corresponding $(C_6Me_6)Ru$ and $(p\text{-cymene})Os$ derivatives were also prepared. ^1H NMR and IR data suggest that these compounds comprise pairs of pseudooctahedral metal centers bridged by the tetrahedral WS_4. Related syntheses gave RuRe and Ru_2PtW_2 compounds from ReS_4^- and $Pt(WS_4)_2^{2-}$, respectively. The reaction of $(p\text{-cymene})RuCl_2(PPh_3)$ and $(PPh_4)_2WS_4$ gave $(p\text{-cymene})RuWS_4(PPh_3)$, whose structure was verified by X-ray crystallography. $(p\text{-cymene})RuWS_4(PPh_3)$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 9.254$ (3) Å, $b = 15.690$ (8) Å, $c = 20.102$ (9) Å, $\beta = 98.77$ (3)°, and $Z = 4$. The analogous reaction of (tetramethylthiophene)-$RuCl_2(PPh_3)$ and $(PPh_4)_2WS_4$ results in the release of free tetramethylthiophene. In contrast, the *p*-cymene ligands were only labilized by further treatment of $[(p\text{-cymene})RuCl]_2WS_4$ with WS_4^{2-}. $[(C_4Me_4)NiCl_2]_2$ and WS_4^{2-} give $[(C_4Me_4)NiCl]_2WS_4$ while $(C_4Me_4)NiWS_4(PMe_2Ph)$ was prepared from $(C_4Me_4)NiCl_2(PMe_2Ph)$. $(C_4Me_4)NiWS_4(PMe_2Ph)$ crystallizes in the monoclinic space group *Ia* (No. 9) with $a = 13.294$ (6) Å, $b = 25.519$ (11) Å, $c = 13.186$ (6) Å, $\beta = 97.44°$, and $Z = 8$. Treatment of $[(C_4Me_4)NiCl]_2WS_4$ with $(Me_3Si)_2S$ gives a polymeric sulfided material, which upon pyrolysis evolves tetramethylthiophene.

Introduction

Organometallic derivatives of the tetrathio- and tetraselenometalates are a relatively new class of compounds comprised of organometallic subunits ligated to chalcogenometalate anions.[1-3] These bi- and multimetallic compounds have a rich chemistry with regard to their structural diversity, substitution reactions, and electrochemistry. Certain organometallic thiometalates show promise as precursors to new ternary chalcogenides.[3] Our work on platinum metal thiometalates has provided complexes with a variety of π-acidic ligands including carbon monoxide, olefins, isocyanides, allyl, and cyclopentadienyl.[4] Related work by Coucouvanis, Müller, and co-workers has afforded heterometallic thiometalates containing nitrosyl coligands.[5,6]

The present work concerns the synthesis of organometallic thiometalates containing arene, thiophene, and cyclobutadiene substituents. This project was originally undertaken to prepare structural models for the chemisorption of arenes and thiophenes on metal sulfides since it is well-known that certain metal sulfides catalyze the hydrogenation of arenes and the hydrogenolysis of thiophenes.[7] We expected to obtain some molecular-level insights into these heterogeneous processes by examining the structures and behavior of molecular analogues. In our scheme, the catalytic substrate is first attached to a metal halide, and this organometallic halide is then metathesized with a thiometalate anion. The strategy is reliable since suitable organometallic halides are available and the coordination chemistry of thiometalate is well established. Thiometalates,[8] typified by WS_4^{2-}, have been shown to coordinate either as $2e^-$ bidentate terminal ligands or as $6e^-$ bridging ligands, e.g., $Pt(WS_4)(\text{diene})$[9] and $[(\text{diene})Rh]_2(\mu\text{-}WS_4)$,[1] respectively.

The original tenet of this modeling effort was that thiometalate complexes would simulate reactivity characteristic of heterogeneous hydrodesulfurization (hds) catalysts. Thus, the complexes contain three known components of an hds catalyst system, i.e., substrates, catalytically active metals, and sulfur. As we will demonstrate, this simple recipe is flawed because it underestimates the effect of M:S stoichiometry, a factor known to be crucial to the activity of heterogeneous catalysts.[10] The effect of M:S stoichiometry is illustrated by a recent surface science study which shows that heavy sulfiding leads to thiophene *synthesis*, not thiophene desulfurization.[11] These experiments find precedent in the old thiophene synthesis from acetylene[12] or butadiene[13] and FeS_2.

Results

Arene Thiometalates. We prepared ruthenium and osmium arene thiometalates following the synthetic protocols used for

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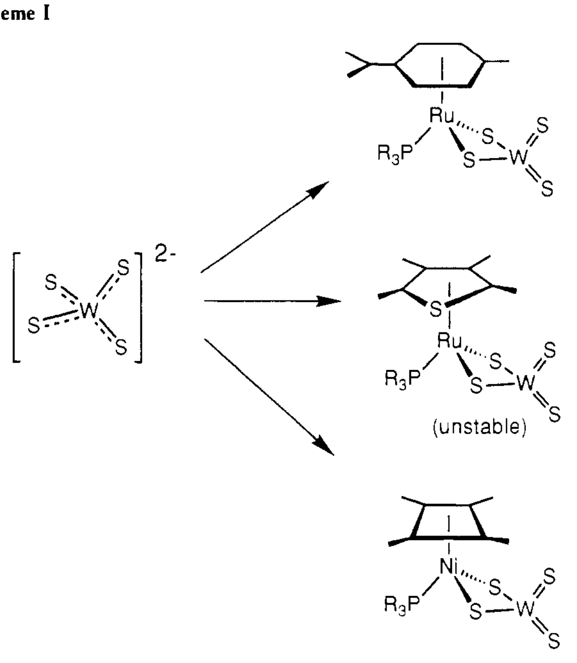
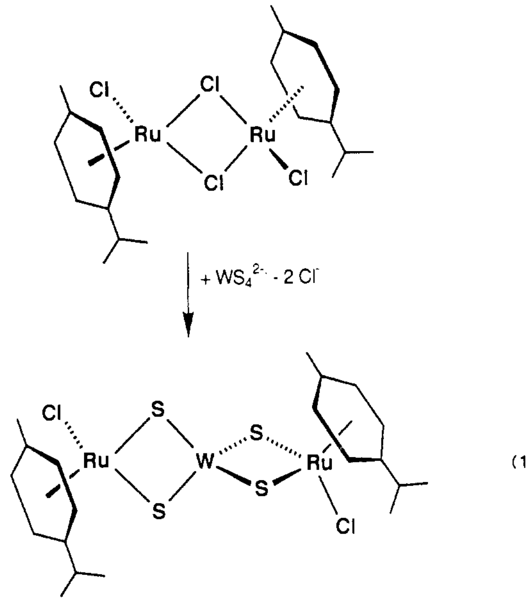
Scheme I



$[(C_5Me_5)RhCl]_2WS_4$.[3] The reaction of acetonitrile solutions of $[(p\text{-cymene})RuCl_2]_2$ and $[(p\text{-cymene})OsCl_2]_2$ (*p*-cymene is 4-methylisopropylbenzene) with $(Ph_4P)_2WS_4$ gave the corresponding $[(p\text{-cymene})MCl]_2WS_4$ as microcrystalline solids (eq 1). The analogous reaction using MoS_4^{2-} did not afford soluble products. $[(C_6Me_6)RuCl]_2WS_4$ was also prepared, but is is noticeably less soluble in $CHCl_3$ and CH_2Cl_2 than the cymene complex. The ^1H NMR spectrum of $[(p\text{-cymene})OsCl]_2WS_4$ shows *two* $(CH_3)_2CH$ doublets separated by 0.02 ppm, as well as two AB quartet patterns for the ring protons.



(1)

The trimetallic $[(arene)MCl]_2(\mu\text{-}WS_4)$ compounds are assumed to be comprised of linear arrays of metals. Analogous structures have been determined for $[Cu(PPh_3)]_2(\mu\text{-}WS_4)$,[14] $[Au(PR_3)]_2(\mu\text{-}WS_4)$,[15] $[Co(NO)_2]_2(\mu\text{-}WS_4)$,[6] and the organometallic compounds $[Rh(COD)]_2WS_4$,[1] $[Pd(allyl)]_2WS_4$,[3] and $[Rh(C_5Me_5)Cl]_2WS_4$.[3] In these compounds the μ-WS_4 subunit is viewed as a three-electron ligand in its interactions with each terminal metal. This representation conforms with the EAN rule, at least as it applies to the ruthenium centers.

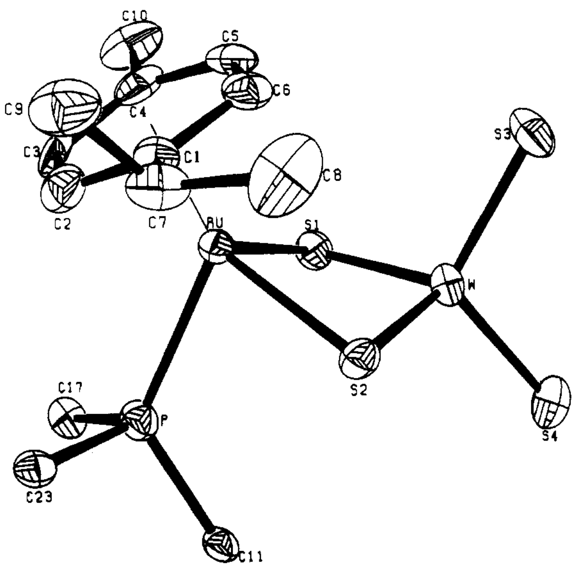


Figure 1. ORTEP drawing of the non-hydrogen atoms in (*p*-cymene)$RuWS_4(PPh_3)$. Phenyl rings omitted for clarity.

Table I. Selected Bond Distances (Å) and Angles (deg) for $(p\text{-cymene})RuWS_4(PPh_3)$ and $(C_4Me_4)NiWS_4(PMe_2Ph)$

	M = Ru	M = Ni[a]
M–W	2.934 (1)	2.813 (3) 2.814 (3)
M–P	2.364 (3)	2.265 (7) 2.253 (7)
M–S1	2.406 (3)	2.290 (7) 2.282 (8)
M–S2	2.416 (3)	2.308 (8) 2.298 (8)
W–S1$_b$	2.238 (3)	2.227 (8) 2.231 (7)
W–S2$_b$	2.236 (3)	2.223 (7) 2.227 (8)
W–S3$_t$	2.154 (3)	2.15 (1) 2.14 (1)
W–S4$_t$	2.151 (4)	2.15 (1) 2.14 (1)
av M–ring C[b]	2.26	2.05 2.06
S1–W–S3	110.9 (1)	110.4 (4) 110.4 (4)
S1–W–S4	109.5 (1)	111.4 (4) 111.8 (4)
S2–W–S3	111.2 (1)	111.4 (4) 111.8 (4)
S2–W–S4	111.2 (1)	109.2 (4) 109.6 (4)
P–M–S1	88.46 (9)	95.3 (3) 95.5 (3)
S1–M–S2	92.48 (9)	99.0 (3) 99.1 (3)
S2–M–P	86.34 (10)	93.3 (3) 93.4 (3)

[a] For M = Ni, the top value is for molecule 1 while the lower value is for molecule 2. [b] For M = Ni, Ni–C1 = 2.03 (3), Ni–C2 = 1.98 (2), Ni–C3 = 2.11 (3), and Ni–C4 = 2.07 (3) Å.

Bennett and Smith showed that $(p\text{-cymene})RuCl_2(PR_3)$ readily undergoes anion metathesis, e.g. with bromide salts to give $(p\text{-cymene})RuBr_2(PR_3)$.[16] Following their example, we combined acetonitrile solutions of $(p\text{-cymene})RuCl_2(PPh_3)$ and $(Ph_4P)_2WS_4$ to obtain orange microcrystals of $(p\text{-cymene})RuWS_4(PPh_3)$ (Scheme I). The ^1H NMR spectrum is well resolved and shows resonances for the PPh_3 and *p*-cymene groups. In contrast to the IR spectrum for the μ-WS_4 compound, this terminal WS_4 complex

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exhibited ν_{WS} bands at 491 and 435 cm^{-1}, assigned to ν_{WS_t} and ν_{WS_b}, respectively. The reaction of MoS_4^{2-} and (*p*-cymene)Ru(PPh_3)Cl_2 failed to give soluble products.

The structure of (*p*-cymene)$RuWS_4(PPh_3)$ consists of isolated bimetallic units (Figure 1). If the cymene is viewed as a unidentate ligand, the core structure resembles an edge-shared bitetrahedron. The coordination sphere of the ruthenium is comprised of an η^6-cymene unit, two sulfur atoms, and a triphenylphosphine ligand. As expected, short terminal W–S distances are observed at 2.154 (3) and 2.151 (4) Å, while the bridging W–S distances are 2.238 (3) and 2.236 (3) Å (Table I). The W–S_t distances are slightly *shorter* than those found in $(NH_4)_2WS_4$ (2.165 Å average).[17] Siedle and co-workers have reported the structure of $PtWS_4(Et_3P)_2$ where a similarly short terminal W–S distances of 2.15 and 2.14 Å were observed.[9] Comparably short terminal W–S distances have been reported for salts of $[X_2FeWS_4]^{2-}$ ($X = {}^1/_2S_5^{2-}$, SPh^-).[18-20] Particularly short W–S_t distances characterize thiotungstates that are supported by weak π-donor ligands, e.g., 2.064 (5) Å in $[WCl_4S]$.[21] The W–S_b distances are slightly longer than those normally observed for μ-WS_4 complexes where bridging W–S bond distances of 2.19–2.23 Å are normal. The bridging W–S distances of 2.238 (3) and 2.236 (3) Å are nearly the same as those reported for $(NEt_4)_2[(PhS)_2FeWS_4]$ (2.239 (2), 2.254 (2) Å).[18] The Ru–S and Ru–W distances are only 0.02 and 0.06 Å longer than those in $[CpRu(MeNC)]_2WS_4$.[2] The S1–W–S2 angle (where S1 and S2 are bridging sulfur atoms) is 102.2°, while the other five S–W–S angles range from 109.5 to 111.4°.

Isoelectronic relationships suggested the potential stability of (arene)RuCl(ReS_4) although no ReS_4^- complex had been previously isolated in pure form.[22] The reaction of dichloromethane solutions of [(*p*-cymene)$RuCl_2]_2$ and $(Et_4N)ReS_4$ produced the desired (*p*-cymene)RuCl(ReS_4). This species is soluble in chlorinated organic solvents although its solutions are quite air-sensitive. The IR spectrum of this bimetallic complex shows bands at 524, 512, and 454 cm^{-1}. The high-frequency bands are assigned to ν_{ReS_t}. A value for ν_{ReS} of 484 cm^{-1} was reported for $(Et_4N)ReS_4$.[22,23]

In a further extension of the use of (*p*-cymene)Ru^{2+}, we reacted [(*p*-cymene)$RuCl_2]_2$ with $[Pt(WS_4)_2]^{2-}$. The product is insoluble in all solvents tested but analyzed reasonably well for the expected formula Pt[WS_4RuCl(*p*-cymene)]$_2$.

Thiophene Thiometalates. Our recent synthesis of [(TMT)$RuCl_2]_2$ (TMT = 2,3,4,5-tetramethylthiophene)[24] prompted attempts to prepare (TMT)$RuWS_4$ complexes (Scheme I). The reaction of [(TMT)$RuCl_2]_2$ and $(PPh_4)_2WS_4$ produces an insoluble solid concomitant with the liberation of free TMT. Similarly, the reaction of (TMT)$RuCl_2(PR_3)$ and WS_4^{2-} also gave insoluble compounds and free TMT. Our difficulties appear to be due to the labilizing influence of the WS_4^{2-} ligand on the tetramethylthiophene ligand, and the experiments described below suggest that the TMT dissociates *after* substitution of chlorides by WS_4^{2-}. In contrast, the precursor complexes (TMT)$RuCl_2(PR_3)$ (R = alkyl, Ar) are very stable.[24]

In order to facilitate the attachment of the WS_4^{2-}, we attempted to preactivate the ruthenium center by replacing chloride with triflate using AgOTf. Combining dichloromethane solutions of $(PPh_4)_2WS_4$ and (TMT)Ru(OTf)$_2(PR_3)$, where R = Me or Ph, resulted in immediate color change to deep red, quickly followed by formation of dark precipitates. The initial solids would not redissolve in common organic solvents. Evaporation of the mother liquor under an N_2 stream sometimes gave an impure material whose ^{1}H NMR spectra were assignable as (TMT)Ru(WS_4)(PR_3). However, after minutes at room temperature in CD_2Cl_2, we observed the formation of *free* TMT. When R = *p*-tolyl, a red solution persists from which an impure solid sample of (TMT)Ru(WS_4)(P(tol)$_3$) can be obtained. The formulation is based on ^{1}H NMR data, which show shifted and well-resolved pairs of TMT methyl peaks not attributable to starting materials. After several hours at room temperature, solutions of such samples also decompose with formation of free TMT and the deposition of dark solids. In contrast, the aforementioned (*p*-cymene)$RuWS_4(PPh_3)$ appears completely robust in solution under these conditions.

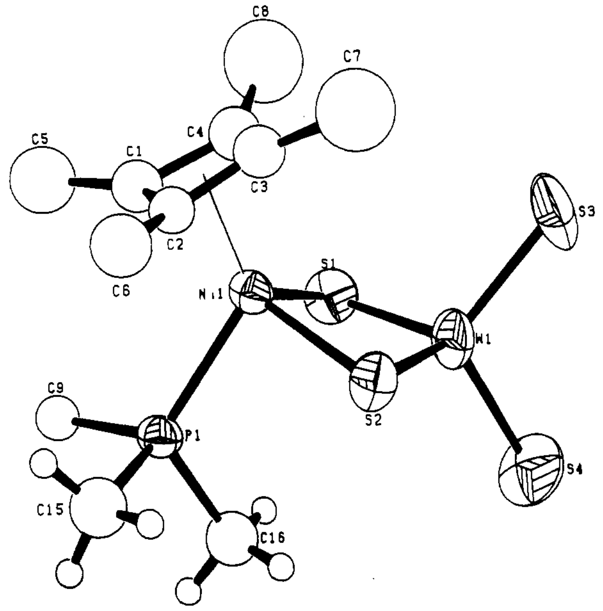

Figure 2. ORTEP drawing of the non-hydrogen atoms in $(C_4Me_4)NiWS_4(PMe_2Ph)$. Phenyl rings omitted for clarity.

Cyclobutadiene Thiometalates. Tetramethylcyclobutadiene, as found in $[(C_4Me_4)NiCl_2]_2$, is formally related to TMT by the addition of one sulfur atom. Because of this stoichiometric relationship, we thought that C_4Me_4 complexes of metal sulfides might provide insights regarding the instability of (TMT)Ru(WS_4)(PR_3). Treatment of the dimeric nickel complex with WS_4^{2-} salts gave $[(C_4Me_4)NiCl]_2(\mu\text{-}WS_4)$. This new compound is red-orange, soluble in polar organic solvents, and fairly air-stable. Analogous to (*p*-cymene)$RuWS_4(PPh_3)$, we also prepared $(C_4Me_4)NiWS_4(PMe_2Ph)$ (eq 2). This conversion is accompanied

$$\begin{array}{lcl} [(C_4Me_4)NiCl_2]_2 & \xrightarrow{WS_4^{2-}} & [(C_4Me_4)NiCl]_2WS_4 \\ \downarrow PMe_2Ph & & \\ (C_4Me_4)NiCl_2(PMe_2Ph) & \xrightarrow{WS_4^{2-}} & (C_4Me_4)NiWS_4(PMe_2Ph) \end{array} \quad (2)$$

by a large change in the $C_4(CH_3)_4$ ^{1}H NMR shifts from δ 1.10 in $(C_4Me_4)NiCl_2(PMe_2Ph)$ to δ 1.55 in $(C_4Me_4)NiWS_4(PMe_2Ph)$.

The structure of solid $(C_4Me_4)NiWS_4(PMe_2Ph)$ consists of two independent molecules; however, the differences are minor (Figure 2). The complex is structurally similar to (*p*-cymene)$RuWS_4(PPh_3)$ since both (*p*-cymene)Ru and (C_4Me_4)Ni are 14e$^-$ fragments. As expected, the terminal W–S distances 2.15 (1) and 2.14 (1) Å are shorter than the bridging W–S distances 2.227 (8)–2.231 (7) Å. In comparison, $(AsPh_4)_2[Ni(WS_4)_2]$ exhibits terminal W–S distances of 2.150 (5) and 2.151 (4) Å and bridging W–S distances of 2.234 (3) and 2.229 (4) Å.[8] The C_4Me_4 ring shows distortions from idealized square geometry. Similar distortions are seen in $[(C_4Me_4)NiCl_2]_2$, but to a lesser extent[25] (Figure 3). The distortions suggest some allyl character for the

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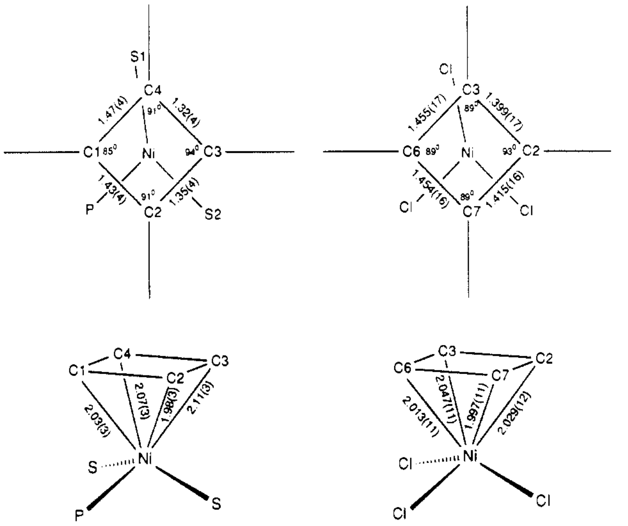

Figure 3. Metrical features of the NiC_4Me_4 parts of $[(C_4Me_4)NiCl_2]_2$ and one of the two crystallographically independent molecules of $(C_4Me_4)NiWS_4(PMe_2Ph)$.

Table II. Yields of Tetramethylthiophene (TMT) from Thermolysis of (Cyclobutadiene)nickel Sulfido Complexes

precursor	thermolysis conditions	% yield of TMT
$[(C_4Me_4)NiCl]_2WS_4$	210 °C, 3 h	4.9
$[(C_4Me_4)NiCl]_2WS_4 + (Me_3Si)_2S$ solid[a]	210 °C, 5 h	16.7
$[(C_4Me_4)NiCl]_2WS_4 + (Me_3Si)_2S$ (CH_2Cl_2 soln)	41 °C, 48 h	1.2
$[(C_4Me_4)NiCl]_2WS_4 + (Me_3Si)_2S$ solid[b]	350 °C, 4 h	20.8
"$[(C_4Me_4)NiS]_x$"[c] (THF soln)	60 °C, 48 h	8.1

[a] % S = 15.41; % Cl = 3.02. [b] % S = 16.5; % Cl = 1.69. [c] This sample consisted of a solution prepared from $[(C_4Me_4)NiCl_2]_2$ and $(Me_3Si)_2S$.

C_4Me_4 ligand involving C2, C3, and C4; this would account for the short C2–C3 and C3–C4 bond lengths of 1.32 and 1.35 Å (vs 1.43 and 1.47 Å for C4–C1 and C1–C2, respectively). Ni–C distances range from 1.98 (2) to 2.11 (3) Å, possibly as a consequence of steric effects since the methyl C7 is positioned over the terminal S3.

Thermolysis of samples of $[(C_4Me_4)NiCl]_2WS_4$ at 300 °C gave small amounts of tetramethylthiophene and 1,2-dichloro-1,2,3,4-tetramethylcyclobutene as proven by gas chromatography/electron-impact mass spectrometry (Table II). By sulfiding the Ni_2W compound using $(Me_3Si)_2S$, we could remove ~85% of the chloride to give solids approaching the formula $(C_4Me_4)_2Ni_2WS_5$. Thermolysis of these sulfided samples gave 15–20% yields of TMT. The formation of TMT commences at the relatively low temperature of 40 °C and continues up until 350 °C (eq 3).

$$[(C_4Me_4)NiCl]_2WS_4 \xrightarrow{(Me_3Si)_2S} \text{“}(C_4Me_4)_2Ni_2WS_5\text{”} \xrightarrow{\Delta} C_4Me_4S + Ni_2WS_x \quad (3)$$

Discussion

The reaction of WS_4^{2-} with organometal halides affords the corresponding organometal thiotungstates. The present study focused on elucidating the influence of the thiometalate on the behavior of the organic coligand with the goal of testing the validity of thiometalate-derived clusters as models for thiophene desulfurization catalysts.

The arene–M–WS_4 complexes represent stabilized analogues of the tetramethylthiophene (TMT) complexes, all of which proved to be very labile. It should be noted that the permethylated thiophene had been specifically selected to stabilize the binding of thiophene to the ruthenium. Maitlis[26] and Angelici[27] had previously demonstrated the increased stability of complexes of tetramethylthiophene vs less substituted analogues.[26,27] Nonetheless, it is clear that replacement of the chlorides in both $[(TMT)RuCl_2]_2$ and $(TMT)RuCl_2(PR_3)$ by WS_4^{2-} destabilizes the Ru···TMT interaction. Since recent work has shown that WS_4^{2-} is a strong acceptor ligand,[2,28] we surmise that it is the acceptor qualities of the thiometalate that weaken the Ru–TMT interaction. The tendency for WS_4 to destabilize π-acid ligands had been noted by us in other studies.[2] Even the cymene–Ru interaction can be labilized as demonstrated by treatment of $[(p\text{-cymene})RuCl]_2WS_4$ with WS_4^{2-}, a reaction that gives an oligomeric material which begins to lose *p*-cymene at room temperature.[29]

The compound $[(C_4Me_4)NiCl]_2(\mu\text{-}WS_4)$ proved to be a well-behaved complex that allowed us to probe the chemistry of the $M\text{–}S_x\text{–}C_4R_4$ system. We observed that several of these Ni/W–S_x–C_4Me_4 species undergo thermal decomposition with loss of TMT. In related work, Gellman had shown that sulfided palladium surfaces react with acetylenes to give thiophenes.[11] It was proposed that this sulfurization occurs via a surface reaction involving a stabilized C_4 intermediate. Gellman tested his mechanism by reacting his sulfided surface with 3,4-dichlorocyclobutene, a "$C_4H_4^{2+}$" source, and observed formation of thiophene. Our experiment is very similar: "$C_4Me_4^{2+}$" is attached to a nickel center (using 3,4-dichlorotetramethylcyclobutene); sulfiding and thermolysis of this compound gave tetramethylthiophene. On the basis of this work, we propose that thiometalate-derived clusters are poor models for desulfurization catalysts. Other studies[30,31] support this view: *low-valent metal complexes with small S/M ratios effect thiophene desulfurization. High-valent metal complexes with high S/M effect hydrocarbon sulfurization, not desulfurization.* These findings illustrate the equilibration of organosulfur/hydrocarbon species on the catalyst. A highly sulfided catalyst will naturally favor the formation of organosulfur compounds.

Experimental Section

Materials and Methods. All compounds described herein are air-stable; however, reactions were routinely carried out under a nitrogen atmosphere. Acetonitrile was distilled from CaH_2 under N_2. Methylene chloride was distilled from P_4O_{10} under N_2. All other solvents were reagent grade and were used without further purification. $[(p\text{-cymene})RuCl_2]_2$,[32] $[(C_6Me_6)RuCl_2]_2$,[32] $[(TMT)RuCl_2]_2$,[24] $[(p\text{-cymene})OsCl_2]_2$,[33] $(NH_4)_2WS_4$,[34] $(Et_4N)ReS_4$,[23] $[(C_4Me_4)NiCl_2]_2$,[35] and $(Et_4N)_2[Pt(WS_4)_2]$[36] were prepared by literature methods. $(PPh_4)_2WS_4$ was prepared by addition of an aqueous $(NH_4)_2WS_4$ solution to an aqueous PPh_4Br solution. The resulting solid was collected by filtration, washed with H_2O, EtOH, and Et_2O, and recrystallized from DMF/Et_2O.

^1H NMR spectra were recorded on Varian XL-200 and General Electric QE-300 spectrometers and are reported in ppm versus TMS. $^{31}P\{^1H\}$ NMR spectra were recorded on a General Electric GN-300 narrow-bore instrument operating at 121.46 MHz; ^{31}P NMR chemical shifts are reported in ppm versus an external standard of 85% H_3PO_4. Infrared spectra were obtained on a Perkin-Elmer 1750 FT-IR spectrophotometer. Elemental analyses were performed by the University of Illinois Microanalytical Laboratory.

$[(p\text{-cymene})RuCl]_2WS_4$. A 30-mL acetonitrile solution of $(Ph_4P)_2WS_4$, 0.325 g (0.328 mmol), was added to a stirred 30-mL

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CH_3CN solution of $[(p\text{-cymene})RuCl_2]_2$, 0.200 g (0.327 mmol), giving a red solution with a microcrystalline red precipitate. After 48 h, the solution was concentrated, and the red-orange solid was filtered in air, washed with acetonitrile and pentane, and dried briefly. The product was recrystallized from CH_2Cl_2/hexane to give maroon crystals. Yield: 0.20 g (71% yield). Anal. Calcd for $C_{20}H_{28}Cl_2S_4Ru_2W$: C, 28.14; H, 3.31; S, 15.03; W, 21.54. Found: C, 28.24; H, 3.34; S, 14.41; W, 21.85. ^1H NMR ($CDCl_3$): δ 1.35 (d, 6 H, J = 10 Hz), 2.17 (s, 3 H), 2.193 (septet, 1 H, J = 10 Hz), 5.88 (m, 2 H), 6.15 (m, 2 H). IR (KI): ν_{W-S} = 456 cm^{-1}.

$[(p\text{-cymene})OsCl]_2WS_4$. A solution of $(PPh_4)_2WS_4$, 0.251 g (0.253 mmol) in 20 mL of CH_3CN, and a solution of $[(p\text{-cymene})OsCl_2]_2$, 0.200 g (0.253 mmol) in 15 mL of CH_3CN, were combined and stirred for 43 h. The precipitate was filtered, washed with CH_3CN (2 × 5 mL), recrystallized from CH_2Cl_2/hexanes, and dried in vacuo at 90 °C for 12 h. Yield: 0.152 g (58%). Anal. Calcd for $C_{20}H_{28}Cl_2S_4Os_2W$: C, 23.28; H, 2.73; Cl, 6.87; S, 12.43. Found: C, 22.89; H, 2.67; Cl, 7.50; S, 12.04. IR (KI): $\nu_{W=S}$ = 466 m, 458 m sh, 451 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.29 (d, 4 H, J = 5.8 Hz), 6.10 (d, 4 H, J = 5.6 Hz), 2.74 (septet, 2 H, J = 6.8 Hz), 2.25 (s, 6 H), 1.38 (d, 6 H, J = 6.8 Hz), 1.27 (d, 6 H, J = 6.8 Hz).

$[(C_6Me_6)RuCl]_2WS_4$. A solution containing 0.247 g (0.250 mmol) of $(Ph_4P)_2WS_4$ in 20 mL of CH_3CN was treated with a slurry of $[(C_6Me_6)RuCl_2]_2$ (0.167 g, 0.250 mmol) in 50 mL of CH_3CN. The red-brown slurry was stirred for 18 h. The resultant brown microcrystalline solid was collected by filtration and washed with CH_3CN (2 × 15 mL) and pentane (3 × 15 mL). Upon recrystallization from CH_2Cl_2/CH_3CN, to remove a large amount of brown CH_2Cl_2-insoluble material, dark orange-red crystals were collected. Yield: 0.05 g (22%). Anal. Calcd for $C_{24}H_{36}Cl_2S_4Ru_2W$: C, 31.69; H, 3.99; Cl, 7.79; S, 14.10. Found: C, 31.85; H, 4.03; Cl, 8.43; S, 13.87. ^1H NMR ($CDCl_3$): δ 2.27 (s). IR (KI): ν_{W-S} = 465, 459 cm^{-1}.

Reaction of $[(TMT)RuCl_2]_2$ and $(PPh_4)_2WS_4$. A slurry of $[(TMT)RuCl_2]_2$ (0.05 g, 0.080 mmol) and $(PPh_4)_2WS_4$ (0.079 g, 0.080 mmol) in methanol (25 mL) was stirred for 24 h, resulting in the formation of a brown precipitate. This mixture was then filtered through Celite, giving a yellow solution. Removal of the solvent by rotary evaporation followed by extraction with hexanes (30 mL) yielded a colorless solution. The presence of TMT was detected and quantified by gas chromatography (0.0054 g, 0.039 mmol). Yield of TMT (based on $[(TMT)RuCl_2]_2$): 24%.

$(p\text{-cymene})RuWS_4(PPh_3)$. A yellow solution of 0.249 g (0.251 mmol) of $(Ph_4P)_2WS_4$ in 20 mL of acetonitrile was treated with a red solution of $(p\text{-cymene})RuCl_2(PPh_3)$ (0.142 g, 0.247 mmol) in 25 mL of acetonitrile. After the mixture was stirred for 18 h, the red-orange microcrystals were collected by filtration in air and washed with CH_3CN (3 × 10 mL) and pentane (3 × 15 mL). Yield: 0.170 g (85%). If necessary, the product may be recrystallized from CH_2Cl_2/hexane. Anal. Calcd for $C_{28}H_{29}PS_4RuW$: C, 41.54; H, 3.61; P, 3.83; S, 15.84. Found: C, 41.74; H, 3.46; P, 3.94; S, 15.81. ^1H NMR (CD_2Cl_2): δ 1.30 (d, 6 H, J = 12 Hz), 2.51 (s, 3 H), 3.10 (septet, 1 H, J = 10 Hz), 5.53 (s, 4 H), 7.20, 7.43 (m, 15 H). ^{31}P NMR: δ 31.5 (s). IR (KI): ν_{W-S} = 491, 435 cm^{-1}.

Reaction of $(TMT)RuCl_2(PR_3)$ with $(PPh_4)_2WS_4$. In a typical reaction $(PPh_4)_2WS_4$ (0.172 g, 0.174 mmol) in 10 mL of CH_2Cl_2 was added slowly to a solution of $(TMT)RuCl_2(PPh_3)$ (0.1 g, 0.178 mmol) in 20 mL of CH_2Cl_2. The previously orange solution soon became red and deposited a dark solid. After the mixture was stirred overnight, the reaction solution was filtered and the filtrate was concentrated and diluted with Et_2O to precipitate the crude product. The solid was washed with Et_2O and dried in vacuo. Extended drying in vacuo resulted in loss of TMT and gave a CH_2Cl_2-insoluble compound. ^1H NMR data were obtainable only for dilute solutions in CD_2Cl_2; the gradual liberation of free TMT was observed concomitant with formation of a black precipitate. When R = Bu or *p*-tolyl, the reaction mixture did not afford a precipitate during the course of the reaction. However, free TMT was observed in the ^1H NMR spectrum.

Reaction of $(TMT)Ru(OTf)_2(P(p\text{-tolyl})_3)$ with $(PPh_4)_2WS_4$. To a solution of $(TMT)RuCl_2(P(tol)_3)$ (0.1 g, 0.162 mmol) was added solid AgOTf (0.083 g, 0.324 mmol). After 2 h, the orange solution was filtered through Celite to remove AgCl. A solution of $(PPh_4)_2WS_4$ (0.16 g, 0.162 mmol) in 15 mL of CH_2Cl_2 was then added to the $(TMT)Ru(OTf)_2(P(tol)_3)$ solution resulting in an immediate color change to red. In this case no precipitate formed, even after 1 h of stirring. The solution was then concentrated to 5 mL, diluted with 5 mL of CH_3NO_2, and further concentrated until a dark solid formed. The solid was filtered, washed with CH_3NO_2 followed by Et_2O, and dried briefly in vacuo. The ^1H NMR spectrum of this solid showed free TMT.

$[(p\text{-cymene})RuCl(\mu\text{-}WS_4)]_2Pt$. A solution of $(Et_4N)_2[Pt(WS_4)_2]$, 0.100 g (0.093 mmol) in 8 mL of CH_3CN, was added to a CH_3CN solution of $[(p\text{-cymene})RuCl_2]_2$, 0.057 g (0.093 mmol). After 18 h, the precipitated product was filtered and washed with CH_3CN until the washings were colorless. Yield: 0.110 g (87%). Anal. Calcd for $C_{20}H_{28}Cl_2S_8Ru_2PtW_2$: C, 17.65; H, 2.07; S, 18.84. Found: C, 17.30; H, 2.32; S, 17.72. IR (KI): ν_{M-S} = 455 (s, br), 442 (sh) cm^{-1}.

Reaction of MoS_4^{2-} and $[(p\text{-cymene})RuCl_2]_2$. A solution of 0.306 g (0.50 mmol) of $[(p\text{-cymene})RuCl_2]_2$ in 15 mL of CH_3CN was treated dropwise with a solution of 0.452 g (0.50 mmol) of $(Ph_4P)_2MoS_4$ in 60 mL of CH_3CN. A brown precipitate and a red-brown solution were obtained. After 18 h, the reaction mixture was filtered and the red-brown filtrate concentrated in vacuo. The resultant brown precipitate did not redissolve in CH_2Cl_2, $CHCl_3$, CH_3CN, acetone, or DMF. The initially formed precipitate, which was removed by filtration, was also insoluble in all of the above solvents.

$(p\text{-cymene})RuClReS_4$. A solution of $(NEt_4)ReS_4$ (0.435 g, 0.980 mmol) and $[(cymene)RuCl_2]_2$ (0.300 g, 0.490 mmol) in 40 mL of CH_2Cl_2 was stirred under nitrogen at room temperature for 10 h. The solvent was removed in vacuo, and the residue was treated with 20 mL of CH_2Cl_2. The dark violet solution was filtered under nitrogen, and the filtrate was concentrated. A 30-mL aliquot of hexane was added to induce the formation of black needle crystals. Yield: 0.26 g (45%). Anal. Calcd for $C_{10}H_{14}S_4ClRuRe$: C, 20.52; H, 2.39; S, 21.89; Cl, 6.06. Found: C, 20.51; H, 2.49; S, 21.75; Cl, 6.37. IR (KI): ν_{M-S} = 524 (m), 512 (s), 454 (m) cm^{-1}. UV-vis (CH_2Cl_2), λ: 560, 351 (sh) nm. ^1H NMR (CD_2Cl_2): δ 1.37 (d, 6 H, J = 6.9 Hz), 2.06 (s, 3 H), 2.92 (septet, 1 H, J = 6.3 Hz), 5.90 (m, 2 H), 6.13 (m, 2 H).

$[(C_4Me_4)NiCl]_2WS_4$. Solid $(PPh_4)_2WS_4$ (0.2138 g, 0.2168 mmol) was added to a stirred solution of $[(C_4Me_4)NiCl_2]_2$ (0.1022 g, 0.2159 mmol) in MeOH (20 mL). A brick red precipitate immediately formed, and the solution was stirred for 30 min. The resulting solid was isolated via vacuum filtration in air and washed with pentane (10 mL). The product was recrystallized twice from CH_2Cl_2/Et_2O to give a brick red solid, which was dried in vacuo. Yield (based on $[(C_4Me_4)NiCl_2]_2$): 0.0926 g (60%). Anal. Calcd: C, 26.81; H, 3.37. Found: C, 26.82; H, 3.39. ^1H NMR (CD_2Cl_2 TMS): δ 1.65 (s). IR (KBr): 2952, 2891, 1543, 1439, 1355, 1070, 993, 625, 467 cm^{-1}.

Reaction of $[(C_4Me_4)NiCl]_2WS_4$ with $(Me_3Si)_2S$. $[(C_4Me_4)NiCl]_2WS_4$ (0.144 g, 0.2019 mmol) was dissolved in CH_2Cl_2 (40 mL) followed by the addition of $(Me_3Si)_2S$ (45 μL, 0.21 mmol). The stirred solution was then heated to reflux for 30 h, after which the dark mixture was filtered and washed with hexanes, giving an amorphous black solid (0.0441 g). Anal. Calcd for $C_{16}H_{24}S_3Ni_2W$: S, 17.32. Found: Cl, 1.91; S, 17.35, 17.50.

$(C_4Me_4)NiCl_2(PMe_2Ph)$. A solution of PMe_2Ph (0.135 g, 0.997 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $[(C_4Me_4)NiCl_2]_2$ (0.211 g, 0.4437 mmol) in CH_2Cl_2 (40 mL). The purple solution quickly turned deep red and was stirred overnight. Hexane (10 mL) was then added to the solution, which was in turn concentrated to approximately 10 mL. The resulting precipitate was isolated via filtration and washed with hexane (10 mL) to give a deep red microcrystalline solid, which was dried in vacuo. Yield (based on $[(C_4Me_4)NiCl_2]_2$): 0.284 g (85.1%). Anal. Calcd for $C_{16}H_{23}Cl_2NiP$: C, 51.12; H, 6.17; Cl, 18.86. Found: C, 50.70; H, 6.35; Cl, 18.35. ^1H NMR ($CDCl_3$, TMS): δ 1.10 (d, J = 7.0 Hz), 1.80 (d, J = 10.2 Hz), 7.46 (d, J = 2.4 Hz, 7.5 (br m).

$(C_4Me_4)NiWS_4(PPhMe_2)$. Solid $(C_4Me_4)NiCl_2(PMe_2Ph)$ (0.059 g, 0.157 mmol) was added to a slurry of $(PPh_4)_2WS_4$ (0.155 g, 0.157 mmol) in MeOH (25 mL). The solution immediately turned orange, and a similarly colored precipitate formed. After the mixture was stirred for 30 min, the volume was reduced to ~10 mL in vacuo. The mixture was filtered in air, and the product was recrystallized from CH_3NO_2/Et_2O to give an orange solid, which was dried in vacuo. Yield (based on $(C_4Me_4)NiCl_2(PMe_2Ph)$): 0.041 g (42%). Anal. Calcd for $C_{16}H_{23}NiPS_4W$: C, 31.14; H, 3.76; S, 20.78. Found: C, 31.20; H, 3.73; S, 16.76. ^1H NMR ($CDCl_3$, TMS): δ 1.55 (d, J = 3.8 Hz), 1.53 (d, J = 3.2 Hz), 7.8 (br m). IR (KBr): 491.0, 434.0 cm^{-1}.

Pyrolysis of $(C_4Me_4)Ni-S$ Compounds. In a typical experiment, approximately 50 mg of material was heated under a 7×10^{-3} mm dynamic vacuum. The volatile products emitted under the conditions were retained in a liquid nitrogen U-trap. The volatiles were dissolved in hexane to give a solution that was analyzed by GC and GC/MS.

X-ray Crystallography. Transparent, red, tabular crystals of $(p\text{-cymene})RuWS_4(PPh_3)$ were obtained by layering a $CHCl_3$ solution of $(p\text{-cymene})RuWS_4(PPh_3)$ with diethyl ether. Translucent, red, platelike crystals of $(C_4Me_4)NiWS_4(PPhMe_2)$ were obtained by vapor diffusion of diethyl ether into a $CHCl_3$ solution of $(C_4Me_4)NiWS_4(PPhMe_2)$; the data collection crystal was cut from a cluster of crystals. Diffraction data were measured at room temperature by using a Syntex $P2_1$ diffractometer in the $\omega/2\theta$ scan mode using monochromated Mo radiation [$\lambda(K\alpha)$ = 0.71073 Å]. Final cell dimensions were obtained by a least-squares fit to the automatically centered settings for 15 reflections (19.5 < 2θ <

Table III. Crystal and Experimental Crystallographic Data for (p-cymene)$RuWS_4(PPh)_3$ and $(C_4Me_4)Ni(WS_4)(PMe_2Ph)$

formula	$C_{28}H_{29}PRuS_4W$	$C_{16}H_{23}NiPS_4W$
fw	809.67	617.13
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	*Ia* (No. 9)
a, Å	9.254 (3)	13.294 (6)
b, Å	15.690 (8)	25.519 (11)
c, Å	20.102 (9)	13.186 (6)
β, deg	98.77 (3)	97.44 (1)
V, Å^3	2885 (2)	4402 (6)
Z	4	8
d(calcd), g/cm^3	1.864	1.862
T, °C	26	26
μ, cm^{-1}	49.34	66.29
transm factor range	0.613–0.247 (numerical)	0.203–0.054 (numerical)
R (based on F_o^2)	0.041	0.054
R_w (for $w = 1/\sigma^2(F_o) = pF_o^2$)	0.047 (p = 0.02)	0.069 (p = 0.02)

Table IV. Atomic Coordinates for Selected Atoms of (p-cymene)$RuWS_4(PPh_3)$

	x/a	y/b	z/c
W	0.22807 (5)	0.11092 (3)	0.17419 (2)
Ru	0.04863 (8)	−0.03200 (5)	0.20850 (4)
P	0.0622 (3)	−0.0157 (2)	0.3262 (1)
S1	0.3093 (3)	−0.0123 (2)	0.2221 (1)
S2	0.0030 (3)	0.1196 (2)	0.2012 (2)
S3	0.2215 (4)	0.1059 (2)	0.0667 (2)
S4	0.3639 (4)	0.2137 (2)	0.2182 (2)
C1	−0.177 (1)	−0.0601 (7)	0.1450 (5)
C2	−0.147 (1)	−0.1174 (6)	0.1983 (6)
C3	−0.020 (1)	−0.1686 (6)	0.2081 (6)
C4	0.083 (1)	−0.1628 (7)	0.1640 (6)
C5	0.060 (1)	−0.1024 (7)	0.1132 (6)
C6	−0.063 (1)	−0.0518 (7)	0.1021 (5)
C11	0.124 (1)	0.0830 (6)	0.3697 (5)
C17	0.177 (1)	−0.0922 (7)	0.3796 (5)
C23	−0.122 (1)	−0.0291 (6)	0.3473 (5)

Table V. Atomic Coordinates for Selected Atoms in $(C_4Me_4)NiWS_4(PMe_2Ph)$

	x/a	y/b	z/c
W1	0.4776	0.15857 (5)	0.2038
Ni1	0.6116 (3)	0.1778 (1)	0.0585 (2)
S1	0.6122 (7)	0.1810 (3)	0.2191 (5)
S2	0.4998 (6)	0.1091 (3)	0.0697 (6)
S3	0.3383 (8)	0.2029 (5)	0.177 (1)
S4	0.478 (1)	0.1094 (5)	0.3364 (7)
P1	0.7515 (5)	0.1269 (2)	0.0993 (5)
C1	0.667 (2)	0.228 (1)	−0.041 (2)
C2	0.601 (2)	0.1886 (8)	−0.091 (2)
C3	0.518 (2)	0.214 (1)	−0.064 (2)
C4	0.573 (2)	0.249 (1)	−0.009 (2)
C5	0.771 (3)	0.251 (2)	−0.044 (3)
C6	0.607 (3)	0.150 (1)	−0.174 (2)
C7	0.400 (4)	0.207 (2)	−0.090 (4)
C8	0.555 (5)	0.301 (2)	0.031 (4)
C9	0.873 (2)	0.1604 (9)	0.110 (2)
C15	0.770 (3)	0.073 (1)	0.011 (2)
C16	0.755 (2)	0.092 (1)	0.222 (2)

20.0°) for the Ru compound and 22 reflections (9.4 < 2θ < 19.6°) for the Ni compound. Three reference reflections monitored during each experiment showed no significant variation. Intensity data were corrected for absorption, anomalous dispersion, Lorentz, and polarization effects. Corrections for the presence of extinction were not applied. Space group assignment for the Ru crystal was unambiguous. For the Ni, crystal space group assignment was suggested by preliminary photographs and average values of the normalized structure factors and then confirmed by successful refinement in the acentric space group.[37] Atomic scattering factors and anomalous dispersion terms were taken from ref 38.

For the Ru compound, the correct tungsten atom position was automatically determined from a Patterson map, and partial structure expansion gave positions for the Ru, S, and P atoms. For the Ni compound, correct positions for the W and Ni atoms were deduced from an E map (SHELXS-86). For both structures, least-squares refinement and subsequent difference Fourier calculations revealed positions for the remaining non-H atoms; H atoms were included as fixed contributors in "idealized" positions. For the Ru compound, C atoms were refined with isotropic thermal coefficients, and anisotropic thermal coefficients were refined for the remaining non-H atoms. For the Ni compound, anisotropic thermal coefficients were refined for all non-H atoms. Common isotropic thermal parameters were varied for the H atoms in both structures, and the highest peaks in both final difference Fourier maps were in the vicinity of the metal atoms. A final analysis of variance between observed and calculated structure factors showed a slight dependence on sin θ for the Ru structure, but there were no apparent systematic errors for the Ni structure. Crystal data and refinement information are given in Table III. Positional parameters for the two crystal structures are given in Tables IV and V.

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Supplementary Material Available: Tables of crystal data, full atomic coordinates, bond angles and distances, and thermal parameters (8 pages); tables of structure factors (27 pages). Ordering information is given on any current masthead page.

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(37) Metrically, the cell parameters reduce to an orthorhombic F-centered space group. Refinement of 208 variables using 1865 observed data in the space group *Fdd*2 (c = 25.518 Å) converged with residuals R = 0.067 and R_w = 0.087. The following discrepancies in chemically similar bond lengths were noted: W–S (terminal), 2.237 (10) and 2.370 (9) Å; W–S (bridging), 2.313 (12) and 2.258 (11) Å; Ni–S, 2.584 (10) and 2.270 (9) Å; Ni–C, from 1.74 (2) to 2.24 (2) Å; P–C, from 1.83 (4) to 2.02 (4) Å. The two independent molecules in the space group *Ia* appear to be unique.

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