Reactivity of a Cationic Non-Hydridic Triruthenium Carbonyl Cluster Complex with Anionic Reagents. Synthesis of New Tri- and Hexanuclear Derivatives

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Summary: The cationic cluster complex [Ru₃(μ₃-ampy)-(CO)₁₀][BF₄] (1) (Hampy = 2-amino-6-methylpyridine) reacts with chloride, iodide, and acetate anions (as [PPN]⁺ or [Bu₄N]⁺ salts) to give the 50-electron neutral compounds [Ru₃(μ-X)(μ₃-ampy)(CO)₉] (X = Cl, I, MeCO₂), whereas its reaction with [PPN][BH₄] affords the known 48-electron neutral hydrido derivative [Ru₃(μ-H)(μ₃-ampy)(CO)₉]. The hexanuclear compound [Ru₆(μ-H)(μ₄-S)(μ₃-ampy)(CO)₁₇], which consists of two closed trimetal units connected by two metal−metal bonds (X-ray structure), has been prepared by reaction of complex 1 with the anionic cluster compound [PPN]₂[Ru₃(μ₃-S)(CO)₉].

Scheme 1

Introduction

In a recent paper, we have described a high-yield synthesis and some carbonyl substitution chemistry of the cluster complex [Ru₃(μ₃-ampy)(CO)₁₀][BF₄] (1, Hampy = 2-amino-6-methylpyridine, Scheme 1).[1] This compound is interesting because it is the first cationic non-hydridic 48-electron triruthenium carbonyl cluster ever reported.[2] These attributes, coupled to its efficient preparation and high thermal and air stability, make complex 1 an excellent candidate for reactivity studies.

As far as the reactivity of cationic carbonyl ruthenium cluster compounds is concerned, only that of some hydrido derivatives has been studied in detail.[3] These studies have demonstrated that such complexes have an enhanced reactivity toward nucleophilic reagents, undergoing carbonyl substitution reactions and nucleophilic additions to coordinated CO ligands under very mild conditions. Sometimes, these hydridic cationic clusters also undergo competitive deprotonation processes.[3]
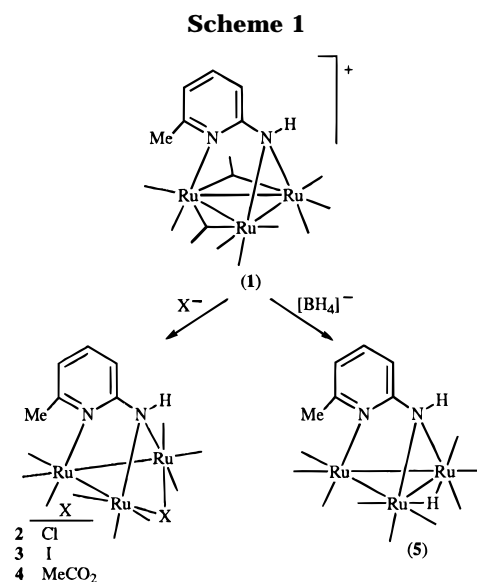
We have already reported that the reaction of compound 1 with aqueous sodium hydroxide renders the novel hexanuclear 94-electron derivative [Ru₆(μ₃-ampy)₂-(CO)₁₈],[4] a rare example of a hexanuclear carbonyl cluster complex consisting of two closed trimetal units connected to each other by only one metal−metal bond. We now report that the reactions of compound 1 with some other anionic reagents, such as the chloride, iodide, and acetate anions, lead to neutral 50-electron cluster compounds, whereas the reaction with the tetrahydroborate anion gives a neutral 48-electron derivative. We also describe that the reaction of compound 1 with the anionic cluster [Ru₃(μ₃-S)(CO)₉]²⁻ renders the hexanuclear 92-electron derivative [Ru₆(μ-H)(μ₄-S)(μ₃-ampy)(CO)₁₇].

Results and Discussion

Reactions with Anionic Ligands. Complex 1 reacted instantaneously with 1 equiv of [PPN]Cl in dichloromethane at room temperature to give a yellow solution. The NMR spectra of this solution indicated the presence of a single cluster complex, subsequently identified as [Ru₃(μ-Cl)(μ-ampy)(CO)₉] (2).[5] Unfortunately, all attempts to separate this product from the

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accompanying [PPN][BF$_4$] were unsuccessful, since the cluster could not be eluted from chromatographic supports (silica and alumina) and it decomposed when its solutions were evaporated to dryness. The structure depicted for compound **2** in Scheme 1 is based on its spectroscopic data.[5] The C_s symmetry of the molecule and the number of CO ligands were unambiguously determined by NMR spectroscopy, since five CO resonances, of intensities 1:2:2:2:2, are observed in the ^{13}C spectrum. The IR spectrum also confirms that the cluster does not contain bridging carbonyl ligands. Therefore, complex **2** is an open 50-electron species in which the chloride ligand spans the same edge as the amido moiety of the ampy ligand. Other known 50-electron trinuclear carbonyl clusters in which a halide ligand spans an open edge are, generally, not neutral[6] but anionic complexes.[7]

The iodide and acetato derivatives [Ru$_3$(μ-X)(μ-ampy)-(CO)$_9$] (X = I (**3**), MeCO$_2$ (**4**)) were also observed in solution when complex **1** was treated with [Bu$_4$N]X (X = I, MeCO$_2$).[8,9] However, as occurred with **2**, they could not be separated from the byproduct [Bu$_4$N][BF$_4$] by either chromatographic methods or fractional crystallization. In an attempt to obtain an isolable derivative of complex **2**, a CD$_2$Cl$_2$ solution of this complex was treated with 1 equiv of triphenylphosphine. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the resulting solution indicated the quantitative formation of a substituted product, presumably [Ru$_3$(μ-Cl)(μ-ampy)(CO)$_8$(PPh$_3$)].[10] Again, it could not be obtained as a solid in pure form.

The compound [PPN][BH$_4$] has been previously reported as the reagent of choice to introduce hydrido ligands into carbonyl cluster compounds for reactions carried out in dichloromethane solvent.[11] In our case, the reaction of [PPN][BH$_4$] with a dichloromethane solution of compound **1** gave the known[12] 48-electron hydrido derivative [Ru$_3$(μ-H)(μ-ampy)(CO)$_9$] (**5**) in quantitative yield (Scheme 1).

The anions of the compounds Li[C$_5$Me$_5$], [NEt$_4$]CN, [PPN]$_2$S, and Li[C≡CPh] were found to react with

Scheme 2

(**6**)
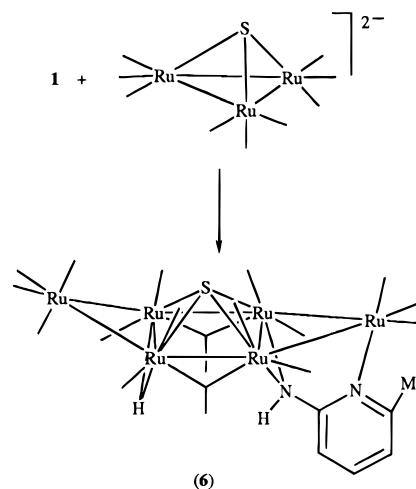
complex **1** in 1,2-dichloroethane at room temperature; however, these reactions gave mixtures of products that we were unable to separate and characterize.

Reactions with Anionic Complexes. The reactions of anionic carbonyl clusters with mononuclear cations have been used before to prepare higher nuclearity cluster compounds;[13,14] however, no reactions of cationic carbonyl clusters with anionic complexes have been reported previously, probably because cationic carbonyl clusters were not readily accessible prior to the publication of compound **1**.[1]

Compound **1** reacted readily with the anionic cluster [PPN]$_2$[Ru$_3$(μ_3-S)(CO)$_9$][13,15] in 2:1 mole ratio to give a mixture of **5**, [Ru$_3$(μ-H)$_2$(μ_3-S)(CO)$_9$],[13,16] and the new hexanuclear derivative [Ru$_6$(μ-H)(μ_4-S)(μ_3-ampy)(CO)$_{17}$] (**6**, Scheme 2). The use of a 1:1 mole ratio did not increase the yield of **6**. As the three compounds are neutral hydrido derivatives, the proton source is believed to be a small amount of moisture in the solvent or in the glassware (although carefully dried solvents and glassware were used) because these clusters were always observed in the reaction mixture by IR spectroscopy prior to the chromatographic separation (thus, ruling out the chromatographic support as the source of protons). All attempts to isolate ionic complexes were unsuccessful.

The data obtained from the IR and NMR spectra of **6** were insufficient to assign a structure to this compound; therefore, an X-ray diffraction study, on the solvate **6**·(C$_6$H$_5$Me)$_{0.3}$, was carried out. The molecular structure of compound **6** in the solid state is shown in Figure 1. Relevant bond distances and angles are given in Table 1. The molecule consists of a square-planar Ru$_4$ unit in which two opposite edges are bridged by two additional Ru atoms, while the other two edges of the square are symmetrically spanned by two CO ligands.

(5) Spectroscopic data for **2**: (a) IR (CH$_2$Cl$_2$), ν(CO): 2085 (w), 2061 (s), 2031 (vs), 2000 (sh), 1986 (s) cm^{-1}. (b) ^{1}H NMR (CD$_2$Cl$_2$): 7.33 (t, J = 7.8 Hz, 1 H, ampy H^4), 6.69 (d, J = 7.8 Hz, 1 H, ampy H^5), 6.47 (d, J = 7.8 Hz, 1 H, ampy H^3), 4.87 (s, br, 1 H, ampy NH), 2.63 (s, 3 H, ampy Me) ppm. (c) ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 201.2 (1 C, CO), 198.5 (2 C, CO), 198.4 (2 C, CO), 197.1 (2 C, CO), 175.6 (2 C, CO) 175.3 (ampy C), 157.2 (ampy C), 137.3 (ampy C), 117.5 (ampy C), 105.5 (ampy C), 27.0 (ampy C) ppm.

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(8) Spectroscopic data for complex **3**: (a) IR (1,2-dichloroethane), ν(CO): 2080 (vw), 2057 (s), 2029 (vs), 1997 (m, sh), 1984 (s) cm^{-1}. (b) ^{1}H NMR (CDCl$_3$): 7.66 (t, J = 8.2 Hz, 1 H, ampy H^4), 7.05 (d, J = 8.2 Hz, 1 H, ampy H^5), 6.91 (s, br, 1 H, ampy NH), 6.56 (d, J = 8.2 Hz, 1 H, ampy H^3), 2.49 (s, 3 H, ampy Me) ppm.

(9) Spectroscopic data for complex **4**: (a) IR (1,2-dichloroethane), ν(CO): 2088 (vw), 2065 (s), 2032 (vs), 1988 (s), 1955 (m, sh) cm^{-1}. (b) ^{1}H NMR (CDCl$_3$): 7.28 (t, J = 7.8 Hz, 1 H, ampy H^4), 6.66 (d, J = 7.8 Hz, 1 H, ampy H^5), 6.52 (d, J = 7.8 Hz, 1 H, ampy H^3), 5.30 (s, br, 1 H, ampy NH), 2.61 (s, 3 H, ampy Me), 2.02 (s, 3 H, acetato Me) ppm.

(10) NMR data for [Ru$_3$(μ-Cl)(μ-ampy)(CO)$_8$(PPh$_3$)]: (a) ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 25.54 (s) ppm. (b) ^{1}H NMR (CD$_2$Cl$_2$): 7.72−7−45 (m, 15 H, PPh$_3$), 7.26 (s, br, 1 H, ampy NH), 7.11 (t, J = 7.8 Hz, 1 H, ampy H^4), 6.56 (d, J = 7.8 Hz, 1 H, ampy H^5), 5.18 (d, J = 7.8 Hz, 1 H, ampy H^3), 2.61 (s, 3 H, ampy Me) ppm.

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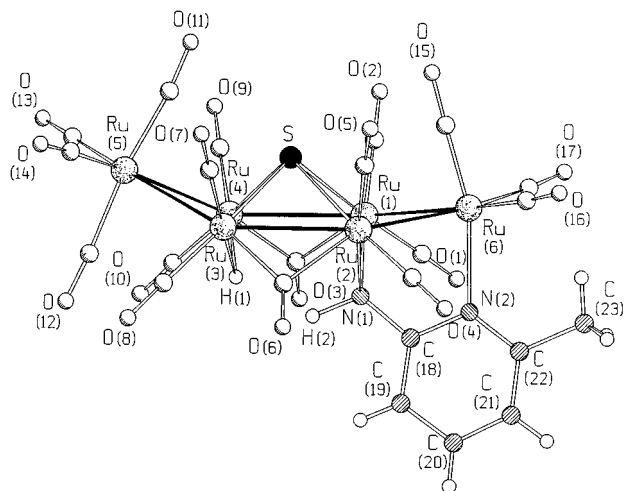
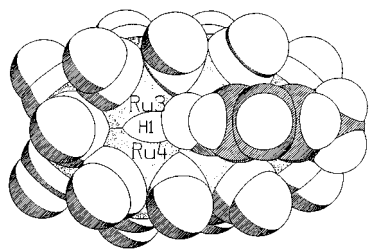**Figure 1.** Molecular structure of compound **6**.

Figure 2. Space-filling diagram of compound **6** viewed perpendicularly to the Ru_4 square plane, showing the large niche in the ligand coverage and the position of the hydride ligand.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in Compound $6 \cdot (C_6H_5Me)_{0.3}$

Ru(1)−Ru(2)	2.911(1)	Ru(1)−Ru(4)	2.868(2)
Ru(1)−Ru(6)	2.713(2)	Ru(2)−Ru(3)	2.875(2)
Ru(2)−Ru(6)	2.733(2)	Ru(3)−Ru(4)	2.873(2)
Ru(3)−Ru(5)	2.817(2)	Ru(4)−Ru(5)	2.808(1)
Ru(1)−S	2.498(3)	Ru(2)−S	2.521(3)
Ru(3)−S	2.396(3)	Ru(4)−S	2.408(3)
Ru(3)−H(1)	1.89(1)	Ru(4)−H(1)	1.81(1)
Ru(1)−N(1)	2.136(9)	Ru(2)−N(1)	2.137(9)
Ru(6)−N(2)	2.202(10)		
mean Ru−C(CO)$_{bridging}$	2.10(1)	mean Ru−C(CO)$_{terminal}$	1.89(2)
Ru(1)−S−Ru(2)	70.90(8)	Ru(3)−S−Ru(2)	71.53(8)
Ru(3)−S−Ru(4)	73.47(9)	Ru(4)−S−Ru(1)	71.54(8)
Ru(1)−N(1)−Ru(2)	85.9(3)	C(18)−N(1)−Ru(1)	118(1)
C(18)−N(1)−Ru(2)	116(1)	C(22)−N(2)−C(18)	118(1)
C(22)−N(2)−Ru(6)	128(1)	C(18)−N(2)−Ru(6)	113(1)
N(2)−C(18)−N(1)	117(1)		

The remaining 15 CO ligands are all terminally bound to the metal frame. The four metal atoms forming the tetragon are capped by a sulfur atom. The ampy ligand is bound to one of the two Ru_3 triangles in its usual μ_3 fashion, with the amido fragment spanning the edge shared by the Ru_4 and Ru_3 units. The edge shared by the Ru_4 and the remaining Ru_3 unit is spanned by a hydride ligand, which was located *via* a Fourier difference map and was observed by solution NMR spectroscopy (see the Experimental Section). The presence of the hydride is also revealed by a large niche in the ligand coverage, as shown in Figure 2.

Other structurally related hexaruthenium carbonyl cluster compounds containing μ_4-S ligands are known,

namely, $[Ru_6(\mu_4\text{-}S)(\mu\text{-}OH)_2(CO)_{18}]$,[17] $[Ru_6(\mu\text{-}SH)(\mu_4\text{-}S)(\mu_3\text{-}Spy)(CO)_{17}]$ (HSpy = pyridine-2-thiol),[18] and $[Ru_6(\mu_4\text{-}S)(\mu_3\text{-}RNCNHR)(\mu_3\text{-}RNCSNHR)(CO)_{16}]$ (R = Ph, Et).[19] The structures of the pyridine-2-thiolato and the thioureato derivatives were published while our work was underway. It is interesting to note that these compounds are electron-rich, since their electron counts (94 electrons) have two electrons in excess from those required by electron-precise hexanuclear clusters containing eight metal-metal bonds (92 electrons).[20] In contrast, cluster **6** is electron precise (the sulfur atom contributes four electrons to the cluster). This is reflected by the Ru−Ru distances associated with the capping sulfur atom: while the tetragons of the 94-electron compounds contain two Ru−Ru distances longer than the other two and longer than those expected for normal Ru−Ru bonds (average values 3.014(1), 3.076(1), and 3.156(3) Å for $[Ru_6(\mu_4\text{-}S)(\mu\text{-}OH)_2(CO)_{18}]$,[17] $[Ru_6(\mu\text{-}SH)(\mu_4\text{-}S)(\mu_3\text{-}Spy)(CO)_{17}]$,[18] and $[Ru_6(\mu_4\text{-}S)(\mu_3\text{-}RNCNHR)(\mu_3\text{-}RNCSNHR)(CO)_{16}]$,[19] respectively) the tetragon of compound **6** is nearly regular, with the four Ru−Ru bond distances ranging from 2.868(2) to 2.911(2) Å.

The crystal structure of compound **6** consists of sheets formed by molecular piles extending along the 101 direction (Figure 3a). The piles are oriented in such a way as to "isolate" the flat ampy ligands in between, allowing a better interlocking of the CO ligands on the opposite side. The toluene solvent molecules, present in a nonstoichiometric amount (0.3 molecules per formula unit), are located between the piles, close to the ampy ligands, as shown in Figure 3b.

The anion $[Ru_3(\mu_3\text{-}S)(CO)_9]^{2-}$ has been used previously as a nucleophile toward mononuclear cationic organometallic compounds. It reacts with $[M(CO)_3(MeCN)_3]^+$ and $[M(CO)_5]^+$ (M = Mn, Re) to give $[Ru_3(\mu\text{-}H)(\mu_4\text{-}S)(CO)_9M(CO)_3(MeCN)_2]$ and $[Ru_3(\mu\text{-}H)(\mu_4\text{-}S)(CO)_9M(CO)_5]$, respectively, in which the sulfur atoms are coordinated to pendant $[M(CO)_3(MeCN)_2]$ or $[M(CO)_5]$ fragments.[13] It should be noted that these products are hydrido derivatives and that the proton source is also uncertain. However, the reactions of $[Ru_3(\mu_3\text{-}S)(CO)_9]^{2-}$ with different amounts of $[Au(PPh_3)]^+$ have been found to give $[Ru_3Au(\mu\text{-}H)(\mu_3\text{-}S)(PPh_3)(CO)_9]$ and $[Ru_3Au_2(\mu_3\text{-}S)(PPh_3)_2(CO)_9]$, in which the gold atoms are attached to ruthenium atoms but not to the sulfur atom.[15]

In our hands, complex **1** also reacted with mononuclear organometallic anions, such as $[Co(CO)_4]^-$ and $[WCp(CO)_3]^-$, but these reactions led to mixtures of compounds from which we could not isolate any well-defined product. It seems that in the reactions of complex **1** with anionic complexes, the presence of a potential bridging ligand in the anionic reagent, such as the sulfur atom of $[Ru_3(\mu_3\text{-}S)(CO)_9]^{2-}$, is essential in order to maintain the integrity of the final products.

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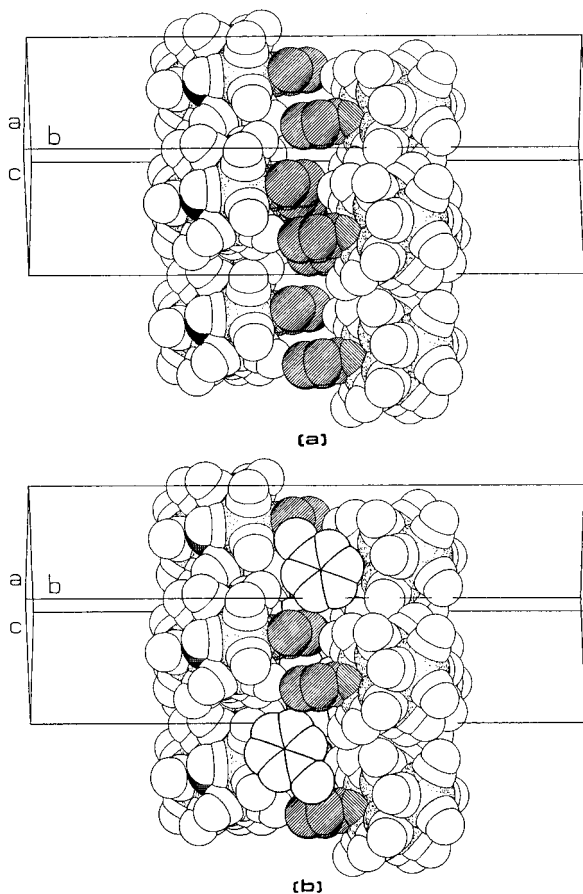
Figure 3. (a) A view of the molecular sheets formed by molecular piles extending the 101 direction in crystalline **6**·(C₆H₅Me)₀.₃, excluding the toluene solvent molecules. The position of the toluene molecules (thick contour) is indicated in (b). In both diagrams, the H atoms have been omitted for clarity.

Experimental Section

General Data. Instrumentation and solvent purification methods were as published previously.[1] Unless otherwise stated, the reactions were carried out under nitrogen at room temperature, using Schlenk–vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Compounds **1**[1] and [PPN]₂[Ru₃(μ_3-S)-(CO)₉][13] were prepared as described previously. The preparations and analytical and spectroscopic data of isolated compounds are described here. Spectroscopic data for nonisolated compounds are given as footnotes associated to their citations in the Results and Discussion section.

Reaction of Compound 1 with [PPN][BH₄]. Solid [PPN]-[BH₄] (35.6 mg, 0.064 mmol) was added to a solution of complex **1** (50 mg, 0.064 mmol) in dichloromethane (10 mL). The color instantaneously changed from red to orange. An IR spectrum of the solution indicated the quantitative formation of complex **5**.[12] The solvent was removed under reduced pressure, and the residue was separated by column chromatography (2 × 10 cm) in neutral alumina (activity I). Hexane–dichloromethane (1:1) eluted an orange band. Removal of the solvent gave [Ru₃(μ-H)(μ-ampy)(CO)₉] (**5**) as an orange solid (36 mg, 85%). Its analytical and spectroscopic data matched those reported in the literature.[12]

Reaction of Compound 1 with [PPN]₂[Ru₃(μ_3-S)(CO)₉]. Complex **1** (55 mg, 0.071 mmol) and [PPN]₂[Ru₃(μ_3-S)(CO)₉] (59 mg, 0.035 mmol) were dissolved in 1,2-dichloroethane (20 mL). The solution was stirred for 15 min, while the color changed from orange to blue. The solvent was removed under reduced pressure, and the residue was separated by column

Table 2. Crystallographic and Refinement Data for Compound 6·(C₆H₅Me)₀.₃

formula	C₂₃H₈N₂O₁₇Ru₆S·(C₇H₈)₀.₃
fw	1250.4
cryst syst	monoclinic
space group	$P2_1/n$
a, b, c, Å	9.626(3), 39.037(5), 11.072(2)
β, deg	108.30(2)
volume, Å³	3950(2)
Z	4
$F(000)$	2364
D_{calcd}, g/cm³	2.103
μ, mm⁻¹	2.173
radiation (λ, Å)	Mo Kα (0.710 69)
θ limits, deg	2.0−25.0
h, k, l ranges	−11 to +10, 0 to +46, 0 to +13
reflcns collected	7320
unique reflcns	6945
refined parameters	446
GOF on F^{2c}	1.078
R_1 (on F, $I > 2\sigma(I)$)	0.0465
wR_2 (on F^2, all data)	0.1772

chromatography (2 × 15 cm) in neutral alumina (activity IV). Pentane eluted three bands. The first band, yellow-orange, contained complex **5** (15 mg). The third band, yellow, contained a small amount of [Ru₃(μ-H)₂(μ_3-S)(CO)₉]. The second band, dark blue, afforded [Ru₆(μ-H)(μ_4-S)(μ_3-ampy)(CO)₁₇] (**6**) as a very dark blue, nearly black, solid (20 mg, 47% based on the amount of [PPN]₂[Ru₃(μ_3-S)(CO)₉]). Anal. Calcd for C₂₃-H₈N₂O₁₇Ru₆S: C, 22.59; H, 0.66; N, 2.29. Found: C, 22.89; H, 0.75; N, 2.29. IR (CH₂Cl₂), ν(CO): 2102 (m), 2068 (vs), 2045 (vs), 2029 (m), 2006 (w), 1988 (w), 1974 (w), 184 (w) cm⁻¹. ¹H NMR (CD₂Cl₂): 7.42 (t, J = 7.8 Hz, 1 H, ampy H⁴), 6.90 (d, J = 7.8 Hz, 1 H, ampy H⁵), 6.19 (d, J = 7.8 Hz, 1 H, ampy H³), 2.82 (s, 3 H, ampy Me), −1.25 (s, br, 1 H, ampy NH), −21.53 (s, 1 H, μ-H) ppm. ¹³C{¹H} NMR (CD₂Cl₂): 202.1 (2 C, CO), 201.0 (2 C, CO), 193.1 (3 C, CO), 192.3 (4 C, CO), 190.8 (2 C, CO), 188.9 (4 C, CO), 176.5 (ampy C), 159.7 (ampy C), 140.0 (ampy C), 119.6 (ampy C), 109.8 (ampy C), 29.2 (ampy C) ppm.

Crystal Structure of 6·(C₆H₅Me)₀.₃. Crystal data and details of measurement for compound **6**·(C₆H₅Me)₀.₃ are summarized in Table 2. The diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.710 69 Å). The intensities were reduced to F_o^2 and the structures were solved by direct methods, followed by difference Fourier syntheses and subsequent full-matrix least-squares refinements (using the programs SHELX86[21a] and SHELXL92[21b]). All non-H atoms were allowed to vibrate anisotropically. The organic H atoms were added in calculated positions and refined riding on their respective parent atoms. The hydride atom could be located from a difference Fourier map, and its position and isotropic thermal parameters were refined without constraints. SCHAKAL92 was used for the graphical presentation of the results.[22]

Supporting Information Available: Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H-atom coordinates for **6**·(C₆H₅Me)₀.₃ and an ORTEP diagram of **6** (10 pages). Ordering information is given on any current masthead page.

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