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Neutral Binuclear and Anionic Trinuclear Rhenium Carbonyl Complexes Containing Bridging Ligands Derived from 2-Amino- and 2-Mercaptopyridines

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The reactions of the nitrile-stabilized complex [$Re_3(\mu\text{-}H)_3(CO)_{11}(MeCN)$] (**1**) and of the unsaturated complex [$Re_4(\mu\text{-}H)_4(CO)_{12}$] (**2**) with 2-amino-6-methylpyridine (Hampy), 2-mercaptopyridine (Hmerpy), and 2-hydroxy-6-methylpyridine (Hhympy) have been studied. Complex **1** reacts slowly with Hampy and Hmerpy (refluxing toluene, 5−7 h) to give the binuclear derivatives [$Re_2(\mu\text{-ampy})_2(CO)_6$] (**3**) and [$Re_2(\mu\text{-merpy})_2(CO)_6$] (**4**), but no reaction is observed between **1** and Hhympy under analogous conditions. Complex **2** reacts with Hampy and Hmerpy (refluxing 1,2-dichloroethane, 10−20 min) to give the trinuclear anionic derivatives [$Re_3(\mu\text{-}H)_3(\mu_3\text{-ampy})(CO)_9$]$^-$ (**5**) and [$Re_3(\mu\text{-}H)_3(\mu_3\text{-merpy})(CO)_9$]$^-$ (**6**), which have been isolated as pyridinium ([H_2ampy]**5**) or triethylammonium ([$HNEt_3$]**5**, [$HNEt_3$]**6**) salts. Under analogous conditions, the reaction of **2** with Hhympy gives an inseparable mixture of compounds. The X-ray structures of [$HNEt_3$]**5** and [$HNEt_3$]**6** confirm that the three edges of the clusters are spanned by hydride ligands, that the ampy (in **5**) and merpy (in **6**) are attached to the three Re atoms, and that there are hydrogen-bonding interactions in the solid state between some carbonyl oxygen atoms and the NH fragments of the ampy ligand (in **5**) and the triethylammonium cation (in **5** and **6**).

Introduction

To date, the carbonyl cluster compounds (three or more metal atoms connected by metal−metal bonds) known for rhenium are still very few[1] in comparison with those known for ruthenium and osmium.[2] This is mainly due to the lack of a convenient rhenium starting material. In fact, the derivative chemistry of the most readily available rhenium carbonyl compound, [$Re_2(CO)_{10}$], leads only to cluster derivatives of interest as starting materials in its reactions with hydrogen,[3] hydrides,[4] and hydroxide anions,[5] but the products are generally isolated in medium to low yields. For example, [$Re_3(\mu\text{-}H)_3(CO)_{12}$], which is isoelectronic with the most important ruthenium and osmium starting clusters [$M_3(CO)_{12}$] (M = Ru, Os), can be prepared from the expensive [$Re_2(CO)_{10}$] by either hydrogenation[3a] or by treatment with Na[BH_4] followed by acidification,[4d,e] but both procedures are rather tedious and the yields are only moderate (50% at best). Moreover, [$Re_3(\mu\text{-}H)_3(CO)_{12}$] is kinetically very stable, and its reactions require high temperatures (which promote changes in cluster and/or ligand integrity, often leading to mixtures

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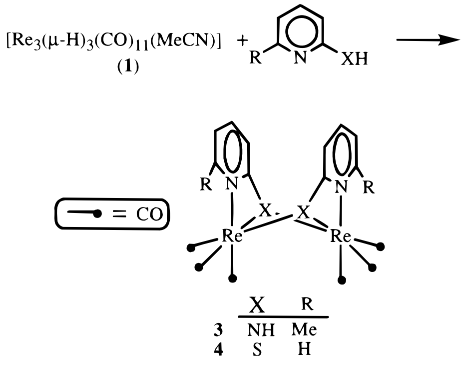
of products)[1] or derivatization to the more reactive $[Re_3(\mu\text{-}H)_3(CO)_{10}(MeCN)_2]$.[6] In addition, although the derivative chemistry of the anionic unsaturated cluster $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ has been extensively studied by Ciani, D'Alfonso, and co-workers,[1] its best preparation requires the hydrogention at high pressure (100 atm) of $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$,[7] which is made by deprotonation of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$.[8]

On the other hand, we (and other authors) have previously studied the reactivity of $[Ru_3(CO)_{12}]$ with ortho-functionalized pyridines such as 2-amino-,[9,10] 2-mercapto-,[10−12] and 2-hydroxypyridines.[9,10] In the case of 2-aminopyridines, the products are trinuclear derivatives that contain the corresponding monodeprotonated ligand in a face-bridging mode, such as $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_{12}]$ (Hampy = 2-amino-6-methylpyridine).[9] The presence of such bridging ligands has profound implications in the reactivity of the clusters, since they help maintain the cluster integrity and provide reaction pathways of low activation energy.[13] Over a hundred ruthenium carbonyl clusters containing μ_3-2-aminopyridinate ligands have already been prepared,[2a] including the first cationic nonhydridic 48-electron triruthenium clusters,[14] some hexanuclear clusters,[15] and some efficient catalyst precursors for alkyne hydrogenation,[16] dimerization,[17] and polymerization[17] reactions.

We now describe some approaches to the synthesis of rhenium carbonyl cluster compounds containing bridging ligands derived from 2-amino-, 2-mercapto-, and 2-hydroxypyridines, using $[Re_3(\mu\text{-}H)_3(CO)_{11}(MeCN)]$ (**1**) and $[Re_4(\mu\text{-}H)_4(CO)_{12}]$ (**2**) as starting materials. We undertook this study prompted by (a) the interesting results obtained with such ligands in ruthenium carbonyl cluster chemistry (mentioned above), (b) the publication of an expeditious preparation of the trinuclear cluster **1** directly from $[Re_2(CO)_8(MeCN)_2]$ and hydrogen (90% isolated yield on a half-gram scale),[18] and (c) the publication of the synthesis of some trinuclear carbonyl derivatives by reaction of the tetranuclear cluster **2** with pyridine[19] and acetonitrile.[20]

Scheme 1



Results and Discussion

Reactions of $[Re_3(\mu\text{-}H)_3(CO)_{11}(MeCN)]$ (1). No reaction was observed between complex **1** and 2-hydroxy-6-methylpyridine (Hhympy) in toluene at reflux temperature. However, under analogous conditions, 2-amino-6-methylpyridine (Hampy) and 2-mercaptopyridine (Hmerpy) reacted slowly with complex **1** (5−7 h) to give the binuclear derivatives $[Re_2(\mu\text{-}ampy)_2(CO)_6]$ (**3**) and $[Re_2(\mu\text{-}merpy)_2(CO)_6]$ (**4**) (Scheme 1). At least 3 equiv of the corresponding pyridine ligand was necessary to consume all the starting rhenium material. Complex **3** is a new compound, but Deeming et al. have previously reported the synthesis of complex **4** by reaction of $[Re_2(CO)_{10}]$ with Hmerpy in refluxing xylene, including an X-ray structural characterization.[21a] Adams et al. have reported the structure of the closely related quinoline-2-thiolate derivative $[Re_2(\mu\text{-}merqui)_2(CO)_6]$ (Hmerqui = 2-mercaptoquinoline).[21b]

The IR spectra of **3** and **4** are very similar in the carbonyl region, suggesting analogous structures. This was confirmed by the NMR spectra of **3**, which indicate C_2 symmetry for the compound, since only three carbonyl resonances of equal intensity are observed in the $^{13}C\{^1H\}$ spectrum and only one set of ampy resomances are observed in both the ^1H and $^{13}C\{^1H\}$ spectra. As far as we are aware, the behavior of 2-aminopyridinate ligands as five-electron donors bridging two metal atoms has no precedent in the chemical literature. However, for 2-mercaptopyridinate ligands, such behavior has been previously observed in binuclear rhenium,[21a] manganese,[22] and molybdenum[23] complexes and in heteronuclear rhenium−ruthenium compounds.[24]

The lower reactivity of Hhympy, as compared with that of Hampy and Hmerpy, may be explained in terms of the high contribution of the ketonic pyridin-2(1*H*)-one tautomer, both in solution[25] and in the solid state.[26] In this tautomer the pyridinic nitrogen bears a proton, and therefore the compound is much less basic than Hampy and Hmerpy.

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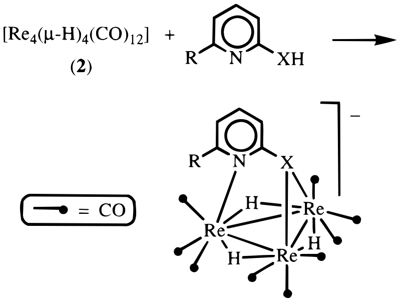
Scheme 2



	X	R
5	NH	Me
6	S	H

Reactions of $[Re_4(\mu\text{-}H)_4(CO)_{12}]$ (2). The deep-red unsaturated tetranuclear compound **2** reacted instantaneously with Hampy (1:2 mol ratio) in dichloromethane or 1,2-dichloroethane at room temperature to give a yellow solution. The ^1H NMR spectrum of a solution obtained by carrying out the reaction in CD_2Cl_2 showed a complex mixture of compounds. This mixture could not be separated by crystallization or by chromatographic means, but, interestingly and fortunately, heating this solution at reflux temperature for a few minutes allowed the isolation of an anionic complex as the corresponding pyridinium salt, namely, $[H_2ampy][Re_3(\mu\text{-}H)_3(\mu_3\text{-}ampy)(CO)_9]$ ($[H_2ampy]$**5**). The best yield of $[H_2ampy]$**5** (77% based on Re) was obtained using a 1:8/3 mol ratio of **2** to Hampy.

As the ^1H NMR spectrum of $[H_2ampy]$**5** is very complicated in the aromatic region and as, in its synthesis, part of the Hampy reagent is used as a base to abstract a hydride ligand as a proton, we thought that a combination of Hampy with a noncoordinating base, such as triethylamine, would lead to a compound having the same anion but with a different cation. Such a compound would have a much simpler ^1H NMR spectrum in the aromatic region, maintaining the resonances of the anion. Thus, when the reaction of **2** with Hampy was carried out in the presence of triethylamine, the triethylammonium salt $[HNEt_3]$**5** was indeed obtained in 70% yield.

Compound **2** also reacted with Hmerpy (in various mol ratios) at room temperature to give mixtures of products. Heating these mixtures in 1,2-dichloroethane at reflux temperature did not allow the preparation of pure $[H_2merpy]$**6**, but led to mixtures of the binuclear compound **4** and the trinuclear $[H_2merpy]$**6**, which could not be separated. However, when the reaction was carried out in the presence of triethylamine, the triethylammonium salt $[HNEt_3]$**6** was separated in pure form in 55% yield.

The structures shown in Scheme 2 for the anions **5** and **6** have been determined by X-ray diffraction methods (see below) and are also validated by the analytical and spectroscopic data of $[H_2ampy]$**5**, $[HNEt_3]$**5**, and $[HNEt_3]$**6**. Their solution IR spectra in the carbonyl region are very similar, showing absorptions that can be assigned only to terminal CO ligands. In addition, the presence of a mirror plane in the anions is indicated by their ^1H and $^{13}C\{^1H\}$ NMR spectra, which, apart from the resonances of the corresponding cation and the ampy or merpy ligands, show two hydride resonances in a 2:1 integral ratio and five carbonyl resonances in a 1:2:2:2:2 ratio.

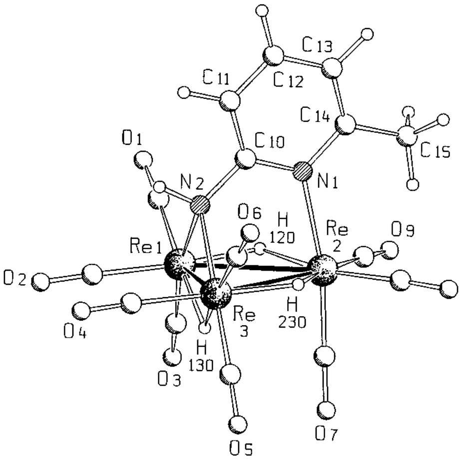


Figure 1. Structure of the anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}ampy)(CO)_9]^-$ (**5**) in $[HNEt_3]$**5**.

Compound **2** did react with Hhympy in 1,2-dichloroethane, in various mol ratios, at room and at reflux temperature, in the absence and in the presence of triethylamine, but in no case could we isolate and characterize a pure compound.

Ligands derived from pyridines or other nitrogen heterocycles containing functionalities liable of further coordination have not been previously used in carbonyl rhenium cluster chemistry, although a number of reactions of rhenium clusters with pyridines[19,27] and pyrazoles[28] have been published. In direct relation with the results described in this paper, it has been reported that the reactions of the tetranuclear complex **2** with nitrogen heterocycles L, such as pyridine, 4-picoline, and piperidine, lead to mixtures of ionic unsaturated $[HL][Re_3(\mu\text{-}H)_4(CO)_9(L)]$ and neutral saturated $[Re_3(\mu\text{-}H)_3(CO)_9(L)_3]$ complexes, whereas the reactions with 2-picoline, 4-cianopyridine, imidazole, and 2,4-dimethylimidazole give only the ionic compounds $[HL][Re_3(\mu\text{-}H)_4(CO)_9(L)]$.[19]

Although no amido derivatives of rhenium carbonyl clusters have been previously reported, it is known that the reactions of $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ with alcohols and thiols give saturated anionic trinuclear clusters containing face- or edge-bridging thiolate or alkoxide ligands, $[Re_3(\mu\text{-}H)_3(\mu_3\text{-}XR)(CO)_9]^-$ (X = S,[29] O[30]) or $[Re_3(\mu\text{-}H)_3(\mu\text{-}OR)(CO)_{10}]^-$.[31]

Crystal Structures of $[HNEt_3]$5 and $[HNEt_3]$6. The structures of the two anions (Figures 1 and 2) are

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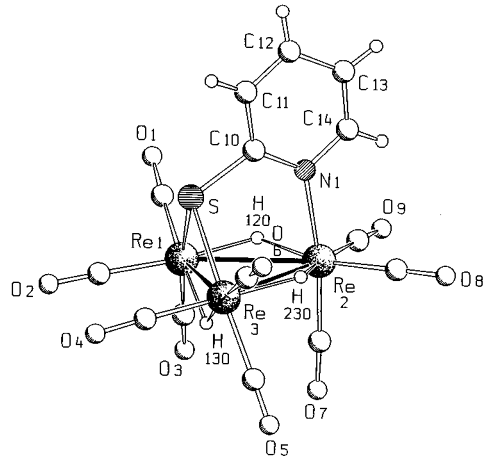

Figure 2. Structure of the anion $[Re_3(\mu\text{-}H)_3(\mu_3\text{-merpy})(CO)_9]^-$ (**6**) in $[HNEt_3]$**6**.

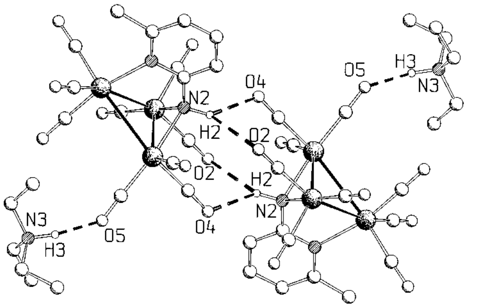

Figure 3. Hydrogen-bonding interactions in $[HNEt_3]$**5**.

Table 1. Relevant Bond Lengths (Å) in the Anions $[Re_3(\mu\text{-}H)_3(\mu_3\text{-ampy})(CO)_9]^-$ (5) and $[Re_3(\mu\text{-}H)_3(\mu_3\text{-merpy})(CO)_9]^-$ (6)

	5	6
Re(1)−Re(2)	3.136(1)	3.113(2)
Re(1)−Re(3)	2.927(1)	2.973(2)
Re(2)−Re(3)	3.154(2)	3.118(2)
Re(1)−C(2)	1.910(8)	1.89(2)
Re(1)−C(1)	1.915(8)	1.91(2)
Re(1)−C(3)	1.906(9)	1.86(2)
Re(3)−C(4)	1.907(9)	1.90(2)
Re(3)−C(5)	1.886(8)	1.96(3)
Re(3)−C(6)	1.928(9)	1.91(2)
Re(2)−C(7)	1.885(8)	1.88(2)
Re(2)−C(8)	1.910(9)	1.93(2)
Re(2)−C(9)	1.924(8)	1.95(2)
mean C−O	1.15(1)	1.16(2)
$Re-H_{hydride}$	1.83	1.83
Re(2)−N(1)	2.250(7)	2.18(1)
Re(1)−N(2)	2.197(6)	
Re(3)−N(2)	2.187(6)	
N(1)−C(10)	1.357(10)	1.35(2)
N(1)−C(14)	1.366(9)	1.33(32)
N(2)−C(10)	1.405(9)	
N(2)−H(2)	1.023(6)	
Re(1)−S		2.450(4)
Re(3)−S		2.453(4)
S−C(10)		1.77(2)
C(10)C(11)	1.38(1)	1.38(2)
C(11)C(12)	1.35(1)	1.36(2)
C(12)C(13)	1.37(1)	1.40(2)
C(13)C(14)	1.37(1)	1.35(2)
C(14)C(15)	1.51(1)	

Table 2. Relevant Hydrogen Bond Interactions in $[HNEt_3]$5 and $[HNEt_3]$6

N−H- - -O	N−H (Å)	H- - -O (Å)	N- - -O (Å)	N−H- - -O (deg)
		$[HNEt_3]$**5**		
N(2)−H(2)- - -O(2)	1.023	2.522	3.340	136.63
N(2)−H(2)- - -O(4)	1.023	2.421	3.243	136.86
N(3)−H(3)- - -O(5)	1.018	1.896	2.889	164.94
		$[HNEt_3]$**6**		
N(2)−H(2)- - -O(2)	1.027	2.227	3.071	138.29
N(2)−H(2)- - -O(6)	1.027	2.437	3.227	131.07

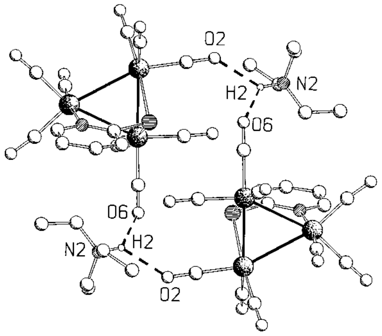

Figure 4. Hydrogen-bonding interactions in $[HNEt_3]$**6**.

closely related and will be described together. Relevant structural parameters for both compounds are given in Table 1. The metal frame consists of a Re triangle, with three hydride ligands bridging the three metal−metal bonds. Two hydride ligands are nearly in the metallic plane, while the plane formed by the remaining hydride ligand and the edge it spans is nearly perpendicular to the Re_3 plane. The pyridine fragment is attached to a Re atom, while the remaining two Re atoms are bridged by the amido (in **5**) or thiolate (in **6**) group. The Re−Re bond distances range from 2.927(1) to 3.154(2) in **5** and from 2.973(2) to 3.118(2) Å in **6**, the shorter distance being that spanned by the amido (in **5**) or thiolate (in **6**) group. The anions have an idealized C_s symmetry, with the pseudomirror plane bisecting the Re(1)−Re(3) bond and comprising the remaining Re atom. Nine carbonyl ligands are terminally bound, three to each Re atom. The ampy and merpy ligands contribute five electrons to the clusters, their coordination parameters being comparable to those previously found in triruthenium clusters.[9−11,14−17]

Crystalline $[HNEt_3]$**5** presents additional interesting structural features. A short N−H- - -O hydrogen-bonding interaction is observed between the hydrogen atom of the ammonium cation and one carbonyl ligand of the anion, resulting in the formation of an ionic pair. In addition, two of these pairs are interconnected via N−H- - -O bifurcated interactions between the N−H group of the ampy ligand and the oxygen atoms of two carbonyl ligands, as shown in Figure 3. The structural parameters of these interactions are listed in Table 2.

The crystal structure of $[HNEt_3]$**6** also shows important N−H- - -O interactions. The basic pattern recognizable in this solid is also a dimer of ionic pairs, in which the H atom of the ammonium cation interacts in a bifurcated way with two carbonyl ligands belonging to two different anionic clusters. This dimeric unit is shown in Figure 4. The relevant structural data of these interactions are listed in Table 2.

The involvement of carbonyl ligands in hydrogen bonding is currently receiving considerable attention in the field of solid-state intermolecular interactions.[32]

Final Remarks

Probably, the most interesting feature of this article is that it reports convenient syntheses of anionic facebridged trinuclear rhenium carbonyl clusters. It is anticipaped that reactivity studies on these compounds will lead to interesting derivatives, which will broaden the so far scarce derivative chemistry known for rhenium carbonyl clusters. Such studies are in progress in our laboratories.

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (diethyl ether, hydrocarbons), sodium sulfate (acetone), or calcium hydride (1,2-dichloroethane, dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot TLC (silica gel). Compounds **1**[18] and **2**[3d] were prepared from literature procedures. The pyridines were purchased from Aldrich. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1 mm CaF_2 cells. ^1H and ^{13}C NMR spectra were run at room temperature with Bruker AC-200 and AC-300 instruments, being referenced to internal $SiMe_4$ (for ^1H, $\delta = 0$ ppm) or acetone-d_6 (for ^{13}C, $\delta = 205.1$ ppm). Microanalyses were obtained from the University of Oviedo Analytical Service.

[$Re_2(\mu$-ampy$)_2(CO)_6$] (3). A solution of **1** (50 mg, 0.055 mmol) and Hampy (24 mg, 0.222 mmol) in toluene (10 mL) was stirred at reflux temperature. After complete conversion of the starting material (5 h, IR monitoring), the reaction mixture was cooled to room temperature, leading to precipitation of a white solid. After decantation of the liquid phase, the solid was recrystallized from dichloromethane−hexane to give compound **3** as colorless crystals (35 mg, 56% based on Re). Anal. Found: C, 28.26; H, 1.52; N, 7.62. Calcd for $C_{18}H_{14}N_4O_6Re_2$: C, 28.65; H, 1.87; N, 7.43. IR (CH_2Cl_2): 2026 (s), 2009 (s), 1916 (sh), 1897 (s), cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.46 (t, $J = 7.7$ Hz, 1 H), 6.53 (d, 7.7 Hz, 1 H), 6.41 (d, 7.7 Hz, 1 H), 3.09 (s, br, 1 H, N*H*), 2.07 (s, 3 H, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ(CO) 198.8, 197.1, 194.1; δ(ampy) 173.8, 155.1, 139.3, 117.2, 114.0, 29.6 ppm.

[$Re_2(\mu$-merpy$)_2(CO)_6$] (4). A solution of **1** (50 mg, 0.055 mmol) and Hampy (25 mg, 0.225 mmol) in toluene (10 mL) was stirred at reflux temperature with constant IR monitoring. After complete conversion of the starting material (7 h), the solvent was removed under reduced pressure and the residue was recrystallized from dichloromethane−hexane to give compound **4** as colorless crystals (53 mg, 85% based on Re). Its analytical (CHN%) and spectroscopic data (IR, ^1H NMR) matched those reported in the literature.[21]

[H_2ampy][$Re_3(\mu$-$H)_3(\mu_3$-ampy$)(CO)_9$] ([H_2ampy]5). A solution of Hampy (18 mg, 0.160 mmol) in 1,2-dichloroethane (5 mL) was added to a solution of compound **2** (65 mg, 0.060 mmol) in the same solvent (5 mL). After 5 min, the color changed from deep-red to yellow. The reaction mixture was then heated at reflux temperature for 10 min. On cooling to room temperature, a small amount of a white solid precipitated. The solid was filtered off and was subsequently found to be insoluble in dichloromethane and acetone. The filtered solution was evaporated to dryness to give a pale yellow oil, which, upon recrystallization from acetone−hexane, afforded [H_2ampy]**5** as an off-white solid (47 mg, 77% based on Re). Anal. Found: C, 24.31; H, 2.05; N, 5.58. Calcd for $C_{21}H_{19}N_4O_9Re_3$: C, 24.49; H, 1.86; N, 5.44. IR (CH_2Cl_2): 2029 (s), 2001 (vs), 1911 (vs, br), cm^{-1}. ^1H NMR (acetone-d_6): δ 7.78−6.66 (complex mixture of signals), 5.68 (s, br, 1 H, N*H*), 2.70 (s, 3 H, Me), 2.49 (s, 3 H, Me), −10.04 (s, 1 H, μ-H), −10.29 (s, 2 H, μ-H) ppm.

Table 3. Crystallographic and Refinement Data for [$HNEt_3$]5 and [$HNEt_3$]6

	[$HNEt_3$]**5**	[$HNEt_3$]**6**
formula	$C_{21}H_{26}N_3O_9Re_3$	$C_{20}H_{23}N_2O_9Re_3S$
fw	1023.05	1026.06
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.479(3)	9.173(6)
b, Å	11.103(3)	11.477(7)
c, Å	13.891(7)	12.922(6)
α, deg	83.51(4)	90.41(4)
β, deg	70.92(4)	91.89(4)
γ, deg	84.78(3)	105.96(5)
volume, Å^3	1370.5(9)	1307.1(13)
Z	2	2
F(000)	940	940
D_{calcd}, g/cm^3	2.479	2.607
μ, mm^{-1}	13.266	13.987
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
monochromator	graphite	graphite
cryst size, mm	0.20 × 0.16 × 0.15	0.18 × 0.16 × 0.16
temp, K	293(2)	293(2)
θ limits, deg	3.0−27.0	3.0−25.0
min/max h, k, l	−11/12, −13/14, 0/17	−10/10, −13/13, 0/15
no. of reflns collected	5768	4305
no. of unique reflns	5758	2244
no. of reflns with $I > 2\sigma(I)$	4851	2122
no. of parameters	325	317
GOF (on F^2)	0.994	1.007
R1 (on F, $I > 2\sigma(I)$)	0.0371	0.0544
wR2 (on F^2, all data)	0.1025	0.1403

[$HNEt_3$][$Re_3(\mu$-$H)_3(\mu_3$-ampy$)(CO)_9$] ([$HNEt_3$]5). A solution of Hampy (8 mg, 0.074 mmol) and triethylamine (10 μL, 0.074 mmol) in 1,2-dichloroethane (5 mL) was added to a solution of compound **2** (60 mg, 0.055 mmol) in the same solvent (5 mL). The resulting solution was worked up as described above for [H_2ampy]**5**, to give [$HNEt_3$]**5** as a white solid (40 mg, 70%). Anal. Found: C, 25.07; H, 2.61; N, 3.88. Calcd for $C_{21}H_{26}N_3O_9Re_3$: C, 24.66; H, 2.54; N, 4.10. IR (CH_2Cl_2): 2029 (s), 2001 (vs), 1911 (vs, br), cm^{-1}. ^1H NMR (acetone-d_6): δ 7.34 (t, $J = 7.2$ Hz, 1 H), 6.87 (d, $J = 7.2$ Hz, 1 H), 6.62 (d, $J = 7.2$ Hz, 1 H), 5.57 (s, br, 1 H, N*H*), 3.50 (q, $J = 7.2$ Hz, 6 H, C*H*$_2$ of Et), 2.69 (s, 3 H, Me), 1.42 (t, $J = 7.2$ Hz, 9 H, C*H*$_3$ of Et), −10.08 (s, 1 H, μ-H), −10.31 (s, 2 H, μ-H) ppm. $^{13}C\{^1H\}$ NMR (acetone-d_6): δ(CO) 195.9 (2 C), 193.5 (1 C), 193.1 (2 C), 188.8 (2 C), 186.1 (2 C); δ(ampy) 181.9, 158.4, 136.9, 116.5, 113.0, 30.1; δ([$HNEt_3$]$^+$) 46.6, 8.3 ppm.

Reaction of Compound 2 with Hmerpy. A solution of Hmerpy (18 mg, 0.162 mmol) in 1,2-dichloroethane (5 mL) was added to a solution of compound **2** (60 mg, 0.055 mmol) in the same solvent (5 mL). After 5 min, the color changed from deep-red to yellow. The reaction mixture was then heated at reflux temperature for 10 min. The solution was evaporated to dryness to give an off-white solid. The ^1H NMR spectrum of this material indicated a ca. 3:1 mixture of the binuclear compound **4** and the trinuclear [H_2merpy]**6** (by comparison with the spectra of pure **4** and [$HNEt_3$]**6**), but the mixture could not be separated.

[$HNEt_3$][$Re_3(\mu$-$H)_3(\mu_3$-merpy$)(CO)_9$] ([$HNEt_3$]6). A solution of Hmerpy (9 mg, 0.081 mmol) and triethylamine (11 μL, 0.08 mmol) in 1,2-dichloroethane (5 mL) was added to a solution of compound **2** (60 mg, 0.055 mmol) in the same solvent (5 mL). The color changed from deep-red to yellow. The solution was heated at reflux temperature for 20 min, and then it was evaporated to dryness. The pale-yellow residue was washed with a small amount of dichloromethane (2 × 1 mL), leaving a white solid. The solid was recrystallized from acetone−hexane to give [$HNEt_3$]**6** as a white solid (31 mg, 55%). Anal. Found: C, 22.93; H, 2.08; N, 2.48. Calcd for $C_{20}H_{23}N_2O_9Re_3S$: C, 23.41; H, 2.26; N, 2.73. IR (CH_2Cl_2): 2035 (s), 2004 (vs), 1917 (vs, br), 1904 (sh) cm^{-1}. ^1H NMR (acetone-d_6): δ 8.83 (d, $J = 7.5$ Hz, 1 H), 7.76 (d, $J = 7.5$ Hz, 1 H), 7.63

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(t, $J = 7.5$ Hz, 1 H), 7.10 (t, $J = 7.7$ Hz, 1 H), 3.48 (q, $J = 7.2$ Hz, 6 H, CH_2 of Et), 1.41 (t, $J = 7.2$ Hz, 9 H, CH_3 of Et), −10.87 (s, 2 H, μ-H), −11.58 (s, 1 H, μ-H) ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ(CO) 194.7 (2 C), 193.5 (1 C), 191.7 (2 C), 187.5 (2 C), 186.9 (2 C); δ(merpy) 175.6, 165.3, 136.0, 129.9, 122.2; δ-($[HNEt_3]^+$) 47.2, 8.3 ppm.

Crystal Structures of Compounds $[HNEt_3]$5 and $[HNEt_3]$6. The X-ray diffraction data collections were carried out on a Nonius CAD-4 diffractometer. Crystal data and details of measurements for compounds $[HNEt_3]$**5** and $[HNEt_3]$**6** are summarized in Table 3.

The structures were solved by direct methods[33a] followed by difference Fourier syntheses and full-matrix least-squares refinement on F^2 using SHELXL92.[33b] All non-H atoms were treated anisotropically. Absorption correction was applied in both cases by azimuthal scanning of high χ reflections (min.−max. absorption correction 0.56−1.00 and 0.49−1.00 for $[HNEt_3]$**5** and $[HNEt_3]$**6**, respectively). H atoms bound to C atoms in the ampy and merpy ligands and in the $[HNEt_3]^+$ cations were added in calculated positions and were refined riding on their respective C atoms. The H atoms bound to N atoms were directly located from the Fourier maps and were not refined. The positions of the hydride H atoms were calculated using the program XHYDEX,[33c] and their coordinates were included in the Fourier calculations but were not refined. The approximate location of the hydride H atoms was also detectable by visual inspection of space-filling diagrams of the two anions, since suitable niches were invariably found corresponding to the calculated positions. The program SCHAKAL97[33d] was used for all graphical representations.

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Supporting Information Available: ORTEP pictures and tables of bond distances and angles, fractional atomic coordinates, and anisotropic thermal parameters for compounds $[HNEt_3]$**5** and $[HNEt_3]$**6** (18 pages). Ordering information is given on any current masthead page.

OM980554Z

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