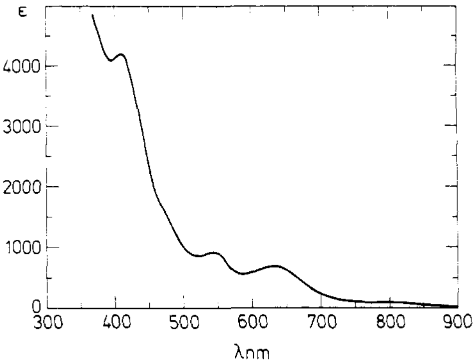

Figure 7. Absorption spectrum of the IV/IV complex $[(\mathrm{bispicen})\mathrm{MnO}]_2(\mathrm{ClO}_4)_4\cdot 3\mathrm{H}_2\mathrm{O}$ in acetonitrile.

phen complex,[19] the bispicen IV/IV complex does not give an EPR signal at 4 K or at higher temperatures; the only signal that is observed must be attributed to the presence of a mixture of a Mn(II) compound and small quantities of the Mn(III)/Mn(IV) dimer, which is consistent with the susceptibility data.

Electronic Spectra. The electronic spectrum of the IV/IV complex, shown in Figure 7, was recorded in acetonitrile; the complex is too unstable in water to allow the spectrum to be recorded in aqueous solution. The spectrum is similar to that of the III/IV complex, but the peaks are shifted. The spectrum exhibits two very intense peaks in the UV region and two medium intensity bands in the visible region at 544 ($\epsilon = 843\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) and 632 nm ($\epsilon = 657\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). The higher energy of the two intense UV peaks has a maximum below 350 nm, while the lower energy peak is at 411 nm ($\epsilon = 3956\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) with a shoulder at 470 nm ($\epsilon = 1544\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). These values may be compared with those at 394 and 470 nm (sh) observed in the tris(μ-oxo)-dimanganese(IV,IV) complex.[15] The intensity in the region near 800 nm, which has been attributed to the intervalence charge-transfer band in the III/IV complexes, is much lower in the IV/IV complex than in the III/IV analogue. The observation of a very weak band at 802 nm ($\epsilon = 159$) in the present spectrum of the IV/IV complex may be due to the presence of a small amount of the III/IV form in solution. The present spectrum is similar to that reported for the tmpa analogue,[7] but very different from that of the phen complex in that the latter shows no peaks in the visible region.[9,21]

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Supplementary Material Available: For $[(\mathrm{bispicen})\mathrm{MnO}]_2(\mathrm{ClO}_4)_4\cdot 2\mathrm{CH}_3\mathrm{CN}$, Tables S1 (hydrogen atom parameters) and S2 (anisotropic thermal parameters) (2 pages); Table S3 (observed and calculated structure amplitudes) (16 pages). Ordering information is given on any current masthead page.

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New Niobium Complexes with Alkynes. 1. Mono- and Dinuclear Complexes

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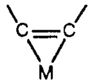
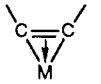
Four alkyne complexes of niobium are reported, and their structures, determined by X-ray crystallography, are presented. $\mathrm{NbCl_3(PhCCPh)(THF)_2}$ (**1**), prepared by the reaction of $\mathrm{NbCl_4(THF)_2}$, sodium amalgam, and PhCCPh in THF, crystallizes in the $P2_1/n$ space group with $a = 12.013$ (3) Å, $b = 15.265$ (4) Å, $c = 13.520$ (3) Å, $\beta = 110.83$ (2)°, $V = 2317$ (1) Å^3, and $Z = 4$. $\mathrm{NbCl_3(PhCCMe)(THF)_2}$ (**2**), prepared by the reaction of $\mathrm{NbCl_4(THF)_2}$, sodium amalgam, and PhCCMe in THF, crystallizes in the $P2_1/n$ space group with $a = 13.751$ (3) Å, $b = 10.867$ (2) Å, $c = 14.592$ (2) Å, $\beta = 116.91$ (1)°, $V = 1944.5$ (6) Å^3, and $Z = 4$. $\mathrm{[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot 0.5THF}$ (**3**), prepared by the reaction of $\mathrm{NbCl_4(THF)_2}$, Mg, and PhCCPh in THF, crystallizes in the $P\bar{1}$ space group with $a = 10.310$ (2) Å, $b = 15.117$ (2) Å, $c = 17.148$ (4) Å, $\alpha = 80.46$ (2)°, $\beta = 89.79$ (2)°, $\gamma = 87.24$ (1)°, $V = 2633$ (1) Å^3, and $Z = 2$. $\mathrm{Nb_2OCl_4(PhCCPh)(THF)_4}$ (**4**), prepared by the same reaction as for **3**, or two other reactions, crystallizes in the $C2/c$ space group with $a = 20.581$ (3) Å, $b = 9.829$ (2) Å, $c = 19.176$ (3) Å, $\beta = 119.406$ (9)°, $V = 3379$ (2) Å^3, and $Z = 4$.

Introduction

Previous work in this laboratory led to the preparation and characterization of the first η^2-alkyne complexes of tantalum. One of these[1] was the anion $[\mathrm{TaCl_4py(PhCCPh)}]^-$, in which a central flat pyramid, $\mathrm{TaCl_4}$, has a py ligand below and a side-on PhCCPh ligand above. From the bond lengths (Ta–C = 2.07 Å; C–C = 1.33 Å) it was concluded that the alkyne was so strongly bonded to the tantalum atom that the oxidation state of the latter should be considered to be V and the bonding represented by I with an



I



II

appreciable contribution from II as well. Shortly thereafter we reported a dinuclear tantalum compound[2] containing two such metal–alkyne linkages, this time with the alkyne $\mathrm{CH_3CCCH_3}$, where the Ta–C distances were even shorter (2.03 Å). In addition, with $\mathrm{Me_3CCCMe_3}$ we obtained a dinuclear compound in which the alkyne formed a skewed (i.e., neither parallel nor perpendicular) bridge across a Ta–Ta bond.[3] The Ta–Ta distance (2.68 Å) was shorter than any previously reported, and the Ta–C distances (2.21 and 2.42 Å) seemed consistent with appreciable Ta–C bond orders.

We now report the preparation and structural characterization of some alkyne complexes of niobium that are very similar to those of tantalum just mentioned. In 1984 Dehnicke and co-workers[4] reported one compound of niobium containing similar, strongly bonded PhCCPh groups. Beyond this, our search of the literature, including the two detailed reviews by Holloway and Melnick,[5] reveals that only two further reports of alkyne complexes of niobium and tantalum have appeared. One deals with $\mathrm{Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(PhCCPh)}$, for which a structure was reported.[6]

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(1) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2352.
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Here the binding of the alkyne was weaker, with Nb–C distances of ca. 2.18 Å. Several alkyne complexes of the type $(C_5Me_5)M(CO)(RCCR')$ with M = Nb and Ta and R and R′ = H, Me, Ph, and C_6H_{11}, have also been prepared,[7] but structural data were not obtained.

Experimental Section

All synthetic work was carried out under an atmosphere of argon by using the standard vacuum, inert-atmosphere double-line techniques or in a nitrogen-filled drybox. $NbCl_5$ was purchased from AESAR, reducing agents, Mg turnings, and sodium were from Fisher Scientific Co., and aluminum powder (200 mesh) was from Aldrich Chemical Co. Mercury was triply distilled grade from the D. F. Goldsmith Chemical & Metal Corp. Diphenylacetylene (PhCCPh) was purchased from Stream Chemical, Inc., and used as received. 1-Phenyl-1-propyne ($PhCCCH_3$) was from Farchen Division, Chemsampco, Inc., and was distilled under nitrogen before use. Solvents: tetrahydrofuran (THF) and benzene were from Fisher Scientific Company, hexane was from J. T. Baker, Inc., and acetonitrile was from Mallickrodt. They were stored over molecular sieves and distilled before use over the drying agent Na–benzophenone or P_2O_5 (for acetonitrile). Stock sodium amalgam, prepared by dissolving 0.46 g of sodium in 20 mL of mercury, was assumed to have a concentration of 1 mmol of Na/mL and handled by a syringe. $NbCl_4(THF)_2$ was prepared by the literature method.[8] A Perkin-Elmer 783 spectrophotometer was used for IR spectroscopy.

Preparation of $NbCl_3(PhCCPh)(THF)_2$ (1). $NbCl_4(THF)_2$ (4.55 g, 12 mmol), PhCCPh (2.14 g, 12 mmol), and sodium amalgam (12 mL, 12 mmol) were stirred overnight in 80 mL of THF. The yellow $NbCl_4(THF)_2$ gradually dissolved to form a green solution, and then the color gradually changed to brown along with the formation of a very fine greenish brown precipitate. After the precipitate and droplets of mercury were removed by filtration through a 4–5.8-μm fritted funnel, 100 mL of hexane was added and the solution was kept in a refrigerator at −10 °C. Big red crystals (several millimeters long), which developed within 3 days, were then filtered out and washed with 2 × 20 mL of hexane (yield 4.5 g, ca. 72%). Sometimes a little fluffy greenish brown or greenish gray precipitate was formed along with the crystals. It was easily removed by stirring up the precipitate followed by decantation. Its presence or absence did not seem to affect the yield. IR (Nujol mull, mineral oil; cm^{-1}): 1684 (s), 1565 (w), 1559 (w), 1446 (w), 1434 (m), 1307 (m), 1168 (7), 1145 (w), 1107 (w), 1064 (m), 1036 (w), 1018 (w), 1005 (s), 921 (s), 860 (vs), 773 (w), 710 (s), 698 (w), 688 (s), 662 (w), 630 (w), 603 (w), 563 (m), 520 (m), 435 (m).

Preparation of $NbCl_3(PhCCCH_3)(THF)_2$ (2). $NbCl_4(THF)_2$ (1.40 g, 3.7 mmol), $PhCCCH_3$ (0.5 mL, 4 mmol), and sodium amalgam (3.7 mL, 3.7 mmol) were stirred overnight in 15 mL of THF. A series of color changes of the solution from light brown to green and finally to reddish brown were observed along with the formation of a little very fine brown precipitate. After the solution was filtered through a 4–5.5-μm fritted funnel, 20 mL of hexane was added and the solution was kept in a refrigerator at −10 °C for about 1 week. Big clusters of red crystals (several millimeters long) were separated by filtration and washed with 2 × 20 mL of hexane (yield 1.2 g, ca. 68%). IR (Nujol mull, mineral oil; cm^{-1}): 1692 (m), 1688 (w), 1438 (w), 1424 (w), 1284 (w), 1240 (w), 1235 (w), 1224 (w), 1219 (w), 1170 (m), 1151 (w), 1130 (w), 1068 (m), 1040 (m), 996 (s), 921 (s), 840 (vs), 772 (s), 698 (vs), 582 (s), 550 (s), 434 (vs).

Preparation of $[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot0.5THF$ (3) and $Nb_2OCl_4(THF)_4(PhCCPh)$ (4). $NbCl_4(THF)_2$ (1.52 g, 4 mmol), Mg turnings (50 mg, 2.06 mmol), and PhCCPh (1.44 g, 8.1 mmol) were stirred overnight at room temperature in 30 mL of THF. The yellow suspension gradually changed to a clear brown solution, which was then transferred to or filtered into a Schlenk tube, layered with 30 mL of hexane, and left alone at room temperature for about a fortnight. As the solvent diffusion proceeded, brown platelike crystals and green-brown rhombohedral crystals were formed. Later, the former were identified as $[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot0.5THF$ and the latter as $Nb_2OCl_4(PhCCPh)(THF)_4$ by X-ray crystallography. The combined yield was 1.10 g, and the weight ratio was about 3:1.

IR spectrum for $Nb_2OCl_4(THF)_4(PhCCPh)$ (Nujol mull, mineral oil; cm^{-1}): 1415 (w), 1410 (w), 1335 (w), 1033 (w), 1024 (w), 1010 (w), 1002 (s), 927 (w), 911 (m), 900 (vs), 770 (m), 753 (m), 701 (m), 687 (m), 577 (w), 560 (w), 553 (m), 508 (m), 406 (w).

IR spectrum for $[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]$ (Nujol mull, mineral oil; cm^{-1}): 1692 (w), 1683 (w), 1636 (w), 1606 (w), 1580 (w), 1560 (m), 1530 (w), 1260 (w), 1165 (m), 1150 (w), 1065 (m), 1020 (vs), 956 (w), 913 (m), 869 (vs), 766 (m), 760 (w), 689 (m), 628 (w), 603 (w), 562 (w), 518 (w), 433 (w).

$Nb_2OCl_4(THF)_4(PhCCPh)$ (**4**) was also prepared in two other ways: (1) $NbCl_5$ (0.54 g, 2 mmol) was reacted overnight with sodium amalgam (4 mL, 4 mmol) and PhCCPh (0.36 g, 2 mmol) in 30 mL of THF. After removal of a gray precipitate by filtration and layering of the brown filtrate with hexane, the product crystallized. Yield: ca. 300 mg, 35%. (2) $^nBu_3SnH$ (1.7 mL, 6 mmol) was used to reduce $NbCl_5$ (0.54 g, 2 mmol) in benzene overnight in the presence of PhCCPh (0.72 g, 4 mmol). A copious brown-black precipitate was isolated by filtration and treated with THF (30 mL), and this THF solution was filtered to remove undissolved precipitate. The dark brown filtrate was layered with hexane. In both cases the brown-green crystals have the same IR spectrum and unit cell parameters as those found for the product as prepared earlier.

X-ray Crystallography. All these four kinds of air-sensitive crystals were examined under a layer of sodium-treated mineral oil on a small dish in a fritted funnel flushed constantly with a stream of argon. Crystals for data collection on a P3 equivalent or Rigaku AFC5 diffractometer were glued with Apiezon grease and sealed by flame in thin-walled capillaries filled with argon.

Routine procedures were followed to determine the unit cell parameters and to collect intensity data. The usual Lp corrections and an empirical absorption correction based on azimuthal scans of seven strong reflections with Eulerian χ angle near 90° were applied. A loss of intensity during data collection (24.2%) was observed for the crystal of $NbCl_3(PhCCCH_3)(THF)_2$, and an anisotropic decay correction based on the time variation of three standards that were monitored every 2 h was thus applied to the data set. Table I summarizes basic data concerning data collection and crystallographic procedures for these four compounds.

$NbCl_3(PhCCPh)(THF)_2$ (1). The interpretation of a supersharp Patterson function (SHELXS-86) gave almost all the coordinates for the non-hydrogen atoms of the independent molecule. The rest of the atoms were located by the subsequent difference Fourier syntheses and least-squares refinement. All these non-hydrogen atoms were refined anisotropically in the final least-squares refinement. A final difference Fourier map indicated the positions for some of the hydrogen atoms, but no attempt was made to locate and refine these hydrogen atoms. The final positional parameters are given in Table II.

$NbCl_3(PhCCCH_3)(THF)_2$ (2). The coordinates of the crystallographically independent Nb atom were derived from a Patterson map. Difference Fourier syntheses and least-squares refinement then provided the positions of the remaining non-hydrogen atoms. After all these atoms were refined anisotropically, a final difference Fourier map revealed the positions of some of the hydrogen atoms, but no effort was made to refine the structure further. The final positional parameters are listed in Table III.

$[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot0.5THF$ (3). The coordinates of the Nb atom were derived from a Patterson map. The rest of the non-hydrogen atoms were then located by alternate difference Fourier syntheses and least-squares refinements. The THF solvent molecule was found disordered around an inversion center in such a manner that two atoms (C(44) and C(44)′) of the five-membered ring were related directly by the inversion center, while the other three atoms (O(8), C(43), and C(45)) resided on two sets of positions related by the inversion, and it was not possible to identify the oxygen atom. Before the final refinement the atom that had the lowest thermal parameter of all the ring atoms, after they were all refined as carbon atoms, was designated as the oxygen atom. The final difference Fourier map was featureless, with the highest peaks around chlorine atoms of the magnesium cation. Table IV lists the final positional parameters.

$Nb_2OCl_4(PhCCPh)(THF)_4$ (4). The position of the crystallographically independent Nb atom was derived from a Patterson map, assuming that the space group was centrosymmetric *C*2/*c*, which was confirmed by successfully locating the rest of the non-hydrogen atoms and the refinement of the structure. All the non-hydrogen atoms were treated anisotropically in the final least-squares refinement, and the top six highest peaks of a final difference Fourier map were all in the vicinity of the Nb atom. The final positional parameters are given in Table V.

Results and Discussion

The three mononuclear compounds have structures that are essentially similar, particularly in regard to the important question of the bonding of the alkyne molecules to the niobium atoms. We shall first report the structure of each of these three compounds and then discuss them in comparison with each other and with the previously reported tantalum compounds.

$NbCl_3(PhCCPh)(THF)_2$ (1). The crystal is formed by a normal packing of neutral molecules, each on a general position. A drawing of the molecule is shown in Figure 1, and selected bond

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Table I. Crystallographic Data

	1	2	3	4
formula	$NbCl_3O_2C_{22}H_{26}$	$NbCl_3O_2C_{17}H_{24}$	$Nb_2Cl_{14}Mg_4O_{15}C_{88}H_{140}$	$Nb_2OCl_4O_5C_{30}H_{42}$
fw	521.72	459.64	2217.49	810.29
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	C2/c
syst absences	$h0l$, $h + l = 2n + 1$	$h0l$, $h + l = 2n + 1$	none	hkl, $h + k = 2n + 1$
	$0k0$, $k = 2n + 1$	$0k0$, $k = 2n + 1$		$h0l$, $l = 2n + 1$
a, Å	12.013 (3)	13.751 (3)	10.310 (2)	20.581 (3)
b, Å	12.265 (4)	10.867 (2)	15.117 (2)	9.829 (2)
c, Å	13.520 (3)	14.592 (2)	17.148 (1)	19.176 (3)
α, deg	90.0	90.0	80.46 (2)	90.0
β, deg	110.83 (2)	116.91 (1)	89.79 (2)	119.406 (9)
γ, deg	90.0	90.0	87.24 (1)	90.0
V, Å^3	2317 (1)	1944.5 (6)	2633 (1)	3379 (2)
Z	4	4	1	4
d_{calc}, g/cm^3	1.495	1.570	1.399	1.593
cryst size, mm	0.55 × 0.32 × 0.30	0.40 × 0.35 × 0.30	0.42 × 0.37 × 0.20	0.40 × 0.25 × 0.10
μ(Mo Kα), cm^{-1}	8.605	10.142	6.440	10.030
data collcn instrument	P3 equivalent	P3 equivalent	CAD-4	Rigaku AFC-5R
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)			
orientation reflcns: no.; range (2θ), deg	25; 30–36	25; 21–29	25; 32–34	25; 40–51
temp, °C	20	20	−80	20
scan method	ω–2θ	ω–2θ	ω–2θ	ω–2θ
data collcn range (2θ), deg	4–46	4–46	4–46	4–55
no. of unique data; tot. no. with $F_0^2 > 3\sigma(F_0^2)$	3208; 2389	2284; 1939	7307; 6050	3901; 2679
no. of params refined	253	208	548	186
transm factors: max; min	0.9989; 0.8697	0.9989; 0.8568	0.9999; 0.9254	1.000; 0.9425
R^a	0.052	0.043	0.065	0.063
R_w^b	0.069	0.064	0.095	0.084
quality-of-fit indicator[c]	1.506	1.437	2.85	1.697
largest shift/esd, final cycle	0.00	0.01	0.03	0.18
largest peak, e/Å^3	0.582	0.775	1.577	0.85

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table II. Positional and Equivalent Isotropic Thermal Parameters for $NbCl_3(THF)_2(PhCCPh)$

atom	x	y	z	B,[a] Å^2
Nb	0.01086 (5)	0.17575 (4)	0.20013 (4)	3.00 (1)
Cl(1)	0.1055 (2)	0.3146 (1)	0.1991 (2)	4.43 (4)
Cl(2)	−0.1299 (2)	0.0586 (1)	0.1550 (2)	5.18 (5)
Cl(3)	0.0207 (2)	0.2054 (2)	0.3762 (1)	5.14 (5)
O(1)	−0.0410 (4)	0.1846 (3)	0.0269 (3)	3.9 (1)
O(2)	−0.1630 (4)	0.2635 (4)	0.1635 (4)	5.0 (1)
C(1)	0.1391 (5)	0.0832 (4)	0.2738 (5)	3.1 (1)
C(2)	0.1809 (5)	0.0249 (4)	0.3646 (5)	3.1 (1)
C(3)	0.1015 (6)	−0.0143 (5)	0.4051 (6)	4.2 (2)
C(4)	0.1448 (8)	−0.0677 (6)	0.4944 (7)	5.7 (2)
C(5)	0.2649 (8)	−0.0809 (6)	0.5443 (6)	5.5 (2)
C(6)	0.3449 (7)	−0.0433 (6)	0.5039 (7)	5.3 (2)
C(7)	0.3033 (6)	0.0095 (5)	0.4150 (6)	4.1 (2)
C(8)	0.1650 (5)	0.1176 (4)	0.1962 (5)	3.0 (1)
C(9)	0.2543 (5)	0.1123 (5)	0.1448 (5)	3.2 (1)
C(10)	0.2694 (6)	0.1805 (5)	0.0842 (5)	4.4 (2)
C(11)	0.3567 (8)	0.1743 (6)	0.0377 (6)	6.0 (2)
C(12)	0.4267 (7)	0.1002 (7)	0.0538 (7)	6.9 (2)
C(13)	0.4078 (8)	0.0318 (7)	0.1116 (7)	6.7 (2)
C(14)	0.3233 (6)	0.0365 (5)	0.1609 (6)	4.7 (2)
C(15)	−0.0998 (7)	0.2591 (5)	−0.0395 (6)	5.1 (2)
C(16)	−0.0608 (9)	0.2507 (6)	−0.1341 (7)	6.3 (2)
C(17)	−0.0508 (9)	0.1540 (6)	−0.1496 (7)	6.7 (3)
C(18)	−0.0373 (8)	0.1116 (5)	−0.0434 (6)	4.7 (2)
C(19)	−0.2763 (8)	0.2250 (8)	0.163 (1)	8.8 (3)
C(20)	−0.3376 (9)	0.304 (1)	0.194 (1)	12.2 (4)
C(21)	−0.267 (1)	0.3769 (9)	0.207 (1)	13.3 (4)
C(22)	−0.1597 (9)	0.3576 (7)	0.187 (1)	9.9 (3)

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

Table III. Positional and Equivalent Isotropic Thermal Parameters for $NbCl_3(PhCCCH_3)(THF)_2$

atom	x	y	z	B,[a] Å^2
Nb	0.67537 (4)	0.25681 (5)	0.47165 (4)	2.88 (1)
Cl(1)	0.4970 (1)	0.2489 (2)	0.4586 (1)	4.81 (4)
Cl(2)	0.8237 (1)	0.2828 (2)	0.4286 (1)	4.39 (4)
Cl(3)	0.7435 (2)	0.4214 (2)	0.5914 (1)	5.13 (5)
C(1)	0.7211 (6)	0.1528 (8)	0.7056 (5)	5.9 (2)
C(2)	0.7189 (5)	0.1547 (6)	0.6008 (4)	3.6 (2)
C(3)	0.7453 (4)	0.0942 (6)	0.5389 (4)	2.9 (1)
C(4)	0.7874 (5)	−0.0261 (6)	0.5294 (4)	3.3 (1)
C(5)	0.7609 (5)	−0.1285 (6)	0.5699 (5)	4.4 (2)
C(6)	0.7983 (7)	−0.2442 (6)	0.5585 (6)	5.1 (2)
C(7)	0.8644 (7)	−0.2573 (7)	0.5111 (6)	5.2 (2)
C(8)	0.8941 (6)	−0.1537 (7)	0.4725 (5)	5.3 (2)
C(9)	0.8527 (5)	−0.0374 (6)	0.4793 (5)	4.2 (2)
O(1)	0.6001 (3)	0.1423 (4)	0.3321 (3)	3.9 (1)
C(10)	0.5871 (7)	0.1685 (8)	0.2292 (5)	7.3 (2)
C(11)	0.5505 (6)	0.0515 (8)	0.1685 (5)	5.7 (2)
C(12)	0.5450 (7)	−0.0430 (7)	0.2424 (6)	6.3 (2)
C(13)	0.5359 (6)	0.0304 (7)	0.3256 (5)	5.6 (2)
O(2)	0.5986 (3)	0.4204 (4)	0.3551 (3)	4.4 (1)
C(14)	0.5202 (6)	0.5061 (8)	0.3634 (7)	7.6 (2)
C(15)	0.5315 (7)	0.6232 (8)	0.3187 (6)	7.4 (2)
C(16)	0.5980 (8)	0.5975 (8)	0.2660 (6)	8.1 (3)
C(17)	0.6447 (8)	0.4819 (9)	0.3009 (7)	11.8 (3)

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

lengths and angles, identified according to the numbering scheme shown in the figure, are listed in Table VI. The two Nb–C distances are equal within the esd's at 2.070 Å, and the C–C distance in the alkyne bond is 1.31 (1) Å.

$NbCl_3(PhCCCH_3)(THF)_2$ (2). Again, the crystal is formed by a packing of discrete molecules on general positions, with no unusual contacts. The molecule and its numbering scheme are shown in Figure 2, while Table VII records the principal distances and angles. Despite the presence of different substituents on the two alkyne carbon atoms, the two Nb–C distances are equal within the esd's at 2.034 Å and the C–C distance is 1.30 (1) Å. The structure of **2** is virtually identical with that of **1** except for the replacement of one phenyl group by a methyl group.

$[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot 0.5THF$ (3). The structures of the cation and the anion in this compound are shown in Figures 3 and 4, respectively, and the principal bond distances and angles in both are listed in Table VIII. The alkyne to metal bonding is again symmetrical, with two Nb–C distances averaging

Table VII. Selected Bond Distances (Å) and Angles (deg) for $NbCl_3(PhCCCH_3)(THF)_2$[a]

Distances			
Nb–Cl(1)	2.374 (2)	Nb–O(1)	2.203 (4)
Nb–Cl(2)	2.407 (2)	Nb–O(2)	2.354 (4)
Nb–Cl(3)	2.377 (2)	C(1)–C(2)	1.515 (10)
Nb–C(2)	2.030 (6)	C(2)–C(3)	1.295 (10)
Nb–C(3)	2.038 (6)	C(3)–C(4)	1.462 (9)
Angles			
Cl(1)–Nb–Cl(2)	161.80 (6)	Cl(3)–Nb–C(3)	110.8 (2)
Cl(1)–Nb–Cl(3)	97.77 (8)	Cl(3)–Nb–O(1)	165.5 (1)
Cl(1)–Nb–C(2)	85.1 (2)	Cl(3)–Nb–O(2)	82.0 (1)
Cl(1)–Nb–C(3)	104.6 (2)	C(2)–Nb–O(1)	111.5 (2)
Cl(1)–Nb–O(1)	82.5 (1)	C(2)–Nb–O(2)	158.6 (2)
Cl(1)–Nb–O(2)	82.0 (1)	C(3)–Nb–O(1)	82.9 (2)
Cl(2)–Nb–Cl(3)	90.28 (7)	C(3)–Nb–O(2)	164.1 (2)
Cl(2)–Nb–C(2)	112.2 (2)	O(1)–Nb–O(2)	83.7 (2)
Cl(2)–Nb–C(3)	87.5 (2)	Nb–C(2)–C(1)	143.8 (5)
Cl(2)–Nb–O(1)	85.7 (1)	C(1)–C(2)–C(3)	144.4 (6)
Cl(2)–Nb–O(2)	83.0 (1)	Nb–C(3)–C(4)	148.3 (5)
Cl(3)–Nb–C(2)	82.9 (2)	C(2)–C(3)–C(4)	140.1 (6)

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

Table VIII. Selected Bond Distances (Å) and Angles (deg) for $[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot 0.5THF$[a]

Distances			
Nb–Cl(1)	2.431 (2)	Mg(1)–Cl(6)	2.482 (3)
Nb–Cl(2)	2.421 (2)	Mg(1)–Cl(7)	2.542 (3)
Nb–Cl(3)	2.434 (2)	Mg(1)–O(2)	2.079 (6)
Nb–Cl(4)	2.442 (2)	Mg(1)–O(3)	2.085 (6)
Nb–C(1)	2.050 (6)	Mg(1)–O(4)	2.061 (5)
Nb–C(8)	2.054 (6)	Mg(2)–Cl(5)	2.525 (3)
Nb–O(1)	2.298 (4)	Mg(2)–Cl(6)	2.488 (3)
C(1)–C(2)	1.477 (8)	Mg(2)–Cl(7)	2.502 (2)
C(1)–C(8)	1.300 (8)	Mg(2)–O(5)	2.093 (5)
C(8)–C(9)	1.487 (9)	Mg(2)–O(6)	2.086 (5)
Mg(1)–Cl(5)	2.470 (3)	Mg(2)–O(7)	2.062 (5)
Angles			
Cl(1)–Nb–Cl(2)	87.44 (6)	Cl(3)–Nb–O(1)	81.6 (1)
Cl(1)–Nb–Cl(3)	163.85 (6)	Cl(4)–Nb–C(1)	111.7 (2)
Cl(1)–Nb–Cl(4)	90.78 (6)	Cl(4)–Nb–C(8)	87.6 (2)
Cl(1)–Nb–C(1)	110.7 (2)	Cl(4)–Nb–O(1)	81.9 (1)
Cl(1)–Nb–C(8)	84.1 (2)	C(1)–Nb–C(8)	36.9 (2)
Cl(1)–Nb–O(1)	82.3 (1)	C(1)–Nb–O(1)	160.4 (2)
Cl(2)–Nb–Cl(3)	90.40 (6)	C(8)–Nb–O(1)	162.6 (2)
Cl(2)–Nb–Cl(4)	163.13 (6)	Nb–C(1)–C(2)	147.3 (5)
Cl(2)–Nb–C(1)	84.6 (2)	Nb–C(1)–C(8)	71.7 (4)
Cl(2)–Nb–C(8)	108.9 (2)	C(2)–C(1)–C(8)	140.9 (6)
Cl(2)–Nb–O(1)	81.3 (1)	Nb–C(8)–C(1)	71.4 (4)
Cl(3)–Nb–Cl(4)	86.65 (6)	Nb–C(8)–C(9)	146.9 (5)
Cl(3)–Nb–C(1)	85.0 (2)	C(1)–C(8)–C(9)	141.3 (6)
Cl(3)–Nb–C(8)	111.7 (2)		

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

through the bridging oxygen atom. Selected distances and angles are given in Table IX.

The most striking and important features of this structure are to be found in the relationship of the bridging PhCCPh molecule to the Nb_2 unit. The C(2)–C(1)–C(1)′–C(2)′ chain is both markedly bent and distinctly nonplanar. The C(2)–C(1)–C(1)′ angle is 125.3 (6)°, and the torsion angle about the C(1)–C(1)′ bond is 43.8 (7)°. In addition, the C(1)–C(1)′ bond is far from being either perpendicular or parallel to the Nb–Nb bond, but instead it makes an angle (θ) of 58.6 (3)° when projected down the 2-fold axis that passes through the midpoints of both. Another way to represent the strongly skewed orientation of the alkyne C–C bond relative to the Nb–Nb bond is to note that the two distinct Nb–C distances are very different, one being strongly bonding (2.014 (6) Å) and the other only weakly bonding (2.453 (7) Å).

This structure is not directly analogous to *any* previously reported structure in *all* respects, but each of its features has some precedent. In comparing it with the previously studied ditantalum compound,[3] $Ta_2Cl_6(Me_3CCCCMe_3)(THF)_2$, we note first that in the tantalum compound there are three bridging ligands and three terminal ligands on each end, while in $Nb_2Cl_4O(PhCCPh)(THF)_4$ there are two bridging ligands and four terminal ligands on each end. However, there are several important similarities: (1) In each case there is a crystallographic 2-fold axis passing through the center of the alkyne C–C bond and the metal–metal bond. (2) The formal oxidation state of the metal atoms is the same. (3) The orientation of the alkyne C–C bond is oblique relative to the M–M direction. Quantitatively, the Ta_2C_2 unit shows differences from the present Nb_2C_2 unit. The latter has a much greater inequality in the two kinds of M–C distances, namely, ca. 0.45 Å as compared to only ca. 0.20 Å in the Ta case.

A much more similar situation is found in the compound $W_2Cl_4(NMe_2)_2(\mu\text{-}MeCCMe)(py)_2$, reported by Chisholm and co-workers.[13] In this case the coordination geometry at the metal

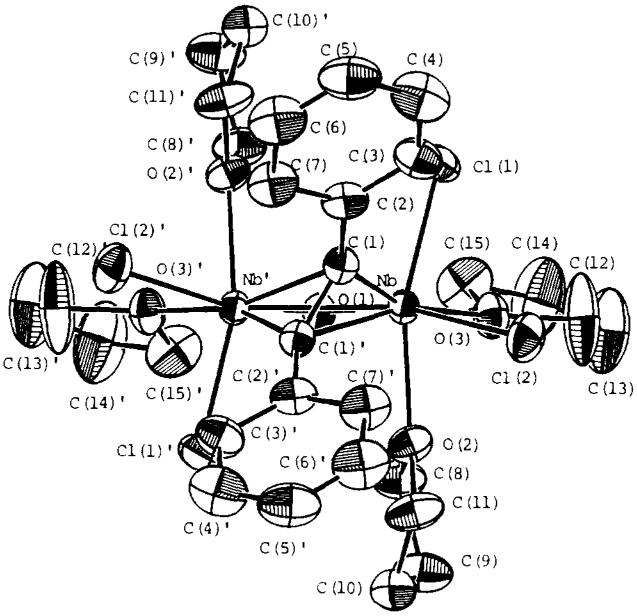

Figure 5. ORTEP drawing of the molecule $Nb_2O(PhCCPh)Cl_4(THF)_4$, showing the atom-labeling scheme. The thermal ellipsoids enclose 50% of electron density. A crystallographic C_2 axis runs through the midpoint of the Nb–Nb′ bond and the bridging atom O(1).

Table IX. Important Bond Distances (Å) and Angles (deg) for $Nb_2O(PhCCPh)Cl_4(THF)_4$[a]

Distances			
Nb–Nb′	2.737 (1)	Nb–O(3)	2.339 (5)
Nb–Cl(1)	2.403 (2)	Nb–C(1)	2.014 (6)
Nb–Cl(2)	2.451 (2)	Nb–C(1)′	2.453 (7)
Nb–O(1)	1.929 (4)	C(1)–C(1)′	1.378 (11)
Nb–O(2)	2.230 (5)		
Angles			
Cl(1)–Nb–Cl(2)	95.07 (8)	O(1)–Nb–O(3)	82.3 (2)
Cl(1)–Nb–O(1)	95.63 (6)	O(1)–Nb–C(1)	102.6 (2)
Cl(1)–Nb–O(2)	156.1 (1)	O(1)–Nb–C(1)′	88.4 (2)
Cl(1)–Nb–O(3)	78.1 (1)	O(2)–Nb–O(3)	78.2 (2)
Cl(1)–Nb–C(1)	85.4 (2)	O(2)–Nb–C(1)	118.1 (2)
Cl(1)–Nb–C(1)′	117.8 (2)	O(2)–Nb–C(1)′	86.1 (2)
Cl(2)–Nb–O(1)	162.85 (9)	O(3)–Nb–C(1)	163.1 (3)
Cl(2)–Nb–O(2)	81.0 (1)	O(3)–Nb–C(1)′	162.5 (2)
Cl(2)–Nb–O(3)	86.8 (1)	C(1)–Nb–C(1)′	34.2 (3)
Cl(2)–Nb–C(1)	91.6 (2)	Nb–O(1)–Nb′	90.4 (2)
Cl(2)–Nb–C(1)′	98.4 (2)	Nb–C(1)–Nb′	74.8 (2)
O(1)–Nb–O(2)	83.8 (1)	C(1)–C(1)′–C(2)′	125.3 (6)

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

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[13] Ahmed, K. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *Organometallics* **1986**, *5*, 2171.

Table IV. Positional and Equivalent Isotropic Thermal Parameters for $[Mg_2Cl_3(THF)_6][NbCl_4(PhCCPh)(THF)]\cdot0.5THF$

atom	*x*	*y*	*z*	*B*,[a] Å^2
Nb	0.56669 (5)	0.67983 (3)	0.31554 (3)	2.24 (1)
Cl(1)	0.3939 (2)	0.7957 (1)	0.2859 (1)	3.44 (3)
Cl(2)	0.6844 (2)	0.7866 (1)	0.3751 (1)	3.53 (3)
Cl(3)	0.7097 (2)	0.5574 (1)	0.3812 (1)	3.31 (3)
Cl(4)	0.4189 (2)	0.5647 (1)	0.2939 (1)	3.64 (3)
C(1)	0.7083 (6)	0.6963 (4)	0.2309 (4)	2.6 (1)
C(2)	0.8486 (6)	0.6964 (4)	0.2132 (4)	2.9 (1)
C(3)	0.8916 (7)	0.7051 (5)	0.1359 (4)	4.0 (2)
C(4)	1.0247 (8)	0.7033 (6)	0.1205 (5)	5.5 (2)
C(5)	1.1133 (7)	0.6952 (6)	0.1818 (5)	5.2 (2)
C(6)	1.0701 (6)	0.6873 (5)	0.2594 (5)	4.0 (2)
C(7)	0.9389 (6)	0.6874 (4)	0.2759 (4)	3.3 (1)
C(8)	0.5960 (6)	0.7035 (4)	0.1955 (4)	2.8 (1)
C(9)	0.5362 (6)	0.7262 (5)	0.1155 (4)	3.7 (1)
C(10)	0.5830 (9)	0.7947 (6)	0.0600 (5)	5.2 (2)
C(11)	0.520 (1)	0.8198 (7)	−0.0138 (5)	6.6 (2)
C(12)	0.4175 (8)	0.7769 (6)	−0.0317 (5)	5.5 (2)
C(13)	0.3736 (7)	0.7069 (7)	0.0196 (5)	5.5 (2)
C(14)	0.4306 (7)	0.6795 (7)	0.0971 (4)	5.3 (2)
O(1)	0.4694 (4)	0.6596 (3)	0.4376 (3)	3.5 (1)
C(15)	0.3323 (6)	0.6507 (6)	0.4564 (5)	4.5 (2)
C(16)	0.3128 (7)	0.6820 (6)	0.5342 (4)	4.4 (2)
C(17)	0.4465 (8)	0.6642 (6)	0.5753 (5)	4.9 (2)
C(18)	0.5386 (8)	0.6397 (8)	0.5148 (5)	6.1 (2)
Mg(1)	0.0204 (2)	0.2944 (1)	0.2303 (1)	3.07 (4)
Mg(2)	−0.0122 (2)	0.0878 (1)	0.2350 (1)	2.98 (4)
Cl(5)	0.1914 (2)	0.1727 (1)	0.2419 (1)	4.49 (4)
Cl(6)	−0.0962 (2)	0.1869 (1)	0.3279 (1)	4.25 (4)
Cl(7)	−0.0803 (2)	0.2145 (1)	0.1277 (1)	4.11 (4)
O(2)	−0.1336 (6)	0.3891 (3)	0.2086 (3)	5.5 (1)
O(3)	0.1302 (6)	0.3763 (3)	0.1481 (3)	5.5 (1)
O(4)	0.0832 (5)	0.3567 (3)	0.3205 (3)	4.1 (1)
O(5)	−0.1933 (5)	0.0328 (3)	0.2275 (3)	4.7 (1)
O(6)	0.0761 (5)	0.0133 (3)	0.1555 (3)	4.2 (1)
O(7)	0.0371 (5)	−0.0140 (3)	0.3273 (3)	4.5 (1)
C(19)	−0.162 (1)	0.4463 (6)	0.1329 (6)	6.5 (2)
C(20)	−0.305 (1)	0.4700 (9)	0.1370 (6)	9.1 (3)
C(21)	−0.360 (1)	0.4020 (9)	0.1967 (7)	10.2 (3)
C(22)	−0.262 (1)	0.378 (1)	0.2506 (8)	12.4 (4)
C(23)	0.229 (1)	0.4319 (8)	0.1674 (6)	10.8 (3)
C(24)	0.307 (1)	0.454 (1)	0.0925 (9)	16.3 (5)
C(25)	0.302 (1)	0.375 (1)	0.0594 (9)	12.2 (4)
C(26)	0.162 (2)	0.355 (1)	0.0704 (6)	13.9 (4)
C(27)	0.1411 (9)	0.3098 (6)	0.3932 (5)	5.8 (2)
C(28)	0.0881 (8)	0.3613 (6)	0.4555 (5)	5.5 (2)
C(29)	0.0805 (8)	0.4571 (5)	0.4121 (4)	5.3 (2)
C(30)	0.048 (1)	0.4523 (6)	0.3288 (6)	8.2 (3)
C(31)	−0.230 (1)	−0.0277 (8)	0.1784 (8)	12.0 (3)
C(32)	−0.3754 (9)	−0.0251 (7)	0.1742 (6)	7.3 (3)
C(33)	−0.4223 (9)	0.0215 (8)	0.2361 (7)	8.1 (3)
C(34)	−0.313 (1)	0.064 (1)	0.2663 (8)	11.7 (3)
C(35)	0.134 (1)	0.0582 (7)	0.0792 (6)	7.5 (3)
C(36)	0.248 (1)	−0.0109 (8)	0.0732 (8)	11.8 (3)
C(37)	0.208 (1)	−0.0922 (8)	0.0995 (7)	10.9 (3)
C(38)	0.126 (2)	−0.0753 (8)	0.1744 (8)	14.3 (4)
C(39)	0.154 (1)	−0.0097 (8)	0.3756 (7)	10.4 (3)
C(40)	0.147 (2)	−0.0971 (9)	0.4366 (8)	12.9 (5)
C(41)	0.035 (1)	−0.1401 (8)	0.4236 (8)	13.6 (4)
C(42)	−0.041 (1)	−0.0789 (9)	0.3668 (9)	12.7 (4)
O(8)	0.365 (3)	0.016 (2)	0.508 (2)	16.8 (9)*
C(43)	0.412 (3)	0.079 (2)	0.472 (2)	11.3 (8)*
C(44)	0.539 (2)	0.069 (1)	0.496 (1)	16.3 (7)*
C(45)	0.527 (5)	−0.030 (4)	0.567 (3)	22 (2)*

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

Table V. Positional and Equivalent Isotropic Thermal Parameters for $Nb_2OCl_4(PhCCPh)(THF)_4$

atom	*x*	*y*	*z*	*B*,[a] Å^2
Nb	0.07421 (3)	0.15756 (6)	0.27245 (3)	2.26 (1)
Cl(1)	0.07505 (9)	0.1330 (2)	0.14822 (9)	3.57 (4)
Cl(2)	0.1887 (1)	0.2936 (2)	0.3378 (1)	4.21 (4)
O(1)	0.000	0.0193 (6)	0.250	2.2 (1)
O(2)	0.1081 (3)	0.1122 (5)	0.3998 (3)	3.2 (1)
O(3)	0.1513 (2)	−0.0321 (5)	0.2980 (3)	3.5 (1)
C(1)	0.0118 (3)	0.3245 (7)	0.2220 (3)	2.6 (1)
C(2)	0.0024 (4)	0.4403 (7)	0.1666 (4)	3.1 (1)
C(3)	0.0585 (4)	0.4682 (9)	0.1484 (4)	4.0 (2)
C(4)	0.0482 (5)	0.5763 (9)	0.0955 (5)	5.2 (2)
C(5)	−0.0174 (6)	0.6529 (9)	0.0610 (5)	5.4 (2)
C(6)	−0.0719 (5)	0.6235 (9)	0.0803 (5)	5.0 (2)
C(7)	−0.0635 (4)	0.5180 (8)	0.1344 (4)	4.0 (2)
C(8)	0.1045 (4)	−0.0269 (8)	0.4250 (4)	4.1 (2)
C(9)	0.1446 (5)	−0.015 (1)	0.5178 (4)	5.2 (2)
C(10)	0.1234 (4)	0.1236 (9)	0.5302 (4)	4.2 (2)
C(11)	0.1262 (5)	0.2084 (9)	0.4659 (4)	4.8 (2)
C(12)	0.2315 (5)	−0.030 (1)	0.3260 (8)	8.6 (3)
C(13)	0.2538 (6)	−0.172 (1)	0.3388 (9)	8.9 (4)
C(14)	0.1880 (6)	−0.256 (1)	0.2888 (8)	8.4 (4)
C(15)	0.1210 (5)	−0.1627 (9)	0.2580 (5)	5.1 (2)

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

Table VI. Important Bond Distances (Å) and Bond Angles (deg) for $NbCl_3(THF)_2(PhCCPh)$[a]

Distances			
Nb–Cl(1)	2.407 (2)	Nb–C(1)	2.067 (6)
Nb–Cl(2)	2.387 (2)	Nb–C(8)	2.072 (7)
Nb–Cl(3)	2.385 (2)	C(1)–C(2)	1.453 (9)
Nb–O(1)	2.203 (4)	C(1)–C(8)	1.307 (10)
Nb–O(2)	2.381 (5)	C(8)–C(9)	1.473 (10)
Angles			
Cl(1)–Nb–Cl(2)	162.02 (6)	Cl(3)–Nb–C(8)	112.3 (2)
Cl(1)–Nb–Cl(3)	89.02 (8)	O(1)–Nb–O(2)	81.3 (2)
Cl(1)–Nb–O(1)	84.0 (1)	O(1)–Nb–C(1)	115.8 (2)
Cl(1)–Nb–O(2)	83.4 (1)	O(1)–Nb–C(8)	85.2 (2)
Cl(1)–Nb–C(1)	109.4 (2)	O(2)–Nb–C(1)	159.0 (3)
Cl(1)–Nb–C(8)	87.1 (2)	O(2)–Nb–C(8)	164.2 (2)
Cl(2)–Nb–Cl(3)	100.17 (8)	C(1)–Nb–C(8)	36.8 (3)
Cl(2)–Nb–O(1)	82.4 (1)	Nb–C(1)–C(2)	143.2 (6)
Cl(2)–Nb–O(2)	83.0 (1)	Nb–C(1)–C(8)	71.8 (4)
Cl(2)–Nb–C(1)	87.1 (2)	C(2)–C(1)–C(8)	144.6 (7)
Cl(2)–Nb–C(8)	103.3 (2)	Nb–C(8)–C(1)	71.4 (4)
Cl(3)–Nb–O(1)	160.8 (1)	Nb–C(8)–C(9)	147.5 (5)
Cl(3)–Nb–O(2)	80.2 (1)	C(1)–C(8)–C(9)	141.1 (6)
Cl(3)–Nb–C(1)	83.4 (2)		

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

Cl–Nb–Cl or Cl–Nb–O angles.

In each case, as in the previously reported $[TaCl_4(PhCCPh)py]^-$ ion, the metal–carbon bonds are in a range, 2.03–2.07 Å, that indicates the existence of M–C single bonds, while the C–C distances of about 1.31 Å are consistent with the retention of a C=C double bond. Moreover, the metal–ligand bond trans to the alkyne is relatively long in relation to the size of the ligand atom. For example, while the two Nb–O distances for THF molecules *cis* to the alkyne are 2.20 Å, those *trans* are in the range 2.30–2.38 Å.

All of these principal features of the structures **1**–**3** and the $[TaCl_4(PhCCPh)py]^-$ ion lead us to the conclusion that the alkynes in these molecules behave like diatomic surrogates for terminal O or NR ligands. The latter have recently been thoroughly reviewed by Nugent and Mayer.[12] The metal atoms in these molecules and anions should thus be assigned formal oxidation states of V. They might be more realistically described as metallacyclopropene compounds than as metal alkyne complexes.

Structure of $Nb_2Cl_4O(PhCCPh)(THF)_4$. A drawing of the molecule is presented in Figure 5. This view was particularly chosen to display the marked deviations from potential orthogonality or coplanarity of equivalent portions of the molecule. The molecule has a crystallographic 2-fold axis of symmetry passing through the midpoints of the C(1)–C(1)′ and Nb–Nb′ bonds and

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[12] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.

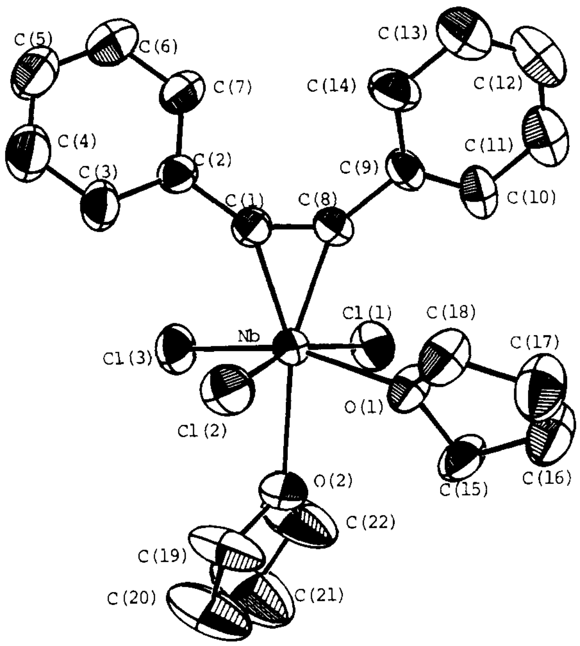

Figure 1. ORTEP drawing of the molecule $NbCl_3(PhCCPh)(THF)_2$ (**1**), showing the atom-labeling scheme. The thermal ellipsoids enclose 50% of electron density.

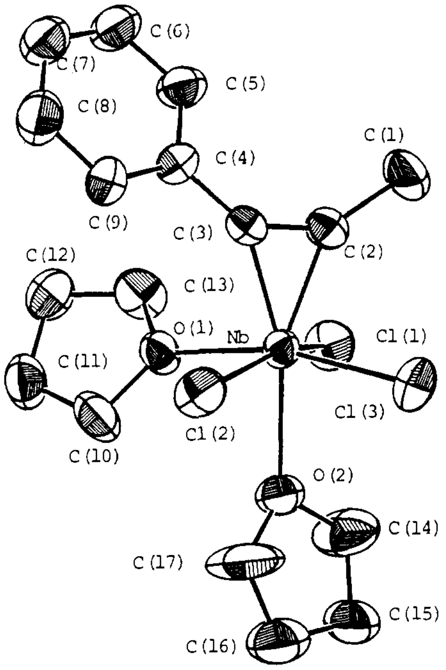

Figure 2. Molecular structure of $NbCl_3(PhCCCH_3)(THF)_2$ (**2**), showing the atomic numbering scheme. The thermal ellipsoids enclose 50% of electron density.

2.052 Å and a C–C distance of 1.30 (1) Å. The four Nb–Cl distances in this anion are all slightly longer (0.03–0.05 Å) than those in **1** and **2**, which is an expected consequence of having four in an anion rather than three in a neutral molecule.

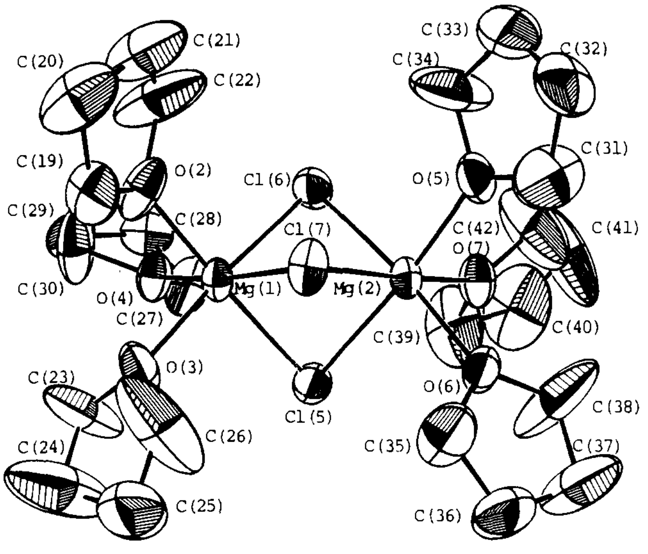

Figure 3. ORTEP view of the cation $[Mg_2Cl_3(THF)_6]^+$, showing 50% probability ellipsoids and the atomic numbering scheme.

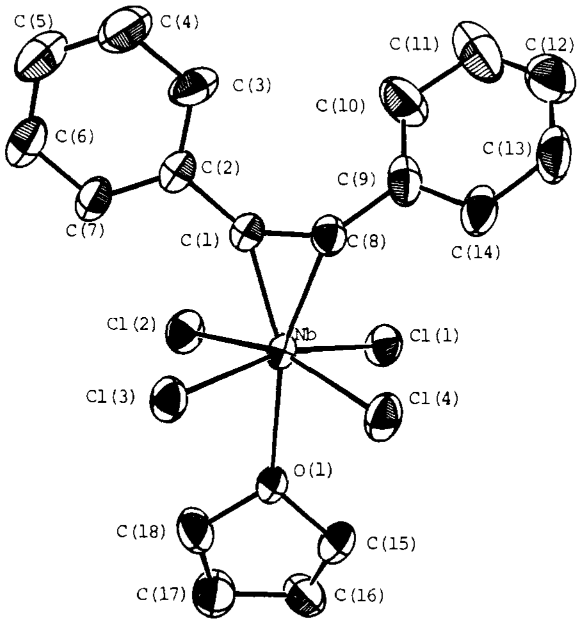

Figure 4. ORTEP view of the anion $[NbCl_4(PhCCPh)(THF)]^-$, showing 50% probability ellipsoids and the atomic numbering scheme.

The binuclear cation is of an unusual type, unprecedented so far as we know for magnesium. However, there are rather similar $[V_2Cl_3(THF)_6]^+$, $[V_2Br_3(THF)_6]^+$, and $[V_2Cl_3(PR_3)_6]^+$ ions$^{9-11}$ with which it may be compared. Whether it exists in solution, we do not know. It is possible that it forms only in the process of crystallization as a counterion of proper charge, size, and shape to combine with the anion in a stable crystalline phase.

The $[NbCl_4(PhCCPh)(THF)]^-$ ions is rather similar to the previously reported $[TaCl_4(PhCCPh)py]^-$ ion. The M–Cl distances in the two cases are virtually identical, and the metal–alkyne interactions are characterized by distances and angles so similar that the differences are barely if at all significant.

Structure and Bonding in the Mononuclear Complexes Generally. The anion and the two molecules described here are essentially similar, and they closely resemble the previously reported^{1,2} tantalum species. In each case the orientation of the alkyne C–C bond is the same. Its projection onto the mean plane of the approximately square-pyramidal array of four Cl atoms or three Cl atoms and an oxygen atom is such as to bisect a pair of opposite

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(9) (a) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377. (b) Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913. (d) Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1987**, *6*, 1433.

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atoms is again rather different from that in the present case, but the characteristics of the RCCR bridge are very similar. Thus, the torsion, C–C–C, and θ angles are 42, 125, and 55°, as compared to 43.8 (7), 125.3 (6), and 58.6 (3)°, respectively, in the present case. To explain the occurrence of the intermediate (i.e., neither perpendicular nor parallel) orientation of the bridging CH_3CCCH_3 molecule in the Chisholm compound, Calhorda and Hoffmann[14] examined model systems by employing extended Hückel calculations and came to the conclusion that the actual geometry could be attributed to second-order Jahn–Teller distortion from a truly perpendicular geometry.

To understand the deviation of the PhCCPh molecule from the perpendicular orientation to the Nb–Nb bond in our case, both SCF-Xα-Sw and Fenske–Hall molecular orbital calculations have been performed[15] on $Nb_2Cl_4O(PhCCPh)(THF)_4$. The results show that the deviation may also be explained in terms of second-order Jahn–Teller distortion. The detailed results and discussion for this and other compounds will be reported later.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for financial support (Grant No. A-494).

Supplementary Material Available: For **1**–**4**, tables of complete bond distances and angles and anisotropic displacements and figures showing stereoviews of unit cell contents and disorder of the THF solvent molecule (27 pages); tables of calculated and observed structure factors (76 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
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Multiply Bonded Dimetal Fluoroalkoxides. 1. Pentafluorophenoxides of Dimolybdenum and Ditungsten

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A series of dimolybdenum and ditungsten pentafluorophenoxides has been prepared by alcoholysis of $M_2(NMe_2)_6$ (M = Mo, W) with pentafluorophenol. $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ has been isolated both from the reaction of $Mo_2(NMe_2)_6$ with 6 equiv of pentafluorophenol (**1a**) and as a disproportionation product with 2 equiv of pentafluorophenol (**1b**). The crystals are different but contain molecules with essentially identical structural features. Eight equivalents of pentafluorophenol react with $Mo_2(NMe_2)_6$ in benzene to yield $Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2{\cdot}2C_6H_6$ (**2**). From reactions with 10 or 12 equiv of pentafluorophenol, only low yields of $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**) and $[(NH_2Me_2)_2][Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4]$ (**4**) have been isolated, both of which are structurally characterized. $W_2(OC_6F_5)_6(NHMe_2)_2$ (**5**) has been prepared from the reaction of 10 equiv of pentafluorophenol with $W_2(NMe_2)_6$ and structurally characterized. Crystallographic parameters of these five alkoxides are as follows. $Mo_2(OC_6F_5)_4(NMe_2)_2(NHMe_2)_2$ (**1a**): space group $C2/c$, a = 21.511 (5) Å, b = 9.057 (2) Å, c = 20.581 (3) Å, β = 103.88 (1)°, V = 3892 (1) Å^3, Z = 4. **1b**: space group $Pbcn$, a = 24.177 (4) Å, b = 10.927 (3) Å, c = 14.475 (3) Å, V = 3824 (1) Å^3, Z = 4. $Mo_2(OC_6F_5)_5(NMe_2)(NHMe_2)_2{\cdot}2C_6H_6$ (**2**) space group $P\bar{1}$, a = 11.785 (3) Å, b = 20.062 (4) Å, c = 11.686 (2) Å, α = 93.14 (2)°, β = 91.39 (2)°, γ = 73.80 (2)°, V = 2649 (1) Å^3, Z = 2. $Mo_2(OC_6F_5)_4(NHMe_2)_4$ (**3**): space group $C2/c$, a = 19.799 (8) Å, b = 8.995 (7) Å, c = 22.248 (6) Å, β = 96.54 (3)°, V = 3937 (1) Å^3, Z = 4. $[(NH_2Me_2)_2][Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4)]$ (**4**): space group $C2/c$, a = 13.233 (2) Å, b = 11.276 (3) Å, c = 25.178 (4) Å, β = 102.82 (1)°, V = 3663 (1) Å^3, Z = 4. $W_2(OC_6F_5)_6(NHMe_2)_2$ (**5**): space group $C2/c$, a = 10.766 (4) Å, b = 22.020 (7) Å, c = 19.463 (5) Å, β = 96.78 (2)°, V = 4582 (3) Å^3, Z = 4.

Introduction

Since the discovery of the first $X_3M{\equiv}MX_3$ type compounds (M = Mo, W; X = CH_2SiMe_3),[1,2] the preparation and characterization of additional group 6 dimers possessing an unbridged $\sigma^2\pi^4$ metal–metal bond has continued to be of much interest. $Mo_2(NMe_2)_6$[3] and $W_2(NMe_2)_6$[4] were the next dimers to be characterized in this series, with the hexakis(amides) soon becoming the starting materials used to produce a host of multiply bonded dimolybdenum and ditungsten alkoxides and mixed-ligand compounds.[5] Although $X_3Cr{\equiv}CrX_3$ compounds have been the subject of theoretical studies, no examples are known.[6]

Alcoholysis of $Mo_2(NMe_2)_6$ results in compounds of the form $Mo_2(OR)_6$ or $Mo_2(OR)_6(NHMe_2)_2$, where R = Pr^i, Bu^t, Bu^{t}CH$_2$, Me$_2$PhC, Me$_3$Si, or Et$_3$Si.[7] $NHMe_2$ groups can be displaced by other σ-donors such as NHMeEt, $NHEt_2$, pyridine, or PR_3, and heating the non-siloxide compounds to 60 °C in vacuo removes two $NHMe_2$ groups, leaving $Mo_2(OR)_6$. $W_2(OSiMe_3)_6(NHMe_2)_2$, isolable by the analogous alcoholysis reaction with $W_2(NMe_2)_6$,[8] exhibits far less thermal stability; heating in vacuum

Table I. Structural Features for Triply Bonded Dimolybdenum Compounds[a]

	bond dist, Å			
compd	Mo–Mo	Mo–N,O	Mo–Cl,C,S	ref
$Mo_2(NMe_2)_6$	2.214 [3]	1.98 [1]		3
$Mo_2(OCH_2Bu^t)_6$	2.222 (2)	1.88 [2]		7
$Mo_2(2,6\text{-}Me_2ArO)_4(OPr^i)_2$	2.245 (4)	1.885 [2] (OPr^i) 1.900 [2] (OAr)		9
$Mo_2(2,6\text{-}Me_2ArO)_4(NMe_2)_2$	2.227 (1)	1.94 [2] (OAr) 1.908 (4) (N)		10
$Mo_2(2\text{-}Bu^t\text{-}6\text{-}MeArO)_2(NMe_2)_4$	2.198 (14)	1.99 [2] (OAr) 1.944 [9] (N)		12
$Mo_2Cl_2(NMe_2)_4$	2.201 [1]	1.93 [1]	2.348 [5]	15
$Mo_2Me_2(NMe_2)_4$	2.201 [1]	1.954 [3]	2.175 [2]	17
$Mo_2(CH_2pyMe)_2(NMe_2)_4$	2.204 (1)	1.952 [8]	2.184 [7]	19
$Mo_2Me_2(OBu^t)_4(py)_2$	2.256 (1)	1.92 [6] (OR) 2.349 (6) (py)	2.167 [7]	20
$Mo_2(SBu^t)_2(NMe_2)_4$	2.2171 (1)	1.954 [5]	2.364 [1]	21

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Standard deviation given in square brackets is calculated as equal to $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$ in which Δ_i is the deviation of the ith of n values from the arithmetic mean of the set.

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