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First Synthesis of Octahedral Tungsten Cluster Chloro Complexes with Trialkylphosphines and Their Conversion to η^1-Ethyl Derivatives

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Hexanuclear tungsten cluster chloro complexes coordinated with two trialkylphosphines were prepared, and *trans*-$[(W_6Cl_8)Cl_4(PR_3)_2]$ complexes (R = n-C_4H_9 (**1**), n-C_5H_{11} (**2**)) were isolated by chromatography. The complex **1** crystallizes in the monoclinic space group $C2/c$ with a = 29.045 (15) Å, b = 10.326 (3) Å, c = 21.485 (9) Å, β = 135.33 (2)°, and Z = 4. The X-ray determination of the structure confirmed that the two tributylphosphine ligands are coordinated to the trans positions of the octahedral tungsten cluster core with eight face-bridging and four terminal chlorines. Selected bond distances are W–W = 2.626 Å (av), $W-Cl^t$ = 2.413 Å (av), $W-Cl^b$ = 2.496 Å (av), and W–P = 2.581 (8) Å. The diethyl and triethyl cluster complexes *all-trans*-$[(W_6Cl_8)Cl_2(C_2H_5)_2(PR_3)_2]$ (R = n-C_4H_9 (**3**), n-C_5H_{11} (**4**)) and *trans,mer*-$[(W_6Cl_8)Cl(C_2H_5)_3(PR_3)_2]$ (R = n-C_4H_9 (**5**), n-C_5H_{11} (**6**)) were synthesized by the reactions of **1** and **2** with triethylaluminum. The ^{13}C NMR spectrum of **6** shows two methylene carbon signals with the W–C coupling satellites (J(W–C) = 74 Hz) indicating that the ethyl groups are bonded to tungsten in an η^1 mode and that the chemical shifts are influenced by the "cis" ligands. In the solid state these ethyl cluster complexes are heat- and air-stable. However, the solutions are very sensitive to visible light and homolysis of the W–C bonds occurs under a short period of irradiation.

Introduction

The well-known hexanuclear metal cluster complexes of the early transition metals[1] having robust skeletons and exo halogen ligands can be good starting compounds for obtaining a variety of multinuclear derivatives having the expanded octahedral coordination sphere, but their chemistry has not been much explored.[2] We isolated pure geometrical isomers of $[(Mo_6Cl_8)Cl_4(PR_3)_2]$ and converted the trans derivatives to the alkyl complexes, which were the first representatives of the class.[3] The alkyl cluster complexes are themselves potential intermediates in the catalysis of hydrocarbons. They yield polymers with intercluster metal–metal bonding, but very few of these have been reported.[4] The present paper reports the tungsten cluster alkyls and is a part of our series of studies on the alkyl cluster complexes of transition metals. Since no report on the preparation of trialkylphosphine complexes of the hexanuclear tungsten cluster halides[5] is available, we have established the preparation of chloro complexes including the separation of their trans isomers and have also determined the crystal structure of a tributylphosphine derivative. The chloro complexes were converted to diethyl and triethyl derivatives by reaction with triethylaluminum.

Experimental Section

Reagents. W_6Cl_{12} was obtained by careful vacuum pyrolysis (50–230 °C) of $(H_3O)_2(W_6Cl_{12})\cdot 6H_2O$, itself prepared by a modification of the method of Schäfer.[5,6] Tributylphosphine (Nihon Kagaku Kogyo) was used as received, and tripentylphosphine was prepared by the reaction of phosphorus trichloride with pentylmagnesium bromide in ether at 0 °C followed by the usual workup. Triethylaluminum (Ethyl Corp.) was used in toluene solution without further purification. Solvents were dried and distilled under dinitrogen.

Spectra. ^1H, ^{13}C, and ^{31}P NMR spectra were run with JEOL FX100 and Bruker AM360 spectrometers. Tetramethylsilane was used as an internal standard for the ^1H and ^{13}C NMR spectra and 5% phosphoric acid (in methanol-d_4) as an external standard for the ^{31}P NMR spectra. Infrared spectra were recorded with Hitachi 295 (4000–250 cm^{-1}) and Hitachi FIS-3 (400–50 cm^{-1}) spectrometers.

Synthesis. All preparative operations were carried out under dinitrogen or argon, and the geometrical isomers of the cluster chloro complexes were separated from chloroform solution by Florisil column chromatography, again under dinitrogen.

The elemental analyses were performed at the analytical laboratory of our department.

***trans*-$[(W_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ (1).** A suspension of W_6Cl_{12} (5.5 g, 3.6 mmol) in THF (55 mL) was stirred with tributylphosphine (2.0 mL, 8.0 mmol) for 24 h at room temperature to dissolve the complex completely. The solvent was removed under reduced pressure and the residue washed with hexane several times and dried to give a yellow powder: yield 7.2 g. The product was chromatographed with chloroform. A light yellow solid was obtained from the first band; yield 0.9 g (13%). Anal. Calcd for $C_{24}H_{54}Cl_{12}P_2W_6$: C, 14.90; H, 2.79; Cl, 22.01. Found: C, 14.93; H, 2.74; Cl, 22.20. IR (Nujol mull): 316, 226 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ −6.56 (J(W–P) = 211.8 Hz).

***trans*-$[(W_8Cl_8)Cl_4\{P(n\text{-}C_5H_{11})_3\}_2]$ (2).** W_6Cl_{12} (5.6 g, 3.7 mmol) was reacted with tripentylphosphine (4.0 mL, 13.7 mmol) in THF (70 mL) followed by chromatography, as for the complex **1**, to give a yellow solid; yield 2.4 g (33%). Anal. Calcd for $C_{30}H_{66}Cl_{12}P_2W_6$: C, 17.86; H, 3.29; Cl, 21.08. Found: C, 17.82; H, 3.27; Cl, 20.87. IR (Nujol mull): 319, 222 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ −6.34 (J(W–P) = 219.1 Hz). ^{13}C NMR (C_6D_6): δ 14.30, 22.42, 23.44, 24.42 (^1J(P–C) = 21.9 Hz), 33.14 (^2J(P–C) = 12.2 Hz).

***all-trans*-$[(W_6Cl_8)Cl_2(C_2H_5)_2\{P(C_4H_9)_3\}_2]$ (3).** A suspension of the chloro complex **1** (0.4 g, 0.2 mmol) in toluene (15 mL) was stirred with triethylaluminum (10 vol %, 2.6 mL, 1.7 mmol) at room temperature for 48 h in darkness. The solvent was removed under reduced pressure from the dark brown solution, and small amounts of ether and acetone were added in succession to the oily residue to form the crude solid product. The product was dissolved in toluene and the solution filtered, concentrated, and cooled at −20 °C to give a yellow powder, which was finally washed with a small amount of toluene: yield 0.05 g (12%). Anal. Calcd for $C_{28}H_{64}Cl_{10}P_2W_6$: C, 17.51; H, 3.35; Cl, 18.46. Found: C, 17.77; H, 3.30; Cl, 18.30. IR (CsI disk): 1355, 460 cm^{-1}. IR (Nujol): 306 cm^{-1}. ^1H NMR (C_6D_6): δ 2.20 (t), 2.50 (q).

***all-trans*-$[(W_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_5H_{11})_3\}_2]$ (4).** The chloro complex **2** (1.5 g, 0.7 mmol) was reacted with triethylaluminum (10 vol %, 3.5 mL, 2.3 mmol) in toluene (25 mL) at −15 °C for 12 h in darkness, and the product was isolated by the same workup as for **3**; yield 0.5 g (34%). Anal. Calcd for $C_{34}H_{76}Cl_{10}P_2W_6$: C, 20.37; H, 3.82; Cl, 17.68. Found: C, 20.45; H, 3.75; Cl, 17.56. IR (CsI disk): 1360, 460 cm^{-1}. IR (Nujol): 310 cm^{-1}. ^1H NMR (C_6D_6): δ 2.20 (t), 2.50 (q). ^{13}C NMR (C_6D_6): δ 14.07, 18.48, 21.68, 22.53, 23.59, 24.80 (^1J(P–C) = 21.5 Hz), 33.33 (^2J(P–C) = 11.7 Hz).

***trans,mer*-$[(W_6Cl_8)Cl(C_2H_5)_3\{P(n\text{-}C_4H_9)_3\}_2]$ (5).** The crude product **3**, as obtained from **1** (0.9 g, 0.5 mmol) and triethylaluminum (10 vol %, 6.6 mL, 4.4 mmol), was dissolved in toluene (6 mL) and reacted with triethylaluminum (10 vol %, 2.6 mL, 1.7 mmol) at 25 °C, for 24 h in darkness. The solvent was removed under reduced pressure, and the

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Table I. Crystal Parameters and X-ray Diffraction Data for *trans*-$[(W_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$

lattice type	monoclinic
space group	*C*2/*c*
a, Å	29.045 (15)
b, Å	10.326 (3)
c, Å	21.485 (9)
β, deg	135.33 (2)
cell vol, $Å^3$	4530 (4)
formula	$C_{24}H_{54}Cl_{12}P_2W_6$
fw	1933.18
systematic absences	*hkl*, *h* + *k* odd; *h*0*l*, *l* odd
Z	4
D_{calcd}, g cm^{-3}	2.83
D_{measd}, g cm^{-3}	2.81 (1)
λ(Mo Kα), Å	0.71069
cryst size, mm	0.13 × 0.33 × 0.10
F(000)	3504
scan method	ω–2θ
scan range (ω), deg	1.2 + 0.35 tan θ
scan rate (2θ), deg min^{-1}	8
bkgd time at each side of peak, s	6
collecn region	$\pm h,k,l$
2θ limit, deg	55
decay	negligible
cor applied	*Lp*
reflecns measd	5552
no. of unique reflecns	5401
R_{int}, F	0.025
no. of obsd reflecns	3629
criterion for obsd *F*	$>4\sigma$
linear abs coeff μ, cm^{-1}	163.2
cor made	yes[a]
rel abs coeff	1.00–1.39
no. of variables	200
R. R_w[b]	0.0641, 0.0678
s[c]	2.27

[a] Correction methods applied were those in: North, A. C. T.; Phillips, D. C.; Matthew, B. W. *Acta Crystallogr., Sect. A: Cryst. Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351–359. [b] $w = 1/\sigma^2(F_o)$. [c] $s = [\sum(|F_o| - |F_c|)^2/(N_{observn} - N_{param})]^{1/2}$.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for *trans*-$[(W_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$[a]

atom	*x*	*y*	*z*	U_{eq}, $Å^2$
W(1)	0.69891 (4)	0.19045 (9)	0.01449 (6)	0.0269 (5)
W(2)	0.70117 (4)	0.15056 (9)	−0.10374 (5)	0.0257 (5)
W(3)	0.69222 (4)	0.38685 (9)	−0.06925 (6)	0.0273 (5)
Cl(1)	0.7101 (3)	−0.0323 (6)	−0.0186 (4)	0.039 (4)
Cl(2)	0.8022 (3)	0.1569 (6)	0.1758 (3)	0.038 (3)
Cl(3)	0.6011 (3)	0.2273 (6)	−0.1431 (3)	0.035 (3)
Cl(4)	0.6922 (3)	0.4202 (6)	0.0481 (4)	0.041 (4)
Cl(5)	0.6333 (3)	0.1117 (7)	0.0385 (4)	0.042 (4)
Cl(6)	0.6173 (3)	0.5613 (7)	−0.1570 (5)	0.054 (5)
P	0.6304 (3)	0.0164 (6)	−0.2476 (4)	0.032 (4)
C(1)	0.5640 (11)	−0.0736 (27)	−0.2712 (14)	0.043 (16)
C(2)	0.5128 (12)	−0.1400 (27)	−0.3629 (16)	0.047 (18)
C(3)	0.4556 (13)	−0.1919 (27)	−0.3823 (17)	0.048 (19)
C(4)	0.4022 (12)	−0.2410 (30)	−0.4741 (18)	0.060 (19)
C(5)	0.5908 (10)	0.1218 (22)	−0.3434 (14)	0.034 (14)
C(6)	0.5428 (10)	0.2179 (26)	−0.3607 (14)	0.041 (14)
C(7)	0.5190 (14)	0.3163 (33)	−0.4281 (17)	0.064 (20)
C(8)	0.4796 (21)	0.4250 (32)	−0.4355 (25)	0.100 (41)
C(9)	0.6706 (11)	−0.1100 (26)	−0.2571 (15)	0.042 (16)
C(10)	0.6974 (13)	−0.2139 (27)	−0.1951 (16)	0.052 (19)
C(11)	0.7232 (18)	−0.3089 (34)	−0.2156 (24)	0.086 (31)
C(12)	0.6704 (14)	−0.3908 (27)	−0.3000 (19)	0.059 (22)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_i{\cdot}a_j$.

Table III. Interatomic Distances (Å) and Esd Values for *trans*-$[(W_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$

W(1)–W(2)	2.620 (2)	W(1)–W(3)	2.625 (2)
W(2)–W(3)	2.616 (2)	W(1)–W(2′)	2.623 (2)
W(1)–W(3′)	2.594 (2)	W(1)–W(1′)	3.652 (2)
W(2)–W(3′)	2.680 (2)	W(2)–W(2′)	3.762 (2)
W(3)–W(3′)	3.729 (2)		
W(1)–Cl(1)	2.496 (8)	W(1)–Cl(2)	2.518 (7)
W(1)–Cl(3)	2.449 (7)	W(1)–Cl(4)	2.527 (8)
W(1)–Cl(5)	2.439 (8)	W(2)–Cl(1)	2.510 (8)
W(2)–Cl(3)	2.509 (7)	W(2)–P	2.581 (8)
W(3)–Cl(3)	2.502 (7)	W(3)–Cl(4)	2.544 (8)
W(3)–Cl(6)	2.387 (9)	W(2)–Cl(2′)	2.478 (7)
W(2)–Cl(4′)	2.507 (8)	W(3)–Cl(1′)	2.500 (8)
W(3)–Cl(2′)	2.447 (7)	P–C(1)	1.86 (3)
P–C(5)	1.84 (3)	P–C(9)	1.86 (3)
C(1)–C(2)	1.55 (5)	C(2)–C(3)	1.50 (5)
C(3)–C(4)	1.48 (5)	C(5)–C(6)	1.53 (4)
C(6)–C(7)	1.48 (5)	C(7)–C(8)	1.53 (6)
C(9)–C(10)	1.43 (5)	C(10)–C(11)	1.48 (6)
C(11)–C(12)	1.55 (6)		

residue was washed with ether and dried. The product was recrystallized from toluene to give a yellow powder; yield 0.2 g (22%). Anal. Calcd for $C_{30}H_{69}Cl_9P_2W_6$: C, 18.82; H, 3.63; Cl, 16.67. Found: C, 18.92; H, 3.62; Cl, 16.55. IR (CsI disk): 1360, 465 cm^{-1}. IR (Nujol mull): 305 cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.20 (m), 2.50 (m).

***trans,mer*-$[(W_6Cl_8)Cl(C_2H_5)_3\{P(n\text{-}C_5H_{11})_3\}_2]$ (6).** The procedure for **5** was followed with **2** (2.7 g, 1.4 mmol) and triethylaluminum being used (10 vol %; first addition 12.2 mL, 8.1 mmol; second addition 13.6 mL, 9.1 mmol); yield 1.0 g (36%). Anal. Calcd for $C_{36}H_{81}Cl_9P_2W_6$: C, 21.63; H, 4.08; Cl, 15.96. Found: C, 21.50; H, 3.98; Cl, 15.86. IR (CsI disk): 1360, 465 cm^{-1}. IR (Nujol mull): 310 cm^{-1}. ^{1}H NMR (C_6D_6, 360 MHz): δ 2.16 (t), 2.23 (t), 2.49 (q), 2.55 (q); ^4J(H–H) = 7.8 Hz. ^{13}C NMR (C_6D_6, 90 MHz): ethyl group, δ 13.21 (J(W–C) = 74 Hz), 15.54 (J(W–C) = 74 Hz), 21.75, 21.82; phosphine, δ 14.03, 22.53, 23.73, 25.31 (^1J(P–C) = 20.9 Hz), 33.45 (^2J(P–C) = 11.9 Hz).

X-ray Determination of the Structure of 1. Yellow crystals were grown by slow diffusion of ether vapor into a dichloromethane solution of the complex in a closed H-shaped vessel. For the X-ray data collection, a crystal was used fixed on the end of a glass fiber with epoxy resin. Systematic absences were consistent with the centric space group *C*2/*c* or noncentric space group *Cc*. Unit cell dimensions were determined by least-squares refinement using 30 reflections (20° < 2θ < 25°). 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 (40 Kv, 200 mA) with graphite-monochromatized Mo Kα radiation. The space group *C*2/*c* was initially assumed, and successful solution and refinement of the structure in this space group supported this choice. The positions of six tungsten atoms were located by MULTAN 78,[7] and the remainder of the non-hydrogen atoms were located in the Fourier maps. All non-hydrogen atoms were refined by the block-diagonal least-squares method with anisotropic thermal parameters. As refinement proceeded, all hydrogen atoms were located in difference Fourier maps. Those atoms were included as fixed contributions in their idealized positions with C–H = 1.08 Å (sp^3-hybridized geometry) and β = 1.93 Å^2. The six low-angle reflections (111, $\bar{1}$11, 311, 200, 002, $\bar{2}$02) were omitted from the final refinement for their extinction. Crystallographic data, experimental information, and structure refinement parameters are given in Table I. Atomic coordinates are listed in Table II. Atomic scattering factors were taken from a standard source,[8] and the effects of anomalous dispersions were included for the W, Cl, P, and C atoms by using the $\Delta f'$ and $\Delta f''$ values of Cromer and Ibers.[9] All calculations were performed with UNICS programs[10] on an ACOS S850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and Discussion

Chloro Cluster Complexes. Synthesis. The coordination of trialkylphosphines to the octahedral cluster skelton of tungsten atoms enhances solubility in such organic solvents as chloroform or aromatic hydrocarbons. The separation of the trans isomers was facilitated by chromatography, but the band separation was not very clear, and the compounds on the column tended to decompose probably due to either oxidation or dissociation of tri-

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Table IV. Interatomic Angles (deg) and Esd Values for *trans*-[$(W_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2$]

W(2)–W(1)–W(3)	59.84 (4)	W(1)–W(2)–W(3)	60.18 (4)
W(1)–W(3)–W(2)	59.99 (4)	W(2)–W(1)–W(2′)	91.69 (5)
W(2)–W(1)–W(3′)	61.86 (4)	W(3)–W(1)–W(2′)	61.42 (4)
W(3)–W(1)–W(3′)	91.19 (5)	W(1)–W(2)–W(1′)	88.31 (5)
W(1)–W(2)–W(3′)	58.60 (4)	W(3)–W(2)–W(1′)	59.36 (4)
W(3)–W(2)–W(3′)	89.49 (5)	W(1)–W(3)–W(1′)	88.81 (5)
W(1)–W(3)–W(2′)	59.25 (4)	W(2)–W(3)–W(1′)	60.45 (4)
W(2)–W(3)–W(2′)	90.51 (5)	W(2)–W(1)–Cl(1)	58.7 (2)
W(2′)–W(1)–W(3′)	60.19 (4)	W(1′)–W(2)–W(3′)	59.33 (4)
W(1′)–W(3)–W(2′)	59.55 (4)		
W(2)–W(1)–Cl(2)	119.0 (2)	W(2)–W(1)–Cl(3)	59.2 (2)
W(2)–W(1)–Cl(4)	119.0 (2)	W(2)–W(1)–Cl(5)	135.6 (2)
W(3)–W(1)–Cl(1)	118.5 (2)	W(3)–W(1)–Cl(2)	119.0 (2)
W(3)–W(1)–Cl(3)	59.0 (2)	W(3)–W(1)–Cl(4)	59.1 (2)
W(3)–W(1)–Cl(5)	135.6 (2)	W(1)–W(2)–Cl(1)	58.2 (2)
W(1)–W(2)–Cl(3)	57.0 (2)	W(3)–W(2)–Cl(1)	118.4 (2)
W(3)–W(2)–Cl(3)	58.4 (2)	W(1)–W(3)–Cl(3)	57.0 (2)
W(1)–W(3)–Cl(4)	58.5 (2)	W(1)–W(3)–Cl(6)	134.9 (2)
W(2)–W(3)–W(3)	58.7 (2)	W(2)–W(3)–Cl(4)	118.5 (2)
W(2)–W(3)–Cl(6)	134.3 (2)	W(1)–W(2′)–Cl(2)	59.1 (2)
W(1)–W(2′)–Cl(4)	59.0 (2)	W(3)–W(2′)–Cl(2)	118.4 (2)
W(3)–W(2′)–Cl(4)	58.6 (2)	W(1)–W(3′)–Cl(1)	58.7 (2)
W(1)–W(3′)–Cl(2)	59.9 (2)	W(2)–W(3′)–Cl(1)	57.8 (2)
W(2)–W(3′)–Cl(2)	119.4 (2)	Cl(2)–W(2′)–W(1′)	117.5 (2)
Cl(2)–W(2′)–W(3′)	57.4 (2)	Cl(4)–W(2′)–W(1′)	117.2 (2)
Cl(4)–W(2′)–W(3′)	118.3 (2)	Cl(1)–W(3′)–W(1′)	117.1 (2)
Cl(1)–W(3′)–W(2′)	119.1 (2)	Cl(2)–W(3′)–W(1′)	118.4 (2)
Cl(2)–W(3′)–W(2′)	58.5 (2)	Cl(1)–W(1)–W(2′)	119.0 (2)
Cl(1)–W(1)–W(3′)	58.8 (2)	Cl(2)–W(1)–W(2′)	57.6 (2)
Cl(2)–W(1)–W(3′)	57.2 (2)	Cl(3)–W(1)–W(2′)	120.4 (2)
Cl(3)–W(1)–W(3′)	121.1 (2)	Cl(4)–W(1)–W(2′)	58.2 (2)
Cl(4)–W(1)–W(3′)	118.4 (2)	Cl(5)–W(1)–W(2′)	132.7 (2)
Cl(5)–W(1)–W(3′)	133.2 (2)	Cl(1)–W(2)–W(1′)	116.8 (2)
Cl(1)–W(2)–W(3′)	57.5 (2)	Cl(3)–W(2)–W(1′)	117.6 (2)
Cl(3)–W(2)–W(3′)	115.6 (2)	Cl(3)–W(3)–W(1′)	118.9 (2)
Cl(3)–W(3)–W(2′)	116.2 (2)	Cl(4)–W(3)–W(1′)	116.8 (2)
Cl(4)–W(3)–W(2′)	57.3 (2)	Cl(6)–W(3)–W(1′)	136.3 (2)
Cl(6)–W(3)–W(2′)	135.2 (2)	W(1)–W(2′)–Cl(2)	59.1 (2)
W(1)–W(2′)–Cl(4)	59.0 (2)	W(2)–W(2′)–Cl(2)	87.9 (2)
W(2)–W(2′)–Cl(4)	87.6 (2)	W(3)–W(2′)–Cl(2)	118.4 (2)
W(3)–W(2′)–Cl(4)	58.6 (2)	W(1)–W(3′)–Cl(1)	58.7 (2)
W(1)–W(3′)–Cl(2)	59.9 (2)	W(2)–W(3′)–Cl(1)	57.8 (2)
W(2)–W(3′)–Cl(2)	119.4 (2)	W(3)–W(3′)–Cl(1)	87.6 (2)
W(3)–W(3′)–Cl(2)	89.2 (2)	W(1)–W(2)–P	134.2 (2)
W(3)–W(2)–P	133.2 (2)	P–W(2)–W(1′)	137.4 (2)
P–W(2)–W(3′)	137.2 (2)	W(1′)–W(1)–Cl(5)	178.4 (2)
W(2′)–W(2)–P	177.9 (2)	W(3′)–W(3)–Cl(6)	179.0 (2)
W(2)–P–C(1)	113 (1)	W(2)–P–C(5)	111 (1)
W(2)–P–C(9)	119 (1)	C(1)–C(2)–C(3)	113 (3)
C(2)–C(3)–C(4)	113 (3)	C(5)–C(6)–C(7)	113 (3)
C(6)–C(7)–C(8)	144 (3)	C(9)–C(10)–C(11)	106 (3)
C(10)–C(11)–C(12)	115 (4)	C(1)–C(2)–C(3)–C(4)	173 (3)
C(5)–C(6)–C(7)–C(8)	171 (3)	C(9)–C(10)–C(11)–C(12)	75 (4)
P–C(1)–C(2)–C(3)	171 (2)	P–C(5)–C(6)–C(7)	171 (2)
P–C(9)–C(10)–C(11)	176 (2)		

alkylphosphines. The isolation of the pure cis isomers has not been successful so far. In the molybdenum case, only one cis isomer of the tripropylphosphine complex was separated.[3]

Structure of 1. Selected interatomic distances and angles are listed in Tables III and IV. The structure determination of *trans*-[$(W_6Cl_8)Cl_4(PBu_3)_2$] has indicated that the crystal is isomorphous with the molybdenum analogue,[3] but its structure was solved independently. The result confirms that the tributylphosphine ligands are coordinated to the tungsten atoms in the trans positions of the octahedral cluster core with eight face-bridging and four terminal chlorine ligands (Figure 1). The ^{31}P NMR spectra showing the W–P coupling satellites are consistent with the structure. The W–W bond distances (2.626 Å (av)) are only slightly longer than those of the molybdenum congener (2.6162 Å (av)),[3] reflecting the similarity of the metallic radii of tungsten and molybdenum.[11] Recent publication[12] of the structure of [$(n\text{-}C_4H_9)_4N]_2W_6Cl_{14}$ has shown that the average W–W bond length is 2.607 Å, which is shorter than the average W–W distance of the present complex. This may be due to the formal dinegative charge on the [$W_6Cl_{14}]^{2-}$ system.

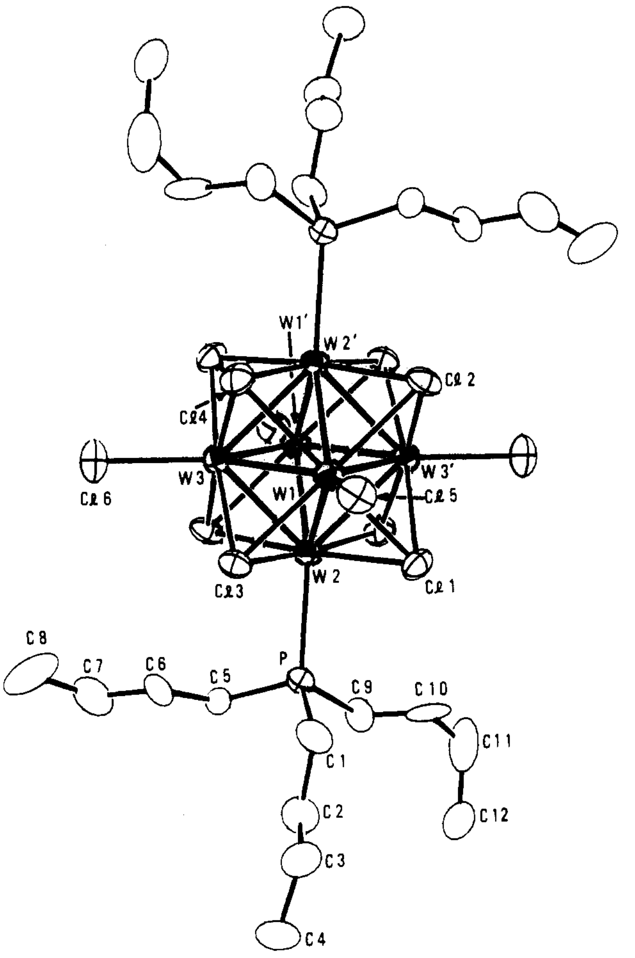

Figure 1. Molecular structure of *trans*-[$W_6Cl_{12}\{P(n\text{-}C_4H_9)_3\}_2$] drawn by ORTEP with ellipsoids corresponding to 50% probability. Distances: W–W = 2.626 Å (av); W–P = 2.581 Å; W–Cl^t = 2.413 Å (av); W–Cl^b = 2.500 A (av).

Ethyl Cluster Complexes. Synthesis. The treatment of the phosphine complexes with triethylaluminum in toluene gave a mixture of ethyl cluster complexes in solution. In the case of the molybdenum cluster alkyl complexes, *all-trans*-dialkyl and *trans,mer*-trialkyl complexes were the major products among the five alkyl complexes that can form from *trans*-[$Mo_6Cl_{12}(PR_3)_2$]. Although chromatographic separation of the products was not possible, the molybdenum cluster alkyl complexes were separated by recrystallization and only dialkyl and trialkyl complexes were obtained.[3] This proved to be also the case for the tungsten cluster ethyl complexes, and only *all-trans*-diethyl and *trans,mer*-triethyl complexes were isolated in the present study.

The alkylation reactions were not very simple, and even if the proportion of triethylaluminum was varied, the product was always a mixture of several alkyl complexes with different degrees of alkylation. Therefore, experimental conditions were chosen such as to make the separation of either diethyl or triethyl complexes most efficient. For this reason the preparation of triethyl complexes was carried out with a two-step addition of triethylaluminum.

Although we have been unable to obtain good single crystals for X-ray crystallography, the geometrical structures of the diethyl and triethyl complexes have been inferred from the comparison of their spectroscopic properties with those of the molybdenum

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(11) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 256.

(12) Zietlow, T. C.; Schaefer, W. P.; Sadeghi, B.; Hua, N.; Gray, H. B. *Inorg. Chem.* **1986**, *25*, 2195.

analogues.[3] For example, the diethyl complex **3** shows ^{1}H, ^{13}C, and ^{31}P NMR spectra almost identical with those of *all-trans*-$[(Mo_6Cl_8)Cl_2Et_2(PBu_3)_2]$, whose crystal structure is known,[3] and **3** can thus be assigned to the all-trans isomer. The ^{1}H NMR spectra of the diethyl complexes **3** and **4** and triethyl complexes **5** and **6** show distorted triplets and quartets for the methyl and methylene protons of the ethyl groups, respectively. The ^{1}H and ^{13}C NMR spectra of **6** were measured with a 360-MHz instrument to effect better peak resolution.

There is a linear relationship between the chemical shift difference Δ of the methyl and methylene protons of ethyl groups and the electronegativity χ of the element X to which the ethyl groups are bonded, namely $\chi = 0.62\Delta + 2.07$.[13] When this equation is applied to the present tungsten cluster diethyl and triethyl complexes, the electronegativity of the tungsten is calculated to be 2.26, which is much larger than Pauling's value of 1.7.[14] This is probably due to the influence of the eight electronegative chlorine atoms, which are face-bridging to the W_6 octahedron. In the case of **6**, there is resolution of the two kinds of methyl and methylene signals from ethyl groups a and b. Although ethyl group b has a higher field resonance than ethyl group a, the chemical shift differences between the CH_3 and CH_2 protons ($\Delta = 0.3$) are almost the same. This indicates that electronegativities for the tungsten atoms to which these ethyl groups are attached are not sufficiently different, and the inductive effects of the metal centers should be similar. Therefore, an alternate suggestion for the difference in chemical shifts of the ethyl groups is some kind of magnetic "cis" ligand influence due to the structure in which ethyl group a has a C_2H_5 group and a Cl atom as "cis" neighbors, whereas ethyl group b has two C_2H_5 groups.

The complex **6** shows two kinds of ethyl carbon resonances with an intensity ratio of ca. 2:1 in a ^{13}C NMR spectrum (90 MHz) (Figure 2, supplementary material), which is consistent with the *trans,mer*-triethyl structure. There are two methyl carbon peaks at δ 21.75 and 21.82 and two methylene carbon peaks at δ 15.54 and 13.21 with the W–C coupling satellites of 74 Hz. The assignment of the methyl and methylene carbon signals was performed by the INEPT measurement.[15] The satellite peaks support the η^1 bonding of the α carbons to the tungsten atoms. The b-group methylene carbon has higher field resonance than the a-group methylene carbons, and the difference must be due to the "cis" ligand influence, as in the case of the ^{1}H NMR spectra. The chemical shift differences between the methyl carbons of groups a and b is small, but the group a methyl has slightly higher field resonance in contrast with that of the methylene carbons. The methylene carbons in the *all*-trans-diethyl complexes **3** and **4** have lower field chemical shifts than those of the triethyl complexes **5** and **6**, because they have two Cl neighbors. As far as the present ethyl complexes are concerned, the more electronegative ligands in the "cis" positions seem to exert a large deshielding influence upon the chemical shifts of the methylene carbons. However, attempts to correlate the trend to any single parameter may be misleading.[16]

The infrared absorptions assignable to $\nu(W-(\mu-Cl))$ are fully consistent with the retention of the octahedral cluster core. The complexes **1**–**6** have the absorptions at around 310 cm^{-1}. The diethyl complexes **3** and **4** and the triethyl complexes **5** and **6** have $\nu(W-C)$ at 460 and 465 cm^{-1}, respectively. There is also the characteristic absorption at around 1360 cm^{-1} ($\delta_{as}(CH_3)$) for the ethyl complexes. The band $\nu(W-Cl)$ in the far-infrared region around 270 cm^{-1} decreases with introduction of the ethyl groups.

Photochemical Reaction of 6. The solid samples of the cluster ethyl complexes are rather stable thermally and decompose at ca. 160 °C. However, the solutions are very sensitive to light, and preliminary ESR measurements of the toluene solution of **6** containing 2,4,6-tris-*tert*-butyl-1-nitrosobenzene as a radical trapping agent showed strong signals of the ethyl radical adduct on irradiation (390 nm) for a few seconds. This photochemical reaction suggests the homolytic cleavage of the tungsten–carbon bond by visible light.[17,18] The possible reductive coupling of clusters[19] by this homolysis is now under investigation.

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Supplementary Material Available: The ^{13}C NMR spectrum of *trans,mer*-$[W_6Cl_9(C_2H_5)_3\{P(n-C_5H_{11})_3\}_2]$ (Figure 2) and listings of hydrogen atom coordinates (Table V) and anisotropic temperature factors (Table VI) (3 pages); a listing of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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