Inorg. Chem. **2004**, *43*, 3327–3328

Inorganic Chemistry
Communication

Synthesis of the New, Cubane-like W_3S_4Co Cluster Core. Completion of the Homologous Series $[(\eta^5\text{-Cp}')_3M_3S_4Co(CO)]$ (M = Cr, Mo, W)

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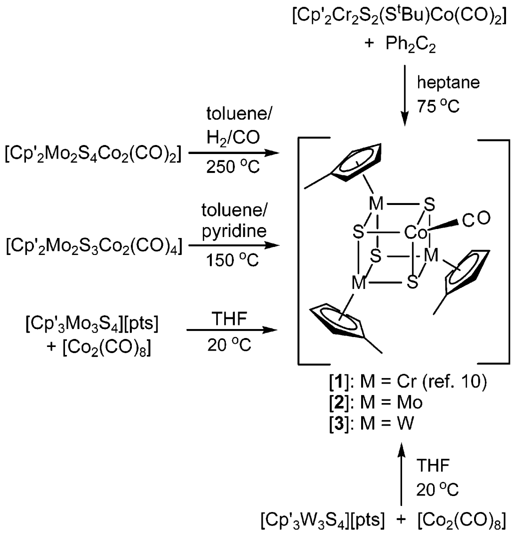
Received February 28, 2004

Reaction between the cluster salts $[(\eta^5\text{-Cp}')_3M_3S_4][\text{pts}]$ (M = Mo, W; Cp′ = methylcyclopentadienyl; pts = *p*-toluenesulfonate) and $[Co_2(CO)_8]$ yielded the electroneutral clusters $[(\eta^5\text{-Cp}')_3M_3S_4Co(CO)]$. The molecular structure of $[(\eta^5\text{-Cp}')_3W_3S_4Co(CO)]$ was determined by single-crystal X-ray diffraction methods. The unprecedented 60 electron W_3S_4Co cluster completes a homologous series of heterobimetallic clusters, $[(\eta^5\text{-Cp}')_3M_3S_4Co(CO)]$ (M = Cr, Mo, W), containing a cubane-like core motif.

During the last two decades, numerous heterobimetallic derivatives of the incomplete cubane-like cluster cores M_3S_4 (M = Mo, W) have been prepared.[1,2] Initially, these M_3S_4M' clusters (M′ = main group or transition metal) were synthesized and studied almost exclusively in aqueous solution. Recently, the preparation of methylcyclopentadienyl-substituted M_3S_4 clusters has enabled the rational synthesis of some hitherto unknown M_3S_4M' cluster cores (M′ = Ru, Os, Ir, Pd) by heterometal insertion in organic media.[3−6]

Heterobimetallic clusters containing a cubane-like Cr_3S_4M' core are much less investigated than the analogous Mo_3S_4M' or W_3S_4M' clusters. Monometallic $[(H_2O)_9Cr_3S_4]^{4+}$ or $[(\eta^5\text{-Cp}')_3Cr_3S_4]^+$ cluster cations have not been prepared to date, and a rational synthesis of Cr_3S_4M' clusters by heterometal insertion into the Cr_3S_4 cluster core has therefore not been possible. The few known bimetallic Cr_3S_4M' clusters (M′ = V,[7] Nb,[7] Fe,[8,9] Co[10]) have all been obtained by self-assembly reactions from precursor complexes of lower nuclearity. $[(\eta^5\text{-Cp}')_3Cr_3S_4Co(CO)]$ ([**1**]) was, for example, prepared by heating a trinuclear Cr_2Co sulfide cluster in heptane in the presence of diphenylacetylene.[10]

Scheme 1. Formation of $[(\eta^5\text{-Cp}')_3M_3S_4Co(CO)]$ clusters (M = Cr, Mo, W)



Our investigations on the reactivity of the $[(\eta^5\text{-Cp}')_3Mo_3S_4]^+$ cluster cation toward dicobalt octacarbonyl have now established a new, high yield synthesis of $[(\eta^5\text{-Cp}')_3Mo_3S_4Co(CO)]$ ([**2**]). Previously [**2**] had been obtained by self-assembly reactions of methylcyclopentadienyl-substituted $Mo_2Co_2S_x$ clusters (*x* = 3, 4) at high temperatures in an autoclave (see Scheme 1).[11] The new synthetic procedure in solution could also be applied to the reaction between the

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10.1021/ic049742+ CCC: $27.50

$[(\eta^5\text{-Cp}')_3W_3S_4]^+$ cation and $[Co_2(CO)_8]$, which led to the isolation of the unprecedented cluster $[(\eta^5\text{-Cp}')_3W_3S_4Co(CO)]$ ([**3**]). This establishes $[(\eta^5\text{-Cp}')_3M_3S_4Co(CO)]$ (M = Cr, Mo, W) as the first homologous series of M_3S_4M' clusters where the variation of the group 6 metal spans all three transition periods.

Clusters [**2**] and [**3**] were prepared at room temperature by contacting a solution of $[Co_2(CO)_8]$ in THF with a suspension of $[(\eta^5\text{-Cp}')_3M_3S_4][\text{pts}]$ (M = Mo, W) in THF. Evolution of CO gas and the concomitant dissolution of the clusters were observed, which led, after 15 min reaction time, to a nonturbid solution. Purification of the reaction product by column chromatography on alumina afforded a single band ([**2**], brown; [**3**], green) that could be eluted with THF. After precipitation by means of pentane, [**2**] and [**3**] were isolated as microcrystalline powders in almost quantitative yields.[12] As dry powders, the clusters are air-stable, whereas solutions of [**2**] and [**3**] require manipulation under strictly inert conditions.

The formation of the electroneutral clusters [**2**] and [**3**] requires the insertion of a $[Co(CO)]^-$ fragment into the $[(\eta^5\text{-Cp}')_3M_3S_4]^+$ cation (M = Mo, W). The fragment was apparently formed by disproportionation of $[Co_2(CO)_8]$ into a Co^{-1} species and a cobalt−pts salt, whose exact composition, however, was not identified. A reactant ratio $[Co_2(CO)_8]$:$[(\eta^5\text{-Cp}')_3M_3S_4]^+$ of 1:1 led to quantitative transformation of $[(\eta^5\text{-Cp}')_3M_3S_4]^+$, whereas application of less than 1 molar equiv of $[Co_2(CO)_8]$ left a part of $[(\eta^5\text{-Cp}')_3M_3S_4][\text{pts}]$ unreacted in suspension. The cobalt−pts salt formed in the disproportionation reaction could be eluted as a second, gray-brown band from the separatory column by a strongly polar mixture of CH_2Cl_2/MeOH (3/1). This material did not display any carbonyl bands in the infrared spectrum, but displayed intense S═O bands that indicate the presence of the pts anion.

The infrared spectrum of [**3**] displayed a sharp carbonyl band at 1881 cm^{-1}. Similar positions have previously been seen for the carbonyl bands of the lighter homologues of [**3**] ([**1**], ν_{CO} = 1900 cm^{-1}; [**2**], ν_{CO} = 1903 cm^{-1}).[10,11] Contrary to previous interpretations, recent Fenske−Hall molecular orbital calculations on the electronic structure in heterobimetallic, cubane-like clusters showed that transition metal heteroatoms M′ do not occur in an oxidized state in a M_3S_4M' cluster core.[13] The low wavenumber of the carbonyl band for Co-containing clusters may be explained by the high energy of the Co orbitals, which enables a strong interaction with the CO $2\pi^*$ orbitals.

Single crystals of [**3**] were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of [**3**]. The molecular structure of [**3**] (see Figure 1) is isostructural with the lighter homologues [**1**] and [**2**].[14] However, due to different temperatures applied during data acquisition, the structural parameters for the chromium-based cluster [**1**] cannot be directly compared with those of its heavier homologues [**2**] and [**3**]. The crystal structure confirmed the presence of 6 M−M bonds between the metal atoms in the cluster core; thus, all metal atoms in the 60 VSE (valence shell electron) cluster obey the 18 electron rule. The interatomic distances of [**3**] show strong similarity with the bond lengths of the molybdenum-based cluster [**2**].[11] However, the average Co−S distance (2.200(11) Å) in [**3**] is slightly elongated compared to $Co-S_{av}$ = 2.178(19) Å in [**2**]. In turn, this is compensated by a shorter Co−carbonyl bond length (Co−C(1) = 1.736(12) Å in [**3**] vs 1.749(30) Å in [**2**]).

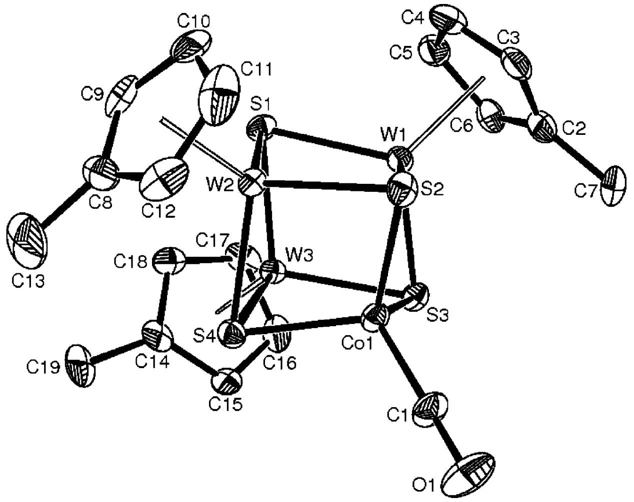

Figure 1. ORTEP drawing of $[(\eta^5\text{-Cp}')_3W_3S_4Co(CO)]$ [**3**] showing thermal ellipsoids at the 30% probability level. All H atoms have been removed for clarity. Selected bond lengths (Å): $W-W_{av}$ 2.833(3), $W-Co_{av}$ 2.773(5), $W-S_{av}$ 2.341(9), Co−S(2) 2.213(4), Co−S(3) 2.191(3), Co−S(4) 2.196(4), Co−C(1) 1.736(12).

The preparation of the new W_3S_4Co cluster core by an organometallic synthesis route is an example of how the extension of cluster synthesis into the organometallic domain may bring about new heterobimetallic M_3S_4M' clusters previously not isolable from aqueous medium. Experiments to insert fragments of early transition metal complexes into the $[(\eta^5\text{-Cp}')_3M_3S_4]^+$ cluster cation (M = Mo, W) are currently in progress.

Supporting Information Available: Synthetic procedure for [**2**] and [**3**]; X-ray structural data for [**3**] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Analytic data for [**3**]: Anal. Calcd for $C_{19}H_{21}Co_3OS_4W_3$: C, 22.73; H, 2.10; S, 12.77. Found: C, 22.99; H, 1.92; S, 12.85. ^1H NMR ($CDCl_3$, δ/ppm): 2.24 (s, 9 H); 5.27 (s, 6 H); 5.44 (s, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ/ppm): 15.77, 86.93, 87.96, 107.65 (CO signal not detected). IR (KBr, cm^{-1}): 1881 (ν_{CO}).

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(14) Crystallographic data for [**3**]: $C_{19}H_{21}CoOS_4W_3$, fw 1004.08 g mol^{-1}, monoclinic, space group $P2_1/n$, $a = 8.150(2)$ Å, $b = 18.309(3)$ Å, $c = 15.111(4)$ Å, $\beta = 91.58(2)°$, $V = 2253.7(9)$ Å^3, $T = 293(2)$ K, $Z = 4$, $\rho_{calc} = 2.959$ Mg m^{-3}, $\mu = 16.365$ mm^{-1}, R1 = 0.0420, wR2 = 0.0982 for $I > 2\sigma(I)$.