Articles

Methylcyclopentadienyl-Substituted Tungsten(IV) Sulfido Cluster $[(\eta^5\text{-Cp}')_3W_3S_4]^+$ and Its Heterobimetallic Derivative $[(\eta^5\text{-Cp}')_3W_3S_4Ni(PPh_3)]^+$

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Received October 31, 2000

The aqueous cluster salt $[(H_2O)_9W_3S_4][pts]_4{\cdot}9H_2O$ (pts = *p*-toluenesulfonate) was converted to the methylcyclopentadienyl (Cp′) substituted cluster $[(\eta^5\text{-Cp}')_3W_3S_4][pts]$ ([**1**][pts]) from which the cubane-like cluster $[(\eta^5\text{-Cp}')_3W_3S_4Ni(PPh_3)][pts]$ ([**2**][pts]) was obtained by reaction with $Ni(cod)_2$ and PPh_3. [**2**][pts] was characterized by X-ray crystal structure analysis.

Introduction

The incomplete cubane-like cluster cores $M_3E_4^{4+}$ (M = Mo, W; E = O,S) play an important role in the chemistry of molybdenum(IV) and tungsten(IV). The $Mo_3S_4^{4+}$ cluster core was first prepared in 1971 in the form of $[(\eta^5\text{-Cp})_3Mo_3S_4][Sn(CH_3)_3Cl_2]$ (Cp = cyclopentadienyl), a product obtained from the reaction of $[Mo(\eta^5\text{-Cp})(CO)_3Cl]$ with $[Sn(CH_3)_3]_2S$ in 1,2-dimethoxyethane.[1] However, it was when aqueous routes to $Mo_3S_4^{4+}$ and $W_3S_4^{4+}$ cluster cores were discovered in the 1980s that the chemistry of these sulfido clusters first flourished.[2−6] Recently we found a rational synthesis route to $[(\eta^5\text{-CpR})_3Mo_3S_4][pts]$ (R = H, CH_3; pts = *p*-toluenesulfonate) that employs $[(H_2O)_9Mo_3S_4][pts]_4{\cdot}9H_2O$ as the starting material.[7,8] By using a similar procedure, we are now able to report the first synthesis of a cyclopentadienyl-type substituted $W_3S_4^{4+}$ cluster.

The incorporation of heterometals, M′, into the geometrically incomplete cubane-like cluster cores $M_3S_4^{4+}$ to form cluster compounds containing the M_3S_4M' motif has been successfully accomplished in a considerable number of cases: for Mo in 22 cases (see ref 9) and for W in 6 cases (In,[10] Ge,[10] Sn,[11] Mo,[12] Ni,[13] and Cu[14,15]). Traditionally, incorporation of heterometal atoms is carried out in aqueous solution by the reaction of $[(H_2O)_9Mo_3S_4]^{4+}$ with metal powder or with metal ions and a reducing agent (typically $NaBH_4$).[16,17] In the case of the less easily reduced $W_3S_4^{4+}$ cluster core, this route is not so likely to be successful, and this may explain[15] why the heterobimetallic chemistry of $W_3S_4^{4+}$ is less well developed than that of $Mo_3S_4^{4+}$. We have recently found that a nonreductive incorporation can be achieved in organic solvents by reacting $[(\eta^5\text{-CpR})_3Mo_3S_4]^+$ with low-oxidation-state (organometallic) compounds of groups 6,[7] 8, 9,[9] and 10[8] heterometals. As we shall exemplify here, this synthetic approach may also be applied in the case of $[(\eta^5\text{-Cp}')_3W_3S_4]^+$ (Cp′ = $CpCH_3$), and a more extensive heterobimetallic chemistry of $W_3S_4^{4+}$ may thus be about to unfold.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents employed were distilled from appropriate drying agents prior to use. NMR spectra were obtained with a Varian UNITY 300 spectrometer (300.1 MHz for ^1H; 121.4 MHz for ^{31}P; 75.5 MHz for ^{13}C) with TMS as an internal standard or H_3PO_4 as an external standard (downfield positive). FAB$^+$ mass spectra were collected with a JEOL SX-102 spectrometer. UV/vis spectra were collected with a Perkin-Elmer UV/vis spectrometer Lambda 16. Elemental analyses were performed by DB Lab, Dansk Bioprotein A/S, Odense, Denmark.

$Ni(cod)_2$ (cod = 1,5-cyclooctadiene) was purchased from Strem Chemicals. TlCp′ was prepared by reaction of thallium ethoxide with Cp′H.[18] $[(H_2O)_9W_3S_4][pts]_4{\cdot}9H_2O$ was prepared according to a published

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precedure.[19]

Synthesis of [(η^5-Cp′)$_3$W$_3$S$_4$][pts] ([1][pts]). [(H$_2$O)$_9$W$_3$S$_4$][pts]$_4$·9H$_2$O (1.0 g, 0.592 mmol) and a catalytic amount (ca. 10 mg) of Hpts were stirred in 20 mL of degassed (C$_2$H$_5$O)$_3$CH for 18 h. The solution was concentrated in a vacuum to approximately 5 mL, from which a brown solid precipitated. Diethyl ether (20 mL) was added, and the solid was allowed to settle. After removal of the supernatant solution, this process was repeated twice until the solution was almost colorless. The mixture was dried in a vacuum, yielding a brown powder. CH$_3$CN (10 mL) was added, and the red solution was stirred for 1 h. The mixture was evaporated to dryness, and the residue was dissolved in 20 mL of THF. A clear solution of 515 mg (1.815 mmol) of TlCp′ in CH$_2$Cl$_2$ (30 mL) was added whereupon a light-brown precipitate formed. After the mixture was stirred for 2 h, the precipitate was removed by filtration and the filtrate was evaporated to dryness. The crude product was purified chromatographically on a silica column (30 cm × 2 cm) using mixtures of CH$_2$Cl$_2$ and CH$_3$OH with increasing polarity (20/1, 15/1, 10/1) as eluent. The intensively purple 10/1 eluate was collected and evaporated to dryness. Yield: 146 mg (0.129 mmol, 22%).

^{1}H NMR (CDCl$_3$; δ/ppm): 2.30 (s, 3 H, pts); 2.33 (s, 9 H, Cp′); 5.93 (t, $J = 2.1$ Hz, 6 H, Cp′); 6.24 (t, 6 H, Cp′); 7.10 (d, $J = 7.8$ Hz, 2 H, pts); 7.80 (d, 2 H, pts). ^{13}C{^{1}H} NMR (CDCl$_3$; δ/ppm): 15.4 (s, Cp′); 21.1 (s, pts); 94.3 (s, Cp′); 95.7 (s, Cp′); 116.9 (s, Cp′); 126.0 (s, pts); 128.2 (s, pts); 138.2 (s, pts); 144.7 (s, pts). FAB$^+$ mass spectrum (*m/z* (% abundance)): 917 (M$^+$ − pts, 84); 838 (M$^+$ − pts - Cp′, 10). UV/vis (MeOH; λ_{max}/nm (ϵ/dm^{3}mol^{-1}cm^{-1})): 342 (4100); 552 (1300). Anal. Calcd for C$_{25}$H$_{28}$O$_3$S$_5$W$_3$·$^1/_2$CH$_2$Cl$_2$ (M_r = 1130.81): C, 27.09; H, 2.59; S, 14.18. Found: C, 26.91; H, 2.83; S, 14.38.

Synthesis of [(η^5-Cp′)$_3$W$_3$S$_4$Ni(PPh$_3$)][pts] ([2][pts]). To a suspension of [**1**][pts] (61 mg, 0.056 mmol) in THF (10 mL) was added a suspension of Ni(cod)$_2$ (15.4 mg, 0.056 mmol) in 5 mL of THF. When the mixture was stirred for 3 h, the suspended solid gradually turned brown and partially went into solution. PPh$_3$ (14.7 mg, 0.056 mmol) was added to the mixture. After the mixture was stirred for 5 min, a green-brown microcrystalline precipitate formed. This was isolated by filtration, washed with pentane, and dried in a vacuum. Yield: 62 mg (0.044 mmol, 78%).

^{1}H NMR (CDCl$_3$; δ/ppm): 2.25 (s, 9 H, Cp′); 2.28 (s, 3 H, pts); 5.58 (t, $J = 2.1$ Hz, 6 H, Cp′); 5.70 (t, 6 H, Cp′); 7.07 (d, $J = 7.8$ Hz, 2 H, pts); 7.15 (m, 6 H, PPh$_3$); 7.36 (m, 9 H, PPh$_3$); 7.85 (d, 2 H, pts). ^{31}P{^{1}H} NMR (CDCl$_3$; δ/ppm): 12.7 (s). FAB$^+$ mass spectrum (*m/z* (% abundance)): 1238 (M$^+$ − pts, 100); 976 (M$^+$ − pts − PPh$_3$, 98); 897 (M$^+$ − pts − PPh$_3$ − Cp′, 14). UV/vis (MeOH; λ_{max}/nm (ϵ/dm^{3}mol^{-1}cm^{-1})): 267 (18200); 479 (1500); 608 (900). Anal. Calcd for C$_{43}$H$_{43}$NiO$_3$PS$_5$W$_3$ (M_r = 1409.33): C, 36.65; H, 3.08; S, 11.37. Found: C, 36.88; H, 3.01; S, 11.23.

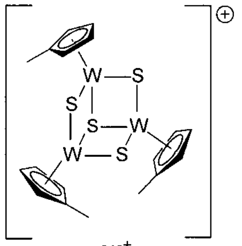
X-ray Crystallography. X-ray data for [**2**][pts] were collected at 293(2) K on a Nonius MACH 3 diffractometer using graphite-monochromated Mo Kα radiation (0.710 69 Å). The structure was solved by direct methods (SIR-97)[20] and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing the WinGX[21] package and the relevant programs (SHELXL-97,[22] ORTEP-3 [23]) implemented therein. H atoms were included in the final structural model, assuming ideal geometry and using appropriate riding models. Crystal and refinement details are given in Table 1.

Table 1. Crystal and Refinement Data for [(η^5-Cp′)$_3$W$_3$S$_4$Ni(PPh$_3$)][pts] ([**2**][pts])

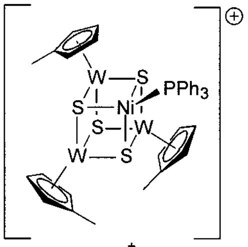
empirical formula	C$_{43}$H$_{43}$NiO$_3$PS$_5$W$_3$
fw	1409.30
cryst syst	monoclinic
space group	$P2_1/n$ (No.14)
reflns for cell measurement (deg)	25 (9.2 < θ < 13.7)
a (Å)	9.469(2)
b (Å)	10.834(1)
c (Å)	41.839(6)
β (deg)	92.04(2)
vol (Å^3)	4289.4(12)
Z	4
calcd density (Mg m^{-3})	2.182
abs coeff (mm^{-1})	8.771
F(000)	2680
cryst dimens (mm)	0.38 × 0.28 × 0.25
θ range for data collection (deg)	2.56−25.08
index ranges	$-11 \le h \le 11$; $0 \le k \le 12$; $0 \le l \le 49$
reflns collected	8359
unique reflns	7597 (R_{int} = 0.032)
abs correction	ψ scans (T_{max} = 0.218; T_{min} = 0.135)
data/restraints/parameters	7597/0/509
GOF on F^2	1.058
final R indices [for 5713 $F_o > 4\,\sigma(F_o)$]	R1 = 0.0459; wR2 = 0.1029
R indices (all data)	R1 = 0.0754; wR2 = 0.1128

Results and Discussion

To convert the aqueous compound [(H$_2$O)$_9$W$_3$S$_4$][pts]$_4$·9H$_2$O into the organically soluble [(η^5-Cp′)$_3$W$_3$S$_4$][pts] cluster compound, the same reaction strategy of a series of ligand exchange reactions was applied as for the transformation of [(H$_2$O)$_9$Mo$_3$S$_4$][pts]$_4$·9H$_2$O to [(η^5-Cp)$_3$Mo$_3$S$_4$][pts], which was recently developed in our laboratory.[7] Purple [(H$_2$O)$_9$W$_3$S$_4$][pts]$_4$·9H$_2$O was reacted with triethyl orthoformate to convert the aqua ligands into ethanol ligands. A further ligand replacement with acetonitrile at the very hydrolysis-sensitive ethanol-substituted cluster was carried out in order to destroy traces of triethyl orthoformate. Finally the cluster material was stirred in THF to coordinate nonprotic thf ligands to the cluster core. At this stage a stoichiometric amount (3 equiv/mol) of methylcyclopentadienyl thallium (TlCp′) was added to the cluster solution. An immediate precipitation of light-brown Tl[pts] and the formation of a purple-brown solution were observed. After separation from Tl[pts], the cluster compound [(η^5-Cp′)$_3$W$_3$S$_4$][pts] ([**1**][pts]) was purified by column chromatography on silica and isolated as an intensely purple solid.



[**1**]$^+$



[**2**]$^+$

An NMR spectroscopic characterization of [**1**][pts] confirmed the high overall symmetry of the cluster cation, the Cp′ ligands giving rise to only one set of signals in the ^{1}H NMR spectrum: a singlet at 2.33 ppm for the methyl groups and two triplets at δ = 5.93 and 6.24 ($^3J_{HH}$ = 2.1 Hz) caused by the AA′BB′ spin systems of the ring protons. Because of a rapid rotation of the Cp′ rings on the NMR time scale at room temperature, no

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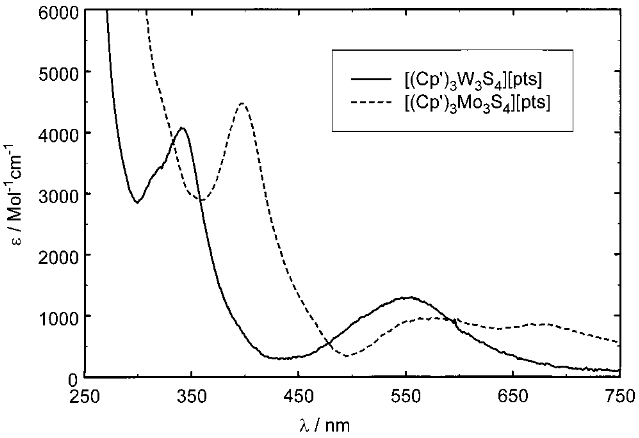

Figure 1. UV/vis spectra of $[(\eta^5\text{-Cp}')_3W_3S_4][pts]$ ([**1**][pts]) and $[(\eta^5\text{-Cp}')_3Mo_3S_4)][pts]$ [8] in methanol.

couplings were detected in the $^{13}C\{^1H\}$ NMR spectrum between ^{13}C nuclei and the NMR-active ^{183}W nuclei. Therefore, the $^{13}C\{^1H\}$ NMR spectrum consisted only of nine singlets (four Cp′, five pts signals). The FAB$^+$ mass spectrum confirmed the presence of the cluster cation $[\mathbf{1}]^+$ at $m/z = 917$ with an 84% relative abundance before the subsequent loss of Cp′ ligands. The UV/vis spectrum is displayed in Figure 1. Relative to the analogous molybdenum compound, all absorption bands are blue-shifted. No decomposition of [**1**][pts] in an aerated methanol solution was observed by UV/vis spectroscopy over a period of 24 h.

In experiments carried out in order to incorporate a Ni atom into the geometrically incomplete cubane-like $Mo_3S_4^{4+}$ cluster,[8] a very high reactivity was found for the $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ cluster toward $Ni(cod)_2$ in THF, visible by the almost instant formation of a brown solution containing the $[(\eta^5\text{-Cp}')_3Mo_3S_4Ni]^+$ cluster cation. An analogous reaction between [**1**][pts] and $Ni(cod)_2$ in THF showed, however, only a very slow transformation presumably due to the very low solubility of [**1**][pts] in THF. After 3 h reaction time, a violet-brown solution containing brown suspended material had formed. The addition of 1 equiv of PPh_3, however, caused the precipitation of a homogeneous, brown-green microcrystalline solid, which, after isolation, was shown by spectroscopic analyses to be the cubane-type cluster compound $[(\eta^5\text{-Cp}')_3W_3S_4Ni(PPh_3)][pts]$ ([**2**][pts]). Most indicative of the formation of [**2**][pts] was the FAB$^+$ mass spectrum with a parent peak for the cluster cation $[\mathbf{2}]^+$ at $m/z = 1238$ with a relative abundance of 100%, followed by a signal of almost equal intensity for the $[(\eta^5\text{-Cp}')_3W_3S_4Ni]^+$ fragment. In the $^{31}P\{^1H\}$ NMR spectrum, the phosphane ligand resonated at $\delta = 12.2$.

To confirm crystallographically the cubane-type structure deduced from spectroscopic analyses, single crystals of [**2**][pts] were grown by slow diffusion of pentane into a CH_2Cl_2 solution of [**2**][pts] at room temperature. The compound crystallized in well-defined, large plates. With a suitable specimen an X-ray structure determination was carried out, and the result is depicted in an ORTEP plot (Figure 2). Details of the data collection and structure refinement can be found in Table 1, and a list of selected bond lengths and angles is given in Table 2.

The crystal structure analysis confirmed the presence of a cubane-like W_3S_4Ni cluster core whose innermost part is formed by a tetrahedral arrangement of three tungsten atoms and one nickel atom. Each tetrahedral face is capped by a μ_3-coordinated sulfido ligand, thus generating the cubane-like structure. With an average W−Ni distance of 2.733 Å and an average W−W distance of 2.809 Å, the bond lengths between the metal atoms are consistent with the presence of single bonds. These bond lengths are, however, considerably longer than the corresponding distances in two other reported W_3S_4Ni clusters compounds, $[\{(H_2O)_9W_3S_4Ni\}_2][pts]_8\cdot 20H_2O$ (W−Ni$_{av}$ = 2.67(3) Å; W−W$_{av}$ = 2.737(7) Å)[13] and $[(H_2O)_9W_3S_4Ni(C_2H_4)][pts]_4\cdot {}^1/_2(Hpts)\cdot 6H_2O$ (W−Ni$_{av}$ = 2.701(2) Å; W−W$_{av}$ = 2.7137(9) Å).[24] These differences can be attributed to a weakening of metal−metal bonds caused by the better electron-accepting properties of the ligands both at the tungsten atoms and the nickel atoms in [**2**][pts] compared to the aqua-substituted $W_3S_4Ni^{4+}$ derivatives. The average W−S distances of 2.329 Å and Ni−S bond lengths of 2.215 Å are in the usual range of metal−sulfur single bonds. Because of the differences in size between the tungsten and the nickel atoms, the cubane-like cluster framework is distorted with respect to the Ni vertex of the cluster cube. This fact is apparent by the size of the S−M−S angles, which lie in a range 99.27(10)−104.64(11)° at the tungsten atoms but are larger than 107° at the Ni atom. Thus, the Ni atom is pulled to the center of the cluster cube.

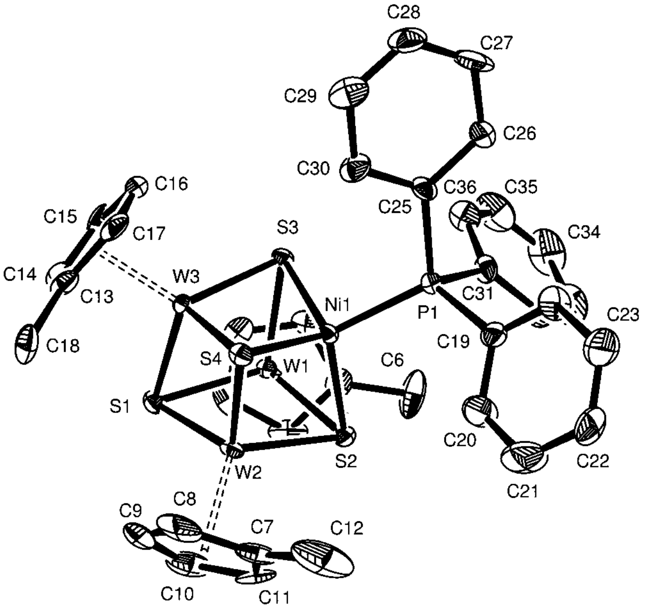

Figure 2. ORTEP plot of the cluster cation $[(\eta^5\text{-Cp}')_3W_3S_4Ni(PPh_3)]^+$ ($[\mathbf{2}^+]$). Atoms are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^5\text{-Cp}')_3W_3S_4Ni(PPh_3)][pts]$ ([**2**][pts])

W(1)−W(2)	2.8108(7)	W(1)−Ni(1)	2.723(2)
W(1)−W(3)	2.8085(8)	W(2)−Ni(1)	2.739(1)
W(2)−W(3)	2.8081(7)	W(3)−Ni(1)	2.737(2)
Ni(1)−S(2)	2.225(3)	Ni(1)−S(4)	2.210(3)
Ni(1)−S(3)	2.209(3)	Ni(1)−P(1)	2.143(3)
W(1)−Ni(1)−W(2)	61.94(3)	S(2)−Ni(1)−S(3)	107.5(1)
W(1)−Ni(1)−W(3)	61.90(3)	S(2)−Ni(1)−S(4)	107.1(1)
W(2)−Ni(1)−W(3)	61.70(3)	S(3)−Ni(1)−S(4)	107.0(1)
W(1)−Ni(1)−P(1)	136.8(1)	S(2)−Ni(1)−P(1)	112.9(1)
W(2)−Ni(1)−P(1)	151.4(1)	S(3)−Ni(1)−P(1)	104.0(1)
W(3)−Ni(1)−P(1)	141.4(1)	S(4)−Ni(1)−P(1)	117.7(1)

The Ni−P distance of 2.143(3) Å is rather short in comparison to other tetrahedral Ni^0−P compounds ($[Ni(CO)_2(PPh_3)_2]$: Ni−P = 2.221 Å).[25] The coordination polyhedron at the Ni atom can

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be described as a tetrahedron (if metal−metal bonds are neglected) but with severe distortion due to a bending of the PPh_3 ligand to one side, the S−Ni−P angles thereby varying from 104.04(12)° to 117.72(13)°. The "oblique" position of the PPh_3 ligand may be due to intermolecular packing forces and the presence of the anion $[pts]^-$, which pushes the phosphane ligand away from a 3-fold axis at the cluster core.

With the successful incorporation of a Ni atom into the geometrically incomplete $W_3S_4^{4+}$ cluster core by a strategy similar to that employed for the analogous $Mo_3S_4^{4+}$ cluster, other late transition metal $W_3S_4^{4+}$ derivatives may be anticipated. A study on the incorporation of platinum metals into the $W_3S_4^{4+}$ core is currently in progess.

Acknowledgment. This work was supported by the European Commission (TMR Network "Metal Clusters in Catalysis and Organic Synthesis", Contract FMRX-CT96-0091, postdoctoral grant to K.H.). We thank our TMR partner at the University of Lund, Sweden, for allowing access to their Varian UNITY 300 MHz NMR spectrometer. We also thank Mrs. A. Nielsen for the preparation of $[(H_2O)_9W_3S_4][pts]_4{\cdot}9H_2O$.

Supporting Information Available: X-ray crystallographic files for [**2**][pts] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001194M