CDS-401 VISTA data system coupled with the chromatograph, operating with an automatic internal standard method (ethanol was the internal standard).

Catalytic Runs. In a typical experiment the catalyst (7.0×10^{-5} mol), the substrate (7.0×10^{-2} mol), the solvent (50 mL), and a stirring bar were placed in a glass-lined stainless-steel autoclave (125 mL, Parr). The autoclave was purged three times with 500 psig of H_2 and then charged to the desired pressure. It was then introduced into a thermostated silicone oil bath and magnetically stirred; this was taken as the zero time of the reaction. The pressure was maintained constant throughout the reaction by continuous supply from a high-pressure reservoir. At the end of the run the autoclave was placed in ice, the excess pressure was released and the mixture was inmediately analyzed by GLC.

Kinetic Measurements and Calculations. For kinetic measurements, series of autoclaves containing 50-mL aliquots of the solutions containing the catalysts and the substrate were used (conditions as above). The reactions were quenched at different times and immediately analyzed. Mass balance showed that the appearance of the alcohol corresponded to >98% of the disappearance of the aldehyde, indicating that <2% of byproducts were formed.

Plots of alcohol production (in millimoles of alcohol per millimole of Ru per minute) vs. time were linear with very small nonzero intercepts up to at least 50% conversion for all the Ru complexes. For the Os complexes no conversion of the aldehyde was observed for the first ~10 min after which hydrogenation was triggered off and also displayed a linear behavior; in these cases the reaction times used in the plot (see for example Figure 1 for complex **21**) were corrected by substracting 10 min, so that the zero point is taken at the time when hydrogenation actually begins.

At constant catalyst concentration and hydrogen pressure the rate law takes the form $-d[\text{aldehyde}]/dt = k_{\text{obsd}}[\text{aldehyde}]$, consistent with linear plots of ln [aldehyde] vs. *t* (see for instance, Figure 2). The corresponding slopes yielded the values of k_{obsd} listed in Table I. In all calculations conventional linear regression programs were used, and the lines were fitted to *r* values >0.99. k_{obsd} values were taken as a measure of catalytic activity for comparison purposes.

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Registry No. **1**, 61521-25-3; **2**, 100678-61-3; **3**, 100678-62-4; **4**, 100678-63-5; **5**, 100678-64-6; **6**, 100514-70-3; **7**, 68853-49-6; **8**, 100678-65-7; **9**, 100514-72-5; **10**, 100514-74-7; **11**, 100514-75-8; **12**, 50661-74-0; **13**, 100514-76-9; **14**, 100514-77-0; **15**, 50661-73-9; **16**, 100514-78-1; **17**, 100514-79-2; **18**, 100514-80-5; **19**, 60451-51-6; **20**, 100678-66-8; **21**, 100678-67-9; **22**, 100514-81-6; **23**, 100678-68-0; propionaldehyde, 123-38-6; acetone, 67-64-1.

Contribution from the Department of Chemistry, Faculty of Engineering Science
and Faculty of Pharmaceutical Sciences, Osaka University, Toyonaka, Osaka 560, Japan

Synthesis of Hexanuclear Molybdenum Cluster Alkyl Complexes Coordinated with Trialkylphosphines: Crystal Structures of *trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ and *all-trans*-$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$

Taro Saito,*[1a] Masakazu Nishida,[1a] Tsuneaki Yamagata,[1a] Yuriko Yamagata,[1b]
and Yoshihiro Yamaguchi[1a]

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Hexanuclear molybdenum cluster chloride complexes coordinated with two trialkylphosphines were prepared, and *trans*-$[(Mo_6Cl_8)Cl_4(PR_3)_2]$ ($R = n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$) and *cis*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_3H_7)_3\}_2]$ were isolated by chromatography. *trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ (**3**) crystallizes in the monoclinic space group *C*2/*c* with $a = 29.076$ (3) Å, $b = 10.301$ (1) Å, $c = 21.508$ (5) Å, $\beta = 135.28$ (1)°, and $Z = 4$. The X-ray structure determination confirmed that the two tributylphosphine ligands are coordinated to the trans positions of the octahedral molybdenum cluster core with eight face-bridging and four terminal chlorines. Pertinent distances are Mo–Mo = 2.6162 (8) Å (av), $\text{Mo–Cl}^t = 2.410$ (2) Å (av), $\text{Mo–Cl}^b = 2.473$ (2) Å (av), and Mo–P = 2.619 (2) Å. Derivatives of the types $[(Mo_6Cl_8)Cl_{4-x}R'_x(PR_3)_2]$ ($x = 2, 3$; $R' = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}$) were prepared by alkylation of *trans*-$[(Mo_6Cl_8)Cl_4(PR_3)_2]$ with AlR'_3. The complex *all-trans*-$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$ (**6**) crystallizes in the monoclinic space group *P*2/*c* with $a = 13.855$ (2) Å, $b = 11.120$ (3) Å, $c = 20.506$ (2) Å, $\beta = 95.81$ (1)°, and $Z = 2$. Two ethyl groups, two chlorines, and two tributylphosphines are bonded to the octahedral Mo_6Cl_8 core in mutually trans positions. The selected bond distances are Mo–C = 2.21 (3) Å, Mo–P = 2.604 (8) Å, and $\text{Mo–Cl}^t = 2.421$ (8) Å. Detailed structural data are reported. Complex **6** decomposed at around 150 °C, evolving dihydrogen, ethane, ethylene, and small amounts of other gaseous products.

Introduction

A number of hexanuclear molybdenum cluster halides with the $(Mo_6X_8)^{4+}$ core and anionic and neutral terminal ligands have been prepared,[2] and structures of some of them have been determined.[3] The similarity of the Mo_6 cluster core to that of Chevrel phases[4] and the interesting photochemical properties[5] have attracted renewed interest in these molybdenum cluster halide systems. Despite the remarkable stability of the cluster framework the chemistry of the cluster complexes has not been much explored.[6]

The purpose of the present study was to effect the hitherto unreported separation of the cis and trans isomers of the tertiary phosphine complexes $[(Mo_6Cl_8)Cl_4(PR_3)_2]$ and to synthesize cluster alkyl complexes by alkylation of the trans isomers. Although alkyl complexes are considered as intermediates in the cluster catalysis of olefins,[7] very few such complexes have been

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isolated and their chemistry is virtually unknown except for some alkyl complexes of Os_3[8] and Re_3.[9] The simplest polymetallic alkyls, $Mo_2R_2(NMe_2)_4$, have recently been synthesized[10] and the reactivity patterns of σ-alkyl groups coordinated to the dinuclear metal centers have been studied.[11] In the communication of the synthesis of Re_3 alkyls, an unsuccessful attempt to prepare Mo_6 alkyls from Mo_6Cl_{12} was described.[12] We consider that alkyl complexes could more probably be prepared from neutral Mo_6 cluster halides coordinated with tertiary phosphines, which often stabilize mononuclear alkyl complexes. Some molybdenum cluster halide complexes with tertiary phosphines have been reported.[2e,i] Because theoretically no fewer than 14 alkyl complexes could form through alkylation of the cis and trans mixtures of the cluster chloride complexes, it was better to start from the pure trans isomer to minimize the subsequent separation problems. We now report the synthesis and isolation of the trans isomers of tri-*n*-alkylphosphine cluster complexes and their conversion to alkylated derivatives, along with X-ray crystal structure determinations on compounds representative of each class.

Experimental Section

Reagents. Mo_6Cl_{12}[13] was prepared by treating $(H_3O)_2[Mo_6Cl_{14}]\cdot 6H_2O$ in vacuum at room temperature for 5 h, at 100 °C for 15 h, and then at 200 °C for 5 h. Tripropylphosphine and tributylphosphine (Nihon Kagaku Kogyo) were used as received and tripentylphosphine was prepared by treating pentylmagnesium bromide in ether with an ethereal solution of phosphorus trichloride at 0 °C followed by the usual workup. The absence of trialkylphosphine oxides was checked by ^{31}P NMR spectra. Trimethylaluminum and triethylaluminum (Ethyl Corp.) and tripropylaluminum, tributylaluminum, and trihexylaluminum (Toyo Stauffer Chemicals) were used without further purification. Solvents were dried and distilled under dinitrogen.

Spectra. ^1H and ^{31}P NMR spectra were measured by a JEOL FX100 spectrometer with tetramethylsilane (internal) and H_3PO_4 (5% methanol-d_4 solution, external) references, respectively, and infrared spectra were recorded by Hitachi 295 (4000–250 cm^{-1}) and Hitachi FIS-3 (400–50 cm^{-1}) spectrometers.

Syntheses. Every operation including chromatography was carried out under dinitrogen. It was essential to prevent air oxidation of trialkylphosphines during the preparations; otherwise, the chromatographic separation of the cluster halide complexes and the alkylation reactions did not proceed satisfactorily because of the ready formation of trialkylphosphine oxides complexes. Chromatographic separations were carried out on Florisil columns. The elemental analyses were performed at the analytical laboratory of our department.

***trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_3H_7)_3\}_2]$ (1).** A suspension of Mo_6Cl_{12} (8.4 g, 8.4 mmol) in THF (400 mL) was treated with $P(n\text{-}C_3H_7)_3$ (6.5 g, 40.5 mmol) for 3 days at room temperature to give a clear orange solution. The solvent was removed under reduced pressure, and the orange residue was washed with hexane (3 × 50 mL) and dried in vacuo; yield 11.1 g. The crude product (5.0 g) was dissolved in chloroform (150 mL) and chromatographed with a mixed solvent of chloroform and ethanol (20:1). A pale yellow solid was obtained from the first band: yield 0.77 g (15%). Anal. Calcd for $C_{18}H_{42}Cl_{12}Mo_6P_2$: C, 16.35; H, 3.20. Found: C, 16.36; H, 3.18. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 2.26.

***cis*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_3H_7)_3\}_2]$ (2).** This was obtained as a yellow product from the second band in the chromatographic purification of the trans isomer (**1**); yield 0.16 g (3%). Anal. Calcd for $C_{18}H_{42}Cl_{12}Mo_6P_2$: C, 16.35; H, 3.20. Found: C, 16.81; H, 3.26. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 2.70.

***trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ (3).** Mo_6Cl_{12} (8.0 g, 8.0 mmol) was treated with $P(n\text{-}C_4H_9)_3$ (8.0 g, 40 mmol) in THF (400 mL) at room temperature until the suspended materials had dissolved (2–3 days). The solvent was removed under reduced pressure and the residue washed with hexane (3 × 50 mL) and dried in vacuo; yield 11.0 g. The $^{31}P\{^1H\}$ NMR spectra showed several bands. The crude product was chromatographed as for the tripropylphosphine complexes, but only pure trans isomer could be isolated; yield 40%. Anal. Calcd for $C_{24}H_{54}Cl_{12}Mo_6P_2$: C, 20.50; H, 3.80; Cl, 30.26; Mo, 40.95. Found: C, 20.47; H, 3.83; Cl, 30.29; Mo, 40.7. $^{31}P\{^1H\}$ NMR: δ 3.80.

***trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_5H_{11})_3\}_2]$ (4).** Mo_6Cl_{12} (20.0 g, 20.0 mmol) was treated with $P(n\text{-}C_5H_{11})_3$ (11.7 g, 8.0 mmol) in THF (600 mL) at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was washed with hexane (3 × 30 mL); yield 29.8 g. The crude product was chromatographed with chloroform. The separation of the bands was incomplete, but a yellow product was obtained from the major part of the first band; yield 50%. Anal. Calcd for $C_{30}H_{66}Cl_{12}Mo_6P_2$: C, 24.18; H, 4.47. Found: C, 24.14; H, 4.47.

$[(Mo_6Cl_8)Cl_2(CH_3)_2\{P(n\text{-}C_4H_9)_3\}_2]$ (5). A toluene solution of $Al(CH_3)_3$ (10 wt %, 1.2 mL, 2.2 mmol) was added to a suspension of **3** (0.8 g, 0.5 mmol) in toluene (20 mL) at –5 °C. The mixture was stirred at –5 °C for 20 h, and the solvent and other volatile materials were removed in vacuo at 0 °C to give a yellow orange oil. Addition of ether precipitated a yellow solid, which was washed with ether and dried in vacuo; yield 0.6 g. The crude product was dissolved in toluene at 60 °C, and the solution was filtered, concentrated, and cooled to –20 °C to give a pale yellow solid. Anal. Calcd for $C_{26}H_{60}Cl_{10}Mo_6P_2$: C, 22.88; H, 4.43. Found: C, 22.48; H, 4.22.

$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]$ (6). A toluene solution of $Al(C_2H_5)_3$ (10 wt %, 21.5 mL, 15.6 mmol) was added to a suspension of **3** (3.6 g, 2.6 mmol) in toluene (180 mL) at –20 °C. After the mixture was stirred for 5 h at –20 °C, the solvent and other volatile materials were removed in vacuo at 0 °C to give a dark oil. A small amount of acetone was added to the oil to precipitate immediately an orange solid, which was washed thoroughly with ether and dried in vacuo; yield 2.5 g. The crude product (2.0 g) was dissolved in toluene at 70 °C, and the filtered solution was cooled to –20 °C to form orange crystals; yield 0.6 g (30%). Anal. Calcd for $C_{28}H_{64}Cl_{10}Mo_6P_2$: C, 24.14; H, 4.64; Cl, 25.45. Found: C, 24.29; H, 4.62; Cl, 25.67.

$[(Mo_6Cl_8)Cl_2(n\text{-}C_3H_7)_2\{P(n\text{-}C_4H_9)_3\}_2]$ (7). A similar procedure to that used for **5**, but using $Al(n\text{-}C_3H_7)_3$ at –15 °C, was followed; yield 11%. Anal. Calcd for $C_{30}H_{68}Cl_{10}Mo_6P_2$: C, 25.35; H, 4.82. Found: C, 25.22; H, 4.73.

$[(Mo_6Cl_8)Cl_2(n\text{-}C_4H_9)_2\{P(n\text{-}C_4H_9)_3\}_2]$ (8). A procedure for **5** was followed, using $Al(n\text{-}C_4H_9)_3$ at –15 °C; yield 11%. Anal. Calcd for $C_{32}H_{72}Cl_{10}Mo_{10}P_2$: C, 26.52; H, 5.00. Found: C, 26.77; H, 5.00.

$[(Mo_6Cl_8)Cl_2(n\text{-}C_6H_{13})_2\{P(n\text{-}C_4H_9)_3\}]$ (9). A procedure for **5** was followed, with $Al(n\text{-}C_6H_{13})_3$ at –15 °C; yield 8%. Anal. Calcd for $C_{36}H_{80}Cl_{10}Mo_6P_2$: C, 28.72; H, 5.35. Found: C, 28.46; H, 5.28.

$[(Mo_6Cl_8)Cl_2(CH_3)_2\{P(n\text{-}C_5H_{11})_3\}_2]$ (10). This was obtained from **4** at –20 °C, with recrystallization from toluene; yield 11%. Anal. Calcd for $C_{32}H_{72}Cl_{10}Mo_6P_2$: C, 26.52; H, 5.00. Found: C, 26.42; H, 4.95.

$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_5H_{11})_3\}_2]$ (11). A procedure as for **6** was followed; yield 19%. Anal. Calcd for $C_{34}H_{76}Cl_{10}Mo_6P_2$: C, 27.64; H, 5.18. Found: C, 27.86; H, 5.24.

$[(Mo_6Cl_8)Cl_2(C_3H_7)_2\{P(C_5H_{11})_3\}_2]$ (12). The complex was obtained from the reaction of **4** with $Al(C_3H_7)_3$ according to the procedure for **5**, with recrystallization from toluene; yield 4%. Anal. Calcd for $C_{36}H_{80}Cl_{10}Mo_6P_2$: C, 28.72; H, 5.35. Found: C, 28.29; H, 5.30.

$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(C_3H_7)_3\}_2]$ (13). A procedure for **12** was followed, using **1** and $Al(C_2H_5)_3$. The product was recrystallized from benzene; yield 17%. Anal. Calcd for $C_{22}H_{52}Cl_{10}Mo_6P_2$: C, 20.19; H, 4.00. Found: C, 20.17; H, 3.98.

$[(Mo_6Cl_8)Cl(n\text{-}C_3H_7)_3\{P(n\text{-}C_4H_9)_3\}_2]$ (14). The crude product of **7** (1.7 g, 1.2 mmol) was treated with a solution of $Al(n\text{-}C_3H_7)_3$ (14 wt %, 5.5 mL, 4.8 mmol) in toluene (30 mL) at –15 °C for 20 h. Ether (10 mL) was added and the solution filtered. The solvent and volatile materials were removed in vacuo, and the residual oil was shaken with ether (3 × 10 mL) to give an orange solid; yield 1.3 g (72%). Anal. Calcd for $C_{33}H_{75}Cl_9Mo_6P_2$: C, 27.74; H, 5.29. Found: C, 27.78; H, 5.27.

$[(Mo_6Cl_8)Cl(C_2H_5)_3\{P(n\text{-}C_5H_{11})_3\}_2]$ (15). The complex was prepared in a manner similar to that for **14**, using **11** and $Al(C_2H_5)_3$; yield 34%. Anal. Calcd for $C_{36}H_{81}Cl_9Mo_6P_2$: C, 29.40; H, 5.55. Found: C, 29.00; H, 5.52.

X-ray Structure Determination of *trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$. Orange crystals of **3** were grown by slow diffusion of ether vapor into a chloroform solution of the complex in a closed H-shaped vessel. For the X-ray measurements, crystals were fixed on the end of glass fibers with epoxy resin. Cell dimensions and the space group were determined from the oscillation and Weissenberg photographs. Systematic absences were consistent with the centric space group *C*2/*c* or noncentric space group *Cc*. Intensity data were collected at 20 °C by using a Rigaku AFC-4 four-circle automated diffractometer equipped with a Rotaflex rotating anode X-ray generator with graphite-monochromatized Mo Kα radiation. The structure was solved with the space group *C*2/*c* by direct methods

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Table I. Crystal Parameters and X-ray Diffraction Data for $[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ (**3**) and $[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$ (**6**)

	3	**6**
lattice type	monoclinic	monoclinic
space group	$C2/c$	$P2/c$
a, Å	29.076 (3)	13.855 (2)
b, Å	10.301 (1)	11.120 (3)
c, Å	21.508 (5)	20.506 (2)
β, deg	135.28 (1)	95.81 (1)
cell vol, Å^3	4532.8 (9)	3114.8 (10)
formula	$C_{24}H_{54}Cl_{12}Mo_6P_2$	$C_{28}H_{64}Cl_{10}Mo_6P_2\cdot 2C_6H_5CH_3$
fw	1405.76	1576.22
syst absences	hkl, $h + k$ odd $h0l$, l odd	$h0l$, l odd
Z	4	2
D_{calcd}, g cm^{-3}	2.06	1.53
D_{measd}, g cm^{-3}	2.03 (1)	not measd
λ(Mo K$\bar{\alpha}$), Å	0.71069	0.71069
cryst size, mm	0.38 × 0.46 × 0.15	0.65 × 0.30 × 0.13
$F(000)$, e	2736	1568
scan method	$\omega-2\theta$	$\omega-2\theta$
scan range (ω), deg	$1.5 + 0.35 \tan\theta$	$2.0 + 0.35 \tan\theta$
scan rate (2θ), deg min^{-1}	8	8
bkgd time at each side of the peak	6	7.5
collcn region	$\pm h,k,l$	$\pm h,k,l$
2θ limit, deg	$2\theta < 60$	$2\theta < 50$
decay	negligible	negligible
corr applied	Lp	Lp
reflecns measd	6793	5653
no. of unique reflecns	6625	5485 (5653)[a]
R_{int}, F	0.011	0.028
no. of obsd reflecns	3894	2989 (3080)[a]
criteria for obsd F	$\geq 4\sigma$	$\geq 3\sigma$
linear abs coeff μ, cm^{-1}	23.78	16.53
corr made	yes[b]	yes[b]
abs factors	1.00–1.79	1.00–1.30
no. of variable params	281	208
R. R_w[c]	0.0323, 0.0326	0.0927, 0.1050
s[d]	1.52	4.41
Δp_{max}, e Å^{-3}	1.32	1.21

[a] Values in parenthese were used for the Pc space group. [b] Correction methods applied were those in: North, A. C. T.; Phillips, D. C.; Matthews, B. W., *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351–359. [c] $w = 1/\sigma^2(F_o)$. [d] $s = [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[(Mo_6Cl_8)Cl_4\{(n\text{-}C_4H_9)_3\}_2]$ (**3**)[a]

atom	x	y	z	U_{eq} Å^2
Mo(1)	0.69904 (2)	0.19032 (4)	0.01584 (3)	0.0303 (2)
Mo(2)	0.70183 (2)	0.15055 (4)	−0.10137 (3)	0.0297 (2)
Mo(3)	0.69268 (2)	0.38693 (4)	−0.06730 (3)	0.0312 (2)
Cl(1)	0.71032 (6)	−0.03114 (12)	−0.01860 (8)	0.0404 (8)
Cl(2)	0.80055 (5)	0.16043 (12)	0.17318 (7)	0.0387 (7)
Cl(3)	0.60227 (5)	0.022717 (13)	−0.14282 (8)	0.0389 (7)
Cl(4)	0.69411 (6)	0.41786 (12)	0.04848 (8)	0.0391 (8)
Cl(5)	0.63356 (6)	0.11056 (14)	0.03838 (9)	0.0472 (9)
Cl(6)	0.61746 (7)	0.56217 (14)	−0.15708 (10)	0.0579 (10)
P	0.63022 (6)	0.01610 (14)	−0.24788 (8)	0.0373 (8)
C(1)	0.5638 (2)	−0.0714 (5)	−0.2725 (3)	0.044 (3)
C(2)	0.5140 (2)	−0.1387 (6)	−0.3620 (3)	0.049 (4)
C(3)	0.4569 (3)	−0.1931 (6)	−0.3806 (4)	0.058 (4)
C(4)	0.4027 (3)	−0.2489 (6)	−0.4727 (4)	0.064 (4)
C(5)	0.5905 (2)	0.1194 (5)	−0.3440 (3)	0.043 (3)
C(6)	0.5439 (2)	0.2191 (5)	−0.3596 (3)	0.046 (3)
C(7)	0.5206 (3)	0.3209 (7)	−0.4272 (4)	0.072 (5)
C(8)	0.4816 (4)	0.4261 (7)	−0.4328 (5)	0.092 (7)
C(9)	0.6715 (2)	−0.1045 (5)	−0.2566 (3)	0.046 (3)
C(10)	0.7042 (3)	−0.2154 (6)	−0.1904 (4)	0.057 (4)
C(11)	0.7303 (3)	−0.3175 (6)	−0.2113 (5)	0.078 (5)
C(12)	0.6749 (4)	−0.3899 (7)	−0.2968 (5)	0.090 (7)

[a] Isotropic equivalent thermal parameters for anisotropically refined atoms are defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $[(Mo_6Cl_8)Cl_2(C_5H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$ (**6**)[a]

atom	x	y	z	U_{eq}, Å^2
Mo(1)	1.1029 (1)	−0.0611 (2)	0.0548 (1)	0.061 (1)
Mo(2)	0.9137 (1)	−0.0770 (2)	0.0485 (1)	0.060 (1)
Mo(3)	0.9962 (2)	0.1353 (2)	0.0521 (1)	0.064 (1)
Cl(1)	0.9821 (4)	0.2592 (6)	−0.0494 (3)	0.073 (3)
Cl(2)	1.1760 (4)	0.1447 (6)	0.0557 (3)	0.077 (3)
Cl(3)	1.0117 (4)	−0.0025 (7)	0.1486 (3)	0.072 (2)
Cl(4)	0.8178 (4)	0.1130 (6)	0.0436 (3)	0.071 (3)
Cl(5)	1.2378 (4)	−0.1411 (7)	0.1263 (3)	0.084 (3)
P	0.7930 (4)	−0.1837 (7)	0.1193 (3)	0.070 (3)
C(1)	0.8572 (15)	−0.2651 (22)	0.1933 (11)	0.074 (11)
C(2)	0.7888 (15)	−0.3441 (22)	0.2256 (10)	0.070 (10)
C(3)	0.8503 (17)	−0.4091 (24)	0.2867 (12)	0.092 (12)
C(4)	0.7933 (20)	−0.4844 (27)	0.3268 (15)	0.124 (16)
C(5)	0.7048 (16)	−0.0822 (23)	0.1550 (13)	0.088 (12)
C(6)	0.7521 (18)	0.0057 (27)	0.2001 (12)	0.101 (13)
C(7)	0.676 (2)	0.100 (3)	0.232 (1)	0.106 (10)*
C(8)	0.733 (2)	0.196 (3)	0.261 (2)	0.135 (12)*
C(9)	0.7100 (16)	−0.2944 (23)	0.0729 (12)	0.081 (11)
C(10)	0.7638 (19)	−0.4000 (24)	0.0511 (12)	0.100 (13)
C(11)	0.680 (2)	−0.493 (3)	0.014 (1)	0.120 (10)*
C(12)	0.745 (3)	−0.581 (3)	−0.003 (2)	0.159 (14)*
C(13)	0.9921 (17)	0.3034 (25)	0.1109 (12)	0.097 (13)
C(14)	0.929 (2)	0.309 (3)	0.165 (2)	0.141 (13)*
C(15)	0.500	−0.225 (4)	0.250	0.137 (17)*
C(16)	0.525 (2)	−0.292 (3)	0.313 (2)	0.149 (13)*
C(17)	0.517 (3)	−0.411 (3)	0.308 (2)	0.174 (15)*
C(18)	0.500	−0.484 (5)	0.250	0.181 (22)*
C(19)	0.441 (2)	−0.001 (3)	0.551 (1)	0.105 (9)*
C(20)	0.443 (2)	0.091 (3)	0.509 (1)	0.109 (10)*
C(21)	0.515 (2)	0.104 (3)	0.460 (1)	0.118 (11)*

[a] Values for isotropically refined atoms are denoted by an asterisk. Isotropic equivalent thermal parameters for anisotroically refined atoms are defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

using the program MULTAN 78[14] and refined by the block-diagonal least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. As refinement proceeded all hydrogen atoms were located in difference Fourier maps. The final refinement including hydrogen atoms with isotropic thermal parameters fixed at $\beta = 4.5$ Å^2 converged to $R = 0.0323$ ($R_w = 0.0326$).

X-ray Structure Determination of *all-trans*-$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$. Single crystals suitable for the X-ray measurements were obtained by repeated recrystallizations of **6** from toluene. As the surface of the orange crystals became rough immediately after removal from the mother liquor due to ready loss of solvate toluene, the crystals were coated with silicone grease and sealed in glass capillaries in the presence of toluene. The measurements were made in a manner similar to that used for the complex **3**. Systematic absences agreed with the centric space group $P2/c$ or noncentric space group Pc. The structure was solved by the heavy-atom method, assuming the space group $P2/c$ initially. The positions of the three crystallographically independent molybdenum atoms were determined from a Patterson map. Subsequent Fourier and difference Fourier syntheses revealed the remaining non-hydrogen atoms except for the methyl carbon atoms of the toluene molecules. One of the two crystallographically independent aromatic rings lay on the 2-fold axis and the other on the center of symmetry, making four and three ring carbon atoms, respectively, independent. The structure was refined by the block-diagonal least-squares method with anisotropic thermal parameters for Mo, Cl, and P atoms and part of the C atoms (denoted by an asterisk in Table III), which were remote from molybdenum and with higher thermal parameters, and isotropic thermal parameters for the remaining C atoms. The final R values converged to 0.093 ($R_w = 0.105$). The final difference Fourier map gave two peaks (1.21 and 1.20 e Å^{-3}), each of which was approximately 1.5 Å away from the aromatic rings. Several smaller residual peaks also appeared near the aromatic rings (>0.5 e Å^{-3}). These peaks together with the high apparent thermal parameters for the carbon atoms of the aromatic rings suggested disorder of the toluenes in the cavity of cluster molecules. The possibility that the noncentrosymmetric space group Pc might provide an alternative solution to the structure was also tested. The final refinement with the same parameters used for the solution with the $P2/c$

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(14) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J.-P.; Woolfson, M. M. "MULTAN78", University of York, England, 1978.

space group converged R to 0.0949 (R_w = 0.1021). However, the results gave abnormal bond distances and angles around the Mo and Cl atoms, and we concluded that space group *Pc* was not suitable and that the structure was to be solved by the space group $P2/c$.

The crystallographic data, experimental information, and structure refinement parameters are given in Table I. Atom coordinates for **3** and **6** are listed in Tables II and III, respectively.

The atomic scattering factors were taken from a standard source,[15] and the effects of anomalous dispersion were included for the Mo, Cl, P, and C atoms by using the $\Delta f'$ and $\Delta f''$ values of Cromer and Ibers.[16] All calculations were performed with UNICS programs[17] on ACOS 900 and 850 computers at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

Cluster Chloride Complexes. Synthesis. Treatment of "molybdenum dichloride" with trialkylphosphines in THF cleaves the chlorine bridges between the cluster units $(Mo_6Cl_8)Cl_2$ and forms cluster complexes $[(Mo_6Cl_8)Cl_4(PR_3)_2]$.[2e,i] The alkylation of the trans isomers would lead to five alkyl complexes; namely *mer*Cl$_3$*trans*P$_2$-$[(Mo_6Cl_8)Cl_3R(PR_3)_2]$, *all-trans*-$[(Mo_6Cl_8)Cl_2R_2(PR_3)_2]$, *cis*Cl$_2$*trans*P$_2$*cis*R$_2$-$[(Mo_6Cl_8)Cl_2R_2(PR_3)_2]$, *trans*P$_2$*mer*R$_3$-$[(Mo_6Cl_8)ClR_3(PR_3)_2]$, and *trans*P$_2$-$[(Mo_6Cl_8)R_4(PR_3)_2]$. On the other hand the cis isomers would form nine alkyl complexes; namely *mer*Cl$_3$*cis*P$_2$-$[(Mo_6Cl_8)Cl_3R(PR_3)_2]$, *fac*Cl$_3$*cis*P$_2$-$[(Mo_6Cl_8)Cl_3R(PR_3)_2]$, *cis*Cl$_2$*cis*P$_2$*trans*R$_2$-$[(Mo_6Cl_8)Cl_2R_2(PR_3)_2]$, *trans*Cl$_2$*cis*P$_2$*cis*R$_2$-$[(Mo_6Cl_8)Cl_2R_2(PR_3)_2]$, *cis*P$_2$*mer*R$_3$-$[(Mo_6Cl_8)ClR_3(PR_3)_2]$, *cis*P$_2$*fac*R$_3$-$[(Mo_6Cl_8)ClR_3(PR_3)_2]$, *cis*P$_2$-$[(Mo_6Cl_8)R_4(PR_3)_2]$, and *R*- and *S-all-cis*-$[(Mo_6Cl_8)Cl_2R_2(PR_3)_2]$. Preliminary experiments indicated that alkylation of the unseparated cis and trans isomers gave an intractable mixture of derivatives, which did not permit chromatographic separation. As the number of possible alkyl complexes is less for the trans isomer, it was necessary to start from pure trans chloride cluster complexes in order to reduce the separation problems. The moderate solubilities of the cluster chloride complexes with normal alkylphosphine ligands in chloroform facilitated the chromatography. The ^{31}P NMR spectra of the crude products obtained in the present study indicated two bands a few ppm downfield from H_3PO_4 (about a 5:1 ratio) and a few minor absorptions. We isolated two compounds from the tripropylphosphine derivative by chromatography that showed analyses almost identical with that of $[(Mo_6Cl_8)Cl_4\{P(C_3H_7)_3\}_2]$ and the same infrared and ^{1}H NMR spectra, but the chemical shifts in their ^{31}P NMR spectra differed slightly (ca. 0.4 ppm). They could only be cis and trans isomers for these complexes. As the X-ray structure determination of the major isomer of the tributylphosphine derivative (**3**) confirmed the trans geometry (vide infra), the major product for the tripropylphosphine derivative indicating higher field chemical shifts in the ^{31}P NMR spectra is probably also the trans isomer. The more polar cis isomers were likely to be eluted from the chromatographic column after the trans isomers, but the band separation was not clear enough to isolate the cis isomers in the case of the tributylphosphine and tripentylphosphine derivatives. Although the structures have not yet been directly determined for the cis isomers, the results demonstrate that the cleavage of the chlorine bridges in $(Mo_6Cl_8)Cl_2Cl_{4/2}$ forms not only trans isomer but also a smaller proportion of the cis isomer.

Table IV. Interatomic Distances (Å) and Esd Values for $[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ (**3**)

Mo(1)–Mo(2)	2.6115 (8)	Mo(1)–Mo(3)	2.6199 (8)
Mo(2)–Mo(3)	2.6103 (8)	Mo(1)–Mo(2′)	2.6162 (8)
Mo(1)–Mo(3′)	2.6114 (8)	Mo(2)–Mo(3′)	2.6277 (8)
Mo(1)–Mo(1′)	3.6918 (8)	Mo(2)–Mo(2′)	3.7012 (8)
Mo(3)–Mo(3′)	3.7064 (8)	Mo(1)–Cl(1)	2.4911 (18)
Mo(1)–Cl(2)	2.4625 (17)	Mo(1)–Cl(3)	2.4619 (17)
Mo(1)–Cl(4)	2.4799 (18)	Mo(1)–Cl(5)	2.4179 (19)
Mo(2)–Cl(1)	2.4715 (18)	Mo(2)–Cl(3)	2.4758 (15)
Mo(2)–P	2.6190 (19)	Mo(3)–Cl(3)	2.4878 (17)
Mo(3)–Cl(4)	2.4813 (18)	Mo(3)–Cl(6)	2.4018 (22)
Mo(2)–Cl(2′)	2.4556 (17)	Mo(2)–Cl(4′)	2.4606 (18)
Mo(3)–Cl(1′)	2.4840 (18)	Mo(3)–Cl(2′)	2.4699 (17)
P–C(1)	1.835 (7)	P–C(5)	1.830 (7)
P–C(9)	1.827 (7)	C(1)–C(2)	1.524 (10)
C(2)–C(3)	1.512 (11)	C(3)–C(4)	1.517 (12)
C(5)–C(6)	1.536 (10)	C(6)–C(7)	1.508 (11)
C(7)–C(8)	1.510 (14)	C(9)–C(10)	1.518 (11)
C(10)–C(11)	1.538 (13)	C(11)–C(12)	1.525 (15)
C(1)–H(11)	1.02 (8)	C(1)–H(12)	1.02 (8)
C(2)–H(21)	0.88 (8)	C(2)–H(22)	0.99 (8)
C(3)–H(31)	0.93 (8)	C(3)–H(32)	0.96 (8)
C(4)–H(41)	0.95 (8)	C(4)–H(42)	1.00 (8)
C(4)–H(43)	1.02 (8)	C(5)–H(51)	1.02 (8)
C(5)–H(52)	0.98 (8)	C(6)–H(61)	1.01 (8)
C(6)–H(62)	1.08 (8)	C(7)–H(71)	1.00 (9)
C(7)–H(72)	1.00 (8)	C(8)–H(81)	1.09 (8)
C(8)–H(82)	1.01 (8)	C(8)–H(83)	0.97 (8)
C(9)–H(91)	0.94 (8)	C(9)–H(92)	0.92 (8)
C(10)–H(101)	0.93 (8)	C(10)–H(102)	1.01 (8)
C(11)–H(111)	0.91 (8)	C(11)–H(112)	1.10 (8)
C(12)–H(121)	0.97 (8)	C(12)–H(122)	0.98 (8)
C(12)–H(123)	0.98 (8)		

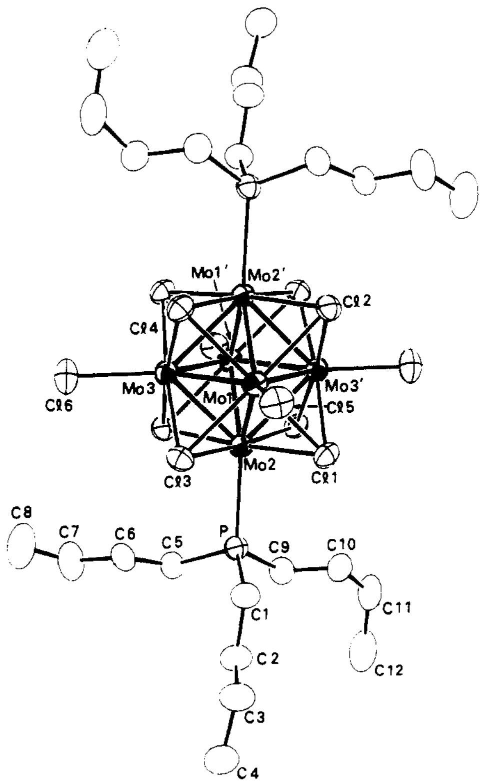

Figure 1. Molecular structure of *trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ (**3**) with the numbering scheme of atoms shown (ORTEP). The thermal ellipsoids are drawn at the 50% probability level.

Structure of 3. Selected interatomic distances and angles are listed in Tables IV and V. The present structure determination provides the first example of the structure of hexanuclear chloride cluster complexes coordinated with tertiary phosphines (Figure 1). The point of immediate importance is the confirmation that the major product is a *trans*-bis(phosphine) complex. The cluster core is an almost regular octahedron of six molybdenum atoms. The Mo–Mo bond distance of 2.616 (2) Å (av) is comparable to those in other similar cluster complexes,[3] and the Mo–Cl^b distance, 2.473 (2) Å (av), is longer than Mo–Cl^t, 2.410 (2) Å (av). The Mo–P distance, 2.619 (2) Å, is significantly longer than the sum

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(15) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(16) Cromer, D. T.; Ibers, J. A. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(17) "The Universal Crystallographic Computing System", Osaka University, Japan.

Table V. Interatomic Angles (deg) and Esd Values for $[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ (3)

Mo(2)–Mo(1)–Mo(3)	59.86 (2)	Mo(1)–Mo(2)–Mo(3)	60.23 (2)	Mo(3′)–Mo(1)–Cl(2)	58.17 (4)	Mo(2′)–Mo(1)–Cl(3)	118.75 (5)
Mo(1)–Mo(3)–Mo(2)	59.91 (2)	Mo(2)–Mo(1)–Mo(2′)	90.15 (2)	Mo(3′)–Mo(1)–Cl(3)	118.73 (5)	Mo(2′)–Mo(1)–Cl(4)	57.67 (4)
Mo(2)–Mo(1)–Mo(3′)	60.41 (2)	Mo(3)–Mo(1)–Mo(2′)	60.24 (2)	Mo(3′)–Mo(1)–Cl(4)	117.57 (5)	Mo(2′)–Mo(1)–Cl(5)	134.68 (5)
Mo(3)–Mo(1)–Mo(3′)	90.23 (3)	Mo(1)–Mo(2)–Mo(1′)	89.85 (2)	Mo(3′)–Mo(1)–Cl(5)	134.06 (5)	Mo(1′)–Mo(2)–Cl(1)	118.15 (5)
Mo(1)–Mo(2)–Mo(3′)	59.79 (2)	Mo(3)–Mo(2)–Mo(1′)	59.95 (2)	Mo(3′)–Mo(2)–Cl(1)	58.21 (4)	Mo(1′)–Mo(2)–Cl(3)	118.40 (4)
Mo(3)–Mo(2)–Mo(3′)	90.08 (2)	Mo(1)–Mo(3)–Mo(1′)	89.77 (3)	Mo(3′)–Mo(2)–Cl(3)	117.60 (4)	Mo(1′)–Mo(3)–Cl(3)	118.14 (5)
Mo(1)–Mo(3)–Mo(2′)	59.81 (2)	Mo(2)–Mo(3)–Mo(1′)	60.14 (2)	Mo(2′)–Mo(3)–Cl(3)	117.36 (4)	Mo(1′)–Mo(3)–Cl(4)	117.28 (5)
Mo(2)–Mo(3)–Mo(2′)	89.92 (2)	Mo(2)–Mo(1)–Cl(1)	57.88 (4)	Mo(2′)–Mo(3)–Cl(4)	57.50 (4)	Mo(1′)–Mo(3)–Cl(6)	134.80 (6)
Mo(2)–Mo(1)–Cl(2)	118.55 (5)	Mo(2)–Mo(1)–Cl(3)	58.33 (4)	Mo(2′)–Mo(3)–Cl(6)	136.32 (6)	Mo(1)–Mo(2′)–Cl(2)	57.99 (4)
Mo(2)–Mo(1)–Cl(4)	117.98 (5)	Mo(2)–Mo(1)–Cl(5)	135.17 (5)	Mo(1)–Mo(2′)–Cl(4)	58.39 (4)	Mo(2)–Mo(2′)–Cl(2)	87.80 (4)
Mo(3)–Mo(1)–Cl(1)	117.73 (5)	Mo(3)–Mo(1)–Cl(2)	117.97 (5)	Mo(2)–Mo(2′)–Cl(4)	87.78 (4)	Mo(3)–Mo(2′)–Cl(2)	117.93 (4)
Mo(3)–Mo(1)–Cl(3)	58.52 (4)	Mo(3)–Mo(1)–Cl(4)	58.15 (4)	Mo(3)–Mo(2′)–Cl(4)	58.26 (4)	Mo(1)–Mo(3′)–Cl(1)	58.47 (4)
Mo(3)–Mo(1)–Cl(5)	135.71 (5)	Mo(1)–Mo(2)–Cl(1)	58.61 (4)	Mo(1)–Mo(3′)–Cl(2)	57.89 (4)	Mo(2)–Mo(3′)–Cl(1)	57.75 (4)
Mo(1)–Mo(2)–Cl(3)	57.81 (4)	Mo(3)–Mo(2)–Cl(1)	118.83 (5)	Mo(2)–Mo(3′)–Cl(2)	117.66 (5)	Mo(3)–Mo(3′)–Cl(1)	87.62 (4)
Mo(3)–Mo(2)–Cl(3)	58.50 (4)	Mo(1)–Mo(3)–Cl(3)	57.56 (4)	Mo(3)–Mo(3′)–Cl(2)	87.31 (4)	Mo(1)–Mo(2)–P	134.51 (5)
Mo(1)–Mo(3)–Cl(4)	58.10 (4)	Mo(1)–Mo(3)–Cl(6)	135.41 (6)	Mo(3)–Mo(2)–P	132.73 (5)	Mo(1′)–Mo(2)–P	135.57 (5)
Mo(2)–Mo(3)–Cl(3)	58.05 (4)	Mo(2)–Mo(3)–Cl(4)	117.97 (5)	Mo(3′)–Mo(2)–P	137.18 (5)	Mo(2)–P–C(1)	112.4 (2)
Mo(2)–Mo(3)–Cl(6)	133.76 (6)	Mo(1)–Mo(2′)–Cl(2)	57.99 (4)	Mo(2)–P–C(5)	112.1 (2)	Mo(2)–P–C(9)	117.7 (2)
Mo(1)–Mo(2′)–Cl(4)	58.39 (4)	Mo(3)–Mo(2′)–Cl(2)	117.93 (4)	C(1)–C(2)–C(3)	112.5 (6)	C(2)–C(3)–C(4)	114.4 (7)
Mo(3)–Mo(2′)–Cl(4)	58.26 (4)	Mo(1)–Mo(3′)–Cl(1)	58.47 (4)	C(5)–C(6)–C(7)	113.4 (6)	C(6)–C(7)–C(8)	111.9 (7)
Mo(1)–Mo(3′)–Cl(2)	57.89 (4)	Mo(2)–Mo(3′)–Cl(1)	57.75 (4)	C(9)–C(10)–C(11)	110.8 (7)	C(10)–C(11)–C(12)	111.6 (8)
Mo(2)–Mo(3′)–Cl(2)	117.66 (5)	Mo(1′)–Mo(2′)–Cl(2)	118.46 (4)	P–C(1)–C(2)–C(3)	172.7 (5)	C(1)–C(2)–C(3)–C(4)	174.1 (6)
Mo(3′)–Mo(2′)–Cl(2)	58.26 (4)	Mo(1′)–Mo(2′)–Cl(4)	118.04 (5)	P–C(5)–C(6)–C(7)	169.1 (5)	C(5)–C(6)–C(7)–C(8)	173.1 (7)
Mo(3′)–Mo(2′)–Cl(4)	118.33 (5)	Mo(1′)–Mo(3′)–Cl(1)	117.55 (5)	P–C(9)–C(10)–C(11)	173.7 (6)	C(9)–C(10)–C(11)–C(12)	68.9 (9)
Mo(2′)–Mo(3′)–Cl(1)	118.57 (5)	Mo(1′)–Mo(3′)–Cl(2)	117.61 (5)	Mo(1′)–Mo(1)–Cl(5)	179.21 (5)	Mo(3′)–Mo(3)–Cl(6)	178.91 (6)
Mo(2′)–Mo(3′)–Cl(2)	57.73 (4)	Mo(2′)–Mo(1)–Cl(1)	118.08 (5)	Mo(2′)–Mo(2)–P	177.91 (4)		
Mo(3′)–Mo(1)–Cl(1)	58.20 (4)	Mo(2′)–Mo(1)–Cl(2)	57.74 (4)				

of the usual covalent radii of molybdenum (1.30 Å) and phosphorus (1.10 Å) atoms[18] and seems to be one of the longest Mo–P bond distances of tertiary phosphine complexes of molybdenum, including some cluster halide complexes such as $[Mo_4Cl_8\{P(C_2H_5)_3\}_4]$ (2.557 (1) Å).[19] This may be associated with the situation that the d_{xz} and d_{yz} orbitals on the molybdenum atoms are mainly used for the molybdenum cluster bonding and are unavailable for the d_π–d_π back-bonding to the phosphines.[20] There is also competition of the use of d_{z^2} and p_z orbitals between the P–Mo σ donation and the cluster bonding. In this regard the argument put forward recently by Chisholm concerning the Mo–O bond distances of the Mo_6 cluster methoxides is instructive.[21]

Cluster Alkyl Complexes. Synthesis. The alkylation reactions of the phosphine complexes with trialkylaluminum compounds were not clean. The solubilities of the reactant complexes in toluene were generally low, and initially the reaction mixtures contained suspended material. The aluminum alkyls were used in excess to bring about complete reaction. The ^{31}P NMR spectra of the crude products obtained by the procedures described in the Experimental Section showed three major bands of almost equal intensities, which are probably assignable to all-trans (ca. δ 0.1) *cis*Cl_2*trans*P_2*cis*R_2 (ca. δ –0.1), and *trans*P_2*mer*R_3 complexes (ca. δ –0.8). Other bands of much weaker intensity are presumably assignable to *trans*P_2R and *trans*P_2R_4 complexes. Three recrystallizations from toluene gave pure complex **6**, which was shown to be an *all-trans*-dialkyl derivative. Attempts to isolate *cis*Cl_2*trans*P_2*cis*R_2 and *trans*P_2*mer*R_3 complexes by chromatography were not successful.

Structure of 6. The full characterization of this diethyl derivative of the tributylphosphine complex was carried out to establish the properties associated with its structure. The elemental analysis was in good agreement with the calculated values. The infrared spectra showed the bands due to the ethyl groups at 1370 and 1150 cm^{-1}, ν(Mo–C) at 460 cm^{-1}, ν(Mo–μ_3-Cl) at 335 and 215 cm^{-1}, ν(Mo–Cl) at 242 cm^{-1}, ν(Mo–P) at 295 cm^{-1}, and ν(Mo–Mo) at 100 cm^{-1} as well as the bands assignable to the coordinated tributylphosphines.[22] The ^1H NMR spectra (benzene-d_6 solution) indicated methyl (triplet) and methylene (quartet) protons of the ethyl groups at δ 1.83 and 2.30, respectively, together with the butyl protons of tributylphosphines in the ratio of 10:54.

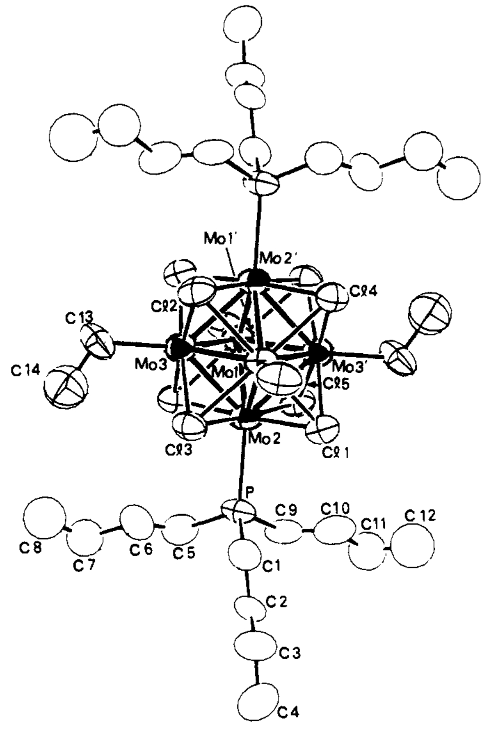

Figure 2. Molecular structure of *all-trans*-$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]$ (**6**) with the numbering scheme of atoms shown (ORTEP). The thermal ellipsoids are drawn at the 50% probability level.

The single-crystal X-ray structure determination of the toluene solvate of the diethyl complex has established that it is the *all-trans*-diethyl complex. The structure is shown in Figure 2, and selected interatomic distances and angles are listed in Tables VI and VII. Two tributylphosphines, two terminal chlorine ligands, and two terminal ethyl groups are bonded to the octahedral Mo_6Cl_8 cluster unit in mutually trans positions. The dimensions of the

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Table VI. Interatomic Distances (Å) and Esd Values for $[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$ (**6**)

Mo(1)–Mo(2)	2.618 (3)	Mo(1)–Mo(3)	2.619 (3)
Mo(2)–Mo(3)	2.602 (3)	Mo(1)–Mo(2′)	2.600 (3)
Mo(1)–Mo(3′)	2.598 (3)	Mo(2)–Mo(3′)	2.597 (3)
Mo(1)–Mo(1′)	3.702 (3)	Mo(2)–Mo(2′)	3.677 (3)
Mo(3)–Mo(3′)	3.676 (3)	Mo(1′)–Cl(1)	2.477 (7)
Mo(2′)–Cl(1)	2.472 (7)	Mo(3)–Cl(1)	2.480 (7)
Mo(1)–Cl(2)	2.483 (7)	Mo(2′)–Cl(2)	2.475 (7)
Mo(3)–Cl(2)	2.486 (7)	Mo(1)–Cl(3)	2.491 (8)
Mo(2)–Cl(3)	2.483 (8)	Mo(3)–Cl(3)	2.486 (8)
Mo(1′)–Cl(4)	2.462 (7)	Mo(2)–Cl(4)	2.475 (7)
Mo(3)–Cl(4)	2.473 (7)	Mo(1)–Cl(5)	2.421 (8)
Mo(2)–P	2.604 (8)	Mo(3)–C(13)	2.21 (3)
P–C(1)	1.90 (3)	P–C(5)	1.86 (3)
P–C(9)	1.87 (3)	C(1)–C(2)	1.49 (4)
C(2)–C(3)	1.61 (4)	C(3)–C(4)	1.46 (4)
C(5)–C(6)	1.45 (4)	C(6)–C(7)	1.66 (4)
C(7)–C(8)	1.42 (4)	C(9)–C(10)	1.48 (4)
C(10)–C(11)	1.67 (4)	C(11)–C(12)	1.40 (5)
C(13)–C(14)	1.48 (4)	C(15)–C(16)	1.49 (6)
C(16)–C(17)	1.32 (5)	C(17)–C(18)	1.44 (7)
C(19)–C(20)	1.33 (4)	C(20)–C(21)	1.50 (4)
C(21)–C(19)	1.32 (4)		

cluster core with eight bridging chlorine atoms on each face of the molybdenum octahedron are almost the same as that of the starting cluster chloride complex **3**. The Mo–C bond distance of 2.21 (3) Å is comparable with that of $Mo_2(C_2H_5)_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2$ (2.21 (1) Å), but the Mo–P bond distance of 2.606 (3) Å is longer than the metal–phosphorus distances of most tertiary phosphine complexes. The ethyl ligands are directed radially from the cluster core, and even if rotation about the Mo–C and C–C bonds is allowed, the shortest metal–β-hydrogen distance is about 2.8 Å to the molybdenum atom to which the ethyl group is coordinated and about 3.7 Å to an adjacent molybdenum atom to which the ethyl group is not bonded. All the molybdenum atoms are nine-coordinate, and no orbital seems to be available for the extra bonding to the methyl hydrogen atom of the ethyl groups without the dissociation of the ligand on the molybdenum.

Other Cluster Alkyl Complexes. Other alkyl derivatives obtained by recrystallization of the crude products appear to be *all-trans*-dialkyl complexes from the comparison of the chemical shifts in ^{31}P NMR spectra with that for **6**. Variation in the number of equivalents of aluminum alkyl from 1 to 4 showed preferential formation of dialkyl derivatives, the reason for which is not evident at present. However when pure dipropyl (**7**) or diethyl (**11**) complex was treated with fresh tripropylaluminum or triethylaluminum, conversion to the cluster trialkyl complexes **14** and **15** did occur.

Table VIII summarizes the spectroscopic data for the cluster complexes. The ν(Mo–C) bands are near those of mononuclear alkyl complexes; their frequencies vary with the alkyl ligand, but are almost independent of the particular trialkylphosphine. Some alkyl complexes show two bands in this region, and the assignments are under investigation. The ^1H NMR signals of the alkyl ligands are at relatively low field. This may be explained by the elec-

Table VII. Interatomic Angles (deg) and Esd Values for $[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$ (**6**)

Mo(2)–Mo(1)–Mo(3)	59.6 (1)	Mo(2)–Mo(1)–Mo(2′)	89.6 (1)	Cl(4)–Mo(1′)–Mo(3)	58.4 (2)	Cl(4)–Mo(1′)–Mo(3′)	118.2 (2)
Mo(3)–Mo(1)–Mo(3′)	89.6 (1)	Mo(2)–Mo(1)–Mo(3′)	59.7 (1)	Cl(4)–Mo(2)–Mo(1′)	58.0 (2)	Cl(4)–Mo(2)–Mo(1)	118.4 (2)
Mo(3)–Mo(1)–Mo(2′)	59.7 (1)	Mo(1)–Mo(2)–Mo(3)	60.2 (1)	Cl(4)–Mo(2)–Mo(3)	58.2 (2)	Cl(4)–Mo(2)–Mo(3′)	118.5 (2)
Mo(1)–Mo(2)–Mo(1′)	90.4 (1)	Mo(1)–Mo(2)–Mo(3′)	59.8 (1)	Cl(4)–Mo(3)–Mo(1′	58.0 (2)	Cl(4)–Mo(3)–Mo(1)	118.5 (2)
Mo(3)–Mo(2)–Mo(3′)	90.0 (1)	Mo(3)–Mo(2)–Mo(1′)	59.9 (1)	Cl(4)–Mo(3)–Mo(2)	58.3 (2)	Cl(4)–Mo(3)–Mo(2′)	118.5 (2)
Mo(1)–Mo(3)–Mo(2)	60.2 (1)	Mo(1)–Mo(3)–Mo(1′)	90.4 (1)	Cl(5)–Mo(1)–Mo(2)	135.5 (2)	Cl(5)–Mo(1)–Mo(2′)	134.9 (2)
Mo(2)–Mo(3)–Mo(2′)	90.0 (1)	Mo(2)–Mo(3)–Mo(1′)	60.0 (1)	Cl(5)–Mo(1)–Mo(3)	135.5 (2)	Cl(5)–Mo(1)–Mo(3′)	134.9 (2)
Mo(1)–Mo(3)–Mo(2′)	118.5 (2)			Cl(5)–Mo(1)–Mo(1′)	179.9 (2)	P–Mo(2)–Mo(1)	134.3 (2)
Cl(1)–Mo(1′)–Mo(2)	119.0 (2)	Cl(1)–Mo(1′)–Mo(2′)	58.0 (2)	P–Mo(2)–Mo(1′)	135.3 (2)	P–Mo(2)–Mo(3)	134.1 (2)
Cl(1)–Mo(1′)–Mo(3)	58.4 (2)	Cl(1)–Mo(1′)–Mo(3′)	117.6 (2)	P–Mo(2)–Mo(3′)	135.9 (2)	P–Mo(2)–Mo(2′)	178.8 (2)
Cl(1)–Mo(2′)–Mo(1)	119.0 (2)	Cl(1)–Mo(2′)–Mo(1′)	58.2 (2)	C(13)–Mo(3)–Mo(1)	136.5 (7)	C(13)–Mo(3)–Mo(1′)	133.0 (7)
Cl(1)–Mo(2′)–Mo(3)	58.5 (2)	Cl(1)–Mo(2′)–Mo(3′)	118.4 (2)	C(13)–Mo(3)–Mo(2)	137.0 (7)	C(13)–Mo(3)–Mo(2′)	132.9 (7)
Cl(1)–Mo(3)–Mo(1)	118.0 (2)	Cl(1)–Mo(3)–Mo(1′)	58.3 (2)	C(13)–Mo(3)–Mo(3′)	177.5 (7)	Mo(2)–P–C(1)	112.5 (8)
Cl(1)–Mo(3)–Mo(2)	118.3 (2)	Cl(1)–Mo(3)–Mo(2′)	58.2 (2)	Mo(2)–P–C(5)	115.6 (9)	Mo(2)–P–C(9)	114.1 (8)
Cl(2)–Mo(1)–Mo(2)	117.8 (2)	Cl(2)–Mo(1)–Mo(2′)	58.2 (2)	P–C(1)–C(2)	111 (2)	C(1)–C(2)–C(3)	107 (2)
Cl(2)–Mo(1)–Mo(3)	58.2 (2)	Cl(2)–Mo(1)–Mo(3′)	118.3 (2)	C(2)–C(3)–C(4)	115 (2)	P–C(5)–C(6)	112 (2)
Cl(2)–Mo(2′)–Mo(1)	58.5 (2)	Cl(2)–Mo(2′)–Mo(1′)	118.4 (2)	C(5)–C(6)–C(7)	114 (2)	C(6)–C(7)–C(8)	106 (2)
Cl(2)–Mo(2′)–Mo(3)	58.6 (2)	Cl(2)–Mo(2′)–Mo(3′)	118.4 (2)	P–C(9)–C(10)	111 (2)	C(9)–C(10)–C(11)	106 (2)
Cl(2)–Mo(3)–Mo(1)	58.1 (2)	Cl(2)–Mo(3)–Mo(1′)	118.7 (2)	C(10)–C(11)–C(12)	96 (3)	Mo(3)–C(13)–C(14)	120 (2)
Cl(2)–Mo(3)–Mo(2)	118.3 (2)	Cl(2)–Mo(3)–Mo(2′)	58.2 (2)	C(16)–C(15)–C(16′)	121 (4)	C(15)–C(16)–C(17)	115 (3)
Cl(3)–Mo(3)–Mo(1)	58.3 (2)	Cl(3)–Mo(3)–Mo(1′)	118.4 (2)	C(16)–C(17)–C(18)	128 (4)	C(17)–C(18)–C(17′)	113 (4)
Cl(3)–Mo(3)–Mo(2)	58.4 (2)	Cl(3)–Mo(3)–Mo(2′)	118.1 (2)	C(20)–C(19)–C(21′)	120 (3)	C(19)–C(20)–C(21)	125 (3)
Cl(3)–Mo(1)–Mo(2)	58.1 (2)	Cl(3)–Mo(1)–Mo(2′)	117.8 (2)	C(20)–C(21)–C(19′)	113 (3)		
Cl(3)–Mo(1)–Mo(3)	58.2 (2)	Cl(3)–Mo(1)–Mo(3′)	117.8 (2)	P–C(1)–C(2)–C(3)	180 (2)	C(1)–C(2)–C(3)–C(4)	176 (2)
Cl(3)–Mo(2)–Mo(1)	58.4 (2)	Cl(3)–Mo(2)–Mo(1′)	118.4 (2)	P–C(5)–C(6)–C(7)	179 (2)	C(5)–C(6)–C(7)–C(8)	166 (2)
Cl(3)–Mo(2)–Mo(3)	58.5 (2)	Cl(3)–Mo(2)–Mo(3′)	118.1 (2)	P–C(9)–C(10)–C(11)	177 (2)	C(9)–C(10)–C(11)–C(12)	179 (2)
Cl(4)–Mo(1′)–Mo(2)	58.5 (2)	Cl(4)–Mo(1′)–Mo(2′)	118.1 (2)				

Table VIII. Spectroscopic Data for *all-trans*-$[(Mo_6Cl_8)Cl_2R'_2(PR_3)_2]$ and $[(Mo_6Cl_8)ClR'_3(PR_3)_2]$

R	R	compd no.	IR[a] ν(Mo–C)/cm^{-1}	^1H NMR[b] δ($Mo\text{–}CH_2$)	^{31}P NMR[c] δ	UV[d] λ, nm (ε, M^{-1} cm^{-1})
C_4H_9	CH_3	**5**	480 s	1.57[f]	0.83	282 (14800)
C_4H_9	C_2H_5	**6**	460 s	2.30	0.11	291 (22900)
C_4H_9	C_3H_7	**7**	550 s, 450 m	2.47	0.32	292 (28200)
C_4H_9	C_4H_9	**8**	555 s	*g*	−0.26	291 (26900)
C_4H_9	C_6H_{13}	**9**	560 s, 430 m	*g*	−1.09	292 (28200)
C_5H_{11}	CH_3	**10**	480 s	1.62[f]	0.00	281 (21400)
C_5H_{11}	C_2H_5	**11**	460 s	2.53	0.09	291 (16200)
C_5H_{11}	C_3H_7	**12**	550 s, 460 m	*g*	0.15	291 (30000)
C_3H_7	C_2H_5	**13**	460 s	2.51	−1.57	290 (18700)
C_5H_{11}	C_2H_5[e]	**14**	450 s	2.49	−1.11	303 (15000)
C_4H_9	C_3H_7[e]	**15**	550 s, 450 m	*g*	−0.80	303 (19800)

[a] CsI disk. [b] In benzene-d_6 (Me_4Si reference). [c] In benzene (^{31}P chemical shifts (positive sign) downfield from external H_3PO_4 (5% in methanol-d_4). [d] In THF. [e] Trialkyl complex. [f] $Mo\text{–}CH_3$. [g] Unresolved multiplet.

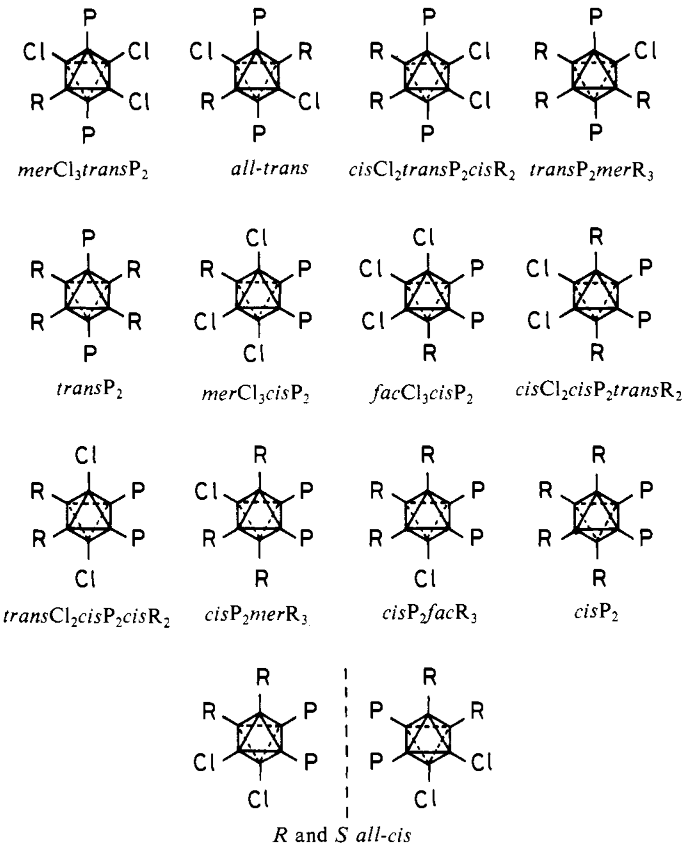

Figure 3. Schematic drawings of possible alkyl complexes derived from *trans*-$[(Mo_6Cl_8)Cl_4(PR_3)_2]$ and *cis*-$[(Mo_6Cl_8)Cl_4(PR_3)_2]$. Molybdenum and face-bridging chlorine atoms are omitted for the sake of clarity, and P denotes PR_3.

tron-attracting character of the cluster core with 10 electronegative chlorine ligands. The chemical shifts of the ethyl protons in the molybdenum ethyl complex with an electronegative oxo ligand have been reported to arise in a similar region.[23]

Thermolysis. A solid sample of **6** began to decompose at 120 °C, and thermolysis became rapid at 160 °C. The gaseous products after heating at 250 °C for 2 h in dinitrogen reached 1.8 mol/mol of the complex; they comprised dihydrogen (0.55 mol), ethane (0.62 mol), ethylene (0.48 mol), butene (0.09 mol), and others (0.06 mol). The amount of *n*-butane (0.02 mol) was at about the same insignificant level as that obtained from a control experiment using the parent nonalkylated complex **3**. It is likely that the molybdenum atoms bonded to the alkyl groups are coordinatively saturated and that the Mo–C bond homolysis is the initial event. However it seems that the ethyl radicals are not so free as to couple to each other and they abstract hydrogen either from tributylphosphine or other ethyl ligand to give ethane. The origin of dihydrogen has not yet been traced, but it is probably linked with the formation of ethylene. Lack of initial β-elimination and other low-energy concerted elimination pathways in the conventional sense for mononuclear alkyl complexes[24,25] may explain the fairly high thermal stability of the cluster diethyl complex; this is in contrast with, for example, the very labile ethyl complexes analogous to $[MoO_2(CH_3)_2(bpy)]$.[26] The details and possible interpretation of the thermolysis will be reported in future publications.

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Appendix

The nomenclature of hexanuclear alkyl complexes coordinated with trialkylphosphines has not been decided, and we propose the tentative terms to describe the structures given in Figure 3. The molybdenum and face-bridging chlorine atoms are omitted for the sake of clarity.

Registry No. 1, 101009-21-6; **2**, 101009-22-7; **3**, 101009-34-1; **4**, 101009-23-8; **5**, 101009-24-9; **6**, 101009-33-0; **6**·$2C_6H_5CH_3$, 101030-80-2; **7**, 101009-25-0; **8**, 101030-81-3; **9**, 101009-26-1; **10**, 101009-27-2; **11**, 101009-28-3; **12**, 101009-29-4; **13**, 101009-30-7; **14**, 101009-31-8; **15**, 101009-32-9; Mo_6Cl_{12}, 11062-51-4.

Supplementary Material Available: Listings of hydrogen atom coordinates, anisotropic temperature factors, and calculated and observed structure factors for **3** and **6** and crystal packing diagrams for **3** and **6** (37 pages). Ordering information is given on any current masthead page.

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