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Summary: The cationic cluster complex [Ru3(μ3-ampy)(CO)10][BF4] (1) (Hampy = 2-amino-6-methylpyridine, Scheme 1). This compound is interesting because it is the first cationic non-hydridic 48-electron triruthenium carbonyl cluster ever reported. 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 ruthenium cluster compounds is concerned, only that of some hydride derivatives has been studied in detail. 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.

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). This compound is interesting because it is the first cationic non-hydridic 48-electron triruthenium carbonyl cluster ever reported. These attributes, coupled to its efficient preparation and high thermal and air stability, make complex 1 an excellent candidate for reactivity studies.

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). Unfortunately, all attempts to separate this product from the mixture of reaction products were unsuccessful.

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], 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 [Ru6(μ3-S)(CO)9]2− renders the hexanuclear 92-electron derivative [Ru6(μ-H)(μ4-S)(μ3-ampy)(CO)17].
accompanying [PPN][BF₄] 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. The C₅ 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 ¹³C 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 but anionic complexes.⁶

The iodide and acetoacetato derivatives [Ru₃(μ-X)₃(μ-ampy)-(CO)₉] (X = 1 (3), MeCO₂ (4)) were also observed in solution when complex 1 was treated with [Bu₄N][X] (X = I, MeCO₂).⁷ However, as occurred with 2, they could not be separated from the byproduct [Bu₄N][BF₄] by either chromatographic methods or fractional crystallization. In an attempt to obtain an isolable derivative of complex 2, a CDCl₃ solution of this complex was treated with 1 equiv of triphenylphosphine. The ¹H and ³¹P (¹H) NMR spectra of the resulting solution indicated the quantitative formation of a substituted product, presumably [Ru₃(μ-Cl)₃(μ-ampy)(CO)₉(PPPh₃)].⁸ Again, it could not be obtained as a solid in pure form.

The compound [PPN][BH₄] 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][BH₄] with a dichloromethane solution of compound 1 gave the known ⁴⁸-electrode hydrido derivative [Ru₃(μ-H)₃(μ-ampy)(CO)₉] (5) in quantitative yield (Scheme 1).

The anions of the complexes Li[C₆Me₃][NEt₂][CN, [PPN]₂S, and Li[C≡CPh] were found to react with 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 [PPN₂][Ru₂(μ-S)(CO)₉] in 2:1 mole ratio to give a mixture of 5, [Ru₂(μ-H)₃(μ-S)(CO)₉] and the new hexanuclear derivative [Ru₆(μ-H)₃(μ-S)(ampy)(CO)₁₂] (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-(C₆H₅Me)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 Ru₄ 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.
The Ru4 and the remaining Ru3 unit is spanned by a perpendicularly to the Ru4 square plane, showing the large niche by the Ru4 and Ru3 units. The edge shared by the metal frame. The four metal atoms forming the edge shared by the amido fragment spanning the edge to the metal frame. The four metal atoms forming the edge.

The remaining 15 CO ligands are all terminally bound with the amido fragment spanning the edge to the metal frame. The four metal atoms forming the edge.

| 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)| Ru(5)–N(2)  | 2.10(2)  |
| mean        | 2.10(1)  | mean        | 1.89(2)  |

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 amido ligand is bound to one of the two Ru3 triangles in its usual μ3 fashion, with the amido fragment spanning the edge shared by the Ru4 and Ru3 units. The edge shared by the Ru4 and the remaining Ru3 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 μ4-S ligands are known, namely, [Ru6(μ4-S)(μ-OH)2(CO)18], [Ru6(μ-SH)(μ4-S)(μ3-Spy)CO17] (HSpy = pyridine-2-thiol), and [Ru6(μ4-S)-[(μ3-RNCNHR)(μ3-RNC5NH)]3] (R = Ph, Et). The structures of the pyridine-2-thiolato and the thiourea 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). 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 [Ru6(μ4-S)(μ-OH)2(CO)18], [Ru6(μ-SH)(μ4-S)(μ3-Spy)CO17] and [Ru6(μ4-S)(μ3-RNCNHR)(μ3-RNC5NH)]3, 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 [Ru3(μ3-S)(CO)3]2– has been used previously as a nucleophile toward mononuclear cationic organometallic compounds. It reacts with [M(CO)3(MeCN)3]+ and [M(CO)4]+ (M = Mn, Re) to give [Ru6(μ3-S)-(CO)3M(CO)3(MeCN)3] and [Ru6(μ3-S)(μ3-S)(CO)3M(CO)3] respectively, in which the sulfur atoms are coordinated to pendant [M(CO)3(MeCN)3] or [M(CO)3] fragments. It should be noted that these products are hydrido derivatives and that the proton source is also uncertain. However, the reactions of [Ru3(μ3-S)(CO)3]2– with different amounts of [Au(PPh3)3] have been found to give [Ru3(μ3-S)(CO)3(μ3-S)(PPh3)3] and [Ru3(μ3-S)(CO)3(μ3-S)(PPh3)2]– (CO)18], in which the gold atoms are attached to ruthenium atoms but not to the sulfur atom.

In our hands, complex 1 also reacted with mononuclear organometallic anions, such as [Co(CO)4]3– and [WCP(CO)3]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 [Ru3(μ3-S)(CO)3]2–, is essential in order to maintain the integrity of the final products.

References:
chroomatography (2 × 15 cm) in neutral alumina (activity IV). Pentane eluted three bands. The first band, yellow-orange, contained complex 5 (15 mg). The second band, dark blue, afforded \( \text{[Ru}_6(\mu_3-S)(\text{CO})_{17}] \) as a very dark blue, nearly black, solid (20 mg, 47% based on the amount of \( \text{[PPN]}_2[\text{Ru}_3(\mu_3-S)(\text{CO})_9] \)). Anal. Calcd for \( \text{C}_{23}\text{H}_{8}\text{N}_2\text{O}_{17}\text{Ru}_6\text{S} \): C, 22.59; H, 0.66; N, 2.29. Found: C, 22.89; H, 0.75; N, 2.29. 1R (CH\(_2\)Cl\(_2\)), ν(CO): 2102 (m), 2068 (vs), 2045 (vs), 2029 (m), 1988 (w), 1974 (w), 184 (w) cm\(^{-1}\). H NMR (CD\(_2\)Cl\(_2\)): 7.42 (t, \( \delta \) = 7.8 Hz, 1 H, ampy H\(_3\)), 6.90 (d, \( \delta \) = 7.8 Hz, 1 H, ampy H\(^3\)), 6.19 (d, \( \delta \) = 7.8 Hz, 1 H, ampy H\(^3\)), 2.82 (s, 3 H, ampy Me), 1.25 (s, br, 1 H, ampy NH) -2153 (s, 1 H, \( \mu \)-H) ppm. \( ^{13}\text{C} \)NMR (CD\(_2\)Cl\(_2\)): 202.1 (2 C, CO), 201.0 (1 C, CO), 193.1 (3 C, CO), 190.8 (4 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**. Crystal data and details of measurement for compound 6(C\(_6\)H\(_5\)Me\(_{0.3}\)) 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 K\(_\alpha\) radiation, \( \lambda = 0.7107 \) 69 Å). The intensities were reduced to \( F^2 \), and the structures were solved by direct methods, followed by difference Fourier syntheses and subsequent full-matrix least-squares refinements (using the programs SHELXS86 and SHELXL92(21)). 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 hydroxide 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

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**Supporting Information Available:** Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H-atom coordinates for 6(C\(_6\)H\(_5\)Me\(_{0.3}\)) and an ORTEP diagram of 6(10 pages). Ordering information is given on any current masthead page.

**OM960552J**

(22) Keller, E. SCHAKAL92 Graphical Representation of Molecular Models; University of Freiburg: Freiburg, Germany, 1992.