Heterobimetallic Cubane-like Cluster Compounds Prepared as the Homologous Series [(η5-Cp′)3Mo3S4M′(PPh3)]+ (M′ = Ni, Pd, Pt). Crystal Structures Show that Platinum Is Smaller than Palladium

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Exchange of the aqua ligands in [(H2O)9Mo3S4][pts]4·9H2O for Cp′ ligands (Cp′ = methylcyclopentadienyl; pts = *p*-toluenesulfonate) yielded the novel cluster salt [(η5-Cp′)3-Mo3S4][pts] ([**1**][pts]). Reactions of [**1**][pts] in the presence of triphenylphosphane with [Ni-(cod)2] (cod = 1,5-cyclooctadiene) or [Pd2(dba)3] (dba = dibenzylideneacetone) afforded the heterobimetallic cubane-like cluster compounds [(η5-Cp′)3Mo3S4M′(PPh3)][pts] ([**2**][pts]: M′ = Ni; [**3**][pts]: M′ = Pd). By reaction of [**1**][pts] with [Pt(nor)3] (nor = 2-norbornene) at ambient temperature [(η5-Cp′)3Mo3S4Pt(nor)][pts] ([**4**][pts]) was isolated and further converted to [(η5-Cp′)3Mo3S4Pt(PPh3)][pts] ([**5**][pts]) at 60 °C. A 31P{1H} NMR spectroscopic characterization of [**5**][pts] revealed a coupling constant 1*J*(PtP) of 6656 Hz, whose size supports the view that the platinum atom is Pt0- rather than PtII-like. Single-crystal X-ray studies of the complete homologous series [**2**][pts], [**3**][pts], and [**5**][pts] demonstrated that the cluster cations are isostructural with M′−P bond lengths in the order Ni < Pt < Pd.

Introduction

The incorporation of metals or metal ions into the geometrically incomplete [Mo3IVS4]4+ cluster core has been effected for an extended array of elements (Cr,[1] Mo,[2] W,[3] Fe,[4] Co,[5] Ni,[6] Pd,[7] Pt,[8] Cu,[9] Cd,[10] Hg,[5] Ga,[11] In,[12] Tl,[13] Sn,[14] Pb,[15,16] As,[17] Sb,[18] and Bi[19]). The hetero-bimetallic cluster cores thereby formed comprise single cubes [Mo3S4M′], edge-shared double cubes [(Mo3S4M′)2], and corner-shared double cubes [(Mo3S4)2M′]. The Mo3S4M′ cluster motif has attracted interest because of the bioinorganic importance of metal sulfide clusters and, in particular, because it provides an unusual opportunity to study, within a homologous series of compounds, how metal−metal bonding and electron density distributions are affected by the nature of M′.[20] Our own interest in the system originates from the oil refinery process of catalytic hydrodesulfurization:[21] The Mo3S4M′ (M′ = Co, Ni) and Co2Mo2Sx (x = 3, 4) cluster cores constitute *molecular* models for the active sites of the industrially used heterogeneous CoMo or NiMo catalysts.[22−25]

Most work with the Mo3S4M′ cluster core motif has been carried out in aqueous solution where heterobi-metallic clusters can be prepared by reaction of [(H2O)9-Mo3S4]4+ with either metal powder or metal ions and a reducing agent (typically NaBH4). The heterobimetallic

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products have been isolated as aqua complexes or as complexes with polydentate ligands with N and/or O ligating atoms. With the exception of a number of cluster complexes with Mo_3S_4Pd[7,26−29] and Mo_3S_4Pt[8,30] cores, no clusters containing noble metal atoms have been described. This is probably due to the low reactivity of these metals in aqueous solution. By avoiding aqueous media we have managed to work around this problem. Recently we described the conversion of $[(H_2O)_9$-$Mo_3^{IV}S_4][pts]_4\cdot9H_2O$ to $[(\eta^5\text{-}Cp)_3Mo_3^{IV}S_4][pts]$ (Cp = cyclopentadienyl; pts = *p*-toluenesulfonate) by a series of ligand substitution reactions.[31] This organically soluble Mo_3S_4 cluster starting material could be reacted in tetrahydrofuran with $[(CH_3CN)_3M'(CO)_3]$ to give the series $[(\eta^5\text{-}Cp)_3Mo_3S_4M'(CO)_3][pts]$ (M' = Cr, Mo, W). Insertion reactions of group 8 and 9 metal alkene complexes into the analogous starting material $[(\eta^5\text{-}Cp')_3Mo_3S_4][pts]$ ([1][pts]; Cp' = *methyl*cyclopentadienyl) resulted in heterobimetallic clusters with cubane-like Mo_3S_4M' cores (M' = Ru, Os, Rh, Ir).[32]

The present paper describes the incorporation of heterometals into [1][pts] by reactions with group 10 metal(0) alkene complexes. After stabilization of the heterometallic site by coordination of triphenylphosphane (PPh_3), the homologous series $[(\eta^5\text{-}Cp')_3Mo_3S_4M'$-$(PPh_3)][pts]$ ([2][pts], M' = Ni; [3][pts], M' = Pd; [5][pts], M' = Pt) was isolated.

Experimental Section

General Procedures, Instrumentation, and Materials. All preparations were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Solvents were dried and distilled from standard drying agents prior to use (pentane, THF: Na/benzophenone; MeOH: Mg; CH_2Cl_2: P_4O_{10}) and stored under nitrogen. Silica gel (70−230 mesh, Aldrich) was dried in vacuo at 160 °C for 14 h and stored under nitrogen. Solvents for column chromatography were degassed before use. NMR spectra were recorded at room temperature on a Varian UNITY 300 MHz spectrometer (300.1 MHz for ^{1}H, 121.4 MHz for ^{31}P) and were referenced to the chemical shift of the nondeuterated part in the deuterated solvents relative to TMS (downfield positive). Elemental analyses were performed at DB-Lab, Dansk Bioprotein A/S, Odense, Denmark.

$[(H_2O)_9Mo_3S_4][pts]_4\cdot9H_2O$[33] and $[Pt(nor)_3]$[34] (nor = 2-norbornene) were prepared according to published procedures; methylcyclopentadienyl thallium (TlCp') was prepared by reaction of thallium ethoxide with Cp'H.[35] $[Pd_2(dba)_3]$ (dba = dibenzylidenacetone) was purchased from Aldrich, and [Ni-(cod)$_2$] (cod = 1,5-cyclooctadiene) from Strem Chemicals.

Synthesis of $[(\eta^5\text{-}Cp')_3Mo_3S_4][pts]$ ([1][pts]). $[(H_2O)_9$-$Mo_3S_4][pts]_4\cdot9H_2O$ (2.0 g, 1.40 mmol) and a catalytic amount (a few crystals) of *p*-toluenesulfonic acid (Hpts) were dissolved

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in triethylorthoformate (25 mL), and the mixture was stirred at room temperature for 16 h. The solution was reduced to half of its volume in vacuo, by which a green-brown solid precipitated. Diethyl ether (30 mL) was added and the solid allowed to settle. The supernatant solution was removed by a pipet. The addition/removal of diethyl ether was repeated twice, after which the solid was dried in a vacuum. The brown powder was dissolved in CH_3CN (30 mL), resulting in a green solution, which was evaporated to dryness after 1 h of stirring. The solid was redissolved in THF (40 mL) and added to a solution of TlCp' (1.25 g, 4.37 mmol) in CH_2Cl_2 (40 mL). The brown-green mixture was stirred for 3 h, filtered (P4), and evaporated to dryness. The crude product was purified by column chromatography on silica gel using mixtures of CH_2-Cl_2/CH_3OH with increasing polarity (20/1, 15/1, 10/1) as eluent. The intensely green 10/1 fraction was collected and evaporated to dryness. Yield: 520 mg (0.63 mmol, 45%). ^{1}H NMR ($CDCl_3$; δ/ppm): 2.12 (s, 9 H, Cp'); 2.31 (s, 3 H, pts); 5.88 (t, J = 2.4 Hz, 6 H, Cp'); 6.21 (t, 6 H, Cp'); 7.10 (d, J = 7.8 Hz, 2 H, pts); 7.80 (d, 2 H, pts). UV/vis (MeOH, λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})): 397 (4400); 576 (1000); 678 (900). FAB$^+$ mass spectrum (m/z (% abundance)): 653 (M$^+$ − pts, 95); 574 (M$^+$ − pts − Cp', 14), 495 (M$^+$ − pts − 2 Cp', 8). Anal. Calcd for $C_{25}H_{28}Mo_3O_3S_5$ (824.62): C, 36.41; H, 3.42; S, 19.44. Found: C, 36.92; H, 3.69; S, 19.67.

Synthesis of $[(\eta^5\text{-}Cp')_3Mo_3S_4Ni(PPh_3)][pts]$ ([2][pts]). A suspension of [Ni(cod)$_2$] (30.0 mg, 0.109 mmol) in THF (5 mL) was added to a suspension (partially solution) of [1][pts] (90.0 mg, 0.109 mmol) in THF (15 mL). After stirring the brown solution for 30 min, PPh_3 (28.6 mg, 0.109 mmol) was added. After 2 h a fine precipitate had formed, which was isolated by filtration. The solid was recrystallized from CH_2Cl_2/pentane to yield a black-red powder. Yield: 112 mg (0.097 mmol, 89%). ^{1}H NMR ($CDCl_3$; δ/ppm): 2.02 (s, 9 H, Cp'); 2.27 (s, 3 H, pts); 5.46 (t, J = 2.1 Hz, 6 H, Cp'); 5.56 (t, 6 H, Cp'); 7.06 (d, J = 8.1 Hz, 2 H, pts); 7.17 (m, 6 H, PPh$_3$); 7.39 (m, 9 H, PPh$_3$); 7.85 (d, 2 H, pts). ^{31}P{^{1}H} NMR ($CDCl_3$; δ/ppm): 34.4 (s). UV/vis (MeOH; λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})): 286 (24300); 513 (1900); 678 (900). FAB$^+$ mass spectrum (m/z): 974 (M$^+$ − pts); 712 (M$^+$ − pts − PPh$_3$). Anal. Calcd for $C_{43}H_{43}Mo_3NiO_3PS_5$ (1145.60): C, 45.08; H, 3.78; S, 13.99. Found: C, 45.09; H, 3.78; S, 13.86.

Synthesis of $[(\eta^5\text{-}Cp')_3Mo_3S_4Pd(PPh_3)][pts]$ ([3][pts]). A solution of [Pd$_2$(dba)$_3$] (61 mg, 0.067 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of [1][pts] (110 mg, 0.133 mmol) in CH_2Cl_2 (20 mL). The dark brown solution was stirred for 20 min at room temperature. Solid PPh_3 (35 mg, 0.133 mmol) was added and the mixture stirred for another 2 h. The solution was concentrated to approximately 5 mL, and pentane (20 mL) was added. The dark precipitate was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 135 mg (0.113 mmol, 85%). ^{1}H NMR ($CDCl_3$; δ/ppm): 2.10 (s, 9 H, Cp'); 2.29 (s, 3 H, pts); 5.60 (t, J = 2.4 Hz, 6 H, Cp'); 5.63 (t, 6 H, Cp'); 7.09 (d, J = 7.8 Hz, 2 H, pts); 7.16 (m, 6 H, PPh$_3$); 7.34 (m, 9 H, PPh$_3$); 7.85 (d, 2 H, pts). ^{31}P{^{1}H} NMR ($CDCl_3$; δ/ppm): 26.0 (s). UV/vis (MeOH; λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})): 291 (27 700); 472 (5600); 682 (900). FAB$^+$ mass spectrum (m/z): 1022 (M$^+$ − pts); 760 (M$^+$ − pts − PPh$_3$). Anal. Calcd for $C_{43}H_{43}Mo_3O_3PPdS_5$ (1193.33): C, 43.28; H, 3.63; S, 13.43. Found: C, 43.02; H, 3.66; S, 13.49.

Synthesis of $[(\eta^5\text{-}Cp')_3Mo_3S_4Pt(nor)][pts]$ ([4][pts]). A solution of [Pt(nor)$_3$] (93 mg, 0.194 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a solution of [1][pts] (160 mg, 0.194 mmol) in CH_2Cl_2 (20 mL). After stirring the green-brown solution for 20 min at room temperature it was concentrated to approximately 5 mL by means of vacuum, and pentane (20 mL) was added. The dark precipitate was isolated by filtration, washed with pentane, and dried in a vacuum. Yield: 147 mg (0.132 mmol, 68%). ^{1}H NMR ($CDCl_3$; δ/ppm): 0.27 (d, J = 9.3 Hz, 1 H, nor); 0.42 (m, 1 H, nor); 0.98 (d, J = 5.4 Hz, 2 H, nor); 1.65 (d, J = 8.1 Hz, 2 H, nor); 2.13 (s, 3 H, Cp'); 2.16 (s,

Table 1. Crystal and Refinement Data for $[(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4\text{M}'(\text{PPh}_3)][\text{pts}]$ ([2][pts], M$'$ = Ni; [3][pts], M$'$ = Pd; [5][pts], M$'$ = Pt)

	[2][pts]	[3][pts]	[5][pts]
empirical formula	$C_{43}H_{43}Mo_3NiO_3PS_5$	$C_{43}H_{43}Mo_3O_3PPdS_5$	$C_{43}H_{43}Mo_3O_3PPtS_5$
fw	1145.57	1193.26	1281.95
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a, Å	9.4781(7)	9.462(2)	9.4431(7)
b, Å	10.872(3)	10.826(1)	10.817(2)
c, Å	41.793(3)	42.891(4)	42.723(4)
β, deg	91.889(6)	92.380(10)	92.179(7)
cell volume, Å^3	4304.3(13)	4389.9(11)	4360.8(10)
Z	4	4	4
D_c, Mg m^{-3}	1.768	1.805	1.953
μ(Mo Kα), mm^{-1}	1.604	1.553	4.356
$F(000)$	2296	2368	2496
cryst size, mm	$0.50 \times 0.18 \times 0.06$	$0.45 \times 0.25 \times 0.16$	$0.40 \times 0.15 \times 0.03$
θ limits, deg	2.22; 23.08	2.23; 25.17	2.23; 22.78
index ranges	$-10 \leq h \leq 10; 0 \leq k \leq 11;$ $0 \leq l \leq 46$	$-11 \leq h \leq 11; 0 \leq k \leq 12;$ $0 \leq l \leq 51$	$-10 \leq h \leq 10; 0 \leq k \leq 11;$ $0 \leq l \leq 46$
no. of reflns collected	6136	7969	5994
no. of ind reflns	6044 [R(int)=0.0254]	7860 [R(int)=0.0148]	5905 [R(int)=0.0747]
no. of data/restraints/params	6044/0/509	7860/0/509	5905/0/509
goodness of fit on F^2	1.127	1.137	1.035
final R indices [$I>2\sigma(I)$]	$R_1 = 0.0366$, $wR_2 = 0.0631$	$R_1 = 0.0352$, $wR_2 = 0.0742$	$R_1 = 0.0607$, $wR_2 = 0.1029$
R indices (all data)	$R_1 = 0.0644$, $wR_2 = 0.0734$	$R_1 = 0.0584$, $wR_2 = 0.0849$	$R_1 = 0.1461$, $wR_2 = 0.1292$
largest diff peak and hole, e Å^{-3}	0.756 and -0.456	0.745 and -0.708	1.306 and -0.932

6 H, Cp$'$); 2.30 (s, 3 H, pts); 2.43 (s, ^3J(PtH) = 17.7 Hz, 2 H, nor); 4.49 (s, ^2J(PtH) = 97.2 Hz, 2 H, nor); 5.60 (m, 6 H, Cp$'$); 5.66 (m, 6 H, Cp$'$); 7.09 (d, J = 8.4 Hz, 2 H, pts); 7.85 (d, 2 H, pts). UV/vis (MeOH; λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})): 424 (2300); 652 (700). FAB$^+$ mass spectrum (m/z (% abundance)): 943 (M$^+$ $-$ pts, 57); 849 (M$^+$ $-$ pts $-$ nor, 100). Anal. Calcd for $C_{32}H_{38}$-$Mo_3O_3PtS_5\cdot CH_2Cl_2$ (1198.79): C, 33.06; H, 3.36; S, 13.37. Found: C, 33.10; H, 3.37; S, 13.94.

**Synthesis of $[(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4\text{Pt}(\text{PPh}_3)][\text{pts}]$ ([5][pts]).** A solution of PPh$_3$ (50 mg, 0.191 mmol) in MeOH (3 mL) was dropped to a solution of [4][pts] (150 mg, 0.135 mmol) in MeOH (10 mL). The mixture was stirred at 60 °C for 3 h. After evaporation of the solvent in a vacuum, the residue was dissolved in CH$_2$Cl$_2$ (5 mL). Addition of pentane (20 mL) caused a green-brown solid to precipitate, which was isolated by filtration, washed with pentane, and dried in a vacuum. Yield: 159 mg (0.124 mmol, 92%). ^{1}H NMR (CDCl$_3$; δ/ppm): 2.13 (s, 9 H, Cp$'$); 2.29 (s, 3 H, pts); 5.49 (t, J = 2.1 Hz, 6 H, Cp$'$); 5.61 (t, 6 H, Cp$'$); 7.08 (d, J = 8.1 Hz, 2 H, pts); 7.20 (m, 6 H, PPh$_3$); 7.35 (m, 9 H, PPh$_3$); 7.86 (d, 2 H, pts). ^{31}P$\{^1$H$\}$ NMR (CDCl$_3$; δ/ppm): 15.4 (s, ^1J(PtP) = 6656 Hz). UV/vis (MeOH; λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})): 287 (23 600); 451 (3900); 652 (700). FAB$^+$ mass spectrum (m/z (% abundance)): 1111 (M$^+$ $-$ pts, 50); 849 (M$^+$ $-$ pts $-$ PPh$_3$, 24). Anal. Calcd for $C_{43}H_{43}Mo_3O_3PPtS_5$ (1281.99): C, 40.29; H, 3.38; S, 12.50. Found: C, 39.88; H, 3.84; S, 12.44.

X-ray Crystallography. X-ray data for [2][pts], [3][pts], and [5][pts] were collected at 293(2) K on a Nonius MACH 3 diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The structures were solved by direct methods (SIR-97)[36] 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[37] package and the relevant programs (SHELXL-97,[38]

ORTEP-3[39]) implemented therein. H atoms were included in the final structural models assuming ideal geometry and using appropriate riding models. Crystal and refinement data are given in Table 1.

Results and Discussion

The purification of heterobimetallic derivatives of $[(\eta^5\text{-}$Cp$)_3\text{Mo}_3\text{S}_4][\text{pts}]$[31] by column chromatography proved to be difficult due to their low solubility even in polar organic solvents. We therefore decided to enhance the solubility of the $[\text{Mo}_3^{IV}\text{S}_4]^{4+}$ cluster and its heterobimetallic derivatives by introducing cyclopentadienyl ligands with aliphatic side chains. For the present study, we have prepared the new homonuclear methyl-cyclopentadienyl cluster compound $[(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4][\text{pts}]$ ([1][pts]). The preparative route is very similar to that for the Cp cluster complex:[31] A conversion of $[(H_2O)_9$-$\text{Mo}_3\text{S}_4][\text{pts}]_4\cdot 9H_2O$ to a water-free thf complex followed by the reaction with methylcyclopentadienyl thallium (TlCp$'$) yielded [1][pts]. After purification by column chromatography, [1][pts] was isolated in 45% yield as an intensely green solid.

[1]$^+$

[2]$^+$: M$'$ = Ni; L = PPh$_3$

[3]$^+$: M$'$ = Pd; L = PPh$_3$

[4]$^+$: M$'$ = Pt; L = nor

[5]$^+$: M$'$ = Pt; L = PPh$_3$
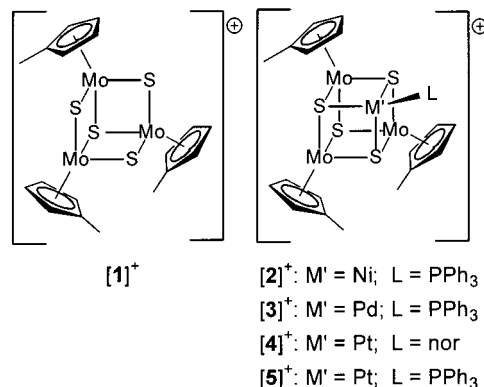
For the preparation of heterobimetallic cubane-like clusters, [1][pts] was reacted with π-alkene complexes

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of group 10 transition metals. Due to an immediate decomposition of [Ni(cod)$_2$] in halogen-containing solvents, the reaction of [**1**][pts] with [Ni(cod)$_2$] had to be carried out in THF. Both starting materials showed only a low solubility in THF, but mixing of two suspensions containing equimolar amounts of [**1**][pts] and [Ni(cod)$_2$] resulted in a rapid color change from green to brown and the formation of a solution. By addition of 1 equiv of PPh$_3$, a fine precipitate was obtained; recrystallization from CH$_2$Cl$_2$/pentane gave [(η^5-Cp′)$_3$Mo$_3$S$_4$Ni(PPh$_3$)]-[pts] ([**2**][pts]) as a dark red powder. A similar procedure using CH$_2$Cl$_2$ as solvent was applied for the reaction of [**1**][pts] with [Pd$_2$(dba)$_3$]. After combination of two CH$_2$Cl$_2$ solutions of [**1**][pts] and [Pd$_2$(dba)$_3$] with a Mo:Pd stoichiometry of 3:1, the instant formation of a nonturbid, dark brown solution was observed. As for the synthesis of [**2**][pts], the Pd site in the cluster was stabilized by the addition of PPh$_3$, resulting in the isolation of [(η^5-Cp′)$_3$Mo$_3$S$_4$Pd(PPh$_3$)][pts] ([**3**][pts]) as a dark brown powder.

While the reactions of [**1**][pts] with [Ni(cod)$_2$] and [Pd$_2$(dba)$_3$] apparently led to a rapid scission of the metal alkene bonds, the analogous procedure applied for the reaction of [**1**][pts] and [Pt(nor)$_3$] resulted in the displacement of only two norbornene ligands. [(η^5-Cp′)$_3$Mo$_3$S$_4$Pt(nor)][pts] ([**4**][pts]) was isolated as an analytically pure green-brown powder after precipitation from pentane. Coordination of alkene ligands to the heterometallic site in Mo$_3$S$_4$M′ clusters was earlier reported for both Mo$_3$S$_4$Ni[40] and Mo$_3$S$_4$Pd[7,26] cores, which took up ethene (or ethene derivatives) in acidic aqueous solution. No reactivity of the norbornene cluster complex [**4**]$^+$ toward PPh$_3$ was observed at room temperature. However at 60 °C in MeOH, a complete substitution of the norbornene ligand in [**4**]$^+$ for PPh$_3$ was achieved within a reaction time of 3 h. The reaction was indicated by only a slight color change to olive, and the isolated product, [(η^5-Cp′)$_3$Mo$_3$S$_4$Pt(PPh$_3$)][pts] ([**5**][pts]), virtually had the same color in the solid state as the starting material [**4**][pts].

The proton NMR spectra of the PPh$_3$ cluster complexes [**2**]$^+$, [**3**]$^+$, and [**5**]$^+$ displayed almost identical chemical shifts. Compared to the resonances in [**1**]$^+$, the Cp′ signals were slightly shifted to higher field. The PPh$_3$ protons resonated at approximately 7.18 and 7.36 ppm. In the ^{1}H NMR spectrum of [**4**]$^+$, well-resolved signals for the norbornene ligand were found. Compared to the data of the starting material [Pt(nor)$_3$],[41] the alkene protons were shifted from 3.36 to 4.49 ppm, thereby indicating a decrease in electron density at the Pt atom after incorporation in the cluster core. The tertiary norbornene protons at δ = 2.43, reported as a singlet at δ = 2.96 in [Pt(nor)$_3$], displayed a ^3J(PtH) coupling constant of 17.7 Hz. The methylene protons were found as AB doublets at higher field in accordance with the reported shifts for [Pt(nor)$_3$].

In the ^{31}P{^{1}H} NMR spectra, the PPh$_3$ ligands in [**2**]$^+$, [**3**]$^+$, and [**5**]$^+$ resonated as singlets in a range 35−15 ppm, the latter flanked by Pt satellites with a coupling constant ^1J(PtP) of 6656 Hz. A similar high ^1J(PtP) coupling constant of 6133 Hz was reported for [Cl$_3$-

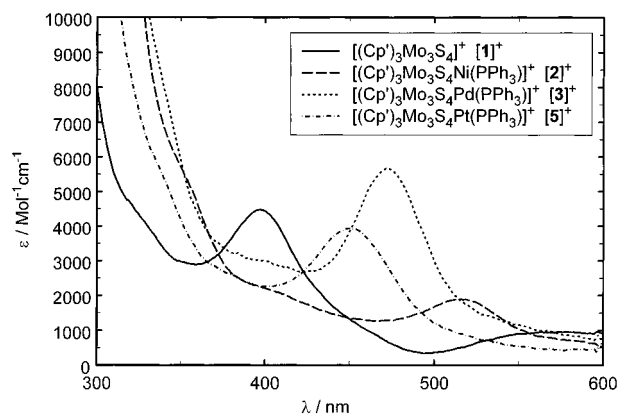**Figure 1.** UV/vis spectra of [(η^5-Cp′)$_3$Mo$_3$S$_4$]$^+$ ([**1**]$^+$) and [(η^5-Cp′)$_3$Mo$_3$S$_4$M′(PPh$_3$)]$^+$ ([**2**]$^+$, M′ = Ni; [**3**]$^+$, M′ = Pd; [**5**]$^+$, M′ = Pt) in methanol.

Mo$_3$S$_4$Pt(dppe)$_4$]Cl (dppe = 1,2-(diphenylphosphanyl)-ethane).[8] Sykes and co-workers[42] observed an unusually high stretching frequency (2060 cm^{-1}) for the carbonyl ligand in [(H$_2$O)$_9$Mo$_3$S$_4$Ni(CO)][pts]$_4$, and this incited a discussion in the literature about the true oxidation state of the heterometal in Mo$_3$S$_4$M′ cluster cores. Originally the high CO stretching frequency was interpreted to have its origin in a metal oxidation state "probably appreciably closer to Ni^{II}" than to Ni^0.[42] Later, Harris and co-workers[20] on the basis of Fenske−Hall molecular orbital calculations explained the appearance of high carbonyl wavenumbers by the ratio of the orbital energy levels of the Mo$_3$ fragment, the heterometal atom, and the carbonyl ligand and concluded that the nickel atom was not oxidized. Since the range for ^1J(Pt^{II}P) coupling constants is reported[43] to be 1400−5000 Hz, whereas ^1J(Pt^{0}P) couplings range up to 9000 Hz, the observation of a ^1J(PtP) coupling constant of 6656 Hz for [**5**][pts] supports the view that its platinum atom is Pt^0- rather than Pt^{II}-like.

The colors of the phosphane cluster complexes [**2**]$^+$ (red), [**3**]$^+$ (brown), and [**5**]$^+$ (green-brown) in MeOH solution were reflected in the presence of charge-transfer bands in the visible region of the UV/Vis spectra (Figure 1). A blue-shift of the dominating absorption band from 513 ([**2**]$^+$) to 472 ([**3**]$^+$) and 451 nm ([**5**]$^+$) was observed when going down the Ni triad. Bands at low wavelengths seem to be due to intraligand transitions, as they show only minor shifts.

Crystallographic Study. Since the triphenylphosphane-containing clusters [**2**][pts], [**3**][pts], and [**5**][pts] differ only in the nature of the heterometal, X-ray crystal structure data would allow the influence of the heterometal on the cluster core to be studied within a complete transition metal group. It was therefore one of our particular aims to obtain X-ray structural information of all three cluster compounds. Single crystals were grown by slow diffusion of pentane into CH$_2$Cl$_2$ solutions of [**2**][pts], [**3**][pts], and [**5**][pts]. Since the three cluster cations proved to be isostructural, Figure 2 shows the ORTEP plot only of [**2**]$^+$. Selected bond distances and angles are collected in Table 2.

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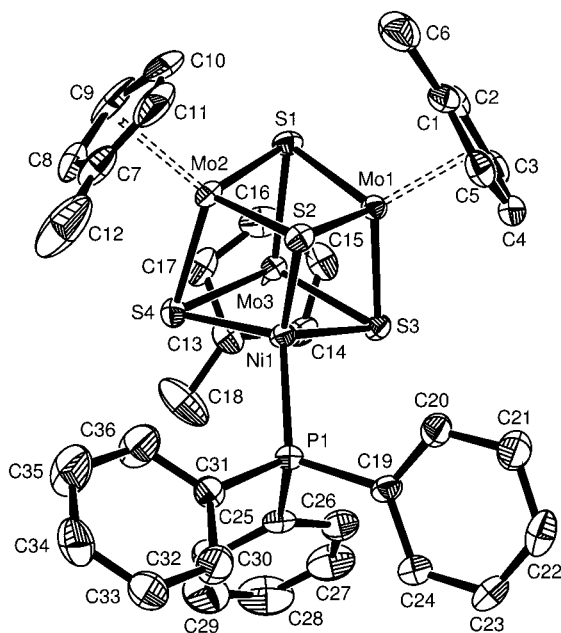
Figure 2. ORTEP plot of the cluster cation $[(\eta^5\text{-Cp}')_3\text{-Mo}_3\text{S}_4\text{Ni}(\text{PPh}_3)]^+$ ($[\mathbf{2}]^+$) representing the isostructural series $[\mathbf{2}]^+$, $[\mathbf{3}]^+$, and $[\mathbf{5}]^+$. Atoms are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4\text{M}'(\text{PPh}_3)][\text{pts}]$ ($[\mathbf{2}][\text{pts}]$, M′ = Ni; $[\mathbf{3}][\text{pts}]$, M′ = Pd; $[\mathbf{5}][\text{pts}]$, M′ = Pt)

	$[\mathbf{2}][\text{pts}]$: M′ = Ni	$[\mathbf{3}][\text{pts}]$: M′ = Pd	$[\mathbf{5}][\text{pts}]$: M′ = Pt
Mo(1)–M′	2.7215(9)	2.8731(6)	2.869(2)
Mo(2)–M′	2.7237(9)	2.8623(6)	2.861(2)
Mo(3)–M′	2.7088(8)	2.8565(7)	2.853(1)
M′–S(2)	2.199(2)	2.382(1)	2.363(4)
M′–S(3)	2.206(2)	2.381(1)	2.379(5)
M′–S(4)	2.211(2)	2.390(1)	2.372(5)
M′–P(1)	2.160(2)	2.277(1)	2.232(4)
Mo(1)–M′–Mo(2)	62.71(3)	59.24(2)	59.35(5)
Mo(1)–M′–Mo(3)	62.72(2)	59.26(2)	59.38(4)
Mo(2)–M′–Mo(3)	62.86(2)	59.58(2)	59.60(4)
Mo(1)–M′–P(1)	141.20(6)	143.24(4)	143.3(1)
Mo(2)–M′–P(1)	150.48(6)	152.82(4)	152.6(1)
Mo(3)–M′–P(1)	136.31(5)	138.00(4)	138.2(1)
S(2)–M′–S(3)	107.46(7)	101.54(5)	101.9(2)
S(2)–M′–S(4)	107.53(7)	102.09(5)	102.7(2)
S(3)–M′–S(4)	108.24(6)	102.12(5)	102.7(2)
S(2)–M′–P(1)	117.35(6)	122.64(5)	122.1(2)
S(3)–M′–P(1)	103.74(7)	108.55(5)	108.5(2)
S(4)–M′–P(1)	112.08(7)	117.10(5)	116.5(2)

The X-ray structures show that each of the cluster cores $[\mathbf{2}]^+$, $[\mathbf{3}]^+$, and $[\mathbf{5}]^+$ are formed by a single cubane-like $\text{Mo}_3\text{S}_4\text{M}'$ array, in which the metal atoms occupy the vertexes of a slightly distorted tetrahedron. Each tetrahedral face is capped by a μ_3-coordinated sulfido ligand, thus generating a cubane-like structure. The Mo–Mo distances (average for $[\mathbf{2}]^+$ 2.831 Å; for $[\mathbf{3}]^+$ 2.836 Å; for $[\mathbf{5}]^+$ 2.837 Å) are consistent with single bonds between the metal atoms and are only slightly affected by the nature of M′. They are, however, significantly shorter than the average Mo–Mo distance of 2.877 Å in the earlier reported cluster $[(\eta^5\text{-Cp})_3\text{-Mo}_3\text{S}_4\text{W}(\text{CO})_3][\text{pts}]$.[31] The most interesting differences between $[\mathbf{2}]^+$, $[\mathbf{3}]^+$, and $[\mathbf{5}]^+$ are found in the M′–S and M′–P bond lengths. These distances generally expand when going from Ni to Pd (e.g., Ni(1)–P(1) = 2.160(2) Å; Pd(1)–P(1) = 2.277(1) Å), but are slightly smaller

for Pt than for Pd (Pt(1)–P(1) = 2.232(4) Å). The same trend is seen for the Mo–M′ bond lengths (Mo–Ni$_{av}$ = 2.718 Å; Mo–Pd$_{av}$ = 2.864 Å; Mo–Pt$_{av}$ = 2.861 Å); these bond lengths are consistent with single bonds between each molybdenum and heterometal atom. With six metal–metal bonds in each cluster core, the cations $[\mathbf{2}]^+$, $[\mathbf{3}]^+$, and $[\mathbf{5}]^+$ represent electron-precise 60 VE clusters according to the Wade–Mingos rules for electron-counting in polyhedra.[44]

The tendency of 5d transition metals to form metal-to-ligand bonds of equal or even shorter distance than their 4d counterparts is a well-known phenomenon categorized under the heading of the "lanthanide contraction". Traditionally this has been explained as a contraction of the valence electron shells due to the poor ability of the 4f electron shell to screen the nuclear charge.[45] Recently, it has been realized that this shell structure explanation is too simplistic and that relativistic effects play a role in the picture.[45–47] Calculations showed this to be most pronounced for the group 10 and 11 elements Pt and Au, but few experimental data exist against which comparisons can be made. As pointed out by Schmidbaur,[48] complexes that can be compared must have identical coordination spheres (in terms of both ligands and counterions) and must crystallize in isomorphous lattices determined at identical experimental conditions. These strict requirements were fulfilled only in a few cases, a prominent example being the bis-(trimesitylphosphane)silver(I) and -gold(I) complexes $[\text{M}(\text{PMes}_3)_2][\text{BF}_4]$, which indeed revealed that the covalent radius of two-coordinated Au^I is more than 0.08 Å smaller than that of the corresponding Ag^I.[48] In isomorphous group 10 metal complexes, the size differences between Pd and Pt covalent radii are less pronounced. For linear two-coordinated complexes $[\text{M}(\text{PhᵗBu}_2)_2]$ (M = Pd, Pt) a size difference of 0.033 Å was recorded,[49] and the tetracoordinated planar dioxygen adducts $[\text{M}(\text{O}_2)(\text{PhᵗBu}_2)_2]$ (M = Pd, Pt) showed a Pd–P/Pt–P bond length difference of 0.068 Å.[50]

The isomorphously crystallizing cluster cations $[\mathbf{2}]^+$, $[\mathbf{3}]^+$, and $[\mathbf{5}]^+$ open the possibility to calculate covalent radius differences for (quasi)tetrahedrally coordinated Ni^0, Pd^0, and Pt^0 atoms. These calculations focus on metal–phosphorus distances, since the coordinating sulfido ligands as a part of the rigid cluster core can hardly be used for comparable studies. In all three clusters, the monodentate PPh$_3$ ligand faces weak interactions with two of the Cp′ methyl groups pointing toward the phenyl groups (closest distance in all clusters found in $[\mathbf{5}]^+$: H12B–H36 2.262 Å). This results in a slight misdirection of the heterometal–P(1) vector with respect to the 3-fold axis of the cubane-like cluster core. An interaction of phenyl protons with the sulfido ligands

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can be excluded (closest S–H$_{phenyl}$ distance $\geq$ 3.0 Å in all clusters). While the metal–phosphorus bond as expected expands (by 0.117 Å) when going from Ni to Pd, the Pt–P bond shows a significant 0.045 Å shortening relative to the corresponding Pd–P bond. Taking r_P = 1.11 Å[51] as a constant value for the covalent radius of tetrahedral phosphorus, the metal atoms contribute to the metal–phosphorus bond length by 1.05 Å (Ni), 1.17 Å (Pd), and 1.12 Å (Pt). This represents a 4% reduction of the Pt as compared to the Pd size.

However, for two reasons the bond length differences in each of the above-mentioned Pd/Pt systems cannot be compared outside their specific isomorphously crystallizing complex pairs: First, a change in metal atom coordination geometry (linear, planar, tetrahedral) affects the orbital energy levels and thereby possibly the metal-to-ligand bond length differences. Second, the geometric and electronic features of the cubane-like cluster core, which partially encapsulates the heterometal, also influence the metal–phosphorus bond length. This fact becomes evident when the Ni–P bond length of 2.160(2) Å in [**2**]$^+$ is compared to the Ni–P bond length of 2.143(3) Å in the isomorphously crystallizing cluster [(η^5-Cp′)$_3$W$_3$S$_4$Ni(PPh$_3$)]$^+$.[52] The shorter Ni–P bond in the tungsten–nickel cluster is most likely explained by the electronic influence of the tungsten-based cluster core. A broadening of the data basis would be possible by crystal structure determinations of the [(η^5-Cp′)$_3$W$_3$S$_4$M′(PPh$_3$)]$^+$ (M′ = Pd, Pt) clusters; this work is currently in progress.

Supporting Information Available: ORTEP plots for the cluster cations [**3**]$^+$ and [**5**]$^+$; tables on atomic coordinates, thermal parameters, bond lengths and angles, and unit cell packing diagrams for [**2**][pts], [**3**][pts], and [**5**][pts]; data are also available in electronic form in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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