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New Niobium Complexes with Alkynes. 3. An Extraordinary Hexaniobium Compound Containing a Central Nb_3 Cluster and Three Outer Nb Atoms Bound to η^4-Tetraphenylcyclobutadiene Ligands

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By reduction of $NbCl_5$ with $(n\text{-}Bu)_3SnH$ in toluene, followed by addition of PhCCPh and then a suitable workup, a crystalline compound of composition $(Bu_3Sn)[Nb_6Cl_{19}C_{12}(C_6H_5)_{12}]\cdot 2C_7H_8$ was obtained in 35% yield. The structure of this material has been determined crystallographically. It forms monoclinic crystals in space group $C2/c$ with unit cell parameters of a = 35.250 (7) Å, b = 24.048 (2) Å, c = 27.956 (6) Å, β = 102.74 (2)°, V = 23115 (13) Å^3, and Z = 8. With the use of 9017 independent data collected at −80 °C, 1225 parameters were refined to R = 0.062, R_w = 0.085. The Bu_3Sn unit has an effectively trigonal-planar structure with Cl atoms occupying axial positions (Sn–Cl, 2.74 Å) to complete a trigonal bipyramid. The hexanuclear entity consists of a central triangular $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3$ cluster with a $Cl_3NbCl_2(c\text{-}C_4Ph_4)$ unit of roughly octahedral shape (if $c\text{-}C_4Ph_4$ is treated as one ligand) attached to each central Nb atom by three mutually cis Cl atoms. The Nb–Nb distances in the central cluster have an average value of 2.87 [1] Å, indicative of Nb–Nb single bonds, while each Nb(inner) to Nb(outer) distance is about 3.50 Å, indicative of no bonding. The $c\text{-}C_4Ph_4$ moieties have square rings (C–C, 1.45 [2] Å) symmetrically bonded to the outer Nb atoms.

Introduction

The ability of lower valent niobium and tantalum halides to form complexes with alkynes,[1-3] to cause oligomerization of polymerization of alkynes,[4,5] and to combine with certain alkyne oligomers to form complexes[6] has become apparent from many investigations over the past decade. In all of this varied chemistry, however, there is no previous report of the dimerization of an alkyne to a cyclic $(RC)_4$ unit that then forms an identifiable complex with the metal.

We report here some chemistry that adds this type of reaction to the already extensive repertoire of reactions of the group V halides with alkynes. In addition to displaying η^4-(c-Ph_4C_4)Nb moieties, where the cyclo-Ph_4C_4 unit has been formed in situ from PhCCPh, the reported compound also contains a $Nb_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)$ cluster unit at the center.

Experimental Section

All reactions were carried out under an atmosphere of argon by using the standard Schlenk techniques or in a nitrogen-filled drybox. $NbCl_5$ was purchased from Aesar. Diphenylacetylene (PhCCPh) and tributyltin hydride ($^nBu_3SnH$) were from Aldrich Chemical Co. Solvents toluene and hexane were well dried over molecular sieves and distilled before use over sodium–potassium–benzophenone. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer.

Preparation. $NbCl_5$ (1.08 g, 4 mmol) was dissolved in toluene (40 mL), and the resulting yellow solution was then cooled down by stirring it in a dry ice/acetone bath. Bu_3SnH (2.2 mL, 8 mmol) was added dropwise. After the bath was removed, the solution was allowed to warm up to room temperature in about an hour, while the color of the solution gradually changed to greenish brown and a brown-black precipitate formed. About 3 h later, PhCCPh (1.1 g, 6 mmol) was added, and the solution was stirred vigorously overnight. During this period of time, the solution first became gelatinous, and after a large quantity of green fluffy precipitate was formed, it gradually became less sticky. After removal of the green precipitate (ca. 0.36 g of vacuum-dried residue) by filtration through a 4–5.5-μm fritted funnel, the brown filtrate was layered with 40 mL of hexane in a Schlenk tube. Though brown-black crystals started growing in several days, interdiffusion of the solvents was completed in about a fortnight. After the liquid was decanted, the crystals were washed with hexane (2 × 30 mL) and dried on a vacuum line (yield: 0.60 g, 35%).

IR (Nujol mull, mineral oil, cm^{-1}): 1592 (m), 1490 (w), 1447 (s), 1263 (w), 1067 (m), 1023 (m), 997 (w), 965 (w), 913 (m), 887 (w), 840 (w), 763 (s), 728 (m), 686 (s), 613 (w), 548 (m), 512 (s).

Table I. Crystal Data for $(SnBu_3)[Nb_6Cl_{19}\{(PhC)_4\}_3]\cdot 2C_7H_8$

compound	$(SnBu_3)[Nb_6Cl_{19}\{(PhC)_4\}_3]\cdot 2C_7H_8$
formula	$SnNb_6Cl_{19}C_{110}H_{108}$
fw	2774.78
space group	$C2/c$
a, Å	35.250 (7)
b, Å	24.048 (2)
c, Å	27.956 (6)
α, deg	90.0
β, deg	102.74 (2)
γ, deg	90.0
V, Å^3	23115 (13)
Z	8
d_{calc}, g/cm^3	1.595
μ(Mo Kα), cm^{-1}	12.496
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.710 73 Å)
temp, °C	−80
trans factors: max; min	0.9996; 0.9708
R^a	0.062
$R_w{}^b$	0.085

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

X-ray Crystallography. The air-sensitive crystals were handled under a layer of well-degassed mineral oil on a small dish that was flushed constantly with a stream of argon in a fritted funnel. Apiezon T grease was used to attach the crystals on tips of quartz fibers. A cold stream of nitrogen gas at −80 °C provided further protection for the crystals from being exposed to air and prevented possible evaporation of interstitial solvent molecules from the crystals during the crystallographic experiments on a CAD-4 diffractometer.

Routine procedures followed to determine the unit cell parameters and to collect intensity data were standard in this laboratory.[7] No crystal decay or movement was observed during the data collection. Lorentz and polarization corrections were applied. An empirical absorption correction based upon azimuthal scans of seven reflections with Eulerian χ angle near 90° was also applied, although the magnitude of the correction was very small.

Direct methods (SHELXS 86) provided the coordinates for all the metal atoms and their surrounding chlorine atoms. A combination of Fourier difference syntheses and least-squares refinements revealed all the non-hydrogen atoms. All these non-hydrogen atoms were treated anisotropically in the final refinement.

The first two peaks (electron densities: 1.314 and 1.169 e/Å^3) in a final difference Fourier map were along a 2-fold axis with a separation of 2.255 Å. Together with the surrounding lower peaks, they did not make explicit chemical sense. Compared with the well-behaved carbon

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Table II. Positional and Isotropic Equivalent Thermal Parameters for $[SnBu_3][Nb_6Cl_{19}\{(PhC)_4\}_3]\cdot 2C_7H_8$

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Nb(1)	0.41011 (4)	0.82550 (6)	0.02985 (5)	2.97 (3)	C(44)	0.3102 (5)	1.1361 (6)	0.1062 (5)	3.6 (4)
Nb(2)	0.36848 (4)	0.89795 (6)	0.08056 (5)	3.01 (3)	C(45)	0.3483 (5)	1.1434 (7)	0.1108 (6)	3.7 (4)
Nb(3)	0.39595 (4)	0.79324 (6)	0.12367 (5)	2.91 (3)	C(46)	0.3647 (6)	1.1956 (7)	0.1004 (6)	5.2 (5)
Cl(1)	0.3469 (1)	0.8060 (2)	0.0488 (1)	3.02 (9)	C(47)	0.3393 (6)	1.2398 (8)	0.0872 (6)	6.0 (5)
Cl(2)	0.4245 (1)	0.9211 (2)	0.0502 (1)	3.8 (1)	C(48)	0.2992 (6)	1.2342 (8)	0.0817 (7)	6.1 (5)
Cl(3)	0.4584 (1)	0.7960 (2)	0.1017 (1)	3.44 (9)	C(49)	0.2834 (5)	1.1814 (7)	0.0922 (6)	5.3 (5)
Cl(4)	0.4073 (1)	0.8833 (2)	0.1624 (1)	3.44 (9)	C(50)	0.2548 (5)	1.0578 (7)	0.1039 (5)	3.7 (4)
Cl(5)	0.4654 (1)	0.8355 (2)	−0.0129 (1)	3.56 (9)	C(51)	0.2162 (5)	1.0776 (6)	0.0788 (6)	4.4 (4)
Cl(6)	0.4114 (1)	0.7303 (2)	−0.0046 (1)	3.17 (9)	C(52)	0.2124 (6)	1.1050 (7)	0.0331 (7)	5.8 (5)
Cl(7)	0.3732 (1)	0.8450 (2)	−0.0518 (1)	3.45 (9)	C(53)	0.1724 (7)	1.1234 (8)	0.0130 (8)	8.3 (7)
Cl(8)	0.3709 (1)	0.9998 (2)	0.1026 (1)	3.51 (9)	C(54)	0.1398 (7)	1.1105 (9)	0.035 (1)	9.6 (7)
Cl(9)	0.3087 (1)	0.9042 (2)	0.1140 (1)	3.30 (9)	C(55)	0.1486 (7)	1.0848 (9)	0.0807 (9)	8.7 (7)
Cl(10)	0.3225 (1)	0.9347 (2)	0.0089 (1)	3.51 (9)	C(56)	0.1867 (5)	1.0692 (7)	0.1026 (7)	5.4 (5)
Cl(11)	0.4303 (1)	0.7532 (2)	0.2061 (1)	3.46 (9)	C(57)	0.3682 (4)	0.7168 (6)	0.2717 (5)	3.1 (4)
Cl(12)	0.3413 (1)	0.7757 (2)	0.1639 (1)	3.42 (9)	C(58)	0.3733 (4)	0.7731 (7)	0.2906 (5)	3.4 (4)
Cl(13)	0.3887 (1)	0.6941 (2)	0.1049 (1)	3.42 (9)	C(59)	0.4094 (5)	0.7889 (7)	0.3174 (6)	4.9 (5)
Nb(4)	0.42617 (4)	0.77914 (6)	−0.08312 (5)	3.15 (3)	C(60)	0.4134 (6)	0.8420 (8)	0.3407 (7)	5.9 (5)
Nb(5)	0.29807 (4)	1.00092 (6)	0.07354 (5)	3.22 (3)	C(61)	0.3807 (6)	0.8781 (8)	0.3353 (6)	5.7 (5)
Nb(6)	0.37573 (4)	0.68248 (6)	0.19486 (5)	3.13 (3)	C(62)	0.3470 (6)	0.8614 (9)	0.3069 (7)	6.3 (6)
Cl(14)	0.3681 (1)	0.7373 (2)	−0.1256 (2)	4.4 (1)	C(63)	0.3431 (5)	0.8096 (7)	0.2846 (6)	4.8 (5)
Cl(15)	0.4241 (1)	0.8566 (2)	−0.1339 (1)	4.5 (1)	C(64)	0.3363 (4)	0.6819 (7)	0.2532 (5)	3.1 (4)
Cl(16)	0.2353 (1)	0.9677 (2)	0.0271 (2)	4.4 (1)	C(65)	0.2941 (5)	0.6869 (7)	0.2474 (5)	4.1 (4)
Cl(17)	0.3031 (1)	1.0661 (2)	0.0134 (2)	4.5 (1)	C(66)	0.2686 (5)	0.7174 (7)	0.2121 (5)	3.7 (4)
Cl(18)	0.4174 (1)	0.6072 (2)	0.1926 (2)	4.4 (1)	C(67)	0.2284 (5)	0.7188 (8)	0.2086 (6)	4.7 (5)
Cl(19)	0.3168 (1)	0.6402 (2)	0.1482 (1)	4.2 (1)	C(68)	0.2123 (6)	0.6876 (9)	0.2414 (7)	7.1 (6)
C(1)	0.4533 (5)	0.7262 (7)	−0.1370 (6)	4.2 (4)	C(69)	0.2390 (6)	0.6514 (9)	0.2771 (7)	7.0 (6)
C(2)	0.4345 (5)	0.7159 (7)	−0.1895 (6)	5.0 (4)	C(70)	0.2772 (5)	0.6522 (8)	0.2803 (6)	5.8 (5)
C(3)	0.4122 (8)	0.7521 (8)	−0.2215 (6)	8.1 (7)	C(71)	0.3594 (5)	0.6327 (7)	0.2599 (5)	3.6 (4)
C(4)	0.3961 (9)	0.7409 (9)	−0.2692 (7)	10.1 (9)	C(72)	0.3529 (5)	0.5720 (7)	0.2569 (5)	4.3 (4)
C(5)	0.4062 (8)	0.695 (1)	−0.2885 (7)	9.3 (8)	C(73)	0.3862 (6)	0.5349 (8)	0.2739 (6)	6.2 (5)
C(6)	0.4294 (9)	0.654 (1)	−0.2596 (9)	11.0 (9)	C(74)	0.3820 (7)	0.4789 (8)	0.2733 (8)	7.5 (6)
C(7)	0.4433 (8)	0.665 (1)	−0.2056 (7)	10.2 (8)	C(75)	0.3450 (6)	0.4590 (9)	0.2528 (8)	7.3 (6)
C(8)	0.4581 (4)	0.6961 (6)	−0.0911 (5)	3.4 (4)	C(76)	0.3139 (6)	0.4926 (9)	0.2365 (7)	6.8 (6)
C(9)	0.4436 (5)	0.6410 (7)	−0.0771 (6)	4.6 (4)	C(77)	0.3177 (6)	0.5508 (7)	0.2381 (7)	6.1 (5)
C(10)	0.4656 (8)	0.6165 (8)	−0.0332 (8)	8.3 (7)	C(78)	0.3937 (5)	0.6692 (7)	0.2795 (5)	4.4 (4)
C(11)	0.4517 (9)	0.560 (1)	−0.0200 (8)	10.4 (8)	C(79)	0.4326 (5)	0.6556 (7)	0.3120 (5)	4.1 (4)
C(12)	0.4184 (7)	0.536 (1)	−0.0496 (8)	9.0 (8)	C(80)	0.4673 (5)	0.6720 (7)	0.3050 (6)	4.2 (4)
C(13)	0.4008 (7)	0.5597 (9)	−0.0940 (9)	8.0 (7)	C(81)	0.5018 (6)	0.6599 (7)	0.3399 (6)	5.5 (5)
C(14)	0.4117 (7)	0.6144 (8)	−0.1072 (9)	8.0 (7)	C(82)	0.4997 (6)	0.6291 (9)	0.3813 (7)	6.4 (6)
C(15)	0.4875 (4)	0.7337 (6)	−0.0678 (6)	3.2 (4)	C(83)	0.4650 (6)	0.609 (1)	0.3882 (7)	8.2 (7)
C(16)	0.5205 (5)	0.7343 (7)	−0.0253 (6)	3.8 (4)	C(84)	0.4307 (6)	0.6237 (9)	0.3535 (7)	6.6 (6)
C(17)	0.5583 (5)	0.7407 (7)	−0.0347 (7)	4.5 (4)	Sn	0.20932 (4)	0.91326 (5)	−0.06048 (4)	3.73 (3)
C(18)	0.5902 (5)	0.7431 (8)	0.0049 (6)	5.2 (5)	C(85)	0.2230 (5)	0.8374 (6)	−0.0205 (5)	3.6 (4)
C(19)	0.5853 (6)	0.7374 (9)	0.0531 (7)	6.2 (6)	C(86)	0.1958 (5)	0.8271 (7)	0.0144 (6)	4.2 (4)
C(20)	0.5470 (5)	0.7288 (8)	0.0618 (7)	5.7 (5)	C(87)	0.2064 (5)	0.7740 (7)	0.0457 (6)	4.1 (4)
C(21)	0.5145 (5)	0.7280 (7)	0.0223 (6)	4.4 (4)	C(88)	0.2428 (5)	0.7809 (7)	0.0862 (6)	4.7 (5)
C(22)	0.4832 (4)	0.7640 (6)	−0.1134 (5)	3.4 (4)	C(89)	0.1545 (6)	0.9488 (7)	−0.0616 (7)	5.7 (5)
C(23)	0.5060 (5)	0.8070 (7)	−0.1315 (6)	4.0 (4)	C(90)	0.1500 (7)	1.005 (1)	−0.092 (1)	10.7 (8)
C(24)	0.5119 (6)	0.8048 (8)	−0.1785 (6)	5.8 (5)	C(91)	0.105 (1)	1.027 (1)	−0.088 (1)	14 (1)
C(25)	0.5341 (6)	0.848 (1)	−0.1940 (7)	6.9 (6)	C(92)	0.097 (1)	1.079 (1)	−0.121 (1)	21 (2)
C(26)	0.5515 (5)	0.8902 (8)	−0.1639 (6)	5.3 (5)	C(93)	0.2494 (5)	0.9550 (7)	−0.0988 (6)	5.3 (5)
C(27)	0.5474 (5)	0.8902 (8)	−0.1154 (7)	5.2 (5)	C(94)	0.2755 (5)	0.917 (1)	−0.1194 (6)	6.7 (5)
C(28)	0.5246 (5)	0.8485 (7)	−0.0994 (6)	4.4 (4)	C(95)	0.3082 (8)	0.949 (1)	−0.1374 (9)	13 (1)
C(29)	0.2686 (5)	1.0143 (6)	0.1400 (5)	3.7 (4)	C(96)	0.302 (1)	0.972 (1)	−0.1750 (9)	15 (1)
C(30)	0.2494 (4)	0.9683 (7)	0.1616 (6)	3.9 (4)	C(97)	0.0502 (8)	0.4836 (9)	0.0604 (8)	8.8 (7)
C(31)	0.2672 (5)	0.9481 (8)	0.2092 (6)	5.2 (5)	C(98)	0.0883 (6)	0.504 (1)	0.0582 (8)	7.9 (7)
C(32)	0.2499 (5)	0.8997 (8)	0.2274 (7)	6.3 (5)	C(99)	0.1102 (6)	0.4695 (9)	0.0412 (8)	7.6 (6)
C(33)	0.2169 (5)	0.8746 (8)	0.1982 (7)	5.8 (5)	C(100)	0.1023 (6)	0.411 (1)	0.0273 (8)	11.6 (9)
C(34)	0.1985 (5)	0.8969 (8)	0.1517 (7)	5.7 (5)	C(101)	0.0665 (8)	0.392 (1)	0.0321 (9)	9.8 (8)
C(35)	0.2155 (5)	0.9423 (7)	0.1346 (6)	4.6 (4)	C(102)	0.0398 (6)	0.427 (1)	0.0471 (8)	7.7 (7)
C(36)	0.3068 (4)	1.0402 (6)	0.1524 (5)	3.2 (4)	C(103)	0.0244 (7)	0.518 (1)	0.0751 (9)	9.1 (8)
C(37)	0.3394 (4)	1.0366 (6)	0.1942 (5)	3.0 (4)	C(104)	0.2206 (7)	0.304 (1)	0.1193 (8)	9.0 (8)
C(38)	0.3563 (5)	0.9854 (7)	0.2133 (5)	3.9 (4)	C(105)	0.2216 (9)	0.341 (1)	0.089 (1)	17 (1)
C(39)	0.3888 (6)	0.9852 (8)	0.2519 (6)	5.3 (5)	C(106)	0.2568 (9)	0.381 (1)	0.102 (1)	14 (1)
C(40)	0.4049 (6)	1.0358 (9)	0.2733 (7)	5.8 (5)	C(107)	0.2833 (9)	0.375 (1)	0.1409 (9)	11 (1)
C(41)	0.3868 (6)	1.0880 (8)	0.2560 (6)	6.0 (5)	C(108)	0.2823 (8)	0.328 (1)	0.1743 (8)	10.5 (8)
C(42)	0.3539 (5)	1.0893 (8)	0.2150 (5)	4.8 (5)	C(109)	0.2489 (7)	0.291 (1)	0.1616 (7)	8.0 (7)
C(43)	0.2938 (5)	1.0828 (6)	0.1173 (5)	3.5 (4)	C(110)	0.1874 (8)	0.265 (1)	0.100 (1)	14 (1)

[a] Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

atoms (C(97)–C(110)) of the two toluene solvent molecules, which had electron densities of more than 2 e/Å^3 in an earlier difference Fourier map, they were so weak and diffuse that we could not assign them any refinable identity.

Crystallographic data and information pertaining to the structure determination are collected in Table I. The atomic positional parameters and equivalent isotropic displacement parameters are listed in Table II.

Results

The crystalline solid consists of planar $(C_4H_9)_3Sn$ units coordinated by Cl atoms from the large $Nb_6Cl_{19}(Ph_4C_4)_3$ unit, as well

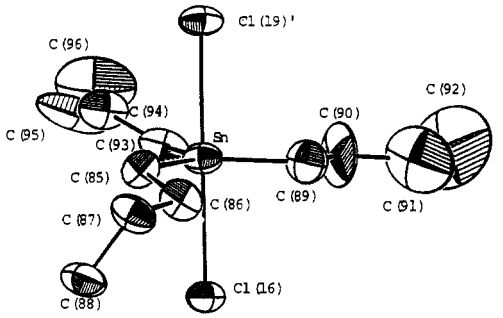

Figure 1. The Bu_3Sn entity and its neighboring Cl atoms. Atoms are represented by their displacement ellipsoids at the 50% probability level.

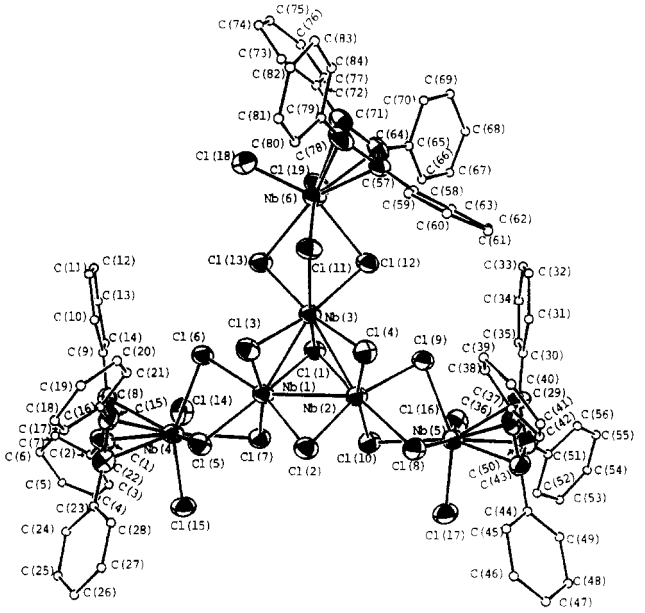

Figure 2. The $Nb_6Cl_{19}(c\text{-}C_4Ph_4)_3$ entity. The phenyl carbon atoms are represented by circles of arbitrarily small size and the other atoms by their displacement ellipsoids at the 50% probability level.

as interstitial toluene molecules. Each of these entities resides on a general position in a unit cell belonging to space group $C2/c$. This space group was chosen in preference to Cc on the basis of the successful refinement of the structure under the constraint imposed by the 2-fold axes. The tin atom and its immediate surroundings are shown in Figure 1 and the hexanuclear niobium species in Figure 2. Tables III and IV list the principal bond distances and angles, respectively.

The configuration of three carbon atoms and two chlorine atoms around the tin atom corresponds to a fairly regular trigonal bipyramid. Such an arrangement, with three alkyl groups in the equatorial plane and anions at the apical positions is a frequent occurrence in trialkyltin(IV) compounds.[8]

The gigantic Nb_6 entity comprises a mixture of both familiar and novel structural elements. At the center is an Nb_3Cl_4 cluster, with the three external coordination sites on each metal atom occupied by chlorine atoms. This is a familiar kind of trinuclear cluster structure, well-known for niobium and also formed by tantalum, molybdenum, and tungsten. The prior examples of such niobium clusters[9] include species with six cluster electrons, $[Nb_3Cl_{10}(PEt_3)_3]^-$ (Nb–Nb = 2.97 Å), seven cluster electrons, $Nb_3Cl_8(S)$ (Nb–Nb = 2.81 Å), and eight cluster electrons,

Table III. Selected Internuclear Distances (Å) for $[SnBu_3][Nb_6Cl_{19}\{(PhC)_4\}_3]\cdot 2C_7H_8$[a]

Nb(1)–Nb(2)	2.849 (2)	Nb(5)–Cl(17)	2.334 (5)
Nb(1)–Nb(3)	2.882 (2)	Nb(5)–C(29)	2.343 (17)
Nb(1)–Cl(1)	2.448 (4)	Nb(5)–C(36)	2.357 (14)
Nb(1)–Cl(2)	2.396 (4)	Nb(5)–C(43)	2.341 (15)
Nb(1)–Cl(3)	2.435 (4)	Nb(5)–C(50)	2.342 (17)
Nb(1)–Cl(5)	2.512 (5)	Nb(6)–Cl(18)	2.339 (5)
Nb(1)–Cl(6)	2.487 (4)	Nb(6)–Cl(19)	2.419 (4)
Nb(1)–Cl(7)	2.411 (4)	Nb(6)–C(57)	2.369 (15)
Nb(1)–Nb(4)	3.511 (2)	Nb(6)–C(64)	2.366 (15)
Nb(2)–Nb(3)	2.866 (2)	Nb(6)–C(71)	2.353 (16)
Nb(2)–Cl(1)	2.442 (4)	Nb(6)–C(78)	2.331 (14)
Nb(2)–Cl(2)	2.381 (5)	Cl(16)–Sn	2.750 (4)
Nb(2)–Cl(4)	2.419 (4)	Cl(19)'–Sn	2.743 (4)
Nb(2)–Cl(8)	2.523 (4)	C(1)–C(2)	1.49 (2)
Nb(2)–Cl(9)	2.491 (5)	C(1)–C(8)	1.45 (2)
Nb(2)–Cl(10)	2.447 (4)	C(1)–C(22)	1.44 (2)
Nb(2)–Nb(5)	3.481 (2)	C(8)–C(9)	1.50 (2)
Nb(3)–Cl(1)	2.422 (4)	C(8)–C(15)	1.42 (2)
Nb(3)–Cl(3)	2.413 (5)	C(15)–C(16)	1.47 (2)
Nb(3)–Cl(4)	2.416 (4)	C(15)–C(22)	1.44 (2)
Nb(3)–Cl(11)	2.545 (4)	C(22)–C(23)	1.47 (2)
Nb(3)–Cl(12)	2.472 (5)	C(29)–C(30)	1.49 (2)
Nb(3)–Cl(13)	2.442 (4)	C(29)–C(36)	1.46 (2)
Nb(3)–Nb(6)	3.491 (2)	C(29)–C(50)	1.46 (2)
Cl(5)–Nb(4)	2.531 (4)	C(36)–C(37)	1.45 (2)
Cl(6)–Nb(4)	2.641 (4)	C(36)–C(43)	1.42 (2)
Cl(7)–Nb(4)	2.735 (5)	C(43)–C(44)	1.47 (2)
Cl(8)–Nb(5)	2.517 (4)	C(43)–C(50)	1.47 (2)
Cl(9)–Nb(5)	2.577 (4)	C(50)–C(51)	1.47 (2)
Cl(10)–Nb(5)	2.687 (4)	C(57)–C(58)	1.45 (2)
Cl(11)–Nb(6)	2.536 (4)	C(57)–C(64)	1.41 (2)
Cl(12)–Nb(6)	2.606 (4)	C(57)–C(78)	1.44 (2)
Cl(13)–Nb(6)	2.668 (4)	C(64)–C(65)	1.46 (2)
Nb(4)–Cl(14)	2.353 (4)	C(64)–C(71)	1.43 (2)
Nb(4)–Cl(15)	2.335 (4)	C(71)–C(72)	1.47 (2)
Nb(4)–C(1)	2.331 (18)	C(71)–C(78)	1.50 (2)
Nb(4)–C(8)	2.327 (15)	C(78)–C(79)	1.51 (2)
Nb(4)–C(15)	2.377 (15)	Sn–C(85)	2.139 (15)
Nb(4)–C(22)	2.375 (17)	Sn–C(89)	2.108 (20)
Nb(5)–Cl(16)	2.441 (4)	Sn–C(93)	2.196 (20)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

$Nb_3Cl_7(PMe_2Ph)_6$ (Nb–Nb = 2.83 Å). In the present case the mean Nb–Nb distance is 2.87 [1] Å. The lengths of Nb–Nb bonds within clusters of this type are determined by steric constraints, by the basicity of the attached ligands, and by the number of cluster electrons. We are justified in concluding from the observed distance that it is consistent with the central cluster being one with six cluster electrons, although from the distance alone we cannot exclude the possible presence of seven or eight cluster electrons.

We believe it is reasonable to assign six electrons to the central cluster for the following reasons. The mean oxidation state for all six niobium atoms is clearly +3, and the three outer ones are chemically equivalent. The only choice of oxidation state to be assigned equally to each of the three outer niobium atoms that is consistent with the structure of the inner cluster is +3. This makes the mean oxidation state of the core Nb atom +3 and leads to the result that there are six cluster electrons.

Each of the three outer niobium atoms has the same coordination sphere with only small, chemically insignificant metrical differences among them. This coordination sphere can be regarded as a distorted octahedron where one vertex is occupied by the centroid of the C_4 ring. Three of the chlorine atoms are shared with one of the cluster niobium atoms so that each such pair of metal atoms can be considered to be in a face-sharing bioctahedron. Face-sharing bioctahedra containing two niobium atoms are, of course, very well-known.[10] However, all those previously

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Table IV. Selected Bond Angles (deg) for $[SnBu_3][Nb_6Cl_{19}\{(PhC)_4\}_3]\cdot 2C_7H_8$[a]

Nb(2)-Nb(1)-Nb(3)	60.01 (5)	Nb(1)-Cl(5)-Nb(4)	88.2 (1)	Cl(10)-Nb(5)-Cl(16)	80.6 (1)	C(9)-C(8)-C(15)	134 (1)
Cl(1)-Nb(1)-Cl(2)	106.7 (2)	Nb(1)-Cl(6)-Nb(4)	86.4 (1)	Cl(10)-Nb(5)-Cl(17)	80.0 (2)	Nb(4)-C(15)-C(16)	132 (1)
Cl(1)-Nb(1)-Cl(3)	105.7 (1)	Nb(1)-Cl(7)-Nb(4)	85.8 (1)	Cl(10)-Nb(5)-C(29)	151.4 (4)	C(8)-C(15)-C(16)	138 (1)
Cl(1)-Nb(1)-Cl(5)	163.8 (1)	Nb(2)-Cl(8)-Nb(5)	87.3 (1)	Cl(10)-Nb(5)-C(36)	150.6 (4)	C(8)-C(15)-C(22)	90 (1)
Cl(1)-Nb(1)-Cl(6)	90.1 (1)	Nb(2)-Cl(9)-Nb(5)	86.7 (1)	Cl(10)-Nb(5)-C(43)	156.4 (4)	C(16)-C(15)-C(22)	128 (1)
Cl(1)-Nb(1)-Cl(7)	85.2 (1)	Nb(2)-Cl(10)-Nb(5)	85.2 (1)	Cl(10)-Nb(5)-C(50)	156.9 (4)	Nb(4)-C(22)-C(23)	126 (1)
Cl(2)-Nb(1)-Cl(3)	90.6 (1)	Nb(3)-Cl(11)-Nb(6)	86.8 (1)	Cl(16)-Nb(5)-Cl(17)	92.3 (2)	C(1)-C(22)-C(15)	91 (1)
Cl(2)-Nb(1)-Cl(5)	82.8 (2)	Nb(3)-Cl(12)-Nb(6)	86.8 (1)	Cl(16)-Nb(5)-C(29)	87.5 (4)	C(1)-C(22)-C(23)	134 (1)
Cl(2)-Nb(1)-Cl(6)	162.6 (2)	Nb(3)-Cl(13)-Nb(6)	86.1 (1)	Cl(16)-Nb(5)-C(36)	123.0 (4)	C(15)-C(22)-C(23)	134 (1)
Cl(2)-Nb(1)-Cl(7)	94.6 (1)	Cl(5)-Nb(4)-Cl(6)	76.6 (1)	Cl(16)-Nb(5)-C(43)	113.4 (4)	Nb(5)-C(29)-C(30)	123 (1)
Cl(3)-Nb(1)-Cl(5)	86.9 (1)	Cl(5)-Nb(4)-Cl(7)	74.7 (1)	Cl(16)-Nb(5)-C(50)	78.3 (4)	C(30)-C(29)-C(36)	134 (1)
Cl(3)-Nb(1)-Cl(6)	89.0 (1)	Cl(5)-Nb(4)-Cl(14)	152.3 (2)	Cl(17)-Nb(5)-C(29)	126.7 (4)	C(30)-C(29)-C(50)	134 (2)
Cl(3)-Nb(1)-Cl(7)	166.1 (2)	Cl(5)-Nb(4)-Cl(15)	89.0 (1)	Cl(17)-Nb(5)-C(36)	113.0 (4)	C(36)-C(29)-C(50)	90 (1)
Cl(5)-Nb(1)-Cl(6)	79.7 (1)	Cl(5)-Nb(4)-C(1)	124.2 (4)	Cl(17)-Nb(5)-C(43)	80.5 (4)	Nb(5)-C(36)-C(37)	130 (1)
Cl(5)-Nb(1)-Cl(7)	81.0 (1)	Cl(5)-Nb(4)-C(8)	109.9 (4)	Cl(17)-Nb(5)-C(50)	91.6 (4)	C(29)-C(36)-C(37)	134 (1)
Cl(6)-Nb(1)-Cl(7)	82.2 (1)	Cl(5)-Nb(4)-C(15)	77.7 (4)	Cl(11)-Nb(6)-Cl(12)	75.5 (1)	C(29)-C(36)-C(43)	90 (1)
Nb(1)-Nb(2)-Nb(3)	60.57 (5)	Cl(5)-Nb(4)-C(22)	89.9 (4)	Cl(11)-Nb(6)-Cl(13)	76.3 (1)	C(37)-C(36)-C(43)	133 (1)
Cl(1)-Nb(2)-Cl(2)	107.4 (2)	Cl(6)-Nb(4)-Cl(7)	73.6 (1)	Cl(11)-Nb(6)-Cl(18)	93.4 (2)	C(40)-C(41)-C(42)	120 (2)
Cl(1)-Nb(2)-Cl(4)	106.1 (1)	Cl(6)-Nb(4)-Cl(14)	85.4 (1)	Cl(11)-Nb(6)-Cl(19)	152.5 (1)	C(37)-C(42)-C(41)	117 (2)
Cl(1)-Nb(2)-Cl(8)	163.7 (1)	Cl(6)-Nb(4)-Cl(15)	151.1 (2)	Cl(11)-Nb(6)-C(57)	83.5 (4)	Nb(5)-C(43)-C(44)	124 (1)
Cl(1)-Nb(2)-Cl(9)	88.3 (1)	Cl(6)-Nb(4)-C(1)	118.6 (4)	Cl(11)-Nb(6)-C(64)	117.6 (4)	C(36)-C(43)-C(44)	134 (1)
Cl(1)-Nb(2)-Cl(10)	86.1 (1)	Cl(6)-Nb(4)-C(8)	83.5 (4)	Cl(11)-Nb(6)-C(71)	123.7 (4)	C(36)-C(43)-C(50)	91 (1)
Cl(2)-Nb(2)-Cl(4)	91.8 (1)	Cl(6)-Nb(4)-C(15)	89.2 (4)	Cl(11)-Nb(6)-C(78)	86.4 (4)	C(44)-C(43)-C(50)	134 (1)
Cl(2)-Nb(2)-Cl(8)	82.7 (2)	Cl(6)-Nb(4)-C(22)	124.5 (4)	Cl(12)-Nb(6)-Cl(13)	76.2 (1)	Nb(5)-C(50)-C(51)	129 (1)
Cl(2)-Nb(2)-Cl(9)	163.0 (2)	Cl(7)-Nb(4)-Cl(14)	80.2 (2)	Cl(12)-Nb(6)-Cl(18)	155.0 (2)	C(29)-C(50)-C(43)	88 (1)
Cl(2)-Nb(2)-Cl(10)	94.4 (2)	Cl(7)-Nb(4)-Cl(15)	78.5 (2)	Cl(12)-Nb(6)-Cl(19)	84.3 (1)	C(29)-C(50)-C(51)	134 (2)
Cl(4)-Nb(2)-Cl(8)	85.9 (1)	Cl(7)-Nb(4)-C(1)	158.3 (4)	Cl(12)-Nb(6)-C(57)	82.2 (4)	C(43)-C(50)-C(51)	135 (1)
Cl(4)-Nb(2)-Cl(9)	90.1 (1)	Cl(7)-Nb(4)-C(8)	155.0 (4)	Cl(12)-Nb(6)-C(64)	86.1 (4)	Nb(6)-C(57)-C(58)	129 (1)
Cl(4)-Nb(2)-Cl(10)	164.0 (2)	Cl(7)-Nb(4)-C(15)	150.1 (4)	Cl(12)-Nb(6)-C(71)	121.3 (4)	C(58)-C(57)-C(64)	136 (1)
Cl(8)-Nb(2)-Cl(9)	80.5 (1)	Cl(7)-Nb(4)-C(22)	153.4 (4)	Cl(12)-Nb(6)-C(78)	117.2 (5)	C(58)-C(57)-C(78)	132 (1)
Cl(8)-Nb(2)-Cl(10)	80.2 (1)	Cl(14)-Nb(4)-Cl(15)	97.3 (2)	Cl(13)-Nb(6)-Cl(18)	79.5 (1)	C(64)-C(57)-C(78)	90 (1)
Cl(9)-Nb(2)-Cl(10)	79.8 (1)	Cl(14)-Nb(4)-C(1)	82.9 (4)	Cl(13)-Nb(6)-Cl(19)	80.9 (1)	Nb(6)-C(64)-C(65)	131 (1)
Nb(1)-Nb(3)-Nb(2)	59.42 (5)	Cl(14)-Nb(4)-C(8)	88.3 (4)	Cl(13)-Nb(6)-C(57)	153.4 (4)	C(57)-C(64)-C(65)	135 (2)
Cl(1)-Nb(3)-Cl(3)	107.1 (1)	Cl(14)-Nb(4)-C(15)	123.4 (4)	Cl(13)-Nb(6)-C(64)	154.1 (3)	C(57)-C(64)-C(71)	94 (1)
Cl(1)-Nb(3)-Cl(4)	106.9 (1)	Cl(14)-Nb(4)-C(22)	117.7 (4)	Cl(13)-Nb(6)-C(71)	154.7 (4)	C(65)-C(64)-C(71)	128 (1)
Cl(1)-Nb(3)-Cl(11)	159.5 (2)	Cl(15)-Nb(4)-C(1)	90.3 (4)	Cl(13)-Nb(6)-C(78)	155.0 (5)	Nb(6)-C(71)-C(72)	121 (1)
Cl(1)-Nb(3)-Cl(12)	86.2 (1)	Cl(15)-Nb(4)-C(8)	125.3 (4)	Cl(18)-Nb(6)-Cl(19)	97.5 (2)	C(64)-C(71)-C(72)	137 (1)
Cl(1)-Nb(3)-Cl(13)	85.2 (1)	Cl(15)-Nb(4)-C(15)	112.4 (4)	Cl(18)-Nb(6)-C(57)	119.3 (4)	C(64)-C(71)-C(78)	87 (1)
Cl(3)-Nb(3)-Cl(4)	91.1 (2)	Cl(15)-Nb(4)-C(22)	79.7 (4)	Cl(18)-Nb(6)-C(64)	118.8 (4)	C(72)-C(71)-C(78)	135 (1)
Cl(3)-Nb(3)-Cl(11)	87.8 (1)	Cl(8)-Nb(5)-Cl(9)	79.0 (1)	Cl(18)-Nb(6)-C(71)	83.6 (4)	Nb(6)-C(78)-C(79)	131 (1)
Cl(3)-Nb(3)-Cl(12)	165.2 (1)	Cl(8)-Nb(5)-Cl(10)	75.9 (1)	Cl(18)-Nb(6)-C(78)	83.7 (5)	C(57)-C(78)-C(71)	89 (1)
Cl(3)-Nb(3)-Cl(13)	91.8 (2)	Cl(8)-Nb(5)-Cl(16)	155.5 (2)	Cl(19)-Nb(6)-C(57)	112.3 (4)	C(57)-C(78)-C(79)	136 (1)
Cl(4)-Nb(3)-Cl(11)	86.2 (1)	Cl(8)-Nb(5)-Cl(17)	90.3 (2)	Cl(19)-Nb(6)-C(64)	78.7 (3)	C(71)-C(78)-C(79)	130 (2)
Cl(4)-Nb(3)-Cl(12)	91.0 (2)	Cl(8)-Nb(5)-C(29)	110.2 (4)	C(19)-Nb(6)-C(71)	82.8 (4)	Cl(16)-Sn-Cl(19)′	179.5 (1)
Cl(4)-Nb(3)-Cl(13)	166.1 (1)	Cl(8)-Nb(5)-C(36)	77.8 (4)	Cl(19)-Nb(6)-C(78)	119.9 (5)	Cl(16)-Sn-C(85)	87.1 (4)
Cl(11)-Nb(3)-Cl(12)	77.7 (1)	Cl(8)-Nb(5)-C(43)	91.1 (4)	Nb(5)-Cl(16)-Sn	135.6 (2)	Cl(16)-Sn-C(89)	86.8 (5)
Cl(11)-Nb(3)-Cl(13)	80.3 (1)	Cl(8)-Nb(5)-C(50)	126.0 (4)	Nb(6)-Cl(19)-Sn′	139.3 (2)	Cl(16)-Sn-C(93)	95.3 (4)
Cl(12)-Nb(3)-Cl(13)	82.9 (2)	Cl(9)-Nb(5)-Cl(10)	73.9 (1)	Nb(4)-C(1)-C(2)	125 (1)	Cl(19)′-Sn-C(85)	93.4 (4)
Nb(1)-Cl(1)-Nb(2)	71.3 (1)	Cl(9)-Nb(5)-Cl(16)	88.0 (1)	C(2)-C(1)-C(8)	137 (2)	Cl(19)′-Sn-C(89)	92.9 (5)
Nb(1)-Cl(1)-Nb(3)	72.6 (1)	Cl(9)-Nb(5)-Cl(17)	153.5 (2)	C(2)-C(1)-C(22)	133 (2)	Cl(19)′-Sn-C(93)	84.5 (4)
Nb(2)-Cl(1)-Nb(3)	72.2 (1)	Cl(9)-Nb(5)-C(29)	79.8 (4)	C(8)-C(1)-C(22)	89 (1)	C(85)-Sn-C(89)	117.0 (7)
Nb(1)-Cl(2)-Nb(2)	73.2 (1)	Cl(9)-Nb(5)-C(36)	88.5 (4)	Nb(4)-C(8)-C(9)	122 (1)	C(85)-Sn-C(93)	123.4 (7)
Nb(1)-Cl(3)-Nb(3)	73.0 (1)	Cl(9)-Nb(5)-C(43)	123.4 (4)	C(1)-C(8)-C(9)	134 (1)	C(89)-Sn-C(93)	119.6 (7)
Nb(2)-Cl(4)-Nb(3)	72.7 (1)	Cl(9)-Nb(5)-C(50)	114.3 (4)	C(1)-C(8)-C(15)	91 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

known have displayed double bonds between the two Nb(III) atoms. In the present case there is clearly no Nb–Nb bond in any of them, since the Nb–Nb distances are 3.51 Å for Nb(1) to Nb(4), 3.48 Å for Nb(2) to Nb(5), and 3.49 Å for Nb(3) to Nb(6). This may be attributed to the fact that in each case the inner niobium atom contributes its electrons to the formation of Nb–Nb bonds within the central cluster and therefore cannot engage in bond formation with its outer partner.

Finally, we turn to the η^4-($-C_4Ph_4$) units. Each of the three is crystallographically independent and they are so positioned as to destroy the potential 3-fold symmetry of the hexaniobium entity. A clockwise rotation carries Nb(4) and its ligands approximately into Nb(6) and its ligands, but the ligand arrangement about Nb(5) is a mirror image of that at the other two. Nevertheless, the three $Nb(C_4Ph_4)$ moieities are effectively identical. The C_4 rings are all square within experimental error. The angles range from 87 (1) to 94 (1)° but the average is 90 ± 1°, and the C–C distances range from 1.41 (2) to 1.51 (2) Å with an average value of 1.445 ± 0.020 Å. The rings are all symmetrically bonded to the niobium atoms, with Nb–C distances that range from 2.33 (2) to 2.38 (2) Å and have an average of 2.35 ± 0.02 Å. The bonds from the ring atoms to the phenyl groups are swept back very slightly, namely by 1–2°, from the mean plane of each ring.

Discussion

Metal η^4-(c-CR)$_4$ complexes have been known since the discovery of $[(MeC)_4NiCl_2]_2$ in 1959,[11] which was followed into the early 1960s by reports of complexes of η^4-C_4 carbocycles with various $M(CO)_n$ fragments. Among these early ones were several containing the $(PhC)_4$ ligand, formed by dimerization of PhCCPh, e.g., $(PhC)_4Fe(CO)_3$.[12] In 1969, the only known (c-RC)$_4$ complex of a group V element, namely, the 18-electron molecule Nb(η^5-C_5H_5)(CO)(Ph_2C_2)(Ph_4C_4), was reported.[13] The previously known (c-RC)$_4$ complexes, however, all (including the one example from group V) seem to be those in which the metal fragment is

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an electron-rich one and the compound has an 18-electron (or, occasionally, a 16-electron) closed configuration. The compound reported here is the first one where a group V metal atom bonds to a $(c\text{-}RC)_4$ ligand and a closed-shell configuration is not attained. If the Nb atom is regarded as Nb(III) with two d electrons and each of the five chlorine ligands is considered to be a two-electron donor, we have a total of 12 valence shell electrons, plus those contributed by the η^4-$-(c\text{-}C_4Ph_4)$ ligand. If this is regarded as a four-electron donor (i.e., as a η^4-cyclobutadiene ligand), the total becomes 16. Thus the metal atom reaches an electron count that, while not strictly speaking a closed shell, is not uncommon among arene–metal complexes of the early transition metals.[14]

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Supplementary Material Available: Tables of detailed crystal data and general displacement parameters, full listings of bond distances and angles, and a drawing of two Nb hexamers connected by Sn–Cl bonding (16 pages); a table of observed and calculated structure factors (46 pages). Ordering information is given on any current masthead page.

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