Heterobimetallic, Cubane-like Mo_3S_4M' Cluster Cores Containing the Noble Metals M′ = Ru, Os, Rh, Ir. Unprecedented Tri(μ-carbonyl) Bridge Between Ruthenium Atoms in $[\{(\eta^5\text{-}Cp')_3Mo_3S_4Ru\}_2(\mu\text{-}CO)_3]^{2+}$

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Reaction of the methylcyclopentadienyl (Cp′) cluster compound $[(\eta^5\text{-}Cp')_3Mo_3S_4]$[pts] (pts = *p*-toluenesulfonate) with noble metal alkene complexes resulted in the formation of four new heterobimetallic cubane-like Mo_3S_4M' cluster cores (M′ = Ru, Os, Rh, Ir). Thus, reaction with $[(1,5\text{-cod})Ru(CO)_3]$ or $[(1,3\text{-cod})Os(CO)_3]$ (cod = cyclooctadiene) afforded $[(\eta^5\text{-}Cp')_3Mo_3S_4M'(CO)_2]$[pts] (M′ = Ru: [**1**][pts]; M′ = Os: [**2**][pts]). When [**1**][pts] was kept in CH_2Cl_2/pentane solution, partial loss of carbonyl ligands occurred and the carbonyl-bridged dicubane cluster $[\{(\eta^5\text{-}Cp')_3Mo_3S_4Ru\}_2(\mu\text{-}CO)_3][pts]_2$ was isolated. An X-ray crystal structure revealed the presence of the hitherto unobserved $Ru(\mu\text{-}CO)_3Ru$ structural element. The formation of cluster compounds containing Mo_3S_4Rh and Mo_3S_4Ir cores was achieved in boiling methanol by reacting $[(\eta^5\text{-}Cp')_3Mo_3S_4]$[pts] with $[M'Cl(cyclooctene)_2]_2$ (M′ = Rh, Ir) in the presence of PPh_3. In this way $[(\eta^5\text{-}Cp')_3Mo_3S_4M'Cl(PPh_3)]$[pts] (M′ = Rh, Ir) could be isolated. An alternative route to the Mo_3S_4Rh cluster core was found in the reaction of $[(\eta^5\text{-}Cp')_3Mo_3S_4]$[pts] with $[RhCl(1,5\text{-cod})]_2$, which yielded $[(\eta^5\text{-}Cp')_3Mo_3S_4Rh(cod)][pts]_2$ ([**7**]$[pts]_2$). Substitution of the cod ligand in [**7**]$[pts]_2$ by 1,3-bis(diphenylphosphanyl)propane (dppp) gave $[(\eta^5\text{-}Cp')_3Mo_3S_4Rh(dppp)][pts]_2$.

Introduction

Recently we described the conversion of $[(H_2O)_9Mo_3S_4][pts]_4\cdot 9H_2O$ to $[(\eta^5\text{-}Cp)_3Mo_3^{IV}S_4]$[pts] (Cp = cyclopentadienyl, pts = *p*-toluenesulfonate) by a series of ligand substitution reactions.[1] This preparative procedure has made readily available cyclopentadienyl derivatives of the geometrically incomplete $[Mo^{IV}{}_3S_4]^{4+}$ cluster core and, by incorporation of a heterometal atom, allowed an extension of cubane-like Mo_3S_4M' cluster chemistry into the organometallic domain.

The present paper describes the synthesis of four new Mo_3S_4M' cluster cores (M′ = Ru, Os, Rh, Ir). Although an extensive array (M′ = Cr,[2] Mo,[3] W,[4] Fe,[5] Co,[6] Ni,[7] Pd,[8] Cu,[9] Cd,[10] Hg,[6] Ga,[11] In,[12] Tl,[13] Sn,[14] Pb,[15,16] As,[17] Sb,[18] and Bi[19]) of clusters containing the Mo_3S_4M' motif has been reported over the last 15 years, the platinum metals are (apart from Pd) not represented among the heterometals. This may be due to the aqueous synthetic route that has prevailed in the chemistry of these compounds; heterobimetallic clusters have been synthesized by reaction of an acidic solution of $[(H_2O)_9Mo_3S_4]^{4+}$ with either metal powder or with metal ions and a reducing agent (typically $NaBH_4$). In this context, the nobleness of the platinum metals may well prevent their incorporation into the Mo_3S_4 cluster core. As we shall describe in the following, a nonaqueous route in which cyclopentadienyl-type complexes of Mo_3S_4 are reacted with alkene complexes of the platinum metals has proven to be very successful in preparing several new Mo_3S_4M' cluster cores.

Noble metal containing, heterobimetallic cubane-like cluster cores of the stoichiometry $Mo_2M'_2S_4$ (M′ = Rh, Ir, Pd) were only prepared very recently.[20−22]

Experimental Section

General Procedures and Materials. All preparations were carried out under an atmosphere of dry dinitrogen using Schlenk techniques.

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Solvents were dried and distilled from standard drying agents prior to use (pentane, THF from Na/benzophenone; MeOH from Mg; and CH_2Cl_2 from P_4O_{10}) and stored under dinitrogen. Silica gel (70−230 mesh, Aldrich) was dried in vacuo at 160 °C for 14 h and stored under dinitrogen. Solvents for column chromatography were degassed before use. Irradiation reactions were carried out by means of a Hg quartz lamp (TQ 150, Heraeus Noblelight GmbH, Germany). Infrared spectra were recorded on a Bio-Rad FTS-60 spectrometer as solids in KBr disks. NMR spectra were recorded at room temperature, on a Varian UNITY 300 MHz spectrometer (300.1 MHz for ^1H, 121.4 MHz for ^{31}P, 75.5 MHz for ^{13}C), and were referenced to the chemical shift of the non-deuterated component of the deuterated solvents relative to TMS. Mass spectra were obtained on a JEOL SX-102 spectrometer. Elemental analyses were performed at DB Lab, Dansk Bioprotein A/S, Odense, Denmark.

The homometallic starting material $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ was prepared in essentially the same manner as the previously described $[(\eta^5\text{-Cp})_3Mo_3S_4][pts]$.[1] Literature procedures (without the final purification steps for the first two compounds) were employed for the preparation of $[(1,5\text{-cod})Ru(CO)_3]$,[23] $[(1,3\text{-cod})Os(CO)_3]$,[24] $[RhCl(cyclooctene)_2]_2$,[25] $[IrCl(cyclooctene)_2]_2$,[25] and $[RhCl(1,5\text{-cod})]_2$[26] (cod = cyclooctadiene).

Syntheses. $[(\eta^5\text{-Cp}')_3Mo_3S_4Ru(CO)_2][pts]$ ([1][pts]). A solution of 190 mg (0.305 mmol) of $[Ru_3(CO)_{12}]$ and 3.0 mL of 1,5-cyclooctadiene in 15 mL of benzene was heated to reflux for 6 h. After cooling to room temperature, the solvent was evaporated; the black-brown residue was extracted with pentane and the extract filtered. The pentane solution was concentrated to 2 mL and added to a solution of 100 mg (0.122 mmol) of $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ in 20 mL of CH_2Cl_2. The mixture was stirred at ambient temperature for 64 h and then concentrated to 5 mL in a vacuum. By addition of 20 mL pentane, a brown solid precipitated. This was isolated by filtration, washed with pentane, and dried in a vacuum. Yield: 101 mg (0.103 mmol, 85%). ^1H NMR ($CDCl_3$; δ/ppm): 2.15 (s, 3 H, Cp′), 2.17 (s, 6 H, Cp′), 2.32 (s, 3 H, pts), 5.66 (t, J = 2.3 Hz, 4 H, Cp′), 5.68 (t, J = 2.4 Hz, 2 H, Cp′), 5.76 (t, 4 H, Cp′), 5.86 (t, 2 H, Cp′), 7.12 (d, J = 7.8 Hz, 2 H, pts), 7.83 (d, 2 H, pts). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ/ppm): 15.5 (s, 2 C, Cp′), 15.6 (s, 1 C, Cp′), 21.3 (s, pts), 93.1 (s, 1 C, Cp′), 93.2 (s, 2 C, Cp′), 93.6 (s, 2 C, Cp′), 93.7 (s, 1 C, Cp′), 114.47 (s, 1 C, Cp′), 114.54 (s, 2 C, Cp′), 126.2 (s, pts), 129.1 (s, pts), 140.6 (s, pts), 142.9 (s, pts), 195.9 (s, CO), 196.0 (s, CO). IR (KBr; ν/cm^{-1}): 1962 (vs), 2012 (vs) ν(CO). FAB$^+$ MS (m/z, % abundance): 811 (M$^+$ − pts, 30), 783 (M$^+$ − pts −CO, 13), 755 (M$^+$ − pts − 2 CO, 68). Anal. Calcd for $C_{27}H_{28}Mo_3O_5RuS_5$ (981.71): C, 33.03; H, 2.87; S, 16.33. Found: C, 33.04; H, 3.25; S, 15.41.

$[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ru\}_2(\mu\text{-CO})_3][pts]_2$ ([2][pts]$_2$). A solution of 30 mg (0.03 mmol) of [**1**][pts] in 5 mL of CH_2Cl_2 was carefully layered with pentane. After keeping this mixture for 7 days, [**2**][pts]$_2$ was isolated as needle-shaped crystals. Yield: 13 mg (0.01 mmol, 26%). IR (KBr; ν/cm^{-1}): 1801 (vs) ν(CO). Anal. Calcd for $C_{53}H_{56}Mo_6O_9Ru_2S_{10}\cdot 2CH_2Cl_2$ (2105.27): C, 31.38; H, 2.87; S, 15.23. Found: C, 31.40; H, 3.11; S, 15.71.

$[(\eta^5\text{-Cp}')_3Mo_3S_4Os(CO)_2][pts]$ ([3][pts]). A mixture of 330 mg (0.364 mmol) of $Os_3(CO)_{12}$ and 2.3 mL of 1,3-cyclooctadiene in 200 mL of benzene was irradiated for 80 h. After removal of all volatile material by vacuum, the brown oily residue was extracted with 100 mL of heptane, filtered, and concentrated in a vacuum to 3 mL. This mixture was added to a solution of 110 mg (0.133 mmol) of $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ in 15 mL of methanol, and was heated at reflux for 5 h. After cooling, the solvent was removed by vacuum; the remaining oil was redissolved in 10 mL of THF. Addition of 20 mL of pentane caused a viscous substance to precipitate. After removal of the solvents and addition of pentane, the oil solidified. The brown−green powder was collected on a filter, washed with pentane, and dried in a vacuum. Yield: 97 mg (0.090 mmol, 68%). ^1H NMR ($CDCl_3$; δ/ppm): 2.13 (s, 6 H, Cp′), 2.22 (s, 3 H, Cp′), 2.32 (s, 3 H, pts), 5.62 (s, br, 2 H, Cp′), 5.73 (s, br, 2 H, Cp′), 5.86 (s, br, 4 H, Cp′), 6.19 (s, br, 4 H, Cp′), 7.12 (d, J = 7.8 Hz, 2 H, pts), 7.82 (d, 2 H, pts). IR (KBr; ν/cm^{-1}): 1941 (vs), 2017 (vs) ν(CO). FAB$^+$ MS (m/z, % abundance): 900 (M$^+$ − pts, 11), 872 (M$^+$ − pts − CO, 46), 844 (M$^+$ − pts − 2 CO, 35).

$[(\eta^5\text{-Cp}')_3Mo_3S_4RhCl(PPh_3)][pts]$ ([4][pts]). To a solution of 135 mg (0.164 mmol) of $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ in 15 mL of methanol was added 41 mg (0.082 mmol) of $[RhCl(cyclooctene)_2]_2$ and 43 mg (0.164 mmol) of triphenylphosphane. The mixture was heated to reflux for 1 h, which caused all solid material to disappear. After the mixture was cooled to room temperature and all volatile components were evaporated, the residue was dissolved in 5 mL of CH_2Cl_2. By addition of 20 mL of pentane, a dark green solid precipitated. This was collected on a filter, washed with pentane, and dried in a vacuum. Yield: 149 mg (0.121 mmol, 74%). ^1H NMR ($CDCl_3$; δ/ppm): 2.10 (s, 6 H, Cp′), 2.12 (s, 3 H, Cp′), 2.31 (s, 3 H, Cp′), 5.61 (m, br, 12 H, Cp′), 7.09 (d, J = 7.2 Hz, 2 H, pts), 7.36−7.56 (m, 15 H, PPh_3), 7.79 (d, 2 H, pts). $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ/ppm): 41.9 (d, ^1J(RhP) = 152.1 Hz). FAB$^+$ MS (m/z, % abundance): 1054 (M$^+$ − pts, 72), 1019 (M$^+$ − pts − Cl, 26), 1064 (M$^+$ − pts − Cp′, 10), 792 (M$^+$ − pts − PPh_3, 84), 756 (M$^+$ − pts − Cl − PPh_3, 76). Anal. Calcd for $C_{43}H_{43}ClMo_3O_3PRhS_5$ (1225.27): C, 42.15; H, 3.54; S, 13.08. Found: C, 41.63; H, 3.46; S, 12.66.

$[(\eta^5\text{-Cp}')_3Mo_3S_4IrCl(cyclooctene)][pts]$ ([5][pts]). To a solution of 80 mg (0.097 mmol) of $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ in 10 mL of methanol was added 44 mg (0.049 mmol) of $[IrCl(cyclooctene)_2]_2$. The mixture was heated at reflux for 3 h until a clear solution was obtained. After cooling, the solvent was removed by vacuum; the olive-green residue was taken up in 5 mL THF. After addition of 10 mL of pentane, a green precipitate formed. This was isolated by filtration, washed with pentane, and dried in a vacuum. Yield: 108 mg (0.093 mmol, 96%). ^1H NMR ($CDCl_3$; δ/ppm): 1.28−1.50 (m, 4 H, cy), 1.56−1.82 (m, 4 H, cy), 2.16−2.24 (m, 4 H, cy), 2.27 (s, 3 H, Cp′), 2.30 (s, 6 H, Cp′), 2.31 (s, 3 H, pts), 4.15 (m, 2 H, cy), 5.55 (t, J = 2.4 Hz, 2 H, Cp′), 5.67 (m, 2 H, Cp′), 5.71 (t, J = 2.1 Hz, 2 H, Cp′), 5.84 (m, 2 H, Cp′), 5.91−5.98 (m, 4 H, Cp′), 7.11 (d, J = 7.8 Hz, 2 H, pts), 7.80 (d, 2 H, pts). FAB$^+$ MS (m/z, % abundance): 991 (M$^+$ − pts, 17), 956 (M$^+$ − pts − Cl, 9), 881 (M$^+$ − pts − cy, 66), 846 (M$^+$ − pts − cy − Cl, 26). Anal. Calcd for $C_{33}H_{42}ClIrMo_3O_3S_5$ (1162.49): C, 34.10; H, 3.64; S, 13.79. Found: C, 33.57; H, 3.95; S, 13.86.

$[(\eta^5\text{-Cp}')_3Mo_3S_4IrCl(PPh_3)][pts]$ ([6][pts]). To a solution of 70 mg (0.060 mmol) of [**5**][pts] in 15 mL of methanol was added 24 mg (0.091 mmol) of PPh_3. The mixture was heated to 60 °C for 2 h. After cooling, the solvent was removed with vacuum; the dark residue was dissolved in 10 mL of CH_2Cl_2. By addition of 10 mL of pentane, an olive-green solid precipitated, which was isolated by filtation, washed with pentane, and dried in a vacuum. Yield: 78 mg (0.056 mmol, 93%). ^1H NMR ($CDCl_3$; δ/ppm): 2.07 (s, 3 H, Cp′), 2.15 (s, 6 H, Cp′), 2.31 (s, 3 H, pts), 5.42 (m, br, 2 H, Cp′), 5.55 (t, J = 1.8 Hz, 4 H, Cp′), 5.62 (t, 4 H, Cp′), 5.66 (m, br, 2 H, Cp′), 7.10 (d, J = 8.4 Hz, 2 H, pts), 7.13−7.22 (m, 2 H, PPh_3), 7.27−7.34 (m, 2 H, PPh_3), 7.36−7.58 (m, 11 H, PPh_3), 7.81 (d, 2 H, pts). $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ/ppm): 20.4 (s). FAB$^+$ MS (m/z, % abundance): 1143 (M$^+$ − pts, 54), 1108 (M$^+$ − pts − Cl, 46), 1064 (M$^+$ − pts − Cp′, 13), 881 (M$^+$ − pts − PPh_3, 32), 846 (M$^+$ − pts − Cl − PPh_3, 17). Anal. Calcd for $C_{43}H_{43}ClIrMo_3O_3PS_5\cdot CH_2Cl_2$ (1399.51): C, 37.76; H, 3.24; S, 11.45. Found: C, 37.78; H, 3.32; S, 12.31.

$[(\eta^5\text{-Cp}')_3Mo_3S_4Rh(cod)][pts]_2$ ([7][pts]$_2$). To a solution of 63 mg (0.127 mmol) of $[RhCl(cod)]_2$ in 10 mL of CH_2Cl_2/THF (1:1) was added 71 mg (0.255 mmol) of Ag[pts]. After 20 min of stirring, the white precipitate was removed by filtration, and the yellow filtrate added dropwise to a solution of 210 mg (0.255 mmol) of $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ in 15 mL of CH_2Cl_2. The olive-green mixture was stirred for 2 h. The almost clear solution was filtered and concentrated to approximately 5 mL. Addition of 20 mL pentane caused a dark solid to precipitate. This was isolated by filtration, washed with pentane, and dried in a vacuum. Yield: 264 mg (0.219 mmol, 86%). ^1H NMR (EtOH-d_6; δ/ppm): 2.14 (s, 6 H, pts), 2.24 (s, 9 H, Cp′), 2.29 (d, br, 4 H, cod), 2.42 (d, br, 4 H, cod), 4.92 (s, br, 4 H, cod), 5.57 (m, 6 H, Cp′), 5.97 (m, 6 H, Cp′), 7.05 (d, J = 7.5 Hz, 4 H, pts), 7.64 (d, 4 H, pts). FAB$^+$ MS (m/z, % abundance): 865 (M$^+$ − 2 pts, 30), 756 (M$^+$ − 2 pts −

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Table 1. Crystal Data and Experimental Details for $[(\eta^5\text{-Cp}')_3Mo_3S_4Ru(CO)_2][pts]$ ([**1**][pts]), $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ru\}_2(\mu\text{-CO})_3][pts]_2$ ([**2**][pts]$_2$ and $[(\eta^5\text{-Cp}')_3Mo_3S_4RhCl(PPh_3)][pts]\cdot{}^1/_2THF$ ([**4**][pts]$\cdot{}^1/_2$THF)

formula	$C_{27}H_{28}Mo_3O_5RuS_5$	$C_{53}H_{56}Mo_6O_9Ru_2S_{10}$	$C_{43}H_{43}ClMo_3O_3PRhS_5\cdot{}^1/_2THF$
M	981.68	1935.36	1225.22($\cdot{}^1/_2$THF)
temp, *K*	293(2)	293(2)	293(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst symmetry	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
a, Å	10.812(2)	23.909(1)	10.058(1)
b, Å	10.868(2)	17.497(1)	13.925(1)
c, Å	15.158(3)	15.854(1)	17.751(1)
α, °	73.09(3)	90	86.354(4)
β, °	69.75(3)	91.067(2)	88.273(4)
γ, °	87.51(3)	90	69.430(4)
cell vol Å^3	1595.6(6)	6631.1(6)	2322.9(4)
Z	2	4	2
D_c Mg m^{-3}	2.043	1.939	1.752
μ(Mo K$_\alpha$) mm^{-1}	1.979	1.902	1.494
F(000)	960	3784	1216
cryst size, mm	0.34 × 0.20 × 0.05	0.35 × 0.25 × 0.20	0.32 × 0.25 × 0.20
θ limits, °	2.61−35.04	2.57−26.99	1.15−34.22
reflns collected	29002($\pm h, \pm k, \pm l$)	35029($\pm h, \pm k, \pm l$)	38299($\pm h, \pm k, \pm l$)
unique observed reflns [$F_o > 4\sigma(F_o)$]	5694	2836	5864
GOF on F^2	0.798	0.984	0.803
R$_1$ (F)^a, wR$_2$ (F^2)^b	0.0527, 0.0936	0.0730, 0.1723	0.0464, 0.0716
weighting scheme	$a = 0.0360$ $b = 0^b$	$a = 0.0975$ $b = 51.4803^b$	$a = 0.0221$ $b = 0^b$
largest diff. peak and hole, eÅ^{-3}	0.99 and −0.76	1.12 and −0.86	0.72 and −0.88

[a] $R_1 = \Sigma||Fo| - |Fc|/\Sigma|Fo|$. [b] $wR_2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$ where $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ and where $P = (Fo^2 + 2Fc^2)/3$.

cod, 95), 677 (M$^+$ − 2 pts − cod − Cp′, 33). Anal. Calcd for $C_{40}H_{47}Mo_3O_6RhS_6\cdot THF$ (1279.00): C, 41.32; H, 4.33; S, 15.04. Found: C, 41.22; H, 3.71; S, 14.72.

$[(\eta^5\text{-Cp}')_3Mo_3S_4Rh(dppp)][pts]_2$ ([8][pts]$_2$). To a solution of 56 mg (0.046 mmol) of [**7**][pts]$_2$ in 10 mL of methanol was added 28 mg (0.068 mmol) of 1,3-bis(diphenylphosphanyl)propane (dppp). The mixture was heated to 60 °C for 1 h until a nonturbid solution was obtained. After evaporation of the solvent, the brown oily residue was dissolved in 5 mL of THF. By addition of 20 mL pentane, a brown solid precipitated, which was isolated by filtration, washed with pentane, and dried in a vacuum. Yield: 64 mg (0.042 mmol, 91%). ^{1}H NMR (CDCl$_3$; δ/ppm): 1.95 (s, 6 H, Cp′), 1.97 (s, 3 H, Cp′), 2.02−2.24 (m, 2 H, dppp), 2.31 (s, 6 H, pts), 2.99 (m, br, 4 H, dppp), 5.31 (t, $J = 1.8$ Hz, 4 H, Cp′), 5.36 (t, 4 H, Cp′), 5.42 (m, 2 H, Cp′), 5.54 (m, 2 H, Cp′), 7.11 (d, $J = 7.8$ Hz, 4 H, pts), 7.30−7.45 (m, 20 H, dppp), 7.86 (d, 4 H, pts). ^{31}P{^{1}H} NMR (CDCl$_3$; δ/ppm): 11.5 (d, ^1J(RhP) = 138.2 Hz). FAB$^+$ MS (*m*/*z*, % abundance): 1169 (M$^+$ − pts, 47), 756 (M$^+$ − pts − dppp, 82), 677 (M$^+$ − pts − dppp − Cp′, 38). Anal. Calcd for $C_{59}H_{61}Mo_3O_6P_2RhS_6\cdot THF$ (1583.27): C, 47.79; H, 4.39; S, 12.15. Found: C, 47.70; H, 4.74; S, 12.34.

X-ray Crystallography. Single crystals suitable for X-ray structure determinations were obtained for [**1**][pts] (from CH$_2$Cl$_2$/pentane), for [**2**][pts]$_2$ (from CH$_2$Cl$_2$/pentane), and for [**4**][pts] (from THF/methanol/pentane). Crystal data and details of the data collections are reported in Table 1. The X-ray intensity data were measured on a Bruker AXS SMART 2000 diffractometer, equipped with a CCD detector, using Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against 3615 (for [**1**][pts]), 4069 (for [**2**][pts]$_2$) and 4154 reflections (for [**4**][pts]$\cdot{}^1/_2$THF). For all crystals, a full sphere of reciprocal space was scanned by 0.3° ω steps, with the detector kept at 5.0 cm from the sample. Intensity decay was monitored by recollecting the initial 50 frames at the end of the data collection and analyzing the duplicate reflections. The collected frames were processed for integration by using the program SAINT, and an empirical absorption correction was applied using SADABS[27] on the basis of the Laue symmetry of the reciprocal space. The structures were solved by direct methods (SIR 97)[28] and subsequent Fourier syntheses, and they were refined by full-matrix-block least-squares on F^2 (SHELXTL),[29] using anisotropic thermal parameters for all non-hydrogen atoms, in [**1**][pts] and [**4**][pts], and only for Mo, Ru, and S in [**2**][pts]$_2$ because of the low reflections/parameters ratio. The methylcyclopentadienyl rings that are bound to Mo(2) and Mo(3) in [**2**][pts]$_2$ and to Mo(3) in [**4**][pts] were found to be disordered over two sites and occupancy factors of 0.55, 0.57, and 0.56 were refined for their main images, respectively. In [**2**][pts]$_2$, a verification of possible voids in the unit cell, performed using the VOID routine of the PLATON[30] program, revealed the presence of four cavities suitable for a small solvent molecule, but it was impossible to identify the nature of the solvent because of the poor data quality. In [**4**][pts], a THF molecule was found disordered around a crystallographic inversion center. All hydrogen atoms were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}(C{-}Me)$], and allowed to ride on their carrier carbons.

Results and Discussion

To facilitate the purification of the heterobimetallic Mo_3S_4M' derivatives by column chromatography, we have chosen to work with the more soluble *methyl*cyclopentadienyl (Cp′) substituted cluster compounds rather than with Cp derivatives. The homometallic starting material required, $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$, was prepared in essentially the same manner as the previously described $[(\eta^5\text{-Cp})_3Mo_3S_4][pts]$.[1]

Ruthenium and Osmium. We intended to add Ru and Os atoms to the Mo_3S_4 cluster core in form of metal(dicarbonyl) groups. Since a direct reaction of binary metal carbonyls with cyclopentadienyl-substituted Mo_3S_4 cores proved to be unsuitable, mononuclear cyclooctadiene (cod) derivatives of dodecacarbonyltriruthenium and dodecacarbonyltriosmium were used

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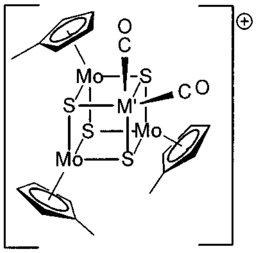
instead. Thus, the reaction of $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ with an excess of $[(1,5\text{-cod})Ru(CO)_3]$ at room temperature in CH_2Cl_2 afforded, after 64 h, a dark brown solution, from which $[(\eta^5\text{-Cp}')_3Mo_3S_4Ru(CO)_2][pts]$ ([**1**][pts]) was isolated in high yield by precipitation with pentane. A combination of NMR, infrared and FAB$^+$ mass spectroscopy, as well as X-ray crystallography revealed the identity of [**1**][pts] and confirmed the loss of one carbonyl ligand at the Ru center during the incorporation reaction. In the $^{13}C\{^1H\}$ NMR spectrum, the two carbonyl ligands gave rise to two singlets of almost equal intensity at $\delta = 195.9$ and 196.0. The Cp′ resonances were split into two sets of signals of 2:1 intensity, both in the $^{13}C\{^1H\}$ and the ^1H NMR spectra, due to the twofold symmetry of the $Ru(CO)_2$ moiety. The FAB$^+$ mass spectrum showed the parent peak for [**1**]$^+$ at $m/z = 811$ and the successive loss of two carbonyl ligands before further fragmentation.



[**1**]$^+$: M' = Ru

[**3**]$^+$: M' = Os

In the infrared, the asymmetric and symmetric carbonyl stretching vibrations expected for a $Ru(CO)_2$ moiety were seen as two strong bands at 2012 and 1962 cm^{-1}. These values fall within the range observed for thiolate/thioether coordinated Ru^{II} carbonyl compounds, such as $[Ru(CO)(PPh_3)(2\text{-}C_6H_4S_2(2\text{-}C_6H_4S)_2)]$ (ν(CO) = 1964 cm^{-1}), which like [**1**]$^+$, have sulfur-dominated coordination spheres for the central metal.[31] However, from discussions[32−35] about the true oxidation state of the heterometal in $[(H_2O)_9Mo_3S_4M'(CO)][pts]_4$ (M′ = Ni, Pd), it has emerged that it is problematic to assign an oxidation state to the heterometal by a comparison between the CO stretching frequencies of a cluster-embedded metal carbonyl fragment and a (mononuclear) noncluster metal carbonyl compound. As discussed in detail by Harris and co-workers,[34] the competitive formation of metal−metal bonds within the cluster leads to a lowering of the heterometal−carbonyl back-bonding, which causes the carbonyl stretching frequency to rise. The situation seems to be similar for [**1**]$^+$; although it is electron poor, the incorporated Ru heteroatom retains five-coordination, as in the 18-electron starting compound $[(1,5\text{-cod})Ru^0(CO)_3]$.

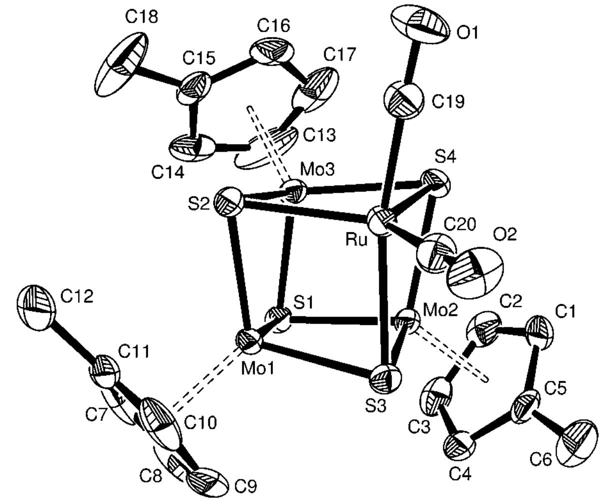


Figure 1. ORTEP drawing of $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ru(CO)_2]^+$ ([**1**]$^+$) with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^5\text{-Cp}')_3Mo_3S_4Ru(CO)_2][pts]$ ([**1**][pts])

Ru−Mo(1)	2.971(1)	Mo(1)−Mo(2)	2.862(1)
Ru−Mo(2)	2.957(1)	Mo(2)−Mo(3)	2.837(1)
Ru−Mo(3)	2.893(1)	Mo(1)−Mo(3)	2.831(1)
Ru−S(2)	2.363(1)	Mo(1)−S(1)	2.325(2)
Ru−S(3)	2.421(1)	Mo(1)−S(2)	2.312(1)
Ru−S(4)	2.384(2)	Mo(1)−S(3)	2.314(1)
Mo(2)−S(3)	2.311(1)	Mo(3)−S(1)	2.322(1)
Mo(2)−S(4)	2.314(1)	Mo(3)−S(2)	2.338(2)
Mo(2)−S(1)	2.326(1)	Mo(3)−S(4)	2.339(1)
Ru−C(19)	1.886(6)	C(19)−O(1)	1.141(7)
Ru−C(20)	1.890(6)	C(20)−O(2)	1.132(6)
Mo−S−Mo(av)	75.2(2)	S(2)−Ru-S(3)	97.89(5)
S−Mo−S(av)	103.0(9)	S(2)−Ru−S(4)	102.23(5)
Ru−S−Mo(av)	77.2(2)	S(3)−Ru−S(4)	98.35(5)
S(2)−Ru−C(19)	94.5(2)	S(2)−Ru−C(20)	123.0(2)
S(3)−Ru−C(19)	166.1(2)	S(3)−Ru−C(20)	81.3(2)
S(4)−Ru−C(19)	85.2(2)	S(4)−Ru−C(20)	134.5(2)
Ru−C(19)−O(1)	178.2(6)	Ru−C(20)−O(2)	177.8(6)
C(19)−Ru−C(20)	86.6(3)		

The structural assignment for [**1**]$^+$ based on spectroscopic techniques was confirmed by a single-crystal X-ray structure of the *p*-toluenesulfonate salt. Selected bond lengths and angles are collected in Table 2. The molecular structure of the cation [**1**]$^+$ (Figure 1) is that of a Mo_3RuS_4 cubane-like core with idealized C_{3v} symmetry. Besides the three sulfur atoms belonging to the cluster core, each of the three Mo atoms coordinate a Cp′ ligand and the Ru atom coordinates two terminal carbonyl ligands, thus depriving the cation of any symmetry element. Each Mo atom adopts a pseudo-octahedral geometry, whereas the Ru atom has a pseudotrigonal bipyramidal geometry if the metal−metal interactions are ignored. The apical sites of the trigonal bipyramid are occupied by S(3) and C(19), respectively (S(3)−Ru−C(19) = 166.1(2)°), whereas S(2), S(4), and C(20) lie in the equatorial plane. Alternatively, the structure of [**1**]$^+$ can be described as a tetrahedral Mo_3Ru framework with a sulfur atom capping each face of the tetrahedron, and thus, generating a cubane structure. The Mo−Mo distances (range 2.831(1)−2.862(1) Å, av. 2.843(9) Å) are consistent with single bonds between each metallic center and are very close to those found in $[(\eta^5\text{-Cp}')_3Mo_3S_4Co(CO)]$ (average 2.838(11) Å),[36] but shorter than found in $[(\eta^5\text{-Cp})_3Mo_3S_4W(CO)_3]$ (average 2.877(17) Å).[1] The Ru−Mo distances are significantly different (range 2.893(1)−2.971(1) Å), the shortest interaction being the Mo(3)−Ru bond trans to the carbonyl ligand C(20)−O(2). Very similar Ru−Mo bond lengths of 2.8989(9) and 2.9129(8) Å were found in the trinuclear cluster $[\{\eta^5\text{-CpMo(CO)}_2\}_2(\mu_3\text{-S})Ru(CO)_3]$.[37] The

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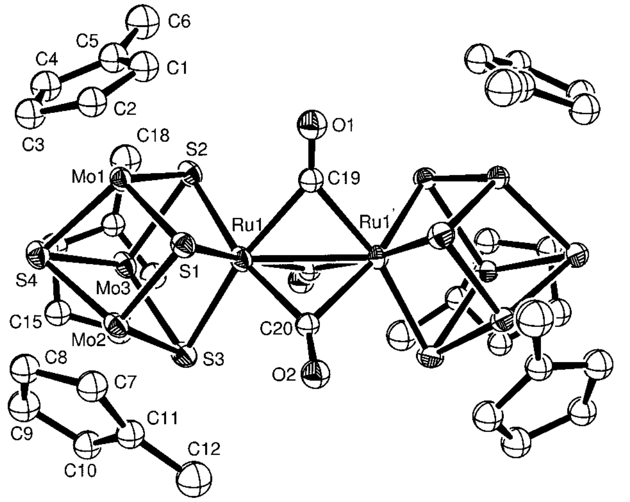
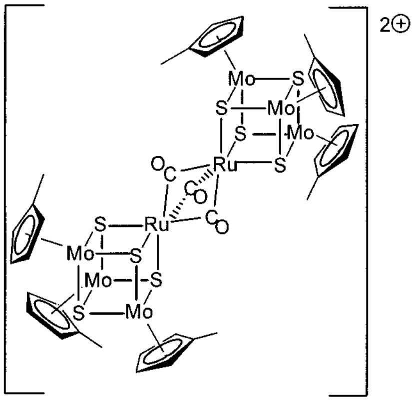


Figure 2. ORTEP drawing of the dimeric dication $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ru\}_2(\mu\text{-CO})_3]^{2+}$ ($[\mathbf{2}]^{2+}$). A C_2 axis that is passing through the bridging carbonyl C(19)−O(1) relates each unlabeled atom to a labeled one (symmetry operation: −x, y, −z + 1/2). Thermal ellipsoids are drawn at the 30% level. Hydrogen atoms have been omitted for clarity.

Mo−S distances (range 2.311(1)−2.338(2) Å, av 2.322(3) Å) are only slightly shorter than the corresponding mean Mo−S interactions in $[(\eta^5\text{-Cp}')_3Mo_3S_4Co(CO)]$ (2.327(10) Å) and in $[(\eta^5\text{-Cp})_3Mo_3S_4W(CO)_3]$ (average 2.336(10) Å). The Ru−S distances range from 2.363(1) to 2.421(1) Å (average 2.389(3) Å), with the longest interaction trans to the carbonyl ligand C(19)−O(1).

When kept in a CH_2Cl_2/pentane solution for several days, the dicarbonyl cluster compound [**1**][pts] proved to be unstable toward a partial loss of its carbonyl ligands. The product that formed crystallized in up to 2 cm long needles and was characterized by X-ray crystallography as the carbonyl-bridged dicubane cluster compound $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ru\}_2(\mu\text{-CO})_3][pts]_2$ ([**2**]$[pts]_2$) (Figure 2). Selected bond lengths and angles are collected in Table 3.



$[\mathbf{2}]^{2+}$

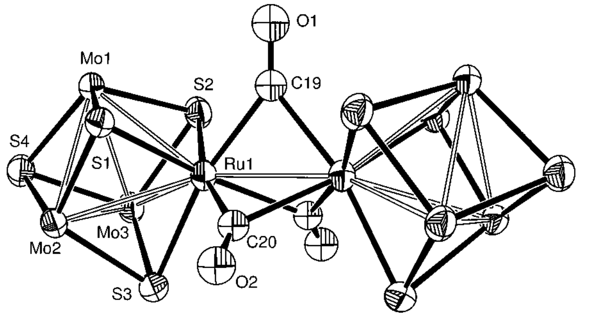


Figure 3. ORTEP view of the cluster cores and the Ru(μ-CO)$_3$Ru structural element of $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ru\}_2(\mu\text{-CO})_3]^{2+}$ ($[\mathbf{2}]^{2+}$).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ru\}_2(\mu\text{-CO})_3][pts]_2$ ([**2**]$[pts]_2$)

Ru(1)−Mo(1)	2.872(2)	Mo(1)−Mo(2)	2.841(2)
Ru(1)−Mo(2)	2.876(2)	Mo(1)−Mo(3)	2.830(2)
Ru(1)−Mo(3)	2.886(2)	Mo(2)−Mo(3)	2.842(2)
Ru(1)−S(1)	2.395(4)	Mo(1)−S(1)	2.313(4)
Ru(1)−S(2)	2.402(4)	Mo(1)−S(2)	2.330(4)
Ru(1)−S(3)	2.407(4)	Mo(1)−S(4)	2.311(4)
Mo(2)−S(1)	2.321(4)	Mo(3)−S(2)	2.322(4)
Mo(2)−S(3)	2.316(4)	Mo(3)−S(3)	2.317(5)
Mo(2)−S(4)	2.308(4)	Mo(3)−S(4)	2.306(4)
Ru(1)−C(19)	2.13(2)	C(19)−O(1)	1.13(2)
Ru(1)−C(20)	2.06(1)	C(20)−O(2)	1.12(1)
Ru(1)−C(20′)	2.23(1)	Ru(1)−Ru(1′)	2.699(2)
Mo−S−Mo(av)	75.6(2)	S(1)−Ru(1)−S(2)	101.3(1)
S−Mo−S(av)	103.5(6)	S(1)−Ru(1)−S(3)	101.1(1)
Ru(1)−S−Mo(av)	75.08(9)	S(2)−Ru(1)−S(3)	100.5(1)
Ru(1)−C(19)−O(1)	140.6(4)	Ru(1)−C(20)−O(2)	148(1)
C(19)−Ru(1)−C(20)	86.2(5)	Ru(1′)−C(20)−O(2)	133(1)

The solid-state structure of $[\mathbf{2}]^{2+}$ consists of two Mo_3S_4Ru cubane units held together by a Ru−Ru bond that is reinforced by three carbonyl ligands (Figure 3). The overall stereochemistry of $[\mathbf{2}]^{2+}$ conforms to a D_{3h} symmetry if the methylcyclopentadienyl rings are ignored. The nonequivalent conformations of the Cp′ groups and their partial disorder reduce the actual symmetry to C_2. In fact, one carbonyl ligand lies on a crystallographically imposed C_2 axis that passes through the midpoint of the Ru(1)−Ru(1′) axis, and therefore only half of the dication is independent. The Mo−Ru bond lengths are slightly shorter than the corresponding Mo−Ru bonds in $[\mathbf{1}]^+$ and are much less scattered (range 2.872(2)−(2.886(2) Å). The Ru(1)−Ru(1′) distance (2.699(2) Å) is rather short in comparison to other molecules containing Ru−Ru single bonds (cf., $Ru_3(CO)_{12}$, d = 2.854(4) Å); this is a consequence of the presence of the three bridging carbonyls that strengthen the metal−metal interaction. Another significant deviation from the idealized symmetry is a marked asymmetry of the bridging carbonyl ligands in the general positions C(20)−O(2) and C(20′)−O(2′). The Ru−μ-C(19) bonds, equivalent by symmetry, are 2.13(1) Å long, whereas the asymmetric Ru−μ-C(20) bonds are 2.06(1) and 2.23(1) Å long. A possible explanation for this effect is in terms of nonbonded C(20)···C(20′) contact optimization. To the best of our knowledge, [**2**]$[pts]_2$ is the first crystallographically characterized example of the Ru(μ-CO)$_3$Ru structural element. Thus, for example, unlike $Fe_2(CO)_9$, which has three bridging CO ligands, the (relatively unstable) analogous ruthenium and osmium compounds adopt the structure $(CO)_4M(\mu\text{-CO})M(CO)_4$ (M = Ru, Os) with M−M single bonds.[38]

Whereas the infrared spectrum of [**1**][pts] was found to be without any band in the bridging carbonyl region (1750−1850 cm^{-1}), the spectrum of [**2**]$[pts]_2$ showed a pronounced band at 1801 cm^{-1}. The general structural type, i.e., two M_3S_4M' cubane-like cluster cores linked by three bridges that extend from the heteroatoms, has been seen previously in $[\{(EtS)_3Fe_3S_4Mo\}_2(\mu\text{-EtS})_3]^{3+}$.[39]

The addition of a Ru atom to the Mo_3S_4 core, by means of $[(1,5\text{-cod})Ru(CO)_3]$, was achieved at very mild reaction conditions, but the corresponding reaction with $[(1,3\text{-cod})Os(CO)_3]$

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Table 4. Cyclopentadienyl-Substituted Mo_3S_4M' Cluster Cores with Carbonyl Ligands at the Heteroatom M′ (M′ = Group 6, Group 8, and Group 10 Metals)

Group 6[a]	Group 8[b]	Group 10[c]
$[(Cp_3)Mo_3S_4Cr(CO)_3]^+$		$[(Cp'_3)Mo_3S_4Ni(CO)]^+$
$[(Cp_3)Mo_3S_4Mo(CO)_3]^+$	$[(Cp'_3)Mo_3S_4Ru(CO)_2]^+$	$[(Cp'_3)Mo_3S_4Pd(CO)]^+$
$[(Cp_3)Mo_3S_4W(CO)_3]^+$	$[(Cp'_3)Mo_3S_4Os(CO)_2]^+$	

[a] Reference 1. [b] Present paper. [c] Reference 40.

required boiling in methanol in order to drive it along. A relatively low reactivity of metal−alkene bonds in 5d transition metal complexes was also observed in the reaction of $[(\eta^5\text{-}Cp')_3Mo_3S_4][pts]$ with Ni, Pd, and Pt alkene complexes.[40] The reaction between $[(\eta^5\text{-}Cp')_3Mo_3S_4][pts]$ and $[(1,3\text{-cod})Os(CO)_3]$, in refluxing methanol, was monitored by IR spectroscopy, which indicated the disappearance of $[(1,3\text{-cod})Os(CO)_3]$ bands at 1980 and 2043 cm^{-1} and the appearance of several new carbonyl bands in the 1900−2120 cm^{-1} range. The isolated material displayed strong carbonyl absorption bands at 1941 and 2017 cm^{-1}, which were assigned to the dicarbonyl cluster compound $[(\eta^5\text{-}Cp')_3Mo_3S_4Os(CO)_2][pts]$ ([**3**][pts]). However, as evidenced by IR spectroscopy, [**3**][pts] was found to be contaminated with a small amount of a carbonyl-containing compound, which could not be removed completely by the chromatographic procedures that we employed. As for [**1**][pts], the proton NMR spectrum of [**3**][pts] shows a splitting of the Cp′ resonances into two sets of signals, and the FAB^+ mass spectrum shows the loss of two carbonyl ligands from the cluster cation $[\mathbf{3}]^+$.

With their two carbonyl ligands, $[\mathbf{1}]^+$ and $[\mathbf{3}]^+$ complete a series of bimetallic Mo_3S_4M' cluster cores bearing carbonyl ligands on the M′ heterometal atom (see Table 4). All these compounds are electron-precise closed shell clusters. The number of carbonyl ligands at each of these clusters is in accordance with the Wade−Mingos rules for counting electrons in cluster compounds; application of these rules for the tetrahedral metal atom arrangement gives a count of 60 valence electrons with six skeletal electron pairs for each cluster core.[41]

Rhodium and Iridium. For the addition of Group 9 metals to $[(\eta^5\text{-}Cp')_3Mo_3S_4]^+$, the chloro-bridged dimers $[M'(\mu\text{-}Cl)(cyclooctene)_2]_2$ (M′ = Rh, Ir) were chosen as reactants. It was expected that the incorporation of a M′Cl fragment into the Mo_3S_4 cluster core would be observed, with a stabilization of the fifth coordination site at the heterometal by a cyclooctene ligand. However, the reaction between $[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2$ with $[(\eta^5\text{-}Cp')_3Mo_3S_4][pts]$ in boiling methanol afforded a mixture, whose cationic components were identified by FAB^+ mass spectroscopy as the cyclooctene-free monomeric cluster cations $(\eta^5\text{-}Cp')_3Mo_3S_4Rh(Cl)]^+$ and $[(\eta^5\text{-}Cp')_3Mo_3S_4Rh(pts)]^+$ as well as the dicubane cluster $[\{(\eta^5\text{-}Cp')_3Mo_3S_4\}_2Rh]^+$, the latter presumably of the corner-shared type[42] (i.e., with six sulfur atoms in the coordination sphere of the Rh atom). Attempts to separate this mixture by column chromatography were unsuccessful. When, on the other hand, $[(\eta^5\text{-}Cp')_3Mo_3S_4][pts]$ was reacted with $[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2$, in the presence of an equimolar amount of triphenylphosphane, $[(\eta^5\text{-}Cp')_3Mo_3S_4RhCl(PPh_3)][pts]$ ([**4**][pts]) could be isolated as a pure compound. The coordination of the phosphane ligand to the rhodium atom was evidenced by the split of its $^{31}P\{^1H\}$ NMR resonance at $\delta = 41.9$ into a doublet with a coupling constant $^1J(RhP)$ of 152.1 Hz.

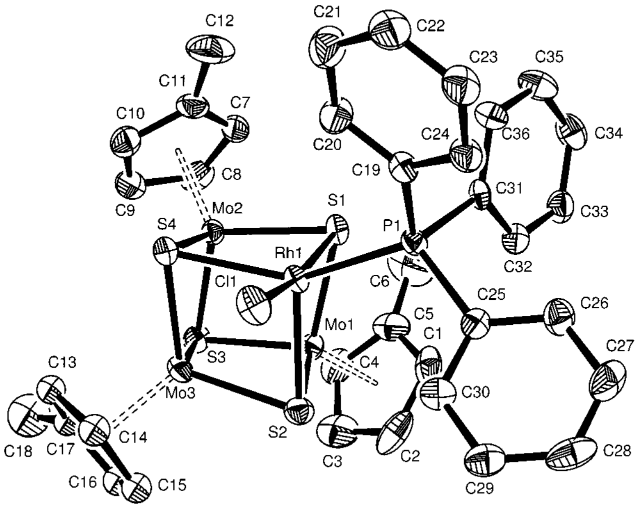
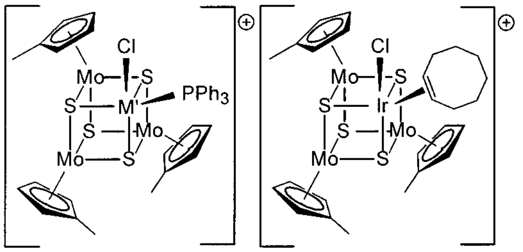


Figure 4. ORTEP drawing of $[\{(\eta^5\text{-}Cp')_3Mo_3S_4RhCl(PPh_3)]^+$ ($[\mathbf{4}]^+$) with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^5\text{-}Cp')_3Mo_3S_4RhCl(PPh_3)][pts]\cdot{}^1/_2THF$ ($[\mathbf{4}][pts]\cdot{}^1/_2THF$)

Rh(1)−Mo(1)	2.935(1)	Mo(1)−Mo(2)	2.850(1)
Rh(1)−Mo(2)	2.954(1)	Mo(1)−Mo(3)	2.812(1)
Rh(1)−Mo(3)	2.883(1)	Mo(2)−Mo(3)	2.838(1)
Rh(1)−S(1)	2.311(1)	Mo(1)−S(1)	2.340(1)
Rh(1)−S(2)	2.417(1)	Mo(1)−S(2)	2.311(1)
Rh(1)−S(4)	2.358(1)	Mo(1)−S(3)	2.317(1)
Mo(2)−S(1)	2.331(1)	Mo(3)−S(2)	2.320(1)
Mo(2)−S(3)	2.318(1)	Mo(3)−S(3)	2.319(1)
Mo(2)−S(4)	2.295(1)	Mo(3)−S(4)	2.325(1)
Rh(1)−Cl(1)	2.395(1)	Rh(1)−P(1)	2.337(1)
Mo−S−Mo(av)	75.3(3)	S(1)−Rh(1)−S(2)	99.83(4)
Rh−S−Mo(av)	77.3(7)	S(1)−Rh(1)−S(4)	98.85(4)
S−Mo−S(av)	102.9(9)	S(2)−Rh(1)−S(4)	101.57(4)
Cl(1)−Rh(1)−S(1)	166.43(5)	S(1)−Rh(1)−P(1)	89.69(4)
Cl(1)−Rh(1)−S(2)	93.49(4)	S(2)−Rh(1)−P(1)	110.60(4)
Cl(1)−Rh(1)−S(4)	80.82(4)	S(4)−Rh(1)−P(1)	144.76(4)
Cl(1)−Rh(1)−P(1)	83.19(4)		



$[\mathbf{4}]^+$: M' = Rh $[\mathbf{5}]^+$

$[\mathbf{6}]^+$: M' = Ir

A single-crystal X-ray structure analysis of $[\mathbf{4}][pts]\cdot{}^1/_2THF$ showed that the molecular structure of $[\mathbf{4}]^+$ (Figure 4) is similar to that of $[(\eta^5\text{-}Cp')_3Mo_3S_4Ru(CO)_2]^+$ ($[\mathbf{1}]^+$), with one $RhCl(PPh_3)$ unit replacing the isoelectronic fragment $Ru(CO)_2$. Selected bond lengths and angles are collected in Table 5. When metal−metal interactions are ignored, the coordination geometry is pseudo-octahedral around the Mo atoms and pseudotrigonal bipyramidal around the Rh atom. Each molybdenum atom coordinates one Cp′ ligand and three S atoms. The Rh atom coordinates, in addition to three S belonging to the cluster core, to one PPh_3 and one chloride ligand; the bulky phosphane ligand

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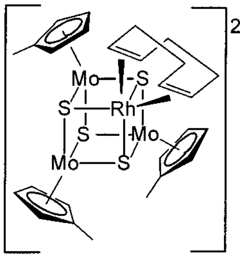
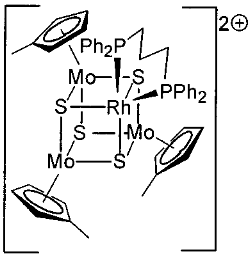
occupies an equatorial position and the chloride an axial position in the distorted trigonal bipyramid. The Mo−S distances average 2.319 Å and are strictly comparable to those found in [**1**]$^+$ and [**2**]$^{2+}$ (see above). The Rh−S distances are rather scattered (range 2.311−2.417(1) Å), the shortest interaction being the one trans to the chloride ligand. The Mo−Mo distances are very similar to those found in [**1**]$^+$ and [**2**]$^{2+}$ (av. Mo−Mo 2.833(1) Å). The Mo−Rh distances in [**4**]$^+$ (range 2.883(1)−2.954(1) Å) tend to be slightly longer than the Mo−Rh bonds in the neutral 62 VE butterfly cluster $[\{(Et_2NCS_2)ClMo\}_2(\mu_3\text{-}S)_4\{Rh(cod)\}_2]$ (range 2.864(2)−2.887(2) Å).[20]

In contrast to these results with rhodium as heterometal, the reaction of $[(\eta^5\text{-}Cp')_3Mo_3S_4][pts]$ with $[Ir(\mu\text{-}Cl)(cyclooctene)_2]_2$ in boiling methanol resulted in the almost quantitative formation of $[(\eta^5\text{-}Cp')_3Mo_3S_4IrCl(cyclooctene)][pts]$ ([**5**][pts]), which was isolated as a green powder. The proton NMR spectrum displayed well-resolved signals for the cyclooctene and the Cp′ ligands in the correct ratio. Subsequent reaction of [**5**][pts] in boiling methanol with one equivalent of triphenylphosphane brought about substitution of the cyclooctene ligand, and $[(\eta^5\text{-}Cp')_3Mo_3S_4IrCl(PPh_3)][pts]$ ([**6**][pts]) could be isolated as an olive green solid. The FAB$^+$ mass spectra of the two PPh_3 substituted cluster cations, [**4**]$^+$ and [**6**]$^+$, showed similar fragmentation pathways; the fragmentation of the parent cation $[(\eta^5\text{-}Cp')_3Mo_3S_4M'Cl(PPh_3)]^+$ (M′ = Rh, Ir) is characterized by the competitive loss of the chloro ligand, the phosphane, and a Cp′ ligand.

An alternative method for adding a rhodium atom to the Mo_3S_4 cluster core was also found; pretreatment of the chloro-bridged dimer $[(cod)Rh(\mu\text{-}Cl)]_2$ with the halogenide abstracting agent Ag[pts] created (cod)Rh fragments stabilized by pts and/or solvent molecules (THF/methanol). After removal of AgCl, the Rh compound reacted readily with an equimolar amount of $[(\eta^5\text{-}Cp')_3Mo_3S_4][pts]$ when the mixture was heated to reflux in methanol. The isolated product was identified as $[(\eta^5\text{-}Cp')_3Mo_3S_4Rh(cod)][pts]_2$ ([**7**][pts]$_2$). The solubility of this dicationic cluster compound in halogenated solvents was much reduced compared to that of the monocations [**4**]$^+$−[**6**]$^+$.



[**7**]$^{2+}$



[**8**]$^{2+}$

The substitution of the presumably labile cod ligand in [**7**][pts]$_2$ would make available two coordination sites at the rhodium atom. This possibility was investigated in the reaction of [**7**][pts]$_2$ with an equimolar amount of the bidentate phosphane ligand, $Ph_2P(CH_2)_3PPh_2$ (dppp). A nearly quantitative transformation to $[(\eta^5\text{-}Cp')_3Mo_3S_4Rh(dppp)][pts]_2$ ([**8**][pts]$_2$) was achieved in boiling methanol. As also seen for the dicarbonylruthenium cluster [**1**]$^+$ (see above), the mirror plane, introduced as a consequence of the bidentate coordination mode of the dppp ligand, caused a split of the Cp′ resonances in the proton NMR spectrum in a 2:1 ratio. The phosphane ligand resonated in the $^{31}P\{^1H\}$ NMR spectrum as a Rh coupled doublet at $\delta = 11.5$ with a typical coupling constant of 138.2 Hz.

Conclusion

The transfer of the geometrically incomplete Mo_3S_4 cluster core from the aqueous to organic phase has enabled the preparation of four new heterobimetallic cubane-like Mo_3S_4M' cluster cores. The potential lability of the hydrocarbon ligands in $[(\eta^5\text{-}Cp')_3Mo_3S_4IrCl(cyclooctene)][pts]$ and $[(\eta^5\text{-}Cp')_3Mo_3S_4Rh(cod)][pts]_2$ opens the possibility that catalytic reactions may be carried out at the noble metal sites. We are currently investigating the chemistry of these new cluster compounds with regard to their suitability as homogeneous catalysts, especially for hydrodesulfurization reactions of thiophene type compounds.

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Note added in proof. We have become aware that photolysis of $Ru_2(\eta^5\text{-}CpR)_2(CO)_4$ in inert gas matrices at 12 K (R=H)[43] or frozen Nujol at 90 K ($R=CH_3$)[44] produce species that on the basis of infrared spectroscopy have been assigned as $[\{(\eta^5\text{-}CpR)Ru\}_2(\mu\text{-}CO)_3]$.

Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[(\eta^5\text{-}Cp')_3Mo_3S_4Ru(CO)_2][pts]$ ([**1**][pts]), $[\{(\eta^5\text{-}Cp')_3Mo_3S_4Ru\}_2(\mu\text{-}CO)_3][pts]_2$ ([**2**][pts]$_2$), and $[(\eta^5\text{-}Cp')_3Mo_3S_4RhCl(PPh_3)][pts]\cdot{}^1/_2THF$ ([**4**][pts]$\cdot{}^1/_2$THF). This material is available free of charge via the Internet at http://pubs.acs.org.

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