Syntheses, Characterization, and Structures of Tri- and Tetraruthenium Clusters Containing Sulfido, Phenylimido, and (Phenylimino)thio Ligands

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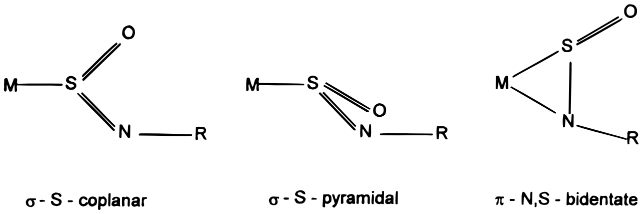
Reaction of $Ru_3(CO)_{12}$ with the SO_2 analog *N*-sulfinylaniline (PhN=S=O) in refluxing toluene produces $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**), $Ru_3(CO)_9(\mu_3\text{-NPh})_2$ (**2**), $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-S})$ (**3**), and $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-NPh})$ (**4**) in low yields. Treatment of $Ru_3(CO)_{10}(NCMe)_2$ with PhN=S=O at room temperature affords **1** as the major product in good yield, accompanied by CO_2 formation. Compounds **1**, **3**, and **4** were characterized by mass, IR, and ^1H NMR spectroscopy, and their structures were determined by single-crystal X-ray diffraction. Crystal data for **1**: triclinic ($P\bar{1}$), $a = 9.585(2)$ Å, $b = 10.151(2)$ Å, $c = 10.555(4)$ Å, $\alpha = 92.32(3)°$, $\beta = 93.21(3)°$, $\gamma = 98.84(2)°$, $Z = 2$, R (R_w) = 0.026 (0.030). Crystal data for **3**: monoclinic ($P2_1/n$), $a = 8.986(7)$ Å, $b = 13.968(3)$ Å, $c = 19.232(9)$ Å, $\beta = 103.06(5)°$, $Z = 4$, R (R_w) = 0.025 (0.025). Crystal data for **4**: monoclinic ($P2_1/c$), $a = 10.319(4)$ Å, $b = 23.354(6)$ Å, $c = 23.329(7)$ Å, $\beta = 100.43(3)°$, $Z = 8$, R (R_w) = 0.051 (0.040).

Introduction

The SO_2 ligand displays an enormous range of coordination modes.[1] This wealth of coordination chemistry can be extended by replacing the essentially "innocent" oxo groups with more strongly donating imino, sulfido, or alkylidene groups.[2] *N*-Sulfinylamine compounds, RN=S=O, are isoelectronic with SO_2 and are obtained by replacing one oxo substituent by an imino group. Theoretical analyses suggest[3] that this replacement does not lead to major changes in the X=S=X angle or the remaining S=O distance, but the N=S bond should be weaker and more reactive than the S=O bond in SO_2, and this offers the opportunity to activate the N=S bond. Three modes of binding have been observed in the interaction of and *N*-sulfinylamine with low-valent mononuclear transition metal centers: σ-S-coplanar,[4] σ-S-pyramidal,[5] and π-N,S-bidentate (Chart 1);[4a,5a,b] the same coordination modes are known for complexes of SO_2. The cluster chemistry of the SO_2 ligand investigated previously in our research group[7] prompted the present research on *N*-sulfinylamine reactions with metal clusters. We describe reactions of triruthenium carbonyl clusters with *N*-sulfinylaniline, which lead to the formation and characterization of several new cluster complexes containing sulfido, phenylimido, and (phenylimino)thio ligands.

Chart 1



Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of purified nitrogen using Schlenk and syringe techniques.[8] Solvents were distilled from the appropriate drying agent before use. The compounds $Ru_3(CO)_{12}$[9] and $Ru_3(CO)_{10}(NCMe)_2$[10] were prepared by literature procedures. ^{13}CO-enriched $Ru_3(CO)_{12}$ (ca. 20% enriched) was prepared by heating a solution of $Ru_3(CO)_{12}$ in dry 1,2-dichloroethane at 80 °C for 48 h under 3 equiv of ^{13}CO in a Schlenk flask. N-Sulfinylaniline (PhN=S=O) and thin-layer chromatography (TLC) plates (2.5-mm silica gel coated on glass with 254-nm fluorescent indicator) from Aldrich were used as received.

Solution infrared data were collected on solutions in CaF_2-windowed cells of 0.1-mm path length with a Bomem MB-100 FTIR spectrometer. The ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-300 spectrometer at 300 and 75.4 MHz, respectively. Electron impact (EI)

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mass spectra were obtained by Dr. D. L. Hung of the Northwestern University Analytical Services Laboratory on a VG 70/250 SE spectrometer. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Reaction of $Ru_3(CO)_{12}$ with PhN=S=O. A 100-mL Schlenk flask containing a sample of $Ru_3(CO)_{12}$ (1 g, 1.56 mmol) was purged with dry N_2, toluene (40 mL) and N-sulfinylaniline (350 μL, 3.1 mmol) were added, and the flask was attached to a water-cooled reflux condenser equipped with a mineral oil bubbler. The solution was heated to reflux (110 °C) for 30 min., at which point the IR spectrum showed no absorptions due to $Ru_3(CO)_{12}$. During reflux, the color changed from bright orange to deep orange-red and finally to brown-red. The solution was cooled to room temperature with a slow N_2 purge and then evaporated to dryness under vacuum. The resulting brown-red oils were extracted with *n*-pentane (2 × 20 mL) to give a red-orange solution and brown solids. The extract was filtered, the solid was dried under vacuum and dissolved in dichloromethane, and the solution was subjected to TLC with an *n*-hexane/dichloromethane (4:1, v/v) eluant. A small amount of unreacted $Ru_3(CO)_{12}$ (<5 mg) was recovered from the first, orange-yellow, band. The material from the second, orange, band was the new compound $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**) (126 mg, 0.186 mmol, 12%). The third, orange-yellow, band afforded the known $Ru_3(CO)_9(\mu_3\text{-NPh})_2$[11] (**2**) (35 mg, 0.046 mmol, 3%). The material from the fourth, orange, band was crystallized from dichloromethane/hexane at −20 °C to produce orange crystals of the new compound $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-S})$ (**3**) (27 mg, 0.08 mmol, 2%). The material from the fifth, orange-yellow, band was crystallized from dichloromethane/hexane at −20 °C, producing orange crystals of another new compound, $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-NPh})$ (**4**) (15 mg, 0.016 mmol, 1%). Five additional minor bands were not identified.

The pentane-insoluble, brown solids were washed with ether (2 × 20 mL) and then extracted with 20 mL of dichloromethane to afford a brown solution. The solution was filtered, and the filtrate was layered with *n*-pentane (50 mL) to yield a brown powder, formulated as $Ru_4(CO)_{12}(PhNS)_2$ (**5**) (410 mg, 0.42 mmol, 36% based on Ru). Formula **5** was assigned on the basis of elemental analysis and spectroscopic data. Anal. Calcd for $Ru_4C_{24}H_{10}N_2S_2O_{12}$: Ru, 40.97; C, 29.21; H, 1.02; N, 2.84; S, 6.50. Found: Ru, 40.06; C, 29.01; H, 1.28; N, 3.36; S, 6.56. ^1H NMR ($CDCl_3$, 20 °C): δ 7.20−6.40 (m, Ph). IR (CH_2Cl_2, ν_{CO}): 2107 (w), 2556 (s, br), 1996 (m, br) cm^{-1}.

Characterization of 1. IR (C_6H_{12}, ν_{CO}): 2098 (w), 2075 (vs), 2053 (vs), 2025 (s), 2019 (vs), 2004 (sh), 1999 (m), 1985 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 7.04−6.72 (m, Ph). ^{13}C NMR ($CDCl_3$, 20 °C): δ 197.4 (3 CO), 191.9 (2 CO), 191.2 (2 CO), 187.0 (2 CO). Mass spectrum (EI): *m/z* 681 (M^+, ^{102}Ru) and successive loss of 9 CO. Anal. Calcd for $Ru_3C_{15}H_5O_9NS$: C, 26.55; H, 0.74; N, 2.06; S, 4.73. Found: C, 26.51; H, 0.44; N, 2.01; S, 4.44.

Characterization of 2. IR (C_6H_{12}, ν_{CO}): 2094 (vw), 2072 (vs), 2049 (vs), 2021 (s), 2015 (s), 2011 (s), 1998 (m), 1978 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 7.10−6.68 (m, Ph). Mass spectrum (EI): *m/z* 740 (M^+, ^{102}Ru) and successive loss of 9 CO. The IR and ^1H NMR data match literature values for this compound.[11]

Characterization of 3. IR (C_6H_{12}, ν_{CO}): 2093 (w), 2053 (s), 2034 (m), 2028 (m), 2006 (sh), 2000 (m), 1824 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 7.11−6.75 (m, Ph). Mass spectrum (EI): *m/z* 871 (M^+, ^{102}Ru) and successive loss of 11 CO. Anal. Calcd for $Ru_4C_{17}H_5O_{11}NS_2$: C, 23.53; H, 0.58; N, 1.61. Found: C, 22.61; H, 0.20; N, 1.61.

Characterization of 4. IR (C_6H_{12}, ν_{CO}): 2086 (vw), 2049 (s), 2033 (w), 2019 (m), 2001 (w), 1991 (sh), 1826 (w) cm^{-1}. ^1H NMR ($CDCl_3$, 20 °C): δ 7.21−6.20 (m, Ph). Mass spectrum (EI): *m/z* 902 (M^+ − CO, ^{102}Ru) and successive loss of 10 CO. Anal. Calcd for $Ru_4C_{23}O_{11}N_2SH_{10}$: C, 29.81; H, 1.09; N, 3.02. Found: C, 30.05; H, 1.21; N, 3.00.

Reaction of $Ru_3(CO)_{10}(NCMe)_2$ and PhNSO. A 30-mL Schlenk flask was charged with 100 mg (0.15 mmol) of $Ru_3(CO)_{10}(NCMe)_2$. The reaction flask was placed in a dry ice/acetone bath (−78 °C), and 10 mL of dichloromethane was slowly added to give a bright yellow solution of $Ru_3(CO)_{10}(NCMe)_2$. After addition of *N*-sulfinylaniline (33 μL, 0.3 mmol), the dry ice/acetone bath was removed, and the reaction mixture was allowed to slowly warm to ambient temperature. This was accompanied by a change in color of the solution from yellow to dark orange-red. The solution was evaporated to dryness under vacuum and the residue subjected to TLC, with *n*-hexane/dichloromethane as eluant (4:1, v/v). Isolation of the material forming the major orange band afforded $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**) (56 mg, 55%).

Table 1. Crystallographic Data for $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (1), $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\eta^2\text{-SNPh})(\mu_4\text{-S})$ (3) and $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\eta^2\text{-SNPh}(\mu_4\text{-NPh})$ (4)

	1	3	4
formula	$Ru_3C_{15}SNO_9H_5$	$Ru_4C_{17}O_{11}NS_2H_5$	$Ru_4C_{23}O_{11}N_2SH_{10}$
fw	678.48	867.63	926.68
temp, °C	−120	−120	−120
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.585(2)	8.986(7)	10.319(4)
b, Å	10.151(2)	13.968(3)	23.354(6)
c, Å	10.555(4)	19.232(9)	23.329(7)
α, deg	92.32(3)		
β, deg	93.21(3)	103.06(5)	100.43(3)
γ, deg	98.84(2)		
V, $Å^3$	1011.9(5)	2351(1)	5529(2)
Z	2	4	8
$R(F)^a$	0.026	0.025	0.051
$R_w(F)^b$	0.030	0.025	0.040
goodness of fit	2.98	1.55	1.27
D_{calc}, g cm^{-3}	2.227	2.451	2.226
μ(Mo Kα), cm^{-1}	23.61	27.57	22.81
λ, Å	0.710 69	0.710 69	0.710 69

[a] $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = 4F_o^2/\sigma^2(F_o^2)$.

During the reaction, gentle bubbling of gas was observed. The gas was transferred into a KBr-windowed cell of 15 cm path length via a high-vacuum line. The strong IR bands at 2359 and 2341 cm^{-1} indicated CO_2 formation.

Reaction of 1 with PhNSO. $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**) (21 mg, 0.03 mmol) was placed in a 30 mL Schlenk flask equipped with a reflux condenser. Methylcyclohexane (5 mL) and PhNSO (13 μL, 0.11 mmol) were added against a nitrogen flow, the mixture was heated to reflux (101 °C) for 4 h, and volatile materials were removed under vacuum. The residue was dissolved in CH_2Cl_2 and isolated by TLC, with dichloromethane/*n*-hexane (1:4, v/v) as the eluant. Compound **1** (11 mg, 52%) and compound **2** (8 mg, 36%) were isolated from the first and second bands, respectively.

X-ray Crystallography. Unit cell constant determination and data collection were performed on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Lattice parameters were determined from 25 randomly selected reflections with 2θ ranging from 22.9 to 24.0° (compound **1**), 19.4 to 24.2° (compound **3**), and 17.9 to 20.7° (compound **4**). The data were collected at −120 ± 1 °C using the $\omega-\theta$ scan technique to maximum 2θ values of 49.9°, 47.9°, and 45.9° for **1**, **3**, and **4**, respectively. Scans of $(1.00 + 0.35 \tan\theta)°$ were made at variable speeds of 3.0−16.0°/min (in ω). The intensities of three representative reflections, which were measured after every 90 min of X-ray exposure time, remained constant throughout data collection, so no decay correction was applied. Lorentz and polarization corrections were applied to the data. A summary of relevant crystallographic data for **1**, **3**, and **4** is provided in Table 1. All calculations were carried out with the TEXSAN crystallographic software package of the Molecular Structure Corp. on a Micro VAX 3600 computer.

Structure Determination for $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (1). Crystals suitable for study by X-ray diffraction were grown from saturated hexane solution of **1** at −20 °C. An orange, translucent triangular crystal of **1** having approximate dimensions 0.4 × 0.3 × 0.2 mm was mounted on a glass fiber and aligned on the diffractometer. On the basis of the statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$. Of the 3768 reflections, 3555 were unique (R_{int} = 0.011). The linear absorption coefficient, μ, for Mo Kα radiation is 23.6 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.85 to 1.00. The structure

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was solved by direct methods using SHELX-86.[12] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions but not refined. The final cycle of full-matrix least-squares refinement was based on 3243 observed reflections ($I > 3.00\sigma(I)$) and 263 variable parameters.

Structure Determination for $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu_4\text{-}S)$ (3). An orange, translucent platelite crystal of **3** was cut from a larger sample; the resultant crystal having approximate dimensions 0.39 × 0.21 × 0.05 mm was mounted on a glass fiber using grease and aligned on the diffractometer. On the basis of the systematic absences of $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) and the successful solution and refinement of the structure, the space group is $P2_1/n$. Of the 4125 reflections which were collected, 3919 were unique ($R_{int} = 0.030$). The linear absorption coefficient, μ, for Mo Kα radiation is 27.6 cm^{-1}. An analytical absorption correction was applied which resulted in transmission factors ranging from 0.59 to 0.87. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2929 observed reflections ($I > 3.00\sigma(I)$) and 317 variable parameters.

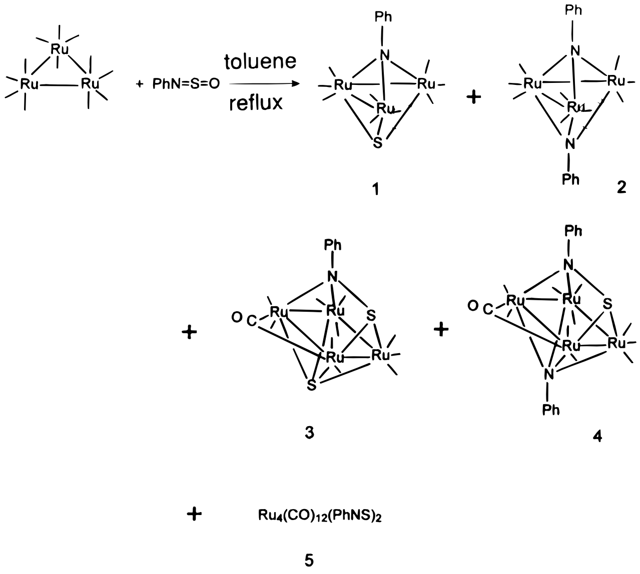
Structure Determination for $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu_4\text{-}NPh)$ (4). An orange, transparent columnar crystal of **4** was cut from a larger sample; the resultant having approximate dimensions 0.26 × 0.06 × 0.07 mm was mounted on a glass fiber and aligned on the diffractometer. The systematic absences of $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) uniquely determined the space group to be $P2_1/c$. Of the 8132 reflections, 7945 were unique ($R_{int} = 0.078$). The linear absorption coefficient, μ, for Mo Kα radiation is 22.8 cm^{-1}. An analytical absorption correction was applied which resulted in transmission factors ranging from 0.78 to 0.87. The structure was solved by direct methods. Two independent molecules were refined in the asymmetric unit. Owing to the paucity of data, carbon atoms were refined isotropically, while the remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions but were not refined. The final cycle of full-matrix least-squares refinement was based on 4147 observed reflections ($I > 2.50\sigma(I)$) and 510 variable parameters.

Results and Discussion

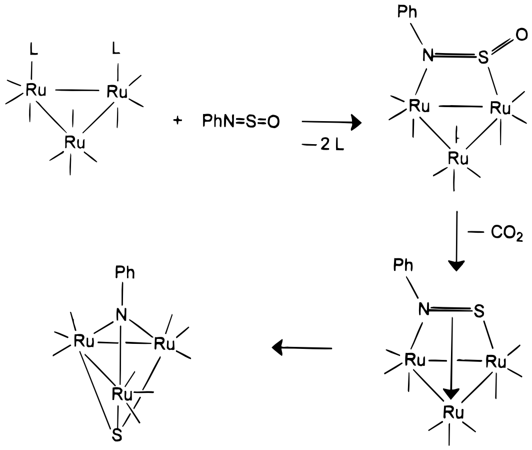
Reaction of $Ru_3(CO)_{12}$ and PhN=S=O. Treatment of $Ru_3(CO)_{12}$ with PhN=S=O in refluxing toluene affords a complex reaction mixture, as indicated by IR spectroscopy. The pentane extract gives a large number of bands upon thin-layer chromatographic separation. Among them, the initial five bands are distinct and can be isolated in order of elution as $Ru_3(CO)_{12}$, $Ru_3(CO)_9(\mu_3\text{-}NPh)(\mu_3\text{-}S)$ (**1**), $Ru_3(CO)_9(\mu_3\text{-}NPh)_2$ (**2**), $Ru_4(CO)_{10}(\mu\text{-}CO)_{10}(\mu_4\text{-}S)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu_4\text{-}S)$ (**3**), and $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu_4\text{-}NPh)$ (**4**) (Scheme 1). The major brown, pentane-insoluble product is purified by washing with diethyl ether and precipitation from dichloromethane/pentane solution to give a brown powder, formulated as $Ru_4(CO)_{12}(SNPh)_2$ (**5**).

In all of the characterized products, the integrity of the thionylaniline moiety is not retained intact. It appears that the sulfido and phenylimido groups are formed by rupture of the S−O and N−S bonds and the (phenylimino)thio group (PhN=S) is formed by S−O bond scission. Similar fragmentation has been observed previously in cothermolysis of metal carbonyls with nitrobenzene[11] and sulfur diimide (RN=S=NR) species.[13−16]

Scheme 1



Scheme 2



To prevent ligand fragmentation, we explored milder conditions, in which carbonyl groups were replaced by the more labile acetonitrile ligands. Surprisingly, treatment of $Ru_3(CO)_{10}(NCMe)_2$ with PhN=S=O at room temperature produces compound **1** as the only metal-containing product, accompanied by the release of CO_2. The reaction of $Ru_3(CO)_{11}(NCMe)$ and PhN=S=O also leads to compound **1** and regenerates $Ru_3(CO)_{12}$. No intermediates are detected in these two reactions. Since *N*-sulfinylaniline may donate two or four electrons to a metal center, successive replacement of two acetonitrile (or carbonyl) ligands from $Ru_3(CO)_{10}(NCMe)_2$ or $Ru_3(CO)_{12}$ may occur to generate $Ru_3(CO)_{10}(PhN{=}S{=}O)$, which apparently is thermally unstable. Subsequent reactions probably proceed via concerted S−O bond scission and C−O bond formation to liberate CO_2 and form $Ru_3(CO)_9(PhN{=}S)$, followed by N−S bond breaking to give **1** (Scheme 2). The sequence of S−O and N−S bond scission is not certain, but the last step resembles the conversion of alkyne complexes into dialkylidyne complexes in trinuclear cluster systems.[17]

Compound **1** is thermally stable up to 101 °C (refluxing methylcyclohexane). However, in the presence of PhN=S=O, slow conversion of **1** to **2** is observed (Scheme 3). It appears

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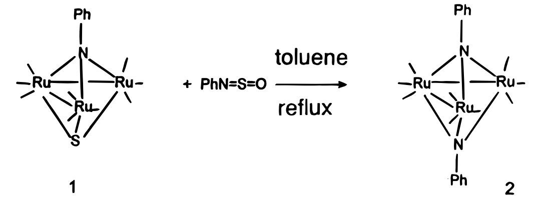
Scheme 3



that nucleophilic attack of the sulfido atom occurs at the thionyl group, inducing ligand transformation to yield **2** and release the unstable species S_2O. Adams[18] has demonstrated the nucleophilicity of sulfido lone-pair electrons in $(H)_2Ru_3(CO)_9(\mu_3\text{-S})$ to give the macrocycle $[(H)_2Ru_3(CO)_8(\mu_4\text{-S})]_3$ upon thermolysis. The reaction pathways leading to formation of compounds **3**−**5** are not clear at this stage. Since the nuclearity of the clusters has changed from 3 to 4, the reactions are likely to be complicated. It is possible that the reactions proceed by partial fragmentation of the trinuclear cluster to give mononuclear fragments, which then combine with remaining trinuclear species to yield the higher nuclearity products.

Characterization of 1 and 2. $Ru_3(CO)_9(\mu_3\text{-NPh})_2$ (**2**) forms air-stable, orange crystals. The ^1H NMR, mass, and IR data agree with those previously reported by Bhaduri and coworkers[11] for compound **2** resulting from the reaction of $Ru_3(CO)_{12}$ with nitrobenzene at elevated temperatures. Compound **2** has a structure consisting of an open triangular Ru_3 cluster with triply-bridging phenylimido ligands on opposite sites of the cluster.[19]

$Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**) forms an air-stable orange crystalline solid, which has been characterized by IR, ^1H and ^{13}C NMR, and mass spectroscopies and by elemental analysis. The EI mass spectrum shows the molecular ion peak at $m/z = 681$ for ^{102}Ru and ion multiplets corresponding to loss of nine carbonyls. The isotopic distribution of the envelope surrounding the molecular ion matches that expected for **1**, and there is a good agreement between the calculated mass distribution and the observed mass spectrum. IR absorptions in the carbonyl region of **1** show a pattern similar to that of **2** (Figure 1), suggesting that their structures are very similar.

The triiron and triosmium analogues of compound **1** are known. $Fe_3(CO)_9(\mu_3\text{-NTol})(\mu_3\text{-S})$[16] and $Os_3(CO)_9(\mu_3\text{-NSiMe}_3)(\mu_3\text{-S})$[13] have been prepared from reactions of $M_3(CO)_{12}$ (M = Fe, Os) with sulfur diimide and TolN=S=NTol and $Me_3SiN{=}S{=}NSiMe_3$, respectively. The reaction of $Ru_3(CO)_{12}$ with $Me_3SiN{=}S{=}NSiMe_3$, however, leads to a complicated binuclear complex.[20]

The ^{13}C NMR spectrum of ^{13}C-enriched $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (ca. 20% ^{13}C) in $CDCl_3$ at 25 °C is illustrated in Figure 2. The carbonyl carbons are in a 3:2:2:2 pattern, which agrees with the proposed C_s symmetry. The signal at δ 197.4 is assigned to the three carbonyls in the central $Ru(CO)_3$ unit, presumably undergoing exchange via 3-fold rotation. The signals at δ 191.9, 191.2, and 187.0 are assigned to the remaining three pairs of carbonyls. This resonance pattern for the carbonyl carbon remains unchanged from 65 to −90 °C (CD_2Cl_2), with no indication of carbonyl scrambling.

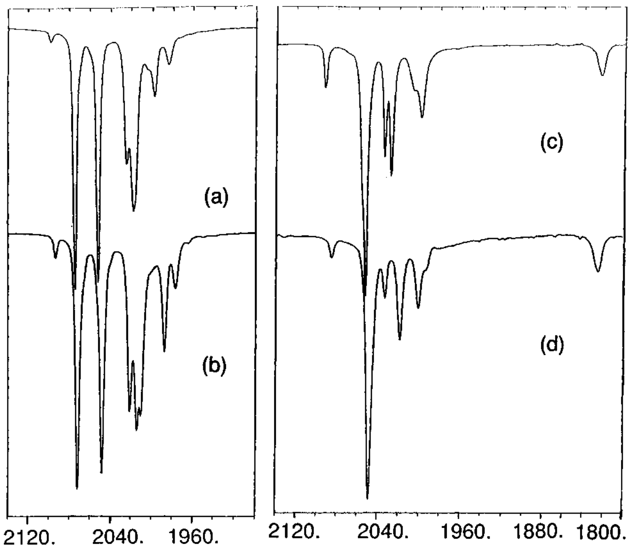


Figure 1. IR spectra in the carbonyl region of (a) $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**), (b) $Ru_3(CO)_9(\mu_3\text{-NPh})_2$ (**2**), (c) $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-S})$ (**3**), and (d) $Ru_4(CO)_{10}(\mu_3\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-NPh})$ (**4**).

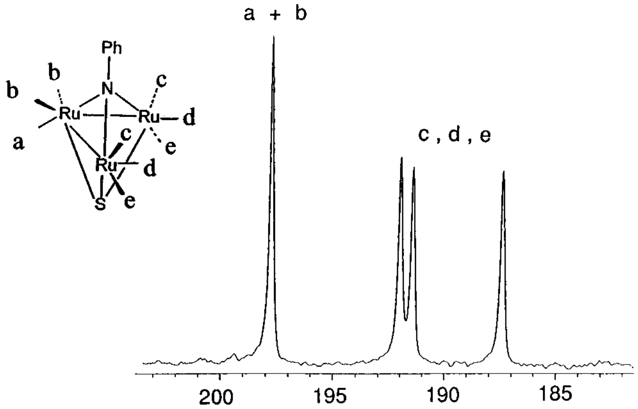


Figure 2. ^{13}C NMR spectrum of $Ru_3(^*CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**) obtained in $CDCl_3$ at 25 °C.

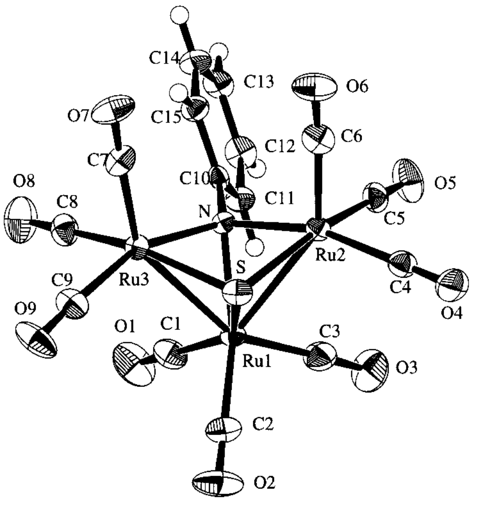


Figure 3. ORTEP drawing of $Ru_3(CO)_9(\mu_3\text{-NPh})(M_3\text{-S})$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.

Crystal Structure of 1. Crystals of **1** contain an ordered array of discrete monomeric molecule units which are mutually separated by normal van der Waals distances. The ORTEP drawing of the molecule is shown in Figure 3. Selected bond distances and bond angles are given in Table 2. The molecule consists of an open triangular cluster of three $Ru(CO)_3$ units, while a phenylimido and a sulfido ligand triply bridge the opposite face of the $Ru_3(CO)_9$ moiety. Structurally, **1** is very similar to $Fe_3(CO)_9(\mu_3\text{-NTol})(\mu_3\text{-S})$,[11] $Os_3(CO)_9(\mu_3\text{-NSiMe}_3)(\mu_3\text{-S})$,[13] $M_3(CO)_9(\mu_3\text{-S})_2$ (M = Fe,[21] Ru,[22] Os[23]), and $Ru_3(CO)_9$-

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $Ru_3(CO)_9(\mu_3\text{-NPh})(\mu_3\text{-S})$ (**1**)

Distances

Ru1−Ru2	2.7233(7)	Ru1−S	2.403(1)
Ru1−Ru3	2.6947(5)	Ru2−S	2.357(1)
Ru1−N	2.136(3)	Ru3−S	2.369(1)
Ru2−N	2.062(3)	N−C10	1.433(5)
Ru3−N	2.078(3)		

Angles

Ru2−Ru1−Ru3	78.53(2)	Ru2−Ru1−S5	54.31(3)
Ru2−Ru1−N	48.37(9)	Ru3−Ru1−S5	55.03(3)
Ru3−Ru1−N	49.31(9)	Ru1−Ru2−S5	55.89(3)
Ru1−Ru2−N	50.76(9)	Ru1−Ru3−S	56.21(3)
Ru1−Ru3−N	51.21(9)	Ru1−S−Ru2	69.79(3)
Ru1−N−Ru2	80.9(1)	Ru1−S−Ru3	68.76(3)
Ru1−N−Ru3	79.5(1)	Ru2−S−Ru3	93.04(4)
Ru2−N−Ru3	111.9(1)	S−Ru1−N	73.44(9)
Ru1−N−C10	129.6(3)	S−Ru2−N	75.74(9)
Ru2−N−C101	118.9(2)	S−Ru3−N	75.17(9)
Ru3−N−C10	123.7(2)		

$(\mu_3\text{-NPh})_2$.[19] The imido and sulfido ligands can be considered as four-electron donors, resulting in a total of 50 valence electrons for the clusters. This electron count requires only two metal−metal bonds to provide an 18-electron configuration on each metal atom, in agreement with the observed M−M bond distances.

In compound **1**, each ruthenium atom is bonded to three terminal carbonyl groups. The individual Ru−CO bond lengths range from 1.905(5) through 1.938(5) Å. The C−O distances range from 1.123(6) through 1.136(6) Å, while Ru−C−O angles are in the range 179.5(4)−176.2(5)°. The imido and sulfido ligands bridge opposite Ru_3 faces asymmetrically; thus the N−Ru and S−Ru bonds to the seven-coordinate central Ru1 atom (2.136(3) and 2.403(1) Å) are significantly longer than those to the six-coordinate Ru3 (2.078(3) and 2.369(1) Å) and the six-coordinate Ru2 (2.062(3) Å and 2.357(1) Å). The slight lengthening of Ru1−Ru2 (2.7233(7) Å) compared with Ru1−Ru3 (2.6947(5) Å is presumably due to the asymmetrical arrangement of the capping ligands.

Characterization of 3 and 4. $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-S})$ (**3**) forms orange, air-stable crystals. It has been characterized by IR, mass, and ^1H NMR spectroscopies and C, H, N elemental analyses. The mass spectrum of **3** shows the parent ion at m/z 871 for ^{102}Ru plus ions corresponding to the loss of 10 carbonyls. The IR spectrum (Figure 1) shows six absorptions ranging from 2093 to 2000 cm^{-1} for the terminal carbonyl stretchings and a weak absorption at 1824 cm^{-1}, indicating the presence of bridging carbonyl. The ^1H NMR spectrum includes a multiplet in the range δ 7.11−6.75 for the phenyl proton resonances.

$Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-NPh})$ (**4**) forms an air-stable, orange crystalline solid. The electron-impact mass spectrum presents the highest mass at m/z 902 for ^{102}Ru, corresponding to the fragment of the molecule ion minus a carbonyl group. The IR absorption pattern, shown in Figure 1, is very similar to that of **3**, again implying an analogous structure. Because of the absence of diagnostic spectral features to reveal the structures of **3** and **4**, single-crystal X-ray diffraction studies were performed.

Crystal Structure of 3. An ORTEP drawing of **3**, shown in Figure 4, consists of a cluster of four ruthenium atoms arranged approximately in the form of a square with one face capped by a (phenylimino)thio group and another face capped by a quadruply-bridging sulfido ligand. Ignoring the carbonyl ligands and the phenyl ring, the geometry can also be viewed as a capped trigonal prism with a skeleton consisting of an Ru_4NS prism, faced-capped by a μ_4-sulfido fragment. Selected bond lengths and bond angles within the molecule are collected in Table 3.

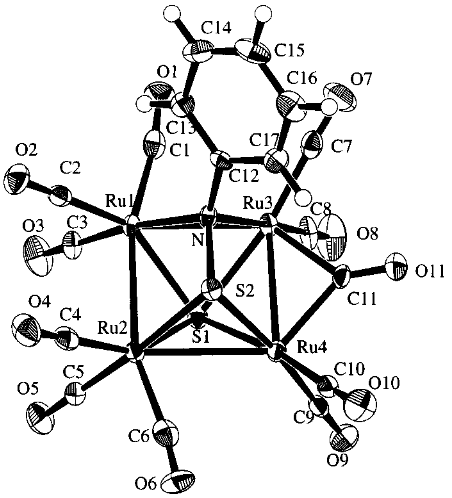

Figure 4. ORTEP drawing of $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})$ $(\mu_4\text{-S})$ (**3**). Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}\eta^2\text{-SNPh})(\mu_4\text{-S})$ (**3**)

Distances

Ru1−Ru2	2.8222(6)	N−S2	1.751(4)
Ru1−Ru3	2.813(2)	N−C12	1.461(7)
Ru2−Ru4	2.905(2)	Ru1−S1	2.425(2)
Ru3−Ru4	2.8340(6)	Ru2−S1	2.424(2)
Ru1−N	2.148(4)	Ru3−S1	2.428(2)
Ru3−N	2.130(4)	Ru4−S1	2.441(2)
Ru2−S2	2.374(2)	Ru3−C11	2.043(6)
Ru4−S2	2.351(2)	Ru4−C11	2.033(6)

Angles

Ru2−Ru1−Ru3	91.21(2)	Ru2−S2−Ru4	75.89(6)
Ru2−Ru4−Ru3	89.11(2)	Ru2−S2−N	99.1(2)
Ru1−Ru2−Ru4	89.02(2)	Ru4−S2−N	98.3(2)
Ru1−Ru3−Ru4	90.62(4)	S2−N−C12	110.6(3)
Ru3−C11−Ru4	88.1(2)	Ru2−Ru1−S1	54.39(4)
Ru3−C11−O11	135.9(5)	Ru3−Ru1−S1	54.61(4)
Ru4−C11−O11	135.9(5)	Ru1−Ru2−S1	54.43(4)
Ru2−Ru1−N	77.8(1)	Ru1−Ru3−S1	54.53(4)
Ru3−Ru1−N	48.6(1)	Ru4−Ru3−S1	54.61(4)
Ru1−Ru3−N	49.2(1)	Ru4−Ru2−S1	53.59(4)
Ru4−Ru3−N	76.6(1)	Ru2−Ru4−S1	53.07(5)
Ru1−Ru2−S2	74.53(4)	Ru3−Ru4−S1	54.20(4)
Ru4−Ru2−S2	51.69(5)	Ru1−S1−Ru2	71.17(4)
Ru2−Ru4−S2	52.42(4)	Ru1−S1−Ru3	70.86(6)
Ru3−Ru4−S2	75.09(4)	Ru1−S1−Ru4	111.22(6)
Ru1−N−Ru3	82.2(2)	Ru2−S1−Ru4	73.34(6)
Ru1−N−S2	108.1(2)	Ru2−S1−Ru3	112.19(6)
Ru3−N−S2	109.8(2)	Ru3−S1−Ru4	71.20(5)

The four ruthenium atoms are essentially coplanar, as evidenced by their torsional angles (±0.84(3)°). Three of the Ru−Ru distances, Ru1−Ru3 = 2.813(2) Å, Ru1−Ru2 = 2.8222(6) Å, and Ru3−Ru4 = 2.834(6) Å, are similar while the fourth, Ru2−Ru4 = 2.905(2) Å, is considerably longer. These are different from those previously measured for $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-PPh})_2$,[24] $Ru_4(CO)_9(\mu\text{-CO})_2(\mu_4\text{-S})_2$,[25] and $Ru_4(CO)_{10}(\mu\text{-CO})(\mu_4\text{-}$

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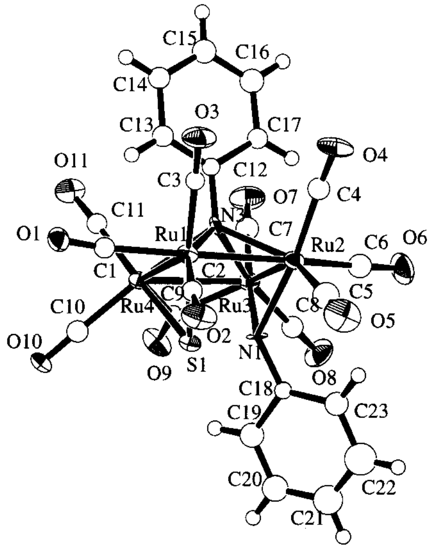

Figure 5. ORTEP drawing of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu_4\text{-}NPh)$ (**4**). Thermal ellipsoids are drawn at the 50% probability level.

$N_2Ph)(\mu_4\text{-}PPh)$,[26] where the Ru−Ru bond bridged by a carbonyl ligand is significantly shorter than the others.

For compound **3**, 10 of the carbonyl groups are terminally bound to the ruthenium atoms with Ru−C distances in the range 1.888(7)−1.927(7) Å, the C−O distances in the range 1.124(7)−1.146(7) Å, and the Ru−C−O angles ranging from 171.4(5) to 179.6(5)°. The 11th carbonyl bridges the Ru3−Ru4 edge symmetrically, tilting 20.2(6)° out of the tetraruthenium plane toward the (phenylimino)thio group.

The (phenylimino)thio ligand caps one Ru_4 face through doubly-bridging nitrogen and sulfur atoms. The two Ru−N bond distances, as well as the two Ru2−S2 and Ru4−S2 lengths, are only slightly different. In this case, all four ruthenium atoms are seven-coordinate. The N−S2 distance of 1.751(4) Å is characteristic of a nitrogen-sulfur single bond.

The quadruply-bridging sulfido ligand lies on the opposite side of the square. The metal−sulfur distance to Ru4, 2.441(2) Å, is slightly longer than all the others, 2.424(2)−2.428(2) Å. As expected, the mean ruthenium−sulfur distance in **3** (2.43 Å) is significantly longer than the ruthenium−sulfur distances to triply-bridging sulfido ligands in **1** (2.38 Å).

Crystal Structure of 4. There are two crystallographically independent molecules in the asymmetric unit, which are structurally equivalent and the molecular stereochemistry of one of these is illustrated in Figure 5. Selected bond lengths and angles are included in Table 4. As predicted from the similarity of IR absorption patterns in the carbonyl region, the structure of **4** closely resembles that of **3**, except that the μ_4-sulfido ligand is replaced by a μ_4-phenylimido species.

The four ruthenium−ruthenium distances are not equal, ranging from 2.727(2) Å (Ru1−Ru2) to 2.818(2) Å (Ru1−Ru4), and the torsional angles between two opposite Ru−Ru vectors are ±2.5(1)°, indicating a slightly distorted square planar framework. The (phenylimino)thio and terminal carbonyl ligands are bound to the tetraruthenium cluster in a fashion identical with that in **3**, while the bridging carbonyl is tilted 21(2)° from the Ru_4 plane toward the (phenylimino)thio group. The phenylimido ligand is quadruply-bridging another square face. The Ru−N3 distances, in the range 2.18−2.28 Å, are considerably longer than the ruthenium-nitrogen distances to the triply-bridging phenylimido ligand in **1** (2.059−2.139 Å).

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}SNPh)(\mu_4\text{-}S)$ (**4**)

Distances			
Ru1−Ru2	2.727(2)	N1−S1	1.76(1)
Ru1−Ru4	2.818(2)	N1−C18	1.42(2)
Ru2−Ru3	2.777(2)	Ru1−N3	2.21(1)
Ru3−Ru4	2.806(2)	Ru2−N3	2.22(1)
Ru2−N1	2.14(1)	Ru3−N3	2.19(1)
Ru3−N1	2.15(1)	Ru4−N3	2.27(1)
Ru1−S1	2.361(4)	N3−C12	1.43(2)
Ru4−S1	2.352(4)	Ru3−C9	2.03(2)
Angles			
Ru1−Ru2−Ru3	90.53(6)	Ru1−S1−N1	98.5(4)
Ru1−Ru4−Ru3	88.10(6)	Ru4−S1−N1	98.7(4)
Ru2−Ru3−Ru4	90.25(6)	S1−N1−C18	110.7(10)
Ru2−Ru1−Ru4	91.01(6)	Ru4−Ru1−N3	52.1(3)
Ru3−C9−Ru4	87.3(6)	Ru2−Ru1−N3	52.2(3)
Ru3−C9−O9	136(1)	Ru3−Ru2−N3	50.5(3)
Ru4−C9−O9	136(1)	Ru1−Ru2−N3	51.7(3)
Ru1−Ru2−N1	79.5(3)	Ru2−Ru3−N3	51.5(3)
Ru3−Ru2−N1	49.8(3)	Ru4−Ru3−N3	52.4(3)
Ru2−Ru3−N1	49.5(3)	Ru1−Ru4−N3	50.0(3)
Ru4−Ru3−N1	77.4(3)	Ru3−Ru4−N3	49.8(3)
Ru2−Ru1−S1	75.3(1)	Ru1−N3−Ru2	76.0(4)
Ru4−Ru1−S1	53.1(1)	Ru1−N3−Ru4	77.9(4)
Ru3−Ru4−S1	75.4(1)	Ru1−N3−Ru3	125.5(6)
Ru1−Ru4−S1	53.4(1)	Ru2−N3−Ru3	78.0(4)
Ru2−N1−Ru3	80.8(4)	Ru2−N3−Ru4	123.2(5)
Ru2−N1−S1	106.1(6)	Ru3−N3−Ru4	77.8(4)
Ru3−N1−S1	108.4(6)	Ru1−N3−C12	116.4(9)
Ru1−S1−Ru4	73.4(1)	Ru2−N3−C12	120.4(9)

If the μ_4-sulfido and μ_4-phenylimido ligands are counted as four-electron donors and the μ_4-η^2-(phenylimino)thio ligand is counted as a six-electron donor, compounds **3** and **4** can be considered as electron-precise square clusters which contain 64 valence electrons. Compounds **3** and **4** are isoelectronic with $Ru_4(CO)_{10}(\mu\text{-}CO)$ $(\mu_4\text{-}\eta^2\text{-}N_2Ph_2)(\mu_4\text{-}PPh)$,[26] whereas the other known tetraruthenium square clusters $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)$,[25] $Ru_4(CO)_7(PMe_2Ph)_2(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$,[25] $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}PPh)_2$,[24] and $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}S)(\mu_4\text{-}PPh)$[24] contain only 62 electrons and are formally electron deficient by two electrons.

Characterization of Compound 5. Compound **5** forms an air-sensitive, brown solid which is insoluble in pentane and diethyl ether but soluble in polar solvents, such as chloroform, dichloromethane, and acetone. Attempts to establish the molecular ion of this compound by electron-impact, fast-atom-bombardment, and field-desorption mass spectrometry proved unsuccessful. However, the presence of a multiplet in the ^1H NMR, ranging from 7.20 to 6.40 ppm, is indicative of the presence of phenyl group. The IR spectrum in the carbonyl region shows three broad bands at 2107, 2055, and 1996 cm^{-1}. The Ru, C, H, N, and S elemental analyses are consistent with the stoichiometry $Ru_4(CO)_{12}(NSPh)_2$. Numerous attempts to grow crystals suitable for X-ray diffraction study have been unsuccessful. Alternative methods of characterization by the synthesis of phosphine derivatives are under way.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1**, **3**, and **4** are available on the Internet only. Access information is given on any current masthead page.

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