and Tc-N3-C10 = 114°). The Tc—S and Tc═O1 distances are unexceptional.[18]

The neutral complexes [TcO(PIC)] and [TcO(PYR)] react rapidly with a variety of thiol compounds to give highly colored polar complexes, which remained bound to silica or alumina on chromatography and thus could not be adequately purified for detailed analysis. Similar results were obtained upon treating the complexes with inorganic reducing agents, such as stannous chloride, stannous tartrate, and sodium dithionite. It is exactly for this reason that the desired neutral complexes [TcO(PIC)] and [TcO(PYR)] could not be satisfactorily prepared from the unprotected thiol forms of the ligands. Indeed, attempts to prepare [TcO(PIC)] from reaction of $(Bu_4N)[TcOCl_4]$ and 1 equiv of H_3PIC (having an -SH group) gave only traces of the neutral product, with the remainder of the technetium as a mixture of highly colored species that no longer showed a Tc═O stretch in the infrared region. In this latter reaction it is likely that the thiol has caused a reduction of the metal center. In contrast, the thiol of the ligands $H_2PIC(Bzm)$ and $H_2PIC(Acm)$ is masked by the protecting group and this stops unwanted redox chemistry from occurring.

The S-deprotection reactions described here that lead to [TcO(PIC)] and [TcO(PYR)] are more simply described as dealkylation reactions. Dealkylation of thioether ligands coordinated to transition metals is well documented.[19] Indeed, we have also characterized intermolecular and intramolecular thioether dealkylations on technetium(V) complexes in which amines and water effect an S_N2 attack on the electrophilic carbon α to the coordinated thioether.[4] The *S*-Acm- and *S*-Bzm-protected ligands described in the present study were synthesized to be very reactive toward S-deprotection (S-dealkylation). Unlike the benzyl group that is removed by a nucleophilic attack of water, the (acetylamino)methyl and (benzoylamino)methyl groups can be eliminated as their respective *N*-methylene amide cations, $H_2C{=}NHCOCH_3^+$ or $H_2C{=}NHCOPh^+$, which are quenched by reaction with the solvent. This elimination reaction was rapid enough that technetium complexes of the *S*-Acm- and *S*-Bzm-protected ligands were not observed.

Acknowledgment. We wish to thank Catherine E. Costello and Cheng-hui Zeng of the NIH Northeast Regional Mass Spectrometry Laboratory for the FAB mass spectra and J. Dewan for collection of the X-ray data.

Supplementary Material Available: Tables SI-SVI, listing complete crystallographic data and collection parameters, final positional and thermal parameters, temperature factor expressions, and complete bond distances and angles (12 pages); a listing of observed and calculated structure factor data (19 pages).

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Synthesis and Structural Characterization of Mixed-Metal Chloro Chalcogenido Cluster Complexes of Molybdenum and Nickel $[Mo_3Ni_2X_4Cl_4\{P(C_2H_5)_3\}_5]$ (X = S, Se)

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Condensation of $[Mo_3X_4Cl_4(PEt_3)_n(MeOH)_{5-n}]$ (X = S, $n = 3$; X = Se, $n = 5$) with $Ni(cod)_2$ formed pentanuclear mixed-metal cluster complexes $[Mo_3Ni_2X_4Cl_4\{P(C_2H_5)_3\}_5]$ (**1**, X = S; **2**, X = Se). X-ray structure determination of **1** has shown that the cluster framework is a square pyramid consisting of three molybdenum and two nickel atoms. A sulfido ligand quadruply bridges the square base of Mo_2Ni_2, and three triply bridging sulfido ligands cap the triangles of Mo_3 and Mo_2Ni. A triply bridging chloro ligand is on the triangular face of $MoNi_2$, and another chloro ligand bridges the basal molybdenum atoms to which terminal chloro ligands are also bonded. One triethylphosphine ligand is coordinated to each of the five metals. Crystal data for $[Mo_3Ni_2S_4Cl_4\{P(C_2H_5)_3\}_5]\cdot CHCl_3$: $C_{31}H_{76}Cl_7Mo_3Ni_2P_5S_4$, triclinic, space group $P\bar{1}$ with $a = 14.628$ (4) Å, $b = 18.095$ (8) Å, $c = 10.594$ (2) Å, $\alpha = 93.68$ (4)°, $\beta = 98.01$ (4)°, $\gamma = 91.22$ (3)°, $V = 2770$ (2) Å^3, $Z = 2$, $R = 0.046$, and $R_w = 0.041$. Selected bond distances (Å) and angles (deg): Mo-Mo(av), 2.677; Mo-Ni(av), 2.586; Ni(1)-Ni(2), 2.710(1); Mo(2)-Mo(3)-Ni(1), 90.23 (3); Mo(3)-Mo(2)-Ni(2), 89.80(3); Mo(2)-Mo(1)-Mo(3), 61.20 (2); Ni(1)-Mo(1)-Ni(2), 65.54 (4); Mo(2)-Mo(1)-Ni(2), 62.05 (3). ^{31}P NMR spectra of the complexes can be interpreted as AA′MXX′ systems, and all the couplings among the phosphorus nuclei have been determined by simulation.

Introduction

The triangular metal framework is ubiquitous in the polyhedral cluster compounds,[1] and some trinuclear cluster complexes are good starting materials for the preparation of larger polyhedra.[2] This has been demonstrated in the syntheses of tetrahedral,[3] square-pyramidal,[4] trigonal-prismatic,[5] bitetrahedral,[6] bicapped-tetrahedral,[7] and octahedral clusters.[8] Our contribution to the area was the preparation of $[M_6S_8(PEt_3)_6]$ (M = Mo,[9] W[10]), which may be regarded as molecular models for the superconducting Chevrel phases.[11] We have now found that trinuclear molybdenum chalcogenido clusters condense with a zerovalent nickel complex to form square-pyramidal mixed-metal cluster complexes.[12]

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Table I. Crystal Parameters and X-ray Diffraction Data for $[Mo_3Ni_2S_4Cl_4(PEt_3)_5]\cdot CHCl_3$

formula	$C_{31}H_{76}Cl_7Mo_3Ni_2P_5S_4$	fw	1385.45
a, Å	14.628 (4)	space group	$P\bar{1}$
b, Å	18.095 (8)	Z	2
c, Å	10.594 (2)	λ(Mo Kα), Å	0.71069
α, deg	93.68 (4)	μ, cm^{-1}	19.69
β, deg	98.01 (4)	no. of obsd rflcns	6814 (>5σ)
γ, deg	91.22 (3)	R, R_w[a]	0.047, 0.042
V, $Å^3$	2770 (2)		

[a] $w = 1/\sigma^2(|F_o|)$.

Table II. Positional and (Equivalent) Thermal Parameters for **1**

atom	$10^4x/a$	$10^4y/b$	$10^4z/c$	10^3U, $Å^2$
Mo(1)	−2198.5 (5)	2509.0 (4)	4175.9 (6)	30.6 (3)
Mo(2)	−1857.8 (4)	1697.2 (4)	2105.1 (6)	30.7 (3)
Mo(3)	−3484.9 (4)	2379.2 (4)	2144.4 (6)	32.3 (3)
Ni(1)	−2582.0 (7)	3649.8 (5)	3000.1 (9)	38.5 (5)
Ni(2)	−955.1 (7)	2960.6 (5)	3001.0 (9)	37.9 (5)
S(1)	−2152 (1)	2921 (1)	1361 (2)	37 (1)
S(2)	−2995 (1)	1382 (1)	3417 (2)	36 (1)
S(3)	−770 (1)	1910 (1)	3948 (2)	39 (1)
S(4)	−3641 (1)	3144 (1)	3992 (2)	40 (1)
Cl(1)	−1342 (1)	3744 (1)	4739 (2)	46 (1)
Cl(2)	−756 (1)	1610 (1)	515 (2)	49 (1)
Cl(3)	−4411 (1)	3112 (1)	536 (2)	53 (1)
Cl(4)	−3262 (1)	1394 (1)	372 (2)	44 (1)
P(1)	−2148 (2)	2277 (1)	6521 (2)	43 (1)
P(2)	−1501 (2)	292 (1)	2094 (2)	51 (1)
P(3)	−5100 (1)	1837 (1)	2369 (2)	45 (1)
P(4)	−3004 (2)	4732 (1	2222 (2)	48 (1)
P(5)	359 (2)	3349 (1)	2393 (2)	50 (1)
C(1)	−1158 (9)	2693 (6)	7541 (9)	92 (8)
C(2)	−226 (7)	2370 (7)	7320 (10)	91 (8)
C(3)	−2110 (9)	1315 (5)	6971 (9)	97 (8)
C(4)	−3006 (8)	867 (6)	6711 (10)	92 (7)
C(5)	−3086 (8)	2643 (7)	7312 (9)	87 (8)
C(6)	−3115 (8)	3486 (6)	7429 (10)	87 (7)
C(7)	−334 (6)	8 (5)	1928 (9)	67 (6)
C(8)	415 (7)	332 (6)	2923 (11)	97 (8)
C(9)	−2180 (9)	−295 (7)	893 (12)	105 (4)
C(10)	−1952 (10)	−286 (8)	−295 (15)	141 (6)
C(11)	−1770 (9)	−141 (6)	3594 (13)	108 (9)
C(12)	−1487 (11)	−887 (7)	3826 (14)	139 (11)
C(13)	−5225 (6)	1555 (5)	3957 (8)	58 (5)
C(14)	−6162 (7)	1229 (6)	4153 (10)	86 (7)
C(15)	−5479 (6)	1009 (5)	1340 (9)	64 (6)
C(16)	−5013 (8)	286 (5)	1708 (11)	85 (7)
C(17)	−6077 (5)	2439 (5)	2003 (10)	66 (6)
C(18)	−6038 (6)	3149 (5)	2833 (12)	83 (7)
C(19)	−2334 (7)	5547 (5)	2973 (10)	72 (6)
C(20)	−1348 (8)	5536 (6)	2839 (12)	97 (8)
C(21)	−2954 (7)	4774 (5)	520 (8)	63 (6)
C(22)	−3252 (8)	5467 (6)	−110 (10)	100 (8)
C(23)	−4190 (7)	4984 (5)	2345 (10)	73 (6)
C(24)	−4406 (9)	5082 (6)	3694 (13)	117 (10)
C(25)	1298 (7)	2709 (6)	2760 (14)	91 (8)
C(26)	1598 (8)	2666 (8)	4189 (16)	125 (10)
C(27)	790 (6)	4235 (5)	3199 (9)	65 (6)
C(28)	1700 (8)	4557 (6)	2920 (12)	103 (8)
C(29)	393 (7)	3454 (6)	707 (10)	74 (7)
C(30)	−276 (10)	4011 (7)	161 (10)	106 (9)
Cl(5)	5780 (3)	7095 (2)	3329 (3)	117 (2)
Cl(6)	7060 (3)	7535 (2)	1680 (4)	143 (3)
Cl(7)	5634 (3)	8505 (2)	2256 (4)	141 (3)
C(31)	5934 (8)	7574 (6)	2016 (10)	88 (8)

Experimental Section

Reagents. $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$[13] and $Ni(cod)_2$ (cod = cycloocta-1,5-diene)[14] were prepared by literature methods. $Mo_3Se_7Cl_4$ was prepared by the reaction of $MoCl_3$ with selenium.[15] PEt_3 (Nippon Chemical Co. Ltd.) was used as received. The solvents were dried and distilled under dinitrogen.

Instruments. ^1H NMR spectra were measured by a JEOL FX100 spectrometer with TMS as internal reference, and ^{31}P NMR spectra by JEOL FX100 (40.25 MHz) and JEOL GX500 (202.35 MHz) spectrometers in 5% toluene-d_8 solutions with 85% H_3PO_4 as an external reference. ^{77}Se NMR spectra were recorded by JEOL GX270 (51.39 MHz) and JEOL GX500 (95.25 MHz) spectrometers in 15% chloroform-d or dichloromethane-d_2 solutions with $(CH_3)_2Se$ as an external reference. Infrared spectra were recorded by a Hitachi 295 spectrometer, UV–vis spectra by a Shimadzu UV-265FS spectrometer, and XPS spectra by a VG Scientific Escalab MkII spectrometer with Mg Kα radiation at the Institute for Molecular Science.

Synthesis. Every operation was carried out under a dinitrogen or argon atmosphere.

$[Mo_3Ni_2S_4Cl_4(PEt_3)_5]$ (1). Treatment of $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$ (0.98 g, 1.0 mmol) with $Ni(cod)_2$ (0.55 g, 2.0 mmol) and PEt_3 (0.3 mL, 2.0 mmol) in tetrahydrofuran (15 mL) under dinitrogen at room temperature for 30 min gave a greenish brown solution. Black crystals were obtained in an isolated yield of 45% after concentration of the solution followed by slow addition of methanol. Anal. Calcd for $C_{30}H_{75}Cl_4Mo_3Ni_2P_5S_4$: C, 28.46; H, 5.97; Cl, 11.20; Mo, 22.73; Ni, 9.27. Found: C, 28.57; H, 5.70; Cl, 11.05; Mo, 22.0; Ni, 8.8. The complex is air-sensitive and decomposes gradually in the solid state and rapidly in solutions when exposed to air. The visible absorption spectrum (benzene solution) shows an absorption at 590 nm (ε = 1400).

$[Mo_3Ni_2Se_4Cl_4(PEt_3)_5]$ (2). $Mo_3Se_7Cl_4$ (1.5 g, 1.5 mmol) and PEt_3 (1.8 g, 15 mmol) were reacted in a mixed solvent of toluene (10 mL) and methanol (10 mL) at room temperature for 12 h. The solution was cooled at −60 °C and $SePEt_3$ was removed by filtration. Solvents and excess triethylphosphine were removed under reduced pressure, the residue was dissolved in THF, and the resulting mixture was added to a solution of $Ni(cod)_2$ (0.68 g, 2.5 mmol) in THF (30 mL). After the solution was stirred for 2 h and filtered, the filtrate was concentrated. Slow addition of methanol formed dark brown needles, which were separated out and washed with methanol. Yield: 43%. Anal. Calcd for $C_{30}H_{75}Cl_4Mo_3Ni_2P_5Se_4$: C, 24.79; H, 5.20; Mo, 19.80; Ni, 8.07; Se, 21.73. Found: C, 24.96; H, 4.99; Mo, 19.0; Ni, 7.5; Se, 20.6. The complex has absorptions at 613 nm (ε = 1200) and at 741 nm (ε = 1100) in benzene.

X-ray Structure Determination. Single crystals of **1** were obtained by slow diffusion of ether onto a chloroform solution in a tube (10-mm diameter) and sealed in a glass capillary under argon for the X-ray measurements. Weissenberg photographs showed no systematic absences and suggested the space group of $P\bar{1}$ or P1, and the structure was successfully solved by using $P\bar{1}$. The intensity data were collected by a Rigaku AFC-4 diffractometer equipped with a Rotaflex rotating-anode X-ray generator. The positions of heavy atoms were determined by direct methods with use of MULTAN78, and the carbon atoms were located on the Fourier maps. Anisotropic refinements yielded large thermal ellipsoids for the C(9) and C(10) atoms and a very short C(9)–C(10) distance. Therefore, these atoms were refined isotropically in the final stages. All other non-hydrogen atoms were treated anisotropically. In the final full-matrix least-squares refinements, hydrogen atoms were included at calculated positions (C–H = 0.92 Å). The hydrogen atoms were classified into two groups (methyl group hydrogen atoms and others), and the isotropic temperature factors of the atoms in each group were refined as one parameter. Data collection and calculations were performed at Research Center for Protein Engineering, Osaka University. The crystallographic data are given in Table I, and other details, in the supplementary material. Atomic coordinates are listed in Table II.

Results

Structure. The X-ray structure of complex **1** recrystallized from chloroform is illustrated in Figure 1. Interatomic distances and angles are given in Table III.

The cluster skeleton of **1** is a square pyramid consisting of an apical molybdenum, two basal molybdenum, and two basal nickel atoms. On each triangular face is a μ_3-ligand, and the basal

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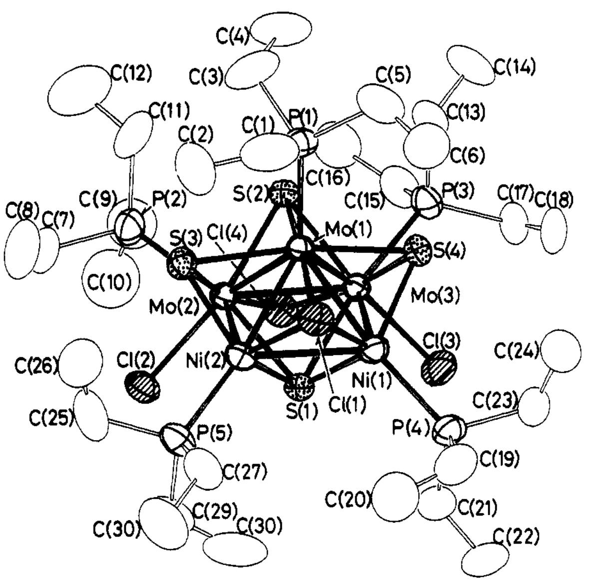

Figure 1. ORTEP drawing of the molecular structure and labeling scheme for **1**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) for **1**

Mo(1)-Mo(2)	2.672 (1)	Ni(1)-S(1)	2.279 (2)
Mo(1)-Mo(3)	2.649 (1)	Ni(1)-S(4)	2.205 (2)
Mo(2)-Mo(3)	2.709 (1)	Ni(2)-S(1)	2.285 (2)
Mo(1)-Ni(1)	2.512 (1)	Ni(2)-S(3)	2.210 (2)
Mo(1)-Ni(2)	2.495 (1)	Mo(1)-Cl(1)	2.534 (2)
Mo(2)-Ni(2)	2.667 (1)	Mo(2)-Cl(2)	2.489 (2)
Mo(3)-Ni(1)	2.669 (1)	Mo(2)-Cl(4)	2.581 (2)
Ni(1)-Ni(2)	2.710 (1)	Mo(3)-Cl(3)	2.494 (2)
Mo(1)-S(2)	2.364 (2)	Mo(3)-Cl(4)	2.564 (2)
Mo(1)-S(3)	2.409 (2)	Ni(1)-Cl(1)	2.394 (2)
Mo(1)-S(4)	2.414 (2)	Ni(2)-Cl(1)	2.390 (2)
Mo(2)-S(1)	2.425 (2)	Mo(1)-P(1)	2.538 (2)
Mo(2)-S(2)	2.393 (2)	Mo(2)-P(2)	2.606 (2)
Mo(2)-S(3)	2.346 (2)	Mo(3)-P(3)	2.587 (2)
Mo(3)-S(1)	2.433 (2)	N(1)-P(4)	2.239 (2)
Mo(3)-S(2)	2.384 (2)	Ni(2)-P(5)	2.225 (3)
Mo(3)-S(4)	2.364 (2)		
Mo(2)-Mo(1)-Mo(3)	61.20 (2)	Ni(1)-S(1)-Ni(2)	72.85 (7)
Mo(3)-Mo(1)-Ni(1)	62.21 (3)	Mo(1)-S(2)-Mo(2)	68.36 (6)
Ni(1)-Mo(1)-Ni(2)	65.54 (4)	Mo(1)-S(2)-Mo(3)	67.82 (6)
Mo(2)-Mo(1)-Ni(2)	62.05 (3)	Mo(2)-S(2)-Mo(3)	69.08 (6)
Mo(1)-Mo(2)-Mo(3)	58.97 (2)	Mo(1)-S(3)-Mo(2)	68.37 (6)
Mo(3)-Mo(2)-Ni(2)	89.80 (3)	Mo(1)-S(3)-Ni(2)	65.22 (6)
Mo(1)-Mo(3)-Ni(1)	56.39 (3)	Mo(2)-S(3)-Ni(2)	71.60 (6)
Mo(2)-Mo(3)-Ni(1)	90.23 (3)	Mo(1)-S(4)-Mo(3)	67.32 (6)
Mo(1)-Ni(1)-Ni(2)	56.92 (3)	Mo(1)-S(4)-Ni(1)	65.72 (6)
Mo(3)-Ni(1)-Ni(2)	89.74 (4)	Mo(3)-S(4)-Ni(1)	71.39 (7)
Mo(1)-Ni(2)-Mo(2)	62.25 (3)	Mo(1)-Cl(1)-Ni(1)	61.22 (5)
Mo(2)-Ni(2)-Ni(1)	90.22 (4)	Mo(1)-Cl(1)-Ni(2)	60.80 (5)
Mo(2)-S(1)-Mo(3)	67.77 (5)	Ni(1)-Cl(1)-Ni(2)	69.02 (6)
Mo(2)-S(1)-Ni(2)	68.92 (6)	Mo(2)-Cl(4)-Mo(3)	63.52 (5)
Mo(3)-S(1)-Ni(1)	68.89 (6)		

Mo–Mo bond is bridged with a μ_2-ligand. The basal Mo_2Ni_2 square is capped by a μ_4-ligand. It is generally difficult to distinguish chlorine from sulfur atoms in the X-ray structure determination because they are adjacent elements. However, the bond distances show unequivocally the kinds of ligands in **1**. Among four μ_3-ligands, the one on the triangle $MoNi_2$ has a uniquely long bond with the apical molybdenum (2.53 Å in contrast with 2.36, 2.41, and 2.41 Å for other three bonds), and it must be assigned as a chlorine, the other three μ_3-ligands being sulfurs. Comparison of the distances between these μ_3-ligands and the Ni atom also supports this assignment (2.39 Å for Ni–Cl vs 2.21 Å for Ni–S). The μ_2-ligand bridging the Mo(2)–Mo(3) bond cannot be a sulfur because the bond distances involving the molybdenum atoms are too long (observed 2.56 and 2.58 Å as compared with 2.29 Å for Mo–μ_2-S in $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$[13]). It must therefore be a chlorine. As three of the four sulfur atoms are μ_3-ligands, the μ_4-ligand on the basal Mo_2Ni square is the remaining sulfur.

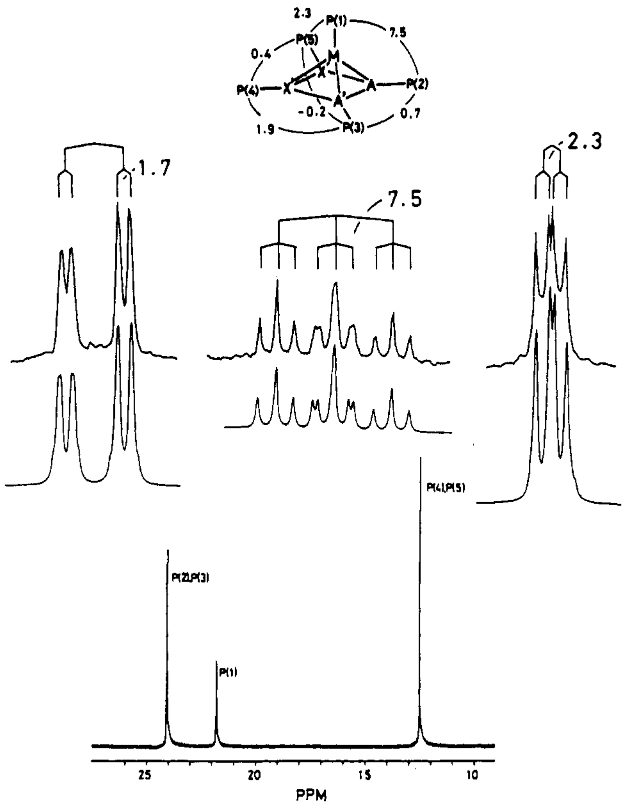

Figure 2. ^1H-decoupled ^{31}P NMR spectrum of **1** with a computer-simulated one shown below. The calculated coupling constants (Hz) between the phosphorus nuclei are indicated in the structure.

Besides the bridging ligands described above, one triethylphosphine ligand is coordinating to each of the five metals, and a terminal chloro ligand is bonded to each basal molybdenum atom. The arrangement of the coordinating ligands around each metal is for the nickel atom tetrahedral (2 S + Cl + P), for the basal molybdenum octahedral (3 S + 2 Cl + P), and for the top molybdenum square pyramidal (3 S + Cl + P). There is a pseudomirror plane passing the apical molybdenum and bisecting the Mo–Mo and Ni–Ni edges of the square base.

The distance Mo(2)–Mo(3) (2.709 Å) is longer than Mo(1)–Mo(2) (2.672 Å) or Mo(1)–Mo(3) (2.649 Å) but is short enough to be a Mo–Mo bond distance. The Mo(1)–Ni(1) (2.512 Å) and Mo(1)–Ni(2) (2.495 Å) distances are shorter than Mo(2)–Ni(2) (2.667 Å) and Mo(3)–Ni(1) (2.669 Å). They are in the range of Mo–Ni bonding. The Ni–Ni interatomic distance of 2.710 Å is short enough to imply Ni–Ni bonding.[16]

^{31}P NMR Study of 1 and 2. Figure 2 shows a proton-decoupled spectrum of **1** recorded at 40.25 MHz. There are three multiplets at 12.52 ppm (dd), 21.90 ppm (tt), and 24.05 ppm (dd) with an intensity ratio of 2:1:2. The magnitudes of peak splittings did not change in the spectra taken at 202.35 MHz (JEOL GX500), indicating that they are the couplings between the five ^{31}P nuclei. The spectrum of the selenium cluster **2** (Figure 3) gives multiplets at 14.8 ppm (dd), 19.7 ppm (septet), and 32.6 ppm (dd).

^{77}Se NMR Study of 2. A proton-decoupled ^{77}Se NMR spectrum of **2** was recorded at 51.39 MHz. There are three peaks at (A) 363 ppm (m), (B) 606 ppm (d), and (C) 806 ppm (d) from $(CH_3)_2Se$ with ^{77}Se–^{31}P splittings. If the structure of **2** is similar to that of **1**, the μ_4-Se should give a triple triplet, Mo_3–μ_3-Se a

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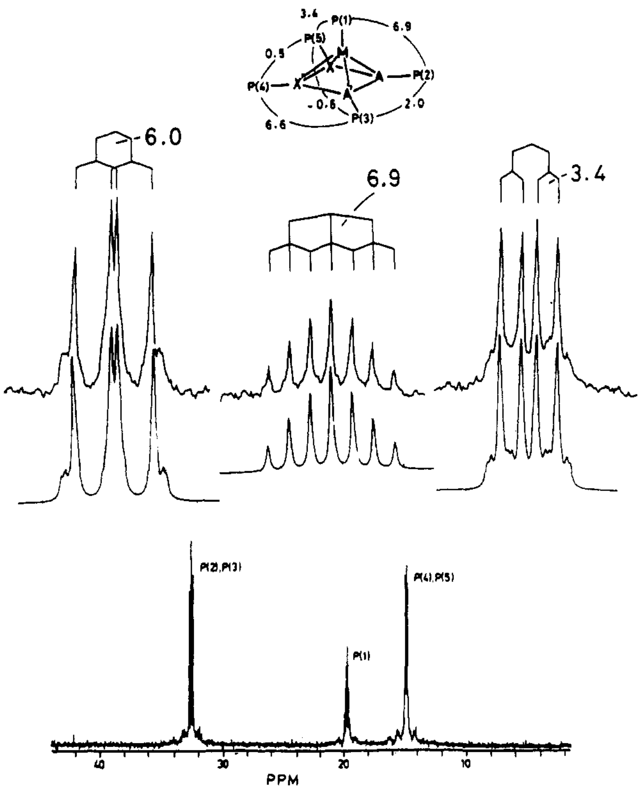

Figure 3. ^1H-decoupled ^{31}P NMR spectrum of **2** with a computer-simulated one shown below. The calculated coupling constants (Hz) between the phosphorus nuclei are indicated in the structure.

Table IV. X-ray Photoelectron Spectral Data (Mg Kα)

	binding energy, eV				
	Mo $3d_{5/2}$	Mo $3d_{3/2}$	Ni $2p_{3/2}$	Ni $2p_{1/2}$	ref
1	228.7	231.9	852.8	870.2	*a*
2	228.6	231.6	852.7	869.9	*a*
$Mo_6S_8(PEt_3)_6$	227.8	231.0			9, *a*
$Mo_6Se_8(PEt_3)_6$	227.8	230.8			9, *a*
MoS_2	228.9				*b*
$MoSe_2$	228.1				*b*
$MoCl_4$	230.4				*b*
$MoCl_3$	229.8				*b*
Ni			852.3	869.7	*b*
NiS			854.9		*b*
$NiCl_2$			856.4		*b*

[a] This work. [b] *PHI Handbook of X-ray Photoelectron Spectroscopy*; Muilenberg, G. E., Ed.; Perkin-Elmer Corp., Physical Electronics Division: Eden Praire, MN, 1979.

double triplet, and Mo_2Ni-μ_3-Se a double double doublet. Therefore tentative assignments are made as follows: (A) μ_4-Se, (B) Mo_3-μ_3-Se, (C) Mo_2Ni-μ_3-Se.

XPS Study of 1 and 2. The binding energies of Mo and Ni measured with reference to the C 1s binding energy (284.6 eV) for **1** and **2** together with the values of the relevant compounds are shown in Table IV.

Discussion

Structure. The arrangement of the ligands indicates that the original Mo_3 cluster bondings are preserved in **1**. The μ_2-S ligands become μ_3- or μ_4-S ligands. The structure suggests that condensation of the triangular cluster with $Ni(cod)_2$ is facilitated by the μ_2-bridging sulfido ligands,[17] which capture the nickel atoms and become the μ_3 or μ_4 capping ligands with concomitant formation of new metal-metal bonds (eq 1). Extra triethylphosphines replace the cyclooctadiene ligands on the nickel atoms.

$$[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2] + 2Ni(cod)_2 + 2PEt_3 \rightarrow [Mo_3Ni_2S_4Cl_4(PEt_3)_5] + 2MeOH + 4cod \quad (1)$$

In the tetranuclear $[Cp'_2Mo_2Ni_2(CO)_2S_4]$ cluster reported by Curtis,[16d] the Mo–Mo (2.829 Å), Mo–Ni (average 2.722 Å), and Ni–Ni (2.96 Å) distances are considerably longer than those in **1**. The Mo_2Ni_2 core in this cluster is regarded as a butterfly with Ni atoms at the wing tips, and the structure is consistent with the 62-VSE count.

^{31}P NMR Study of 1 and 2. The ^{31}P NMR spectrum of **1** can be approximated as A_2MX_2 with the chemical shifts of A at 24.05 ppm (dd), that of M at 21.90 ppm (tt), and those of X at 12.52 ppm (dd) and with the coupling constants of $J(AM) = 7.5$ Hz, $J(MX) = 2.3$ Hz, and $J(AX) = 1.7$ Hz. The deviation of the observed spectrum from the A_2MX_2 system is small but evident, and the spin system must be treated as an AA'MXX' system to make an exact fitting between the observed and calculated spectra. As the coupling constants other than those described above cannot be determined directly, we have estimated them by performing a computer simulation to obtain the best fit between the measured and calculated spectra. (The coupling $J(AX)$ in the A_2MX_2 system corresponds to $J(AX) + J(AX')$ in the AA'MXX' system.[18]) The nucleus P(1) connected to the top molybdenum is assigned to M in the AA'MXX' system, since it is the unique one. Though it is difficult to determine definitely which of P(2)P(3) and P(4)P(5) corresponds to AA', we prefer the assignment of AA' as P(2)P(3) and XX' as P(4)P(5) because of the similarity of the environments of P(2) and P(3) to that of P(1), which is reflected in the proximity of the chemical shift.

The ^{31}P NMR spectrum of **2** also shows the spin system of AA'MXX', and a similar procedure revealed the coupling constants indicated in Figure 3. The couplings $J(MX)$, $J(AX)$, and $J(AA')$ are larger for the selenide. We defer correlating the difference of the coupling constants to that of the bond distances and angles till the structures of **2** and related cluster complexes are determined. The couplings between the phosphorus atoms can be transmitted through a number of routes in these square-pyramidal frameworks, but it would be conceivable that only the contribution from the shortest circuits is significant. The present cluster complexes are rare examples of tertiary phosphine complexes with five magnetically nonequivalent phosphine ligands capable of showing clear couplings among them.

XPS Spectra. The binding energies of Mo $3d_{5/2}$ (228.7 eV) and Ni $2p_{3/2}$ (852.9 eV) in the X-ray photoelectron spectra (Mg Kα) are in the regions assignable to Mo^{4+} and Ni^0, respectively.[19,20] Consequently the oxidation states of the two metals are apparently near the formal oxidation states of the starting compounds. Harris has recently shown by MO calculations that $[Cp_4Mo_2Ni_2(CO)_2S_4]$ contains Mo^{5+} and Ni^0.[21]

Electron Counting. To clarify the discussion of the electron counting, we will assign the oxidation state of +4 and 0 for Mo and nickel, respectively, as the results of XPS indicate. Every ligand donates two electrons to each of the bonded metal atoms except for the μ_4-sulfido ligand, which has a total of only six electrons for four bonds. Because two electrons on the molybdenum atoms must be used for the Mo–Mo bonds, the electrons for the Mo–Ni bond must be afforded by nickel atoms. Then, the top molybdenum atom (Mo(1)), which has five coordinating ligands, two Mo–Ni bonds, and two Mo–Mo bonds, achieves the 18-electron configuration. Similarly, the basal molybdenum atom has 18 electrons. The μ_4-sulfido ligand, donates six electrons, and four of them must be used for Mo–S bonds. Therefore, only one electron is donated to each nickel atom from the μ_4-sulfido ligand. With other ligands and a Ni–Ni bond, the nickel atom also attains the 18-electron configuration.

For square pyramidal clusters, the 18-electron configuration of all metals automatically leads to the 74 cluster electrons (18

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× 5 − 2 × 8), as found in this complex and in many carbonyl cluster compounds.[22] Though the square-pyramidal clusters with π-acceptor ligands usually have 74 electrons, those with π-donor ligands may have a smaller number of electrons due to the destabilization of the valence-shell d orbitals by the repulsion with π-electrons of the ligands. For example, a square-pyramidal cluster, $[Mo_5Cl_{13}]^-$, has only 68 electrons.[23] The existence of complexes **1** and **2** shows that the square-pyramidal cluster can achieve the upper limit of electrons even with π-donor ligands. As the relationship between the cluster shape and the number of valence electrons in the present class of sulfido clusters is interesting, we are currently preparing other metal derivatives.

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Supplementary Material Available: Listings of detailed crystal data, positional parameters for hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for non-hydrogen atoms (7 pages); a Table of calculated and observed structure factors (38 pages). Ordering information is given on any current masthead page.

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Deprotonation of $Re_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8$ for Synthesis of Mixed Rhenium–Gold Clusters with Re_2Au_n Cores (n = 1–3)

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The dirhenium complex $Re_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8$ (**1**) is deprotonated with NaOEt (or 1,8-diazabicyclo[5.4.0]undec-7-ene, DBU) to give the anion $[(\mu\text{-}PPh_2)(CO)_8Re_2]^-$ ($\mathbf{2}^-$), which was isolated as tetraethylammonium salt $[C_8H_{20}N]$[**2**]. The exchange of the isolobal fragment $AuPPh_3$ for H in **1** (via $\mathbf{2}^-$) generates $[(\mu\text{-}PPh_2(CO)_8Re_2AuPPh_3]$ (**3**). The treatment of **1** in THF solution with lithium organyls RLi (R = Me, *n*-Bu, Ph) gives products of two types: first, $[(\mu\text{-}C(R)O)(\mu\text{-}PPh_2)(CO)_6Re_2(AuPPh_3)_2]$ (R = Ph (**4**), Me (**5**), *n*-Bu (**6**)) and, second, $[(\mu\text{-}PPh_2)(CO)_6Re_2(AuPPh_3)_3]$ (**7**). Complex **1** was also reacted with diphenylacetylene to give $[(\mu\text{-}\sigma{:}\eta^2\text{-}CPh{=}CHPh)(\mu\text{-}PPh_2)(CO)_7Re_2]$ (**8**). ^{31}P NMR data have been measured for the newly synthesized compounds. The molecular structures of $[C_8H_{20}N]$[**2**], **3**, **4**, **7**, and **8** have been determined from X-ray data collected on an automated diffractometer with monochromatized Mo Kα radiation. Compounds **3**, **7**, and **8** crystallize in the triclinic space group $P\bar{1}$ with $Z = 2$, while **2** and **4** crystallize in the monoclinic space groups $C2/c$ with $Z = 8$ and $P2_1/n$ with $Z = 4$, respectively. For **2**, a = 18.007 (3) Å, b = 17.165 (3) Å, c = 21.368 (5) Å, and β = 109.36 (1)°; for **3**, a = 14.918 (7) Å, b = 15.456 (4) Å, c = 9.229 (4) Å, α = 93.12 (1)°, β = 97.10 (1)°, and γ = 83.27 (1)°; for **4**, a = 24.434 (4) Å, b = 10.284 (2) Å, c = 24.618 (4) Å, and β = 113.75 (1)°; for **7**, a = 13.676 (5) Å, b = 13.817 (4) Å, c = 21.723 (7) Å, α = 71.26 (1)°, β = 87.05 (1)°, and γ = 82.37 (1)°; and for **8**, a = 9.436 (2) Å, b = 11.774 (3) Å, c = 14.353 (4) Å, α = 95.91 (2)°, β = 99.57 (2)°, and γ = 95.71 (2)°. The molecular structure of the diamagnetic anion $\mathbf{2}^-$ as the $[NEt_4^+]$ salt contains an $Re_2(\mu\text{-}P)$ ring with four cis-terminal carbonyl ligands at each Re atom of an idealized C_{2v} symmetry. The Re–Re bond length is 3.062 (2) Å with bond angle Re–P–Re = 78.6 (1)°. The addition of the sterically demanding $[AuPPh_3^+]$ cation to $\mathbf{2}^-$ leads to a planar four-membered $AuPRe_2$ ring in **3**. The Re–Re bond of 3.225 (2) Å is elongated and the angle Re–P–Re = 83.8 (3)° enlarged compared to those of $[C_8H_{20}N]$[**2**]. The average Au–Re single-bond length is 2.787 (2) Å. The molecular structure of **4** shows an Re_2Au_2 metallatetrahedron core in which the Re–Re bond is bridged through the acylic C(Ph)O group (Re–C = 2.17 (3) Å, C–O = 1.24 (4) Å). The Re–Re bond length is 3.122 (2) Å, and the other metal–metal distances are 2.734 (2) Å (Au–Au) and 2.901 (2) Å (average Au–Re). These values are consistent with metal–metal single bonds. The molecular structure of **7** contains a trigonal-bipyramidal Re_2Au_3 core. The Re–Re bond length of 2.914 (3) Å, of double-bond character, is shorter than that of **4**, whereas the average Au–Au bond length of 2.829 (2) Å is elongated; the average Au–Re bond length is 2.830 (2) Å. The molecular structure of **8**, which results from a release of one CO ligand from **1** and a hydride transfer to coordinated diphenylacetylene, contains the vinylic $\mu\text{-}\sigma{:}\eta^2\text{-}CPh{=}CHPh$ ligand (C=C = 1.394 (16) Å) bridging an Re–Re bond, Re–Re = 2.998 (1) Å. In the isoelectronic series of compounds **1**–**3** in which the H^+ in **1** is substituted by the isolobal fragment $[PPh_3Au^+]$ via the anion $\mathbf{2}^-$, the Re_2 core becomes more electron-rich, which facilitates the anodic one-electron transfer as measured by cyclic voltammetry; i.e., $E_{p,a1}$ decreases from 1508 mV in **1** to 1132 mV in $[C_8H_{20}N]$[**2**] to 241 mV in **3**. The same is observed for the Re_2 core in the exchange of an electron-poor phenyl acyl against an electron-rich diisopropylamino acyl group in the isoelectronic compounds of the type $[(\mu\text{-}C(R)O)(\mu\text{-}PPh_2)\text{-}(CO)_6Re_2(AuPPh_3)_2]$ (R = Ph, E^f = 682 mV; R = N(i-Pr$_2$), E^f = 576 mV). For **7** the E^f values of the reversible one-electron-transfer processes are 289 and 752 mV.

Introduction

This study continues our recent work on the reactions between dirhenium decacarbonyl and diphenylphosphine at different molar ratios, which have yielded $Re_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_8$[1] (**1**) and $Re_2(\mu\text{-}PPh_2)_2(CO)_8$.[2] We describe now the deprotonation of the hydrido-bridged compound **1** with different bases such as sodium ethanolate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and especially nucleophiles R^- in LiR (R = Me, *n*-Bu, Ph). Anionic intermediates have been isolated and identified as well as different dirhenium gold clusters obtained from the reaction of the anionic intermediates with PPh_3AuCl. It might be anticipated from the isolobal relationship of H with $AuPPh_3$[3] that the basic property of such reagents possibly generates via the intermediate $[(\mu\text{-}PPh_2)(CO)_8Re_2]^-$ ($\mathbf{2}^-$) the substance $[(\mu\text{-}PPh_2)(CO)_8Re_2AuPPh_3]$ (**3**). By contrast, the assumption of gold atom uptake in the reaction of PPh_3AuCl with anionic intermediates obtained in the reaction of **1** with RLi followed by release of RH and acylation of coordinated carbonyls cannot reasonably be made without related experiments. It can only be said that the intented auration of **1** may be limited as the consequence of a reduced capability of C atoms in CO ligands to be converted into acyl fragments. Each acylation process then produces a higher electron density

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