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Dimethyl sulfide-substituted mixed-metal clusters: synthesis, structure, and characterization of HRuCo3(CO)11(SMe2) and [HRuRh3(CO)9]2[SMe2]3

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B. Wave Functions. The geometries of the stationary points were generated with analytic gradient techniques using restricted Hartree–Fock wave functions. For the final optimized geometries, GVB wave functions[17] were obtained, and CI calculations[18] were performed consisting of RCI quadruples plus a Pol(2/1)-CI[19] including the GVB orbitals and the entire virtual space. For each structure all of the valence electrons on carbon, hydrogen, and scandium were correlated.

C. Geometry Optimizations. As mentioned above, the geometries of the reactants, transition states, and products were determined by using analytic derivatives of the form

$$d_{li} = \partial E(\Psi_{\mathrm{HF}})/\partial q_{li}$$

for all Cartesian coordinates ql of each atom i in the molecule, using the numerical procedure of Dupuis and King.[20] Second derivatives $k_{li,mj}$ were estimated by using Badger's rules[21] and updated with finite difference of the first derivatives at each geometry by using a procedure implemented by Upton and Rappé.[22] Assuming the total potential near the minimum to be of the form

$$V(\mathbf{r}) = V_0 + \mathbf{d}\cdot\mathbf{r} + \tfrac{1}{2}\mathbf{k}\cdot\mathbf{r}^2$$

the global minimum in the potential was found by using successive Newton–Raphson steps,[23] $\Delta\mathbf{r} = -\mathbf{d}/\mathbf{k}$ to define new test geometries. To locate the transition state, the Lagrange multiplier technique of Simons and co-workers[24] was used. The final geometries and CI total energies are collected in Table I. For each equilibrium structure six zero eigenvalues were found corresponding to the translational and rotational degrees of freedom—the remaining eigenvalues were positive. For the saddlepoint structures a single negative eigenvalue was obtained corresponding to the reaction coordinate, six zero eigenvalues were found corresponding to the translational and rotational degrees of freedom, and the remaining eigenvalues were positive.

For the acetylide transition state where a C_{2v} saddlepoint was found, steps away from C_{2v} symmetry were carried out to assess whether or not the C_{2v} structure was indeed a saddlepoint or merely an arbitrary point on the potential energy surface or an equilibrium structure. The single negative eigenvalue found was indeed for a distortion from C_{2v} to C_s symmetry. In contrast to the work of Steigerwald and Goddard[4a] for the parent $Cl_2ScH + H_2$ case, the reaction coordinate here (not surprisingly) predominately consists of motion of the terminal hydrogen of the acetylene. The eigenvector corresponding to the reaction coordinate is given in Table III.

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Dimethyl Sulfide Substituted Mixed-Metal Clusters: Synthesis, Structure, and Characterization of $HRuCo_3(CO)_{11}(SMe_2)$ and $[HRuRh_3(CO)_9]_2[SMe_2]_3$

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Ligand substitution reactions of dimethyl sulfide with mixed-metal clusters are described. The clusters $HRuCo_3(CO)_{11}(SMe_2)$ (1) and $[HRuRh_3(CO)_9]_2[SMe_2]_3$ (2) have been prepared by reactions of SMe_2 with the neutral parent clusters. Their crystal structures have been established: 1, monoclinic, space group $P2_1/n$, $a = 11.459$ (5) Å, $b = 12.484$ (4) Å, $c = 14.384$ (4) Å, $\beta = 96.40$ (3)°, $Z = 4$; 2, trigonal, space group $R\bar{3}c$, $a = 13.181$ (7) Å, $\alpha = 75.54$ (5)°, $Z = 2$. Dimethyl sulfide coordinates terminally as a two-electron donor on basal cobalt in 1 and as a bridging four-electron donor causing unusual dimerization of clusters in 2. The carbonyl arrangement of the parent clusters was not changed during the ligand substitution, and hydride ligands bridge the three basal metals in both compounds.

Introduction

Mixed-metal clusters and their ligand substitution reactions have been studied extensively. Among the most commonly used ligands are phosphines and phosphites, but also a variety of sulfur ligands have been employed.[1] Reactions of metal clusters with sulfur-containing ligands are important, when catalytic processes are studied, sulfur being one of the foremost catalyst poisons.[2]

Sulfur ligands can be classified as S^{2-}, SR^-, or SR_2 analogues. S^{2-} or elemental sulfur is commonly found to

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Table I. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $HRuCo_3(CO)_{11}(SMe_2)$

atom	*x*	*y*	*z*	U^a
Ru(1)	−930 (1)	1622 (1)	7121 (1)	38 (1)
Co(1)	1293 (1)	2131 (1)	7069 (1)	32 (1)
Co(2)	796 (1)	800 (1)	8273 (1)	33 (1)
Co(3)	303 (1)	2744 (1)	8449 (1)	36 (1)
S	3217 (2)	2603 (2)	7119 (2)	40 (1)
O(1)	−2123 (8)	3262 (7)	5779 (6)	93 (4)
O(2)	−3202 (7)	943 (8)	7878 (7)	98 (4)
O(3)	−1084 (7)	−65 (6)	5591 (5)	72 (3)
O(4)	782 (8)	2428 (6)	5063 (5)	80 (3)
O(6)	−773 (6)	−1030 (6)	8036 (5)	65 (3)
O(7)	2670 (6)	−254 (6)	9513 (5)	66 (3)
O(8)	−2004 (7)	3674 (7)	8450 (6)	90 (4)
O(9)	1365 (8)	4099 (7)	9972 (6)	91 (4)
O(12)	1815 (6)	−105 (5)	6633 (5)	52 (2)
O(13)	637 (7)	4418 (5)	7044 (5)	61 (3)
O(23)	−456 (7)	1298 (6)	9888 (5)	75 (3)
C(1)	−1673 (9)	2665 (8)	6302 (8)	58 (4)
C(2)	−2360 (10)	1200 (9)	7607 (8)	60 (4)
C(3)	−1026 (8)	559 (8)	6159 (7)	48 (3)
C(4)	956 (8)	2285 (7)	5849 (6)	43 (3)
C(6)	−205 (8)	−282 (8)	8091 (7)	46 (3)
C(7)	1985 (8)	188 (7)	9039 (6)	41 (3)
C(8)	−1135 (9)	3238 (8)	8387 (7)	55 (4)
C(9)	1002 (9)	3553 (8)	9359 (7)	49 (3)
C(12)	1494 (7)	598 (7)	7056 (6)	35 (3)
C(13)	731 (8)	3566 (7)	7352 (7)	43 (3)
C(23)	−3 (9)	1500 (8)	9241 (7)	49 (3)
C(101)	4000 (8)	2249 (8)	8225 (6)	55 (4)
C(102)	3929 (9)	1730 (8)	6354 (7)	66 (4)
H(1)[b]	149 (9)	199 (8)	825 (7)	9 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U** tensor. [b] $\times 10^3$ (coordinates) and $Å^2 \times 10^2$ (U_{eq}).

incorporate into the cluster core. Both SH^- and SR^- usually form μ_2 bridges. This is a well-known type; one example is $HOs_3(CO)_{10}(SEt)$.[3]

Thioethers SR_2 have two unshared electron pairs; they have two possible coordination modes. In mononuclear metal compounds such as *cis*-$[Pt(SR_2)_2Cl_2]$ (R = Me, Et, Pr, Bu) one electron pair is used for terminal coordination.[4] In dinuclear complexes bidentate four-electron-donor dialkyl sulfides are found, as in $[Cl_3W(\mu\text{-}Me_2S)WCl_3]$.[5]

In polynuclear metal compounds dialkyl sulfides as ligands are rather rare. They have been reported, for example, in metal boranes,[6,7] but in metal clusters they are known only in the SMe_2 derivatives of $Co_4(CO)_{12}$, which were characterized by IR spectroscopy.[8] We have given a preliminary report of the mixed-metal cluster $HRuRhCo_2(CO)_{11}(SMe_2)$, where SMe_2 is bound terminally.[9] In order to start the systematic development of the cluster chemistry of thioethers, we have studied the reactions of dimethyl sulfide with the clusters $HRuCo_3(CO)_{12}$[10] and $HRuRh_3(CO)_{12}$.[11] They belong to the family of $H_xRu_xCo_yRh_z(CO)_{12}$ (x, y, z = 0–4; $x + y + z$ = 4) clusters,

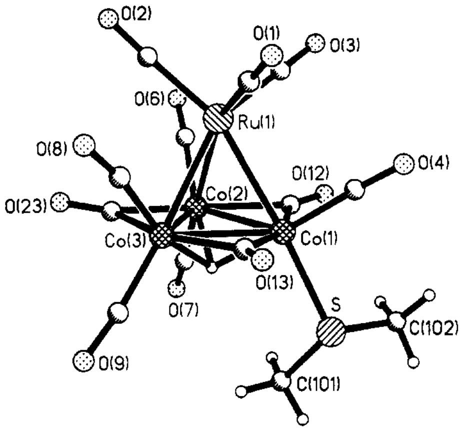

Figure 1. Structure and numbering scheme for $HRuCo_3(CO)_{11}(SMe_2)$ (1).

Table II. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $[HRuRh_3(CO)_9]_2[SMe_2]_3$

atom	*x*	*y*	*z*	U^a
Rh(1)	6195 (1)	4228 (1)	5450 (1)	29 (1)
Rh(2)	7737 (1)	5778 (1)	7048 (1)	31 (1)
Ru(1)	4515 (1)	4515 (1)	4515 (1)	35 (1)
Ru(2)	7628 (1)	7628 (1)	7628 (1)	39 (1)
S	7550 (2)	4225 (2)	6451 (2)	32 (1)
O(11)	3921 (9)	2353 (8)	5590 (9)	81 (5)
O(12)	6870 (10)	1943 (7)	5195 (9)	92 (5)
O(13)	4816 (6)	3195 (6)	7518 (7)	58 (3)
O(21)	8009 (11)	6667 (9)	9902 (8)	92 (6)
O(22)	9714 (7)	4885 (8)	8006 (8)	72 (4)
O(23)	6512 (7)	5008 (7)	9348 (6)	64 (3)
C(11)	4128 (11)	3170 (11)	5166 (10)	51 (5)
C(12)	6622 (10)	2810 (8)	5294 (9)	50 (4)
C(13)	4963 (7)	3915 (8)	6823 (7)	36 (3)
C(21)	7867 (12)	7031 (12)	9036 (12)	60 (6)
C(22)	8982 (8)	5185 (8)	7630 (9)	44 (4)
C(23)	6616 (8)	5592 (8)	8514 (8)	40 (4)
C(31)	7369 (9)	3166 (8)	7621 (9)	50 (4)
C(32)	8865 (8)	3652 (10)	5749 (10)	56 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized **U** tensor.

Table III. Selected Bond Lengths (Å) for $HRuCo_3(CO)_{11}(SMe_2)$

Ru(1)–Co(1)	2.634 (2)	Ru(1)–Co(2)	2.643 (2)
Ru(1)–Co(3)	2.646 (2)	Ru(1)–C(1)	1.89 (1)
Ru(1)–C(2)	1.93 (1)	Ru(1)–C(3)	1.91 (1)
Co(1)–Co(2)	2.511 (2)	Co(1)–Co(3)	2.513 (2)
Co(1)–S	2.275 (3)	Co(1)–C(4)	1.765 (9)
Co(1)–C(12)	1.928 (8)	Co(1)–C(13)	1.962 (9)
Co(1)–H(1)	1.70 (9)	Co(2)–Co(3)	2.511 (2)
Co(2)–C(6)	1.77 (1)	Co(2)–C(7)	1.822 (9)
Co(2)–C(12)	2.020 (9)	Co(2)–C(23)	1.96 (1)
Co(2)–H(1)	1.69 (9)	Co(3)–C(8)	1.75 (1)
Co(3)–C(9)	1.772 (9)	Co(3)–C(13)	1.99 (1)
Co(3)–C(23)	1.98 (1)	Co(3)–H(1)	1.7 (1)
S–C(101)	1.792 (9)	S–C(102)	1.81 (1)
O(1)–C(1)	1.14 (1)	O(2)–C(2)	1.13 (1)
O(3)–C(3)	1.13 (1)	O(4)–C(4)	1.14 (1)
O(6)–C(6)	1.14 (1)	O(7)–C(7)	1.12 (1)
O(8)–C(8)	1.15 (1)	O(9)–C(9)	1.15 (1)
O(12)–C(12)	1.15 (1)	O(13)–C(13)	1.15 (1)
O(23)–C(23)	1.14 (1)		

which is one of the best characterized mixed-metal systems.[12] Earlier studies within this group have revealed systematic trends in hydride ligand location, activity, and reactivity in phosphine substitution.[13] Linear relation-

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Table IV. Selected Bond Lengths (Å) for $[HRuRh_3(CO)_9]_2[SMe_2]_3$

Rh(1)–Ru(1)	2.697 (2)	Rh(1)–S	2.470 (3)
Rh(1)–C(12)	1.86 (1)	Rh(1)–C(13)	2.139 (8)
Rh(1)–Rh(1A)	2.777 (2)	Rh(1)–C(13A)	2.075 (9)
Rh(2)–Ru(2)	2.693 (2)	Rh(2)–S	2.454 (3)
Rh(2)–C(22)	1.89 (1)	Rh(2)–C(23)	2.120 (9)
Rh(2)–Rh(2A)	2.778 (2)	Rh(2)–C(23A)	2.116 (9)
Ru(1)–C(11)	1.90 (1)	Ru(2)–C(21)	1.90 (2)
S–C(31)	1.81 (1)	S–C(32)	1.82 (1)
O(11)–C(11)	1.15 (2)	O(12)–C(12)	1.14 (2)
O(13)–C(13)	1.16 (1)	O(21)–C(21)	1.17 (2)
O(22)–C(22)	1.13 (2)	O(23)–C(23)	1.17 (1)

Table V. Selected Bond Angles (deg) for $HRuCo_3(CO)_{11}(SMe_2)$

Co(1)–Ru(1)–C(1)	100.7 (3)	Co(2)–Ru(1)–C(1)	155.6 (3)
Co(3)–Ru(1)–C(1)	104.6 (3)	Co(1)–Ru(1)–C(2)	160.3 (3)
Co(2)–Ru(1)–C(2)	105.9 (3)	Co(3)–Ru(1)–C(2)	106.9 (3)
Co(1)–Ru(1)–C(3)	97.2 (3)	Co(2)–Ru(1)–C(3)	99.4 (3)
Co(3)–Ru(1)–C(3)	150.8 (3)	Ru(1)–Co(1)–S	176.4 (1)
Co(2)–Co(1)–S	116.3 (1)	Co(3)–Co(1)–S	114.7 (1)
Ru(1)–Co(1)–C(4)	87.1 (3)	Co(2)–Co(1)–C(4)	135.8 (3)
Co(3)–Co(1)–C(4)	133.2 (3)	Ru(1)–Co(1)–C(12)	83.0 (3)
Co(2)–Co(1)–C(12)	52.1 (3)	Co(3)–Co(1)–C(12)	112.0 (3)
Ru(1)–Co(1)–C(13)	82.7 (3)	Co(2)–Co(1)–C(13)	110.9 (3)
Co(3)–Co(1)–C(13)	51.0 (3)	Ru(1)–Co(1)–H(1)	88 (3)
Co(2)–Co(1)–H(1)	42 (3)	Co(3)–Co(1)–H(1)	42 (3)
Ru(1)–Co(2)–C(6)	77.1 (3)	Co(1)–Co(2)–C(6)	126.5 (3)
Co(3)–Co(2)–C(6)	127.0 (3)	Ru(1)–Co(2)–C(7)	177.8 (3)
Co(1)–Co(2)–C(7)	118.9 (3)	Co(3)–Co(2)–C(7)	120.4 (3)
Ru(1)–Co(2)–C(12)	81.1 (2)	Co(1)–Co(2)–C(12)	48.9 (2)
Co(3)–Co(2)–C(12)	108.9 (2)	Ru(1)–Co(2)–C(23)	84.0 (3)
Co(1)–Co(2)–C(23)	110.8 (3)	Co(3)–Co(2)–C(23)	50.8 (3)
Ru(1)–Co(2)–H(1)	88 (3)	Co(1)–Co(2)–H(1)	42 (3)
Co(3)–Co(2)–H(1)	42 (4)	Ru(1)–Co(3)–C(8)	74.1 (3)
Co(1)–Co(3)–C(8)	124.9 (3)	Co(2)–Co(3)–C(8)	123.8 (3)
Ru(1)–Co(3)–C(9)	174.6 (3)	Co(1)–Co(3)–C(9)	123.3 (3)
Co(2)–Co(3)–C(9)	122.5 (3)	Ru(1)–Co(3)–C(13)	81.9 (3)
Co(1)–Co(3)–C(13)	50.0 (3)	Co(2)–Co(3)–C(13)	109.9 (3)
Ru(1)–Co(3)–C(23)	83.5 (3)	Co(1)–Co(3)–C(23)	109.9 (3)
Co(2)–Co(3)–C(23)	49.9 (3)	Ru(1)–Co(3)–H(1)	88 (3)
Co(1)–Co(3)–H(1)	42 (3)	Co(2)–Co(3)–H(1)	42 (3)
Co(1)–S–C(101)	110.6 (3)	Co(1)–S–C(102)	109.0 (3)
C(101)–S–C(102)	100.2 (5)	Ru(1)–C(1)–O(1)	177.1 (9)
Ru(1)–C(2)–O(2)	178.9 (8)	Ru(1)–C(3)–O(3)	179.8 (9)
Co(1)–C(4)–O(4)	176.3 (9)	Co(2)–C(6)–O(6)	173.2 (8)
Co(2)–C(7)–O(7)	175.0 (8)	Co(3)–C(8)–O(8)	169.3 (9)
Co(3)–C(9)–O(9)	174 (1)	Co(1)–C(12)–Co(2)	79.0 (3)
Co(1)–C(12)–O(12)	143.8 (7)	Co(2)–C(12)–O(12)	137.2 (7)
Co(1)–C(13)–Co(3)	79.0 (3)	Co(1)–C(13)–O(13)	141.5 (8)
Co(3)–C(13)–O(13)	139.5 (8)	Co(2)–C(23)–Co(3)	79.3 (4)
Co(2)–C(23)–O(23)	140.5 (8)	Co(3)–C(23)–O(23)	140.1 (8)
Co(1)–H(1)–Co(2)	96 (5)	Co(1)–H(1)–Co(3)	96 (5)
Co(2)–H(1)–Co(3)	96 (5)		

ships between the cluster structure and the chemical shift of the cluster proton in ^1H NMR spectra have turned out to be fruitful to develop an easy and rapid method for the analysis of the products in this system.[12]

Results and Discussion

Synthesis and Structure of $HRuCo_3(CO)_{11}(SMe_2)$ (1). The preparation was a simple substitution of a carbonyl ligand by SMe_2 in CH_2Cl_2 solution. The reaction between $HRuCo_3(CO)_{12}$ and dimethyl sulfide was accelerated by refluxing the CH_2Cl_2 solvent and by using excess SMe_2 so that a reasonable 58% yield was obtained after a 2-h reaction. A small amount of $HRuCo_3(CO)_{10}(SMe_2)_2$ was formed as a byproduct (10% yield after a 22-h reaction).[14]

Table VI. Selected Bond Angles (deg) for $[HRuRh_3(CO)_9]_2[SMe_2]_3$

Ru(1)–Rh(1)–S	170.1 (1)	Ru(1)–Rh(1)–C(12)	91.4 (4)
Ru(1)–Rh(1)–C(13)	79.2 (3)	S–Rh(1)–Rh(1A)	115.2 (1)
C(12)–Rh(1)–Rh(1A)	137.4 (4)	C(13)–Rh(1)–Rh(1A)	107.6 (2)
S–Rh(1)–Rh(1B)	111.4 (1)	C(12)–Rh(1)–Rh(1B)	132.7 (4)
C(13)–Rh(1)–Rh(1B)	47.8 (2)	Ru(1)–Rh(1)–C(13A)	80.3 (3)
Rh(1A)–Rh(1)–C(13A)	49.8 (2)	Rh(1B)–Rh(1)–C(13A)	109.6 (2)
Ru(2)–Rh(2)–S	170.8 (1)	Ru(2)–Rh(2)–C(22)	89.1 (4)
Ru(2)–Rh(2)–C(23)	80.2 (3)	S–Rh(2)–Rh(2A)	114.3 (1)
C(22)–Rh(2)–Rh(2A)	133.1 (3)	C(23)–Rh(2)–Rh(2A)	108.8 (2)
S–Rh(2)–Rh(2B)	112.7 (1)	C(22)–Rh(2)–Rh(2B)	133.8 (3)
C(23)–Rh(2)–Rh(2B)	49.0 (2)	Ru(2)–Rh(2)–C(23A)	80.2 (3)
Rh(2A)–Rh(2)–C(23A)	49.1 (3)	Rh(2B)–Rh(2)–C(23A)	108.9 (3)
Rh(1)–Ru(1)–C(11)	97.2 (5)	Rh(1)–Ru(1)–C(11A)	103.1 (4)
Rh(1)–Ru(1)–C(11B)	158.0 (5)	Rh(2)–Ru(2)–C(21)	97.3 (5)
Rh(2)–Ru(2)–C(21A)	101.1 (5)	C(21)–Ru(2)–C(21A)	95.8 (7)
Rh(2)–Ru(2)–C(21B)	157.4 (5)	Rh(1)–S–Rh(2)	125.1 (1)
Rh(1)–S–C(31)	104.7 (4)	Rh(2)–S–C(31)	107.7 (4)
Rh(1)–S–C(32)	108.8 (5)	Rh(2)–S–C(32)	107.5 (5)
C(31)–S–C(32)	100.3 (5)	Ru(1)–C(11)–O(11)	177 (2)
Rh(1)–C(12)–O(12)	179 (1)	Rh(1)–C(13)–O(13)	136.0 (7)
Rh(1)–C(13)–Rh(1B)	82.5 (3)	O(13)–C(13)–Rh(1B)	141.4 (7)
Ru(2)–C(21)–O(21)	180 (1)	Rh(2)–C(22)–O(22)	176 (1)
Rh(2)–C(23)–O(23)	139.8 (8)	Rh(2)–C(23)–Rh(2)	82.0 (3)
O(23)–C(23)–Rh(2B)	138.2 (8)		

The crystal structure and the numbering scheme of 1 are presented in Figure 1. Atomic coordinates are shown in Table I, bond distances in Table III, and selected bond angles in Table V.

This compound shows a closed-tetrahedral metal core with three terminal carbonyls on apical ruthenium, three carbonyl bridges connecting the three basal metals, and an axially coordinated SMe_2 ligand.

In this type of cluster the hydrides bridge either one of the $Ru–M_{bas}$ edges or the basal face of the metals. The hydride ligand was located in the $Co_3(\mu_3\text{-}H)$ position from a difference map and refined. The presence of a $Ru_{ap}(\mu_2\text{-}H)Co$ bridge can be excluded by the Ru–Co distances, which show no lengthening due to bridging hydrides, and by the $Ru_{ap}–Co_{bas}–C_{eq}$ bond angles (less than 90°), which are typical nonbridged values (Table V). For example, the corresponding bond angles in $H_2Ru_2Rh_2(CO)_{12}$ for $Ru_{ap}(\mu_2\text{-}H)M_{bas}$ edges are 110.7 and 115.8°.[15] The $M_{bas}–M_{bas}–S_{ax}$ values (average 115.5°) are lower than, for example, the $M_{bas}–M_{bas}–P_{ax}$ value in $HRuCo_3(CO)_{10}(PPh_3)_2$ (average 120.5°).[13] However, the $Co–Co–C_{ax}$ angles (average 121.3°) are reasonably large for a $Co_3(\mu_3\text{-}H)$ hydride.

The broad hydride resonance of 1 at −19.6 ppm corresponds well with the $Co_3(\mu_3\text{-}H)$ resonances of $HRuCo_3(CO)_{12}$ and its phosphine derivatives.[11,16] The methyl proton peak is at 2.2 ppm instead of the 2.0 ppm of free SMe_2. One of the methyl groups (but not the free electron pair) is oriented to "cover" the hydride ligand. There are previous observations that the repulsion caused by a hydride against the nearest ligands opens more space above the hydride, as seen for example for the R groups of PR_3.[17] In the present case it can be suggested that the total steric repulsion of ligands is minimized when one methyl group is above the hydride.

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(14) $HRuCo_3(CO)_{10}(SMe_2)_2$ crystal data: monoclinic, space group $P2/c$, $a = 15.45$ (2) Å, $b = 10.70$ (3) Å, $c = 14.67$ (3) Å, $\beta = 106.5$ (2)°, $Z = 4$. The SMe_2 ligands were axially coordinated on cobalt atoms. IR: $\nu(CO)$ 2067 m, 2035 s, 2003 s, 1863 m, 1844 m cm^{-1}.

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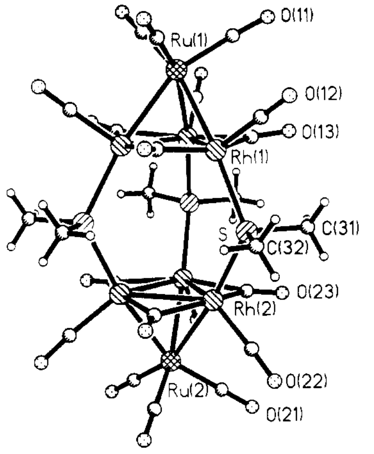

Figure 2. Structure and numbering scheme for $[HRuRh_3(CO)_9]_2[SMe_2]_3$ (2).

The cluster $HRuCo_2Rh(CO)_{11}(SMe_2)$ is isomorphous with 1, having the SMe_2 ligand axially coordinated on rhodium.[9]

Synthesis and Structure of $[HRuRh_3(CO)_9]_2[SMe_2]_3$ (2). $HRuRh_3(CO)_{12}$ was found to be more reactive toward SMe_2 than $HRuCo_3(CO)_{12}$ due to the higher reactivity of rhodium sites. The crystal structure and the numbering scheme are presented in Figure 2. Atomic coordinates are shown in Table II, bond distances in Table IV, and selected bond angles in Table VI. In refluxing CH_2Cl_2 the reaction between $HRuRh_3(CO)_{12}$ and SMe_2 smoothly produced 2 with no ^1H NMR evidence of simple mono- or disubstituted derivatives of the parent cluster. This compound has closed-tetrahedral metal cores with three terminal carbonyls on apical ruthenium, three carbonyl bridges connecting the three basal metals, and axially coordinated SMe_2 ligands. The four-electron capability of SMe_2 is ideal to form intercluster bridges. The bite of the bidentate coordination is wide enough to accommodate the facing triply bridging hydrogens of the cluster monomers. The formation of intermolecular bridges instead of intramolecular is unusual. The presence of $Ru_{ap}(\mu_2\text{-}H)Rh$ bridges can be excluded by the Ru–Rh distances (Table IV), which show no lengthening due to bridging hydrides, and by the Ru_{ap}–M_{bas}–C_{eq} bond angles (Table VI). The M_{bas}–M_{bas}–S_{ax} values (average 113.4°) are lower than the M_{bas}–M_{bas}–P_{ax} values in $HRuRh_3(CO)_{10}(PPh_3)_2$ (average 123.5°).[11] The hydride bridge was evidenced by ^1H NMR spectra. Compound 2 gives a quartet at −17.0 ppm ($^1J_{Rh-H}$ = 12.0 Hz), indicating the $Rh_3(\mu_3\text{-}H)$ hydride. The chemical shift differs from the $Rh_3(\mu_3\text{-}H)$ signals of $HRuRh_3(CO)_{12}$ and its phosphine derivatives (ca. −15.5 ppm) as a result of the unique dimer structure.

Substitution occurred even at −60 °C. The dimer cluster, however, was not formed at this low temperature. After a 5-h reaction with a 2-fold excess of SMe_2 practically all the $HRuRh_3(CO)_{12}$ was consumed. ^1H NMR spectra (samples were handled below 0 °C) showed a doublet of triplets at −15.5 ppm ($^1J_{Rh(A)-H}$ = 10.5 Hz and $^1J_{Rh(B)-H}$ = $^1J_{Rh(C)-H}$ = 11.8 Hz) together with a small quartet due to the parent cluster but no signal of 2. These parameters correspond to the data of mono- or disubstituted phosphine derivatives of $HRuRh_3(CO)_{12}$ and suggest therefore the formation of mono- or disubstituted derivatives with terminal SMe_2 ligands. These are obvious intermediate steps in the formation of the trisubstituted cluster dimer 2, since after the mixture is warmed to room temperature proton NMR spectra showed the quartet of 2 but not the peaks near −15.5 ppm. Attempts to obtain monomeric products by chromatographic separations at −20 °C failed.

Table VII. Crystallographic Data for $HRuCo_3(CO)_{11}(SMe_2)$ (1) and $[HRuRh_3(CO)_9]_2[SMe_2]_3$ (2)

	1	2
fw	649.12	1512.22
cryst syst	monoclinic	trigonal
space group	$P2_1/n$	$R\bar{3}c$
a, Å	11.459 (5)	13.181 (7)
b, Å	12.484 (4)	
c, Å	14.384 (4)	
α, deg	90.00	75.54 (5)
β, deg	96.40 (3)	
γ, deg	90.00	
V, Å^3	2045 (1)	2103 (2)
Z	4	2
D_{calc}, g cm^{-3}	2.11	2.39
cryst dimens, mm	0.3 × 0.3 × 0.3	0.2 × 0.2 × 0.2
radiation	Mo Kα	Mo Kα
monochromator	graphite	graphite
2θ limits, deg	4–55	4–55
hkl range	+14,+16,±20	+17,±16,±16
no. of unique rflns	4752	2571
no. of obsd data, $I \geq 3\sigma(I)$	2205	2094
μ, cm^{-1}	32.2	31.5
no. of params	266	160
R^a	0.0406	0.0312
$R_w{}^b$	0.0377	0.0294

[a] $R = \sum||F_o| - |F_c|| / \sum|F_o|$. [b] weight = $1/(\sigma^2(F) + 0.0005F^2)$.

Conclusion

Dimethyl sulfide has been demonstrated to be a useful ligand for substitution reactions in tetranuclear Ru–Co–Rh mixed-metal clusters. It can act as a standard two-electron ligand, forming monosubstituted and multiply substituted derivatives. Dimethyl sulfide also forms intercluster bridges as a four-electron donor, facilitating novel cluster polymerization reactions.

Dialkyl and diaryl sulfides in general are a promising group of ligands for cluster studies.

Experimental Section

General Comments. All reactions up to the chromatographic separations were carried out under a nitrogen atmosphere with deoxygenated solvents. SMe_2 was of commercial origin (Aldrich Chemie). $HRuCo_3(CO)_{12}$[10] and $HRuRh_3(CO)_{12}$[11] were prepared by published methods.

Infrared spectra were recorded in dichloromethane on a Nicolet 20SXC spectrometer.

^1H NMR spectra were measured on a Bruker AM-250 spectrometer with $CDCl_3$ as solvent at 0 °C with TMS as reference.

Synthesis of $HRuCo_3(CO)_{11}(SMe_2)$ (1). The compound SMe_2 (3.6 mL, 49 mmol) was added to a solution of $HRuCo_3(CO)_{12}$ (300 mg, 0.49 mmol) in CH_2Cl_2 (40 mL). The solution was refluxed for 2 h. The solvent was evaporated in vacuo and the residue chromatographed on a silica column. Elution with hexane gave yellow and orange bands that showed CO-stretching vibrations characteristic for $Ru_3(CO)_{12}$ (14 mg) and unreacted $HRuCo_3(CO)_{12}$ (4 mg, 1%), respectively. Further elution with a hexane–dichloromethane (4:1) mixture gave reddish brown and violet bands. The former band of 1 was dried in vacuo and recrystallized from hexane–dichloromethane at −40 °C. Air-stable black cubic crystals of 1 were formed; yield 183 mg (58%). IR: ν(CO) 2085 m, 2046 s, 2012 m, 1864 m, 1846 m cm^{-1}. ^1H NMR: −19.6 ppm (broad singlet). The violet product was identified as $HRuCo_3(CO)_{10}(SMe_2)_2$, yield 4 mg, 1%.[14]

Synthesis of $[HRuRh_3(CO)_9]_2[SMe_2]_3$ (2). The compound SMe_2 (2.9 mL, 40.2 mmol) was added to the solution of $HRuRh_3(CO)_{12}$ (300 mg, 0.402 mmol) in CH_2Cl_2 (40 mL) and refluxed for 1 h. After evaporation of the solvent in vacuo the products were chromatographed on silica. Elution with hexane and a hexane–dichloromethane (4:1) mixture gave minor fractions that consisted of impurities of starting material and some byproducts. Further elution with dichloromethane gave a red band of the title compound, yield 130 mg (43%). IR: ν(CO) 2054 s, 2013 m, 1975 w, 1844 w, 1843 w cm^{-1}. ^{1}H NMR: −17.0 ppm (q, $^1J_{Rh-H}$ = 12.0 Hz). Recrystallization from CH_2Cl_2 by slow evaporation of the solvent gave dark red air-stable crystals.

Crystallographic Studies. Data were collected on a Nicolet R3m diffractometer using Mo Kα radiation (λ = 0.71073 Å). Accurate cell parameters were obtained from 25 automatically centered reflections in the range 15° < 2θ < 35° and 8° < 2θ < 22° for 1 and 2, respectively. Intensities were corrected for background, polarization, and Lorentz factors. Empirical absorption corrections were made from ψ-scan data. Table VII presents further crystallographic information.

The metal atom positions were solved by direct methods with use of the SHELXTL program package.[18] All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. Metal, sulfur, oxygen, and carbon atoms were anisotropically refined for both structures. Methyl protons were placed on idealized positions (C–H = 0.96 Å, U = 0.08 Å^2) and not refined.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond lengths and angles for 1, 2, and $HRuCo_3(CO)_{10}(SMe_2)_2$[14] (11 pages); listings of structure factors (38 pages). Ordering information is given on any current masthead page.

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Ligand Behavior of the $[HRu_3(CO)_{10}(\mu\text{-}CO)]^-$ Cluster Anion toward a Borane: Synthesis of and Molecular and Electronic Structure of $[HRu_3(CO)_{10}(\mu\text{-}COBH_2NMe_3)]$

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The compound $[HRu_3(CO)_{10}(\mu\text{-}COBH_2NMe_3)]$ (1) has been obtained as a minor product from the reaction of $Ru_3(CO)_{12-x}(NCMe)_x$ (x = 1, 2) either with $THF{\cdot}BH_3$ in the presence of NMe_3 or directly with $Me_3N{\cdot}BH_3$. The second boron-containing product is proposed from spectroscopic data to be $[Ru_6(CO)_{17}B][HNMe_3]$. The structure of 1 has been determined by single-crystal X-ray crystallography: monoclinic, $P2_1/c$, a = 14.938 (2) Å, b = 9.153 (1) Å, c = 16.872 (1) Å, β = 100.66 (1)°, V = 2267 Å^3, Z = 4, R_F = 2.44%. In 1, the $[HRu_3(CO)_{10}(\mu\text{-}CO)]^-$ anion formally functions as a base toward the borane; the observed bond length of the cluster μ-CO group (1.262 (4) Å) in 1 is longer than that of the corresponding bond in $[HRu_3(CO)_{10}(\mu\text{-}CO)]^-$. A Fenske–Hall quantum-chemical analysis of the bonding in 1 illustrates that the cluster–borane interaction is localized and results in subtle changes to the cluster bonding within the $[HRu_3(CO)_{10}(\mu\text{-}CO)]^-$ fragment.

We have previously reported that the reaction of $Ru_3(CO)_{12}$ with $THF{\cdot}BH_3$ and $Li[BHEt_3]$ in hexane solution leads to the formation of $Ru_3(CO)_9BH_5$.[1] However, the reaction is far from specific, and difficulties encountered in the separation of the products have encouraged us to explore other synthetic strategies. The bis(acetonitrile) derivative of ruthenium carbonyl $Ru_3(CO)_{10}(NCMe)_2$[2] appeared to be a potential precursor for Ru–B bond formation. The acetonitrile ligands are labile, and the compound has been used as an intermediate in the formation of several ruthenium-based clusters.[2] Here we illustrate that, in addition to the formation of the ruthenaboride cluster anion $[Ru_6(CO)_{17}B]^-$, the reaction of $Ru_3(CO)_{12-x}(NCMe)_x$ (x = 1, 2) with $THF{\cdot}BH_3$ in the presence of NMe_3 leads to $[HRu_3(CO)_{10}(\mu\text{-}COBH_2NMe_3)]$, in which a bridging carbonyl ligand of the triruthenium cluster acts as a Lewis base toward the borane fragment. The formation of adducts between transition-metal carbonyl compounds, including $Ru_3(CO)_{12}$,[3] and group III alkyls and halides has been studied previously, and infrared spectroscopic data suggest that carbonyl ligand rearrangement may, in some cases, accompany adduct formation.[3]

Crystallographic characterization of transition-metal carbonyl–group III Lewis acid adducts is confined to the tricobalt species $Co_3(CO)_9(\mu_3\text{-}COBH_2NEt_3)$,[4] $Co_3(CO)_9(\mu_3\text{-}COBCl_2NEt_3)$,[5] and $Co_3(CO)_9(\mu_3\text{-}COBBr_2NEt_3)$.[6] In each compound, the bridging carbonyl ligand exhibits a lengthened C–O bond, in keeping with the donation of electron density from the carbonyl to the coordinated Lewis acid. We present here the synthesis and structural characterization of $[HRu_3(CO)_{10}(\mu\text{-}COBH_2NMe_3)]$ (1) as well as an investigation of the electronic structure of the complex. The extent to which the interaction of the bridging carbonyl ligand with the borane fragment affects the bonding within the triruthenium cluster fragment is examined.

Experimental Section

General Data. FT-NMR spectra were recorded on a Bruker WM 250 or AM 400 spectrometer. ^{1}H NMR shifts are reported

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