Notes

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Synthesis and Crystal and Molecular Structure of the Neutral Cluster Compound $[Rh_9(CO)_{19}(NCMe)\{Cu(NCMe)_2\}]$

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In the course of a study of the rhodium carbonyl clusters of medium nuclearity (8–12 metal atoms), we reported the synthesis and structure of the anion $[Rh_9(CO)_{19}]^{3-}$ (**1**),[2] containing a metal cluster formed by two face-to-face condensed octahedra, and we are presently investigating its reactivity. We first began to study the behavior of **1** toward electrophiles, like H^+ and complex cations such as $[Rh(CO)_2(NCMe)_2]^+$. In the latter case, for a reagent ratio of 1:1, insertion of a $[Rh(CO)_2]^+$ unit is observed to give the compact decanuclear anion $[Rh_{10}(CO)_{21}]^{2-}$.[3] The reaction with acids affords unstable hydridic species that are presently under investigation. Since it is known that frequently metal fragments of group IB behave like hydride ligands from the electronic point of view, we decided to study the reactivity of compound **1** with these metal complexes, which could help the understanding of the unstable hydridic systems.

In this paper we report on the reactions of **1** with $[Cu(NCMe)_4](BF_4)$, which led us to the isolation of the novel neutral cluster species $[Rh_9(CO)_{19}(NCMe)\{Cu(NCMe)_2\}]$, containing an unusual edge-bridging $Cu(NCMe)_2$ group.

Results and Discussion

$[Rh_9(CO)_{19}(NCMe)\{Cu(NCMe)_2\}]$ (**2**) has been synthesized by reaction in acetone of $[Rh_9(CO)_{19}]^{3-}$ with $[Cu(NCMe)_4](BF_4)$ in slight excess over the molar ratio of 1:3. During the reaction copper metal separates out; thus, the net result looks formally as an oxidation of the trianion to the isoelectronic $[Rh_9(CO)_{19}(NCMe)]^-$ monoanion, followed by reaction of this species with Cu(I) to give the mixed cluster. However, things are not so simple, because performing the reaction with a stepwise addition of the Cu(I) complex, it has been possible to ascertain, by IR spectroscopy, the existence of at least two unstable intermediate products; this could be consistent with the existence of a complex path involving both the Rh_9 tri-, di- and mono- anions, and their derivatives with Cu(I).

Table I. Bond Distances (Å) and Main Angles (deg) within $[Rh_9(CO)_{19}(NCMe)\{Cu(NCMe)_2\}]$

Bond Distances			
Rh1–Rh2	2.771 (1)	Rh4–Rh8	2.719 (1)
Rh1–Rh3	2.780 (1)	Rh4–Rh9	2.723 (1)
Rh1–Rh5	2.720 (1)	Rh5–Rh6	2.735 (1)
Rh1–Rh6	2.689 (1)	Rh5–Rh7	2.740 (1)
Rh2–Rh3	2.938 (1)	Rh5–Rh9	2.773 (1)
Rh2–Rh4	2.712 (1)	Rh6–Rh7	2.719 (1)
Rh2–Rh5	2.706 (1)	Rh6–Rh8	2.747 (1)
Rh3–Rh4	2.721 (1)	Rh7–Rh8	2.815 (1)
Rh3–Rh6	2.694 (1)	Rh7–Rh9	2.805 (1)
Rh4–Rh5	2.756 (1)	Rh8–Rh9	2.764 (1)
Rh4–Rh6	2.742 (1)		
Rh2–Cu	2.692 (1)	Rh3–Cu	2.709 (1)
Rh2–C1	1.898 (7)	Rh2–C13	2.239 (8)
Rh3–C2	1.910 (8)	Rh4–C13	1.965 (8)
Rh7–C3	1.895 (8)	Rh2–C14	2.085 (7)
Rh7–C4	1.903 (8)	Rh5–C14	2.064 (7)
Rh8–C5	1.902 (8)	Rh3–C15	2.178 (8)
Rh8–C6	1.892 (8)	Rh4–C15	1.995 (7)
Rh9–C7	1.896 (8)	Rh3–C16	2.092 (7)
Rh9–C8	1.893 (8)	Rh6–C16	2.022 (7)
Rh1–C9	2.059 (7)	Rh4–C17	2.155 (7)
Rh2–C9	2.031 (7)	Rh8–C17	2.208 (7)
Rh1–C10	2.039 (7)	Rh9–C17	2.184 (7)
Rh3–C10	2.035 (7)	Rh6–C18	2.018 (7)
Rh1–C11	2.339 (8)	Rh7–C18	2.253 (7)
Rh5–C11	1.939 (7)	Rh8–C18	2.308 (7)
Rh1–C12	2.230 (7)	Rh5–C19	2.042 (7)
Rh6–C12	1.967 (7)	Rh7–C19	2.284 (7)
		Rh9–C19	2.270 (7)
C–O	1.108 (9)–1.160 (8)		
Rh1N1	2.126 (6)	Cu–N2	1.956 (8)
Cu–N3	1.950 (8)	Cu···C1	2.577 (8)
Cu···C2	2.697 (8)		
N1–C20	1.126 (8)	C20–C21	1.490 (10)
N2–C22	1.161 (11)	C22–C23	1.447 (15)
N3–C24	1.151 (11)	C24–C25	1.444 (13)
Bond Angles			
Rh1–N1–C20	173.7 (6)	N1–C20–C21	178.1 (9)
Cu–N2–C22	160.8 (7)	N2–C22–C23	175.7 (10)
Cu–N3–C24	178.6 (8)	N3–C24–C25	179.4 (11)
Rh2–Cu–Rh3	65.93 (3)	Rh3–Cu–N2	108.8 (2)
Rh2–Cu–N2	109.3 (2)	Rh3–Cu–N3	117.9 (2)
Rh2–Cu–N3	118.4 (2)	N2–Cu–N3	123.0 (3)

Compound **2** has been crystallized from tetrahydrofuran (thf) and *n*-hexane by the slow diffusion technique. During the long time required for the crystal growth, some decomposition was observed. The product obtained in this way was constituted of a mixture of black crystals, mostly in thin needles, among which a few larger prismatic specimens suitable for X-ray analysis were found. The IR spectrum of these crystals is very similar to that of the bulk product. Since analytical data indicate that the bulk product, in contrast to the crystals used for the X-ray analysis, does not contain solvated thf, but possibly some acetonitrile, this could explain the different crystal forms. However, due to the presence of an acetonitrile molecule coordinated to a rhodium atom (see later), we suspect that the other crystal species could also be produced from substitution of this solvent molecule by CO coming from the partial decomposition. This substitution should not cause relevant differences in the IR spectrum.

The crystals are stable in air for a few days, while solutions are oxidized. Solutions of **2** in thf or acetone under nitrogen undergo a very slow decomposition with formation of traces of $Rh_6(CO)_{16}$ and of other uncharacterized products. In acetonitrile, compound **2** is unstable, giving within a few hours an IR spectrum similar to that of one of the intermediate species observed during its synthesis.

The IR spectrum in thf solution shows bands at 2030 vs, 2018 sh, 1878 m, and 1845 w, br cm^{-1}.

The structure of the novel compound is shown in Figure 1, and bond distances and important angles are given inTable I. It exhibits an overall idealized (noncrystallographic) C_s symmetry, the mirror plane passing through the Rh1, Rh4, Rh7, and Cu atoms. The Rh_9 metal cluster (of D_{3h} idealized symmetry) is the same present in the parent anion **1**, consisting of two condensed face-sharing octahedral units, a nine-metal array observed also in the mixed-metal cluster anion $[PtRh_8(CO)_{19}]^{2-}$[4] and in the

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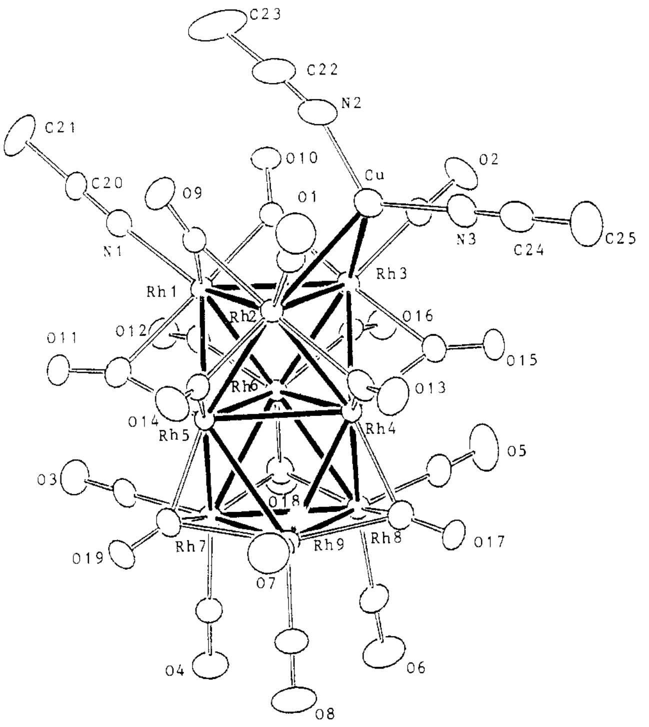

Figure 1. View of the cluster compound $[Rh_9(CO)_{19}(NCMe)\{Cu(NCMe)_2\}]$. The carbonyl ligands are indicated by the numbers of their oxygen atoms.

nickel cationic cluster $[Ni_9S_9(PEt_3)_6]^{2+}$.[5] Different nine-metal cores of stacked metal triangles were observed in the $[M_9(CO)_{18}]^{2-}$ anions (M = Ni,[6] Pt[7]).

The copper atom, bearing two acetonitrile molecules, is bound on an edge of an outer Rh_3 triangle.

The carbonyl ligands are bonded as follows: eight terminally, eight doubly bridging, and three triply bridging. One metal atom, Rh1, bears a linearly bonded acetonitrile molecule [Rh–N–C = 173.7 (6)°]. The CO arrangement is quite changed with respect to **1**, and in the octahedral moiety not interacting with copper, it resembles the ligand disposition of $[Rh_6(CO)_{16}]$.[8]

All but one of the 21 Rh–Rh bond lengths fall in a normal range, 2.689 (1)–2.815 (1) Å (mean 2.742 Å; comparable with the mean value of 2.759 Å in the parent trianion), with no clear distinction between bridged and unbridged edges. The Rh2–Rh3 edge, spanned by the μ-$Cu(NCMe)_2$ group, is particularly long, 2.938 (1) Å, the lengthening being similar to that observed in many $M(\mu$-$X)M$ systems (X = H, CuL, AuL, and similar ML).

The Rh–Cu bonds, mean 2.701 Å, are slightly longer than in $[Rh_6C(CO)_{15}\{\mu_3$-$Cu(NCMe)\}_2]$ (mean 2.660 Å),[9] but markedly longer than in $[Rh_2(\eta^5$-$C_5H_5)_2(\mu$-$CO)(\mu$-dppm$)(\mu$-$CuI)]$ [2.588 (2) Å].[10] The copper atom may be considered as sp^2 hybridized [N–Cu–N = 123.0 (3)°], with one lobe pointing toward the midpoint of the Rh2–Rh3 edge and involved in a three-center–two-electron bond. This bonding situation is similar to that of the μ-$HgCl_2$ group in $[Rh_2(\eta^5$-$C_5H_5)_2(\mu$-$CO)(\mu$-dppm$)(\mu$-$HgCl_2)]$.[11] The two Cu–N bonds, mean 1.953 Å, are, as expected, longer (ca. 0.05 Å) than those in Cu(NCMe)-bonded groups containing a single nitrile ligand.[9,12-14] One NCMe molecule is linearly bonded, Cu–N–C = 178.6 (8)°, while the other one shows a bent interaction, Cu–N–C = 160.8 (7)°.

Table II. Summary of Crystal Data for $[Rh_9(CO)_{19}(NCMe)\{Cu(NCMe)_2\}]\cdot C_4H_8O$

formula	$C_{29}H_{17}CuN_3O_{20}Rh_9$
fw	1717.1
space group	$P2_1/C$ (No. 14)
a	12.848 (2) Å
b	25.057 (5) Å
c	13.643 (3) Å
β	98.70 (2)°
V	4341.6 Å^3
D_c	2.627 g cm^{-3}
Z	4
radiation	Mo Kα, λ = 0.71073 Å
μ(Mo Kα)	38.36 cm^{-1}
no. of reflecns with $I > 3\sigma(I)$	4587
R	0.026
R_w	0.034

The copper atom exhibits two long-range interactions with the carbon atoms of adjacent terminal carbonyl ligands [Cu···C(CO) = 2.577 (8) and 2.697 (8) Å], reflected also in a moderate bending of the two corresponding Rh–C–O angles [170.2 (7) and 172.6 (7)° vs a mean value for the other terminal CO of 177.9°]. Analogous and even shorter contacts have been observed in other cluster species.[12-17]

The mean values of the Rh–C and C–O bonds for the terminal CO groups, 1.900 and 1.124 Å, compared with the corresponding mean values in **1** (1.86 and 1.15 Å), show the expected variations related to the different net charge in the two species. Four μ-CO groups are asymmetric, on edges Rh1–Rh5, Rh1–Rh6, Rh2–Rh4, and Rh3–Rh4, with shorter bonds to the metals of the central triangle. Also two of the μ_3-CO ligands are markedly asymmetric, on faces Rh5–Rh7–Rh9 and Rh6–Rh7–Rh8, with one shorter and two longer Rh–C bonds.

Finally, the possibility of placing two further ligands [μ-$Cu(NCMe)_2$ and NCMe] on the cluster surface of **1** suggests that the parent anion has a relatively low crowding, and this can account for the observed fluxional behavior of the CO groups in the parent $[Rh_9(CO)_{19}]^{3-}$[18] and in the isostructural $[PtRh_8(CO)_{19}]^{2-}$.[4]

Experimental Section

All of the operations were carried out under nitrogen atmosphere. The starting $Cs_3[Rh_9(CO)_{19}]$ was prepared as already described,[2] while $[Cu(NCMe)_4](BF_4)$ was prepared as the corresponding hexafluorophosphate[19] by using HBF_4 in place of HPF_6.

Synthesis of $[Rh_9(CO)_{19}(NCMe)\{Cu(NCMe)_2\}]$. A stirred solution of $Cs_3[Rh_9(CO)_{19}]$ (0.209 g, 0.113 mmol) in acetone (16 mL) was treated dropwise with a 0.1 M solution of $[Cu(NCMe)_4](BF_4)$ in acetone (3.9 mL). During the reaction, copper metal separated out as a fine powder. At the end of the addition the mixture was left to stir for 1 h; then, the solvent was evaporated off in vacuum at room temperature. The residue was treated with thf (12 mL) and the insoluble material filtered off. The clear extract was collected into a 100-mL Schlenk tube. A layer of *n*-hexane (40 mL) was cautiously placed over the solution, and the system was left to stand until the diffusion of the solvents was complete (about 1 week). During this period, some decomposition occurred to give a thin dark veil on the tube walls. The black crystalline product was filtered

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off, washed with *n*-hexane, and vacuum dried. Yield: 60–70%. Anal. Calcd for the unsolvated cluster $C_{25}H_9CuN_3O_{19}Rh_9$: C, 18.25; H, 0.55; N, 2.55. Found: C, 18.13; H, 0.64; N, 2.85. These analytical data indicate that, with the exception of the few larger crystals used for the X-ray analysis, the bulk of the product does not contain solvated thf, but possibly does contain some acetonitrile.

X-ray Analysis

The crystal data are summarized in Table II. A crystal sample of 0.10 × 0.21 × 0.30 mm, on a glass fiber in the air, was mounted on an Enraf-Nonius CAD4 automated diffractometer. Cell parameters and the orientation matrix were obtained on the basis of 25 random intense reflections ($16 < 2\theta < 25°$). The intensity data were collected by using graphite-monochromatized Mo Kα radiation, by the ω-scan method, within the limits $3 < \theta < 24°$. A variable scan speed (from 2 to 20°/min) and a variable scan range of $(1.1 + 0.35 \tan \theta)°$ were used, with a 25% extension at each end of the scan range for background determination. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to the intensities, based on ψ scans (ψ = 0–360° every 10°) of suitable reflections with χ values close to 90°; the relative transmission factors had values in the range 0.71–1.00.

The structure was solved by direct methods and Fourier techniques, and refined by full-matrix least-squares techniques, on the basis of 4587 independent significant [$I > 3\sigma(I)$] reflections. All atoms but those of the solvated tetrahydrofuran molecules were refined anisotropically. The hydrogen atoms were neglected. The final conventional agreement indices R and R_w were 0.026 and 0.034, respectively. The final difference Fourier map was rather flat, showing residual peaks not exceeding ca. 1.2 e/Å^3. All computations were performed by using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants therein tabulated.

Registry No. [1]Cs_3, 84179-28-2; **2**, 119787-09-6; **2**·C_4H_8O, 119793-83-8; $[Cu(NCMe)_4](BF_4)$, 15418-29-8; Cu, 7440-50-8; Rh, 7440-16-6.

Supplementary Material Available: Listings of atomic coordinates (Table 1S), thermal parameters (Table 2S), and bond angles (Table 3S) and a summary of the crystal data (Table 4S) (8 pages); a listing of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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Four-Electron Oxidations by Dioxo Complexes of Osmium(VI)

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Among a growing body of examples of higher oxidation state oxo and dioxo complexes of osmium and ruthenium[1] are the complexes *cis*- and *trans*-$[Os^{VI}(bpy)_2(O)_2](ClO_4)_2$ (bpy is 2,2′-bipyridine).[1a,b] From the results of a series of experiments in water, it is known that the Os(VI) complexes undergo reversible electron–proton additions via the intermediate oxidation states Os(V), Os(IV), and Os(III) to give, ultimately, $[Os^{II}(bpy)_2(OH_2)_2]^{2+}$. Oxidation state VI for the cis isomer in acetonitrile is unstable with regard to isomerization to the trans isomer. In aqueous solution, a more rapid process than isomerism occurs in which a bpy ligand is lost, giving *trans*-$Os^{VI}(bpy)(O)_2(OH)_2$. In oxidation state II, *trans*-$[Os(bpy)_2(OH_2)_2]^{2+}$ is unstable with regard to isomerization to *cis*-$[Os(bpy)_2(OH_2)_2]^{2+}$.[1a]

One of the reasons for our interest in dioxo complexes of Os(VI) and Ru(VI) is their implied reactivity as four-electron oxidants. Given the implied multiple electron character and the shared *cis*-dioxo structures, the cis complexes could conceivably mimic such oxidants as OsO_4 or RuO_4 in their reactivity.[2] They are also potential electrocatalysts given the known capabilities of Ru(IV/II) couples are electrocatalysts.[3-5] An additional question arises concerning the role of stereochemistry at the metal in determining oxidative reactivity. Electrochemical studies show that the cis complexes of Os(VI) or Ru(VI) are stronger oxidants thermodynamically than are the trans complexes. The major factor is the special electronic stabilization associated with the d^2 *trans*-dioxo structure for oxidation state VI. Electronic stabilization effects also affect the pattern of stable oxidation states. In acidic solution, oxidation states Os(IV) and Os(V) are actually stronger oxidants than Os(VI), and only the three-electron, three-proton couple *trans*-$[Os^{VI}(bpy)_2(O)_2]^{2+}$/*trans*-$[Os^{III}(bpy)_2(OH_2)(OH)]^{2+}$ is observed.[1a,6]

The osmium(VI) dioxo complexes are not especially strong oxidizing agents. Compared to analogous complexes of ruthenium, which are more strongly oxidizing, the rates of oxidation of organic substrates like benzyl alcohol are quite slow. Earlier work with *cis*-$[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ showed that the rate of oxidation of PPh_3 is rapid.[7]

$$\textit{cis-}[Ru^{IV}(bpy)_2(py)(O)]^{2+} + PPh_3 \rightarrow \textit{cis-}[Ru^{II}(bpy)_2(py)(O{=}PPh_3)]^{2+} \quad (1)$$

$$k(25\ °C \text{ in } CH_3CN) = 1.75 \times 10^5\ M^{-1}\ s^{-1}$$

The coordinated $OPPh_3$ complex which is formed is unstable toward loss of phosphine oxide in a slower step.

$$\textit{cis-}[Ru^{II}(bpy)_2(py)(O{=}PPh_3)]^{2+} + CH_3CN \rightarrow \textit{cis-}[Ru^{II}(bpy)_2(py)(CH_3CN)]^{2+} + O{=}PPh_3 \quad (2)$$

Che and co-workers have shown that the reduction of a dioxoosmium(VI) porphyrin complex by PPh_3 gives the four-electron reduction product $Os^{II}(OEP)(OPPh_3)_2$ (H_2OEP = octaethylporphyrin).[8] Related work has shown that *trans*-dioxo complexes of Ru(VI) containing macrocyclic tertiary amines such as 14-TMC (14-TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) react with PPh_3 to give stable monooxo complexes of Ru(IV)[9]

$$\textit{trans-}Ru^{VI}(14\text{-}TMC)(O)_2 + PPh_3 + CH_3CN \rightarrow \textit{trans-}Ru^{IV}(14\text{-}TMC)(O)(CH_3CN) + O{=}PPh_3 \quad (3)$$

Groves and Ahn have shown that *trans*-$Ru^{VI}(TMP)(O)_2$ (TMP = tetramesitylporphyrin) is reduced in the presence of PPh_3 to give $Ru^{II}(TMP)(PPh_3)$ and $OPPh_3$ via a $Ru^{IV}{=}O$ intermediate.[10] In order to probe the implied four-electron oxidative character of the cis and trans dioxo complexes of Os(VI), we have inves-

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