$[(\mu_2\text{-H})Ru_3(CO)_9\{\mu_3\text{-NS(O)MePh}\}]$: An Electron-Deficient Trinuclear Cluster Containing a Chiral Sulfoximido Cap[†]

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Trinuclear clusters with optically active ligands have found interest as potential catalysts for enantioselective reactions.[1] Most of the trinuclear organometallic clusters, however, are electron-precise systems which satisfy the effective atomic number rule with 48 electrons.[2,3] Trinuclear 46e clusters are rare;[4] in the iron triad only osmium representatives are known. Apart from $[(\mu_2\text{-H})Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-PPh}_2CH_2PPhC_6H_4)]$,[5] only the famous cluster $[(\mu_2\text{-H})_2Os_3(CO)_{10}]$[6] and its derivatives $[(\mu_2\text{-H})_2Os_3(CO)_9L]$ (L = PMe_2Ph,[7] PPr^i [8]), $[(\mu_2\text{-H})Os_3(CO)_{10}(\mu_2\text{-AuPh})]$,[9] and $[Os_3(CO)_{10}(\mu_2\text{-AuPh})_2]$[9] have been reported so far. No Ru_3 cluster with an electron count of 46 is mentioned in Deeming's review of 1995.[4]

The thermal reaction of triruthenium dodecacarbonyl with racemic or optically pure methylphenylsulfoximine in tetrahydrofuran gives, within 2 h in good yields, the cluster $[(\mu_2\text{-H})Ru_3(CO)_9\{\mu_3\text{-NS(O)MePh}\}]$ (**1**)[10] which is obtained, depending on the substrate employed, as a racemic mixture or enantiopure.

$$[Ru_3(CO)_{12}] + MePhS(O)NH \rightarrow$$
$$[(\mu_2\text{-H})Ru_3(CO)_9\{\mu_3\text{-NS(O)MePh}\}] + 3CO$$

1

The N−H activation and coordination of the sulfoximido fragment to the triruthenium framework does not change the configuration at the stereogenic S atom, as demonstrated by the strictly symmetrical CD spectra of *(R)*-**1** and *(S)*-**1** (Figure 1, Supporting Information). The X-ray structure analysis[11] of a single crystal of **1**, prepared by using *(R)*-methylphenylsulfoximine, revealed that the chirality of the ligand is preserved in the complex. Figure 2 therefore, corresponds to the absolute configuration of **1**.

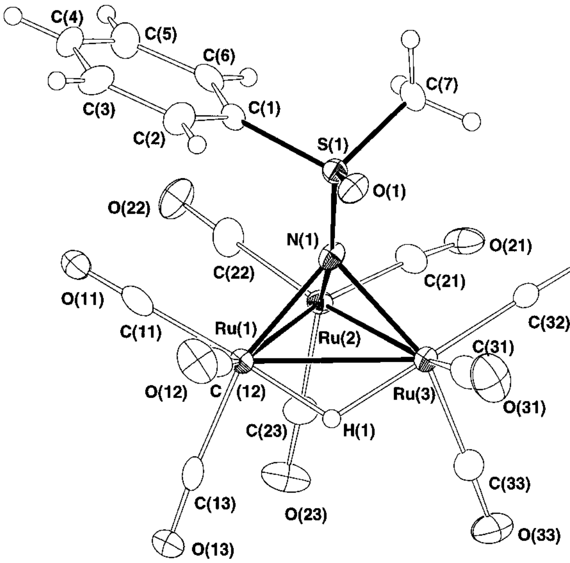

Figure 2. Molecular structure of $[(\mu_2\text{-H})Ru_3(CO)_9(\mu_3\text{-}(R)\text{-NS(O)MePh})]$ [(*R*)-**1**] as Zortep plot,[27] with the following selected bond distances (Å) and angles (deg): Ru(1)−Ru(2) 2.674(1), Ru(2)−Ru(3) 2.683(1), Ru(1)−Ru(3) 2.831(1), Ru(1)−H(1) 1.63(1), Ru(3)−H(1) 1.75(5), Ru(1)−N(1) 2.106(7), Ru(2)−N(1) 2.120(7), Ru(3)−N(1) 2.112(7), S(1)−N(1) 1.566(7), S(1)−O(1) 1.449(6), S(1)−C(1) 1.761(9), S(1)−C(7) 1.775(9), Ru(1)−H(1) 1.63(1), Ru(3)−H(1) 1.75(5); S(1)−N(1)−Ru(1) 124.5(4), S(1)−N(1)−Ru(2) 144.5(5), S(1)−N(1)−Ru(3) 125.8(4), O(1)−S(1)−N(1) 115.1(4), O(1)−S(1)−C(1) 108.2(4), N(1)−S(1)−C(1) 108.0(4), O(1)−S(1)−C(7) 110.2(4), N(1)−S(1)−C(7) 108.7(4), C(1)−S(1)−C(7) 106.2(4).

The formal electron count for cluster **1** is 46: While the H bridge counts one electron, the N═S(O)MePh cap is considered as a three-electron donor. With the three $Ru(CO)_3$ units, providing 14 electrons each, a total of 46 electrons makes cluster **1** formally electron-deficient. An alternative description, giving

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[†] Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

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(10) Synthesis of **1**. A solution of $[Ru_3(CO)_{12}]$ (200 mg, 0.312 mmol) and MePhS(O)NH (50 mg, 0.322 mmol) in THF (25 mL) was heated in a pressure Schlenk tube to 100 °C for 2 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and separated by thin-layer chromatography (silica gel, CH_2Cl_2/cyclohexane 3:1). From the yellow main band, **1** was extracted with THF and crystallized from a CH_2Cl_2/hexane mixture (yield 180 mg, 81%). A second pale-yellow band contained a small quantity of **2**.

(11) X-ray Structure Analysis of (*R*)-**1**. Crystal data: $C_{16}H_9NO_{10}Ru_3S$, M_r = 710.51, crystal dimensions 0.46 mm × 0.46 mm × 0.06 mm, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 11.891$ (1) Å, $b = 12.857(1)$ Å, $c = 14.187(2)$ Å, $V = 2168.9(4)$ Å^3, $\delta_{calcd} = 2.176$ g/cm^3, $2\theta_{max} = 60°$, Mo Kα (λ = 0.71073 Å), ω/θ-scan, −120 °C, 3685 measured reflections, 3600 independent and used, 3098 with $I > 2\sigma(I)$. No absorption correction was applied, and the structure was solved by direct methods using SHELXS-86[24] and refined anisotropically (non hydrogen atoms) using SHELXL-93[25] (281 parameters). The methyl and phenyl protons were included in the theoretical positions, and the hydride was located from a difference map and fixed (U_{iso} = 0.003 Å^3. R1 ($I > 2\sigma(I)$/all) = 0.046/0.061, wR2 ($I > 2\sigma(I)$/all) = 0.087/0.096, refinement against $|F|^2$, residual electron density max/min = 1.302/−1.063 e Å^3. Absolute structure paramater (asp) = −0.07(8) [asp = 0 (within 3 esd's) for correct absolute structrue[26]]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre, 12 Union Road, Cambridge, U.K. CB2 1EZ.

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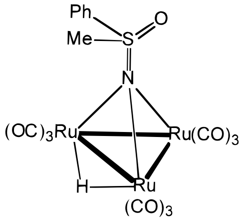
a formal electron count of 48 for **1**, would imply the nitrogen cap to act as a five-electron donor ligand [$N^{-}-S^{+}OMePh$)], however, no 5e-μ_3-NR cap has been reported so far.[4] Furthermore, the lack of two electrons with respect to the effective atomic number rule is in accordance with the structural data of **1** (Figure 2): The sulfur−nitrogen bond in *(R)*-**1** (1.566 Å) lies within the range of N═S double bonds; in comparison with methionylsulfoximine (1.529 Å),[12] the sulfur−nitrogen distance in *(R)*-**1** is only slightly longer.

The bond angles at the sulfur atom reveal the stereogenic center to be tetrahedrally coordinated; the three nitrogen−ruthenium distances display an almost symmetrical coodination of the sulfoximido ligand to the metal core. The Ru_3 triangle, however, is distincly unsymmetrical, the longer Ru−Ru distance (2.831 Å) being due to the μ_2-H bridge (see Figure 2 for details). The other two ruthenium−ruthenium distances are significantly shorter than the average value of 2.854 Å found in [$Ru_3(CO)_{12}$].[13] This shortening of Ru(1)−Ru(2) [2.674(1) Å] and Ru(2)−Ru(3) [2.683(1) Å] may be interpreted in terms of the electron-deficient character of the metal triangle, since these distances are already close to values observed for ruthenium−ruthenium double bonds (2.26−2.67 Å).[14] On the other hand, rather short distances have been observed also for Ru−Ru single bonds in other closed Ru_3 clusters containing μ_3-NR capping ligands: 2.669, 2.784, and 2.865 Å in [(μ_2-H)$Ru_3(CO)_8$(μ_3-NPh) (μ_1-η^2-$MeOC_6H_3NNC_6H_4OMe$)][15] and 2.740, 2.740, and 2.762 Å in [$Ru_3(CO)_9$(μ_3-CO)(μ_3-NOMe)].[16] The short values of these Ru−Ru bonds, however, may be explained by the action of the μ_1-η^2 ligand in the first case and by the presence of two μ_3 ligands in the second case, as argued by the authors.[16]

The unsaturated character of **1** is further reflected in the reversible addition of carbon monoxide: In THF, **1** takes up CO (1.5 bar, 20 °C) and yields quantitatively the saturated cluster [(μ_2-H)$Ru_3(CO)_{10}$\{μ_2-NS(O)MePh\}] (**2**).[17] Heating a THF solution of **2** to 100 °C in a pressure Schlenk tube causes a release of CO and results in the restoration of **1**. A somewhat related, but not reversible process has been reported for the doubly bridged complex [(μ_2-H)$Ru_3(CO)_{10}$(μ_2-NCHPh)], which converts with H_2 into the triply bridged complex [(μ_2-H)$_2$-$Ru_3(CO)_{10}$(μ_3-NCH_2Ph)].[18]

$$\underset{\mathbf{1}}{[(\mu_2\text{-H})Ru_3(CO)_9\{\mu_3\text{-NS(O)MePh}\}]} + CO \rightleftharpoons \underset{\mathbf{2}}{[(\mu_2\text{-H})Ru_3(CO)_{10}\{\mu_2\text{-NS(O)MePh}\}]}$$

The two trinuclear clusters **1** and **2** can be separated by chromatography on silica gel and are obtained as orange-yellow solids. Whereas **1** crystallizes easily from dichloromethane−hexane mixtures, attempts to obtain X-ray quality crystals of **2** failed. The structure proposed for **2** is based on the spectroscopic data (Table 1, Supporting Information). The infrared spectrum of **1** displays the typical carbonyl pattern (2082 m, 2056 s, 2029 vs, 1997 s, 1954 m cm^{-1}) of the $Ru_3(CO)_9$ fragment,[19] while **2** gives rise to a ν(CO) absorption pattern (2099 w, 2062 s, 2051 s, 2013 vs, 1980 w, 1952 m cm^{-1}) characteristic of a $Ru_3(CO)_{10}$ base bridged by two μ_2-ligands.[20] This is in line with complexes related to **2**, such as [(μ_2-H)-$Ru_3(CO)_{10}$(μ_2-NO)][21] and [(μ_2-H)$Ru_3(CO)_{10}$(μ_2-NCO)].[22] The ^{1}H NMR spectrum of **2** shows, in addition to the expected signals for the phenyl and methyl protons, a singlet at −14.16 ppm for the μ_2-hydrido ligand; in the ^{13}C NMR spectrum of **2** all the carbonyl ligands show up as 10 individual signals (Table 1, Supporting Information). The FAB mass spectrum of **2** (matrix: *o*-nitropenyl octyl ether) exhibits all the fragments of the series [$HRu_3(CO)_n(NSOMePh)]^+$ (n = 1−10) with the expected isotope distribution (molecular peak *m/z*= 740).[23]



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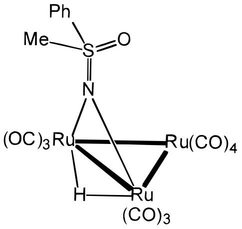

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As opposed to the electron-precise cluster **2**, which shows a rigid molecular structure in solution over a temperature range of +25 to −80 °C, the variable-temperature ^{13}C NMR spectra of the electron-deficient cluster **1** reveals a fluxional behaviour in solution. At ambient temperature, a single carbonyl resonance at δ = 194.3 ppm indicates the equivalence of all the nine CO ligands of **1** in solution, either by a complete carbonyl scrambling about the Ru_3 core or by the scrambling of the hydride over the three edges coupled with the pseudorotation of the three $Ru(CO)_3$ units. After coalescence at −20 °C, three CO signals appear at −80 °C, being indicative of three groups of equivalent CO ligands in **1**. A complete freezing out of the intramolecular carbonyl exchange to give the solid state structure with nine individual carbonyl ligands was not attained down to −80 °C.

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Supporting Information Available: Table 1 (IR and NMR data of **1** and **2**) and Figure 1 (CD spectra of *(R)*-**1** and *(S)*-**1**) as well as tables (Tables 1S-8S) giving crystal data and details of the structure determination and refinement, atomic coordinates and equivalent isotropic dsiplacement parameters, bond lengths and angles, torsion angles, anisotropic displacement parameters, and hydrogen atom coordinates (10 pages). Ordering information is given on any current masthead page.

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