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Reactions of $Nb_2Cl_6(SMe_2)_3$ and $Ta_2Cl_6(SMe_2)_3$ with Compounds Containing N–N Single Bonds

JO ANN M. CANICH, F. ALBERT COTTON*, LARRY R. FALVELLO

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Tex. 77843, U.S.A.

and STAN A. DURAJ

Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115, U.S.A.

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Abstract

$Ta_2Cl_6(SMe_2)_3$ reacts with PhHNNHPh to afford $Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}PhN)(PhNH_2)_3$ (1) a compound with a Ta^{IV}–Ta^{IV} single bond, with a length of 2.644(1) Å. The compound crystallizes in space group *Pnma* with unit cell dimensions $a = 22.960(8)$, $b = 16.875(4)$, $c = 6.367(3)$ Å, $V = 2467(1)$ Å^3, and $Z = 4$. The reaction of $Nb_2Cl_6(SMe_2)_3$ with PhHC=NN=CHPh, merely on mixing at room temperature produced $Nb_2Cl_6(SMe_2)[PhHC(N)PhHCNHN{=}CHPh]\cdot C_7H_8$ (2) as large red crystals in *ca.* 50% yield. The molecule consists of two Nb^{IV} atoms, one six-coordinate and the other seven-coordinate, united by three bridging atoms (Cl, Cl, N) and a Nb–Nb bond of length 2.681(1) Å. The way in which the tridentate triazo ligand is generated is completely obscure. Crystallographic data for 2: space group $P2_1/n$ with $a = 11.393(3)$, $b = 11.988(3)$, $c = 27.233(7)$ Å, $\beta = 100.75(2)°$, $V = 3654(3)$ Å, and $Z = 4$.

Introduction

One of the reasons why multiple bonds between metal atoms are interesting is that they are versatile reactive centers [1]. They can be employed in the synthesis of other compounds in which the M–M bond order is lower, or even zero. Many of these reactions have as their first (and perhaps only) step oxidative addition of a main group single or multiple bond across the M–M bond. To mention just a few illustrative cases, the reactions of –S–S– bonds with Mo=Mo [2] and Ta=Ta [3] bonds, the reactions of –O–O– and Cl–Cl bonds with Mo=Mo [4], the reactions of –N=N– bonds with Nb=Nb [5] and Ta=Ta [6] bonds, and the reactions of –N=O with W=W [7] have all been observed and products characterized.

The results reported here were obtained by examining the reactions of several compounds containing =N–N= bonds with the M=M bonds of the $M_2Cl_6(SMe_2)_3$ molecules in which M = Nb or Ta. The reactions proceed readily under mild conditions, but the products so far isolated and characterized are surprising (in one case bizarre is not too strong a word) and the way in which they are formed is quite unknown.

Experimental

All manipulations were carried out under an atmosphere of argon using standard Schlenk and vacuum line techniques. Commercial grade benzene, toluene and hexane were distilled from benzophenone ketyl prior to use. The compounds $Ta_2Cl_6(SMe_2)_3$ and $Nb_2Cl_6(SMe_2)_3$ were prepared by literature methods [8] which involved the sodium amalgam reduction of $TaCl_5$ or $NbCl_5$ in the presence of dimethylsulfide. Benzaldehyde azine was purchased from Lancaster Synthesis Ltd. and 1,2-diphenylhydrazine was purchased from Aldrich Chemical Company. Both reagents were used without further purification. The infrared spectrum was recorded on a Perkin-Elmer 783 spectrophotometer. Peaks coinciding with Nujol are not reported. Elemental analyses were performed by Galbraith Laboratories, Inc.

Preparation and Crystallization of $Ta_2(\mu\text{-}NPh)(\mu\text{-}Cl)_2Cl_4(H_2NPh)_2$ (1)

A benzene solution (15 ml) of $Ta_2Cl_6(SMe_2)_3$ (0.50 g, 0.66 mmol) was filtered into a round bottom flask equipped with a side arm and stir bar. To this, 0.18 g PhHNNHPh (0.98 mmol) in 10 ml benzene was added. The reaction mixture was stirred at room temperature for one week to form a fine yellow–green precipitate. Yield: 0.21 g, 38.0%. IR (CsI, Nujol) cm^{-1}: 3280(s), 3220(s), 3105(w), 1594(s),

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*Author to whom correspondence should be addressed.

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1560(s), 1487(s), 1475(s), 1282(vw), 1250(w), 1234(vw), 1212(m), 1178(m), 1150(vw), 1092(vs, br), 1067(s, sh), 1020(s), 997(w), 983(vw), 975(vw), 938(w), 930(w), 888(mw), 858(w, br), 835(w), 813(w), 798(s), 768(s), 754(vw), 722(w), 690(s), 680(s), 640(m), 630(w), 610(mw), 554(w), 542(mw), 522(s), 470(w), 442(vw, br), 388(mw), 368(s), 343(s), 322(vs, br), 262(s). *Anal.* Calc. for $Ta_2Cl_6N_3C_{18}H_{19}$: C, 25.37; H, 2.25; N, 4.93. Found: C, 25.21; H, 3.11; N, 4.99%.

X-ray quality crystals of **1** were grown in the following manner. $Ta_2Cl_6(SMe_2)_3$ (0.31 g, 0.41 mmol) was dissolved in 12 ml benzene, and filtered into a Schlenk tube. A 0.10 g (0.54 mmol) PhHN-NHPh solution (5 ml benzene, 10 ml hexane) was carefully layered on top. After one month, the Schlenk tube contained a brown solution and no crystals. After being left undisturbed for an additional two months, large block-shaped brown crystals had formed. They were shown by IR to be identical with the fine precipitate originally obtained.

Preparation and Crystallization of $Nb_2Cl_6(SMe_2)$-(NCHPhCHPhHNNCHPh) (2)

A toluene solution (12 ml) of $Nb_2Cl_6(SMe_2)_3$ (0.12 g, 0.21 mmol) was filtered into a Schlenk tube and layered with 0.043 g (0.21 mmol) PhHC=N–N=CHPh dissolved in a 10 ml 25/75 mixture of toluene and hexane. Diffusion of layers produced large red crystals which were identified as **2** by X-ray diffraction. Yield: 0.086 g, 48.6%.

Crystallographic Study

Crystals of **1** and **2** were grown as described above. Each compound was mounted in a glass capillary tube using epoxy resin. The geometric and intensity data for **1** and **2** were gathered on four-circle Syntex P$\bar{1}$ and Enraf-Nonius CAD-4 diffractometers, respectively. Routine unit cell identification and intensity data collection procedures have been described previously [9]. Compound **1** crystallizes in an orthorhombic primitive unit cell while compound **2** was found to be monoclinic. Symmetry and lattice dimensions were verified by axial photographs. Three standard reflections were monitored throughout the data collection, and showed no significant variation in intensity. Data sets were reduced by routine procedures using the Enraf-Nonius Structure Determination Package (SDP). Polarization, Lorentz and empirical absorption corrections based on azimuthal scans of nine reflections were applied to the intensity data. Experimental parameters pertaining to the crystallography are collected in Table I.

TABLE I. Crystal Data

Formula	$Ta_2Cl_6N_3C_{18}H_{19}$	$Nb_2Cl_6N_3SC_{30}H_{33}$
Formula weight	851.98	865.20
Space group	*Pnma*	$P2_1/n$
Systematic absences	$(0kl)$: $k + l = 2n + 1$ $(hk0)$: $h = 2n + 1$	$(hk0)$; $h + k = 2n$ $(0k0)$: $k \neq 2n$
a (Å)	22.960(8)	11.393(3)
b (Å)	16.875(4)	11.988(3)
c (Å)	6.367(3)	27.233(7)
β (°)		100.75(2)
V (Å^3)	2467(1)	3654(3)
Z	4	4
D_{calc} (g/cm^3)	2.29	1.574
Crystal size (mm)	0.65 × 0.25 × 0.20	0.5 × 0.3 × 0.2
μ(Mo Kα) (cm^{-1})	99.8	11.224
Data collection instrument	Syntex P$\bar{1}$	CAD-4
Radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
Orientation reflections, number, range (2θ)	15; 18 < 2θ < 40°	25, 17, 16 $\leqslant 2\theta \leqslant$ 31.02
Temperature (°C)	4 ± 2	22
Scan method	$\omega - 2\theta$	ω
Data collection range, 2θ (°)	3, 55	4, 45
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2356; 1379	4759; 3089
No. parameters refined	139	344
Transmission factors, max., min.	observed 1.00, 0.71	0.9992, 0.9043
R^a	0.0334	0.05087
$R_w{}^b$	0.0476	0.06582
Quality-of-fit indicator^c	1.016	1.858
Largest shift (e.s.d.), final cycle	0.07	0.01
Largest peak (e/Å^3)	1.02	0.901

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

Solution and Structure Refinement for Compound 1

Systematic absences in the intensity data narrowed the choice of space groups to $Pn2_1a$ or $Pnma$. The position of the unique tantalum atom was determined from the Patterson map and the space group $Pn2_1a$ was initially chosen, but found to be incorrect. The space group $Pnma$ was then tried, and allowed for a satisfactory solution and refinement. The remaining non-hydrogen atoms were located by use of alternating least-squares refinements and difference Fourier maps. A second empirical absorption correction [9] was made prior to final anisotropic refinement which converged to 0.0334 e/Å^3 (R_w = 0.0476 e/Å^3).

Solution and Structure Refinement for Compound 2

Systematic absences in the intensity data uniquely determined the space group as $P2_1/n$. The unique niobium atoms were located by use of a Patterson map. All other non-hydrogen atoms were found by using a series of least-squares refinement cycles and difference Fourier maps. An additional empirical absorption correction [9] was applied prior to anisotropic refinement of 2. All atoms with the exception of those in the interstitial toluene molecule were refined anisotropically.

The results of the normal refinement showed carbon atoms C(4) and C(5) to possess extremely large thermal parameters [B (Å^2) = 34(1), 27.5(8)], and unreasonably short S–C bond distances [S(1)–C(4) 1.61(3) Å and S(1)–C(5) 1.64(2) Å]. The actual S–C bond distances were calculated (1.954(29) Å for S(1)–C(4) and 1.874(23) Å for S(1)–C(5)) using the program ORRFE, whereby the bond distances were corrected for thermal motion with C(4) and C(5) treated as 'riding' on S(1). The reasonable S–C bond distances calculated from this procedure indicate that the bond distances calculated previously were artifically short because of the large thermal motion.

Results and Discussion

Compound 1

The atomic positional parameters resulting from the X-ray crystallographic study are listed in Table II. A drawing of the molecule is presented in Fig. 1, and bond distances and angles are listed in Table III. Crystallographic mirror symmetry is imposed on the molecule, with the atoms Cl(1), Cl(2), N(1), C(2) and C(4) lying in the mirror plane. The molecule is a face-sharing bioctahedron, structurally similar in a general way to the starting material, $Ta_2Cl_6(SMe_2)_3$, but with the SMe_2 ligands all replaced by others. The bridging ligand is a phenyl nitrene, C_6H_5N, group, and is structurally similar to other μ-nitrene ligands [10]. The three bonds to the bridging nitro-

TABLE II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for $Cl_2(NH_2Ph)Ta(\mu\text{-}Cl)_2(\mu\text{-}NPh)Ta(NH_2Ph)Cl_2$^{a}

Atom	x	y	z	B (Å^2)
Ta(1)	0.00181(2)	0.32833(2)	0.15838(6)	2.422(7)
Cl(1)	−0.0107(2)	0.250	0.4811(6)	3.24(9)
Cl(2)	−0.0860(2)	0.250	0.0678(8)	3.26(9)
Cl(3)	−0.0135(2)	0.4040(2)	−0.1495(5)	3.27(6)
Cl(4)	0.0769(2)	0.4024(2)	0.3118(6)	3.83(7)
N(1)	0.0538(6)	0.250	0.021(2)	2.9(3)
N(2)	−0.0547(5)	0.4272(6)	0.324(2)	3.4(2)
C(1)	0.1026(8)	0.250	−0.112(3)	3.0(4)
C(2)	0.1266(7)	0.3208(8)	−0.173(2)	4.4(3)
C(3)	0.1738(6)	0.321(1)	−0.311(2)	5.3(4)
C(4)	0.1977(9)	0.250	−0.388(4)	4.9(5)
C(5)	−0.1180(6)	0.4193(7)	0.312(2)	3.3(3)
C(6)	−0.1501(7)	0.4491(9)	0.144(2)	4.8(3)
C(7)	−0.2092(8)	0.437(1)	0.142(3)	7.4(5)
C(8)	−0.2377(9)	0.393(1)	0.303(3)	8.0(6)
C(9)	−0.2055(8)	0.367(1)	0.467(3)	6.6(5)
C(10)	−0.1468(7)	0.3798(9)	0.483(3)	5.7(4)

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

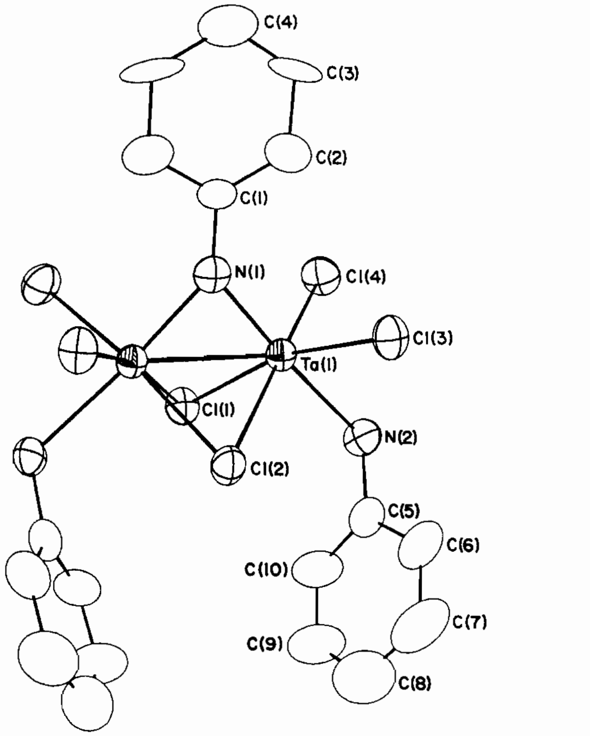


Fig. 1. An ORTEP drawing of the $Cl_2(NH_2Ph)Ta(\mu\text{-}Cl)_2(\mu\text{-}NPh)Ta(NH_2Ph)Cl_2$ molecule which also defines the labeling scheme. The thermal ellipsoids enclose 40% of electron density.

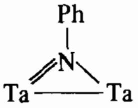
TABLE III. Table of Bond Distances (Å) and Angles (°) for Cl$_2$(NH$_2$Ph)Ta(μ-Cl)$_2$(μ-NPh)Ta(NH$_2$Ph)Cl$_2$[a]

Atom 1	Atom 2	Distance
Distances		
Ta(1)	Ta(1′)	2.644(1)
Ta(1)	Cl(1)	2.460(4)
Ta(1)	Cl(2)	2.478(4)
Ta(1)	Cl(3)	2.366(3)
Ta(1)	Cl(4)	2.342(3)
Ta(1)	N(1)	1.984(12)
Ta(1)	N(2)	2.363(11)
N(1)	C(1)	1.41(2)
N(2)	C(5)	1.46(2)
C(1)	C(2)	1.37(2)
C(2)	C(3)	1.40(2)
C(3)	C(4)	1.41(2)
C(5)	C(6)	1.40(2)
C(5)	C(10)	1.43(2)
C(6)	C(7)	1.37(3)
C(7)	C(8)	1.43(3)
C(8)	C(9)	1.35(3)
C(9)	C(10)	1.37(2)

Atom 1	Atom 2	Atom 3	Angle
Angles			
Ta(1′)	Ta(1)	Cl(1)	57.50(6)
Ta(1′)	Ta(1)	Cl(2)	57.77(6)
Ta(1′)	Ta(1)	Cl(3)	122.66(7)
Ta(1′)	Ta(1)	Cl(4)	122.26(9)
Ta(1′)	Ta(1)	N(1)	48.2(3)
Ta(1′)	Ta(1)	N(2)	134.9(3)
Cl(1)	Ta(1)	Cl(2)	79.2(2)
Cl(1)	Ta(1)	Cl(3)	164.7(1)
Cl(1)	Ta(1)	Cl(4)	91.4(1)
Cl(1)	Ta(1)	N(1)	94.6(4)
Cl(1)	Ta(1)	N(2)	86.7(3)
Cl(2)	Ta(1)	Cl(3)	88.5(1)
Cl(2)	Ta(1)	Cl(4)	168.5(2)
Cl(2)	Ta(1)	N(1)	91.8(4)
Cl(2)	Ta(1)	N(2)	91.9(3)
Cl(3)	Ta(1)	Cl(4)	99.6(1)
Cl(3)	Ta(1)	N(1)	94.8(4)
Cl(3)	Ta(1)	N(2)	84.7(3)
Cl(4)	Ta(1)	N(1)	95.6(4)
Cl(4)	Ta(1)	N(2)	80.8(3)
N(1)	Ta(1)	N(2)	176.2(4)
Ta(1)	Cl(1)	Ta(1′)	65.0(1)
Ta(1)	Cl(2)	Ta(1′)	64.5(1)
Ta(1)	N(1)	Ta(1′)	83.5(6)
Ta(1)	N(1)	C(1)	138.2(3)
Ta(1)	N(2)	C(5)	117.3(8)
N(1)	C(1)	C(2)	119(1)
C(2)	C(1)	C(2′)	121(2)
C(1)	C(2)	C(3)	120(2)
C(2)	C(3)	C(4)	121(2)
C(3)	C(4)	C(3′)	117(2)
N(2)	C(5)	C(6)	122(1)
N(2)	C(5)	C(10)	118(1)
C(6)	C(5)	C(10)	120(2)
C(5)	C(6)	C(7)	118(2)
C(6)	C(7)	C(8)	122(2)
C(7)	C(8)	C(9)	118(2)
C(8)	C(9)	C(10)	123(2)
C(5)	C(10)	C(9)	118(2)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

gen atom are coplanar within experimental error and the Ta–N distances (equal by symmetry) are short, 1.98(1) Å. The oxidation state of the Ta atoms is clearly IV and the Ta–Ta distance of 2.644(1) Å is indicative of a metal–metal bond. It appears that the nitrene bridge bonding can be formulated as the resonance hybrid **I**, where the N to Ta π bonds are dative in character and formed with the use of the formal lone pair of electrons on the N atom.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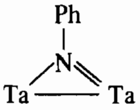

Ib

Other features of the structure of **1** are quite normal. The Ta–Cl bridge bonds are about 0.11 Å longer than the Ta–Cl terminal bonds. The other terminal ligands are undoubtedly aniline molecules, even though the amine hydrogen atoms were not observed. The infrared spectrum shows two N–H stretching bands at 3220 and 3280 cm^{-1} and the Ta–N(2) distance, 2.36(1) Å is appropriate.

The problem in fully understanding this compound is a chemical one concerning the way in which the three ligands, two C$_6$H$_5$NH$_2$ and one C$_6$H$_5$N, arise from the PhHNNHPh starting material. We have no evidence on this point and will refrain from speculating. Redox processes entailing hydrogen atom transfers must be involved and need not be considered surprising in a general sense.

Compound 2

This compound crystallizes as a toluene solvate, but the toluene molecule is interstitial and has no chemical interaction with the dinuclear complex. The atomic positional parameters are listed in Table IV and a drawing of the molecule is presented in Fig. 2. The entire molecule (together with a molecule of toluene) constitutes the crystallographic asymmetric unit. Thus no rigorous symmetry element occurs, nor does the molecule have any approximate symmetry. The interatomic distances and angles are listed in Tables V and VI, respectively.

TABLE IV. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for $Nb_2Cl_6(SMe_2)$(NCHPhCHPhHNNCHPh)$\cdot C_7H_8$[a]

Atom	*x*	*y*	*z*	*B* (Å^2)
Nb(1)	0.08443(7)	0.15083(7)	0.31470(3)	3.52(2)
Nb(2)	0.06045(7)	0.07401(7)	0.40475(3)	3.10(2)
Cl(1)	0.2194(2)	0.2112(2)	0.3911(1)	5.21(6)
Cl(2)	0.1804(2)	−0.0288(2)	0.3485(1)	4.57(6)
Cl(3)	0.0302(3)	0.3343(2)	0.2946(1)	6.08(7)
Cl(4)	0.0118(3)	0.0596(2)	0.2387(1)	5.41(7)
Cl(5)	0.0099(2)	0.2237(2)	0.4544(1)	4.80(6)
Cl(6)	0.1924(2)	−0.0164(2)	0.47613(9)	4.50(6)
S(1)	0.2728(3)	0.1853(4)	0.2685(1)	8.3(1)
N(1)	−0.0529(6)	0.1022(6)	0.3412(3)	3.3(2)
N(2)	−0.1128(6)	0.0154(6)	0.4185(3)	3.2(2)
N(3)	−0.0473(6)	−0.0809(6)	0.4072(3)	3.3(2)
C(1)	−0.1744(7)	0.0577(7)	0.3291(3)	2.9(2)
C(2)	−0.2182(7)	0.0503(7)	0.3792(3)	3.2(2)
C(3)	−0.0769(9)	−0.1758(7)	0.4220(4)	4.1(2)
C(4)	0.372(2)	0.261(3)	0.303(1)	34(1)
C(5)	0.359(2)	0.075(2)	0.275(1)	27.5(8)
C(11)	−0.2563(7)	0.1297(7)	0.2918(3)	3.3(2)
C(12)	−0.3195(8)	0.0817(9)	0.2482(4)	4.4(2)
C(13)	−0.3955(9)	0.147(1)	0.2134(4)	5.8(3)
C(14)	−0.4073(9)	0.260(1)	0.2216(4)	5.5(3)
C(15)	−0.3446(9)	0.3096(9)	0.2664(4)	5.6(3)
C(16)	−0.2657(8)	0.2442(8)	0.3018(4)	4.5(2)
C(21)	−0.3263(8)	−0.0234(8)	0.3782(4)	3.6(2)
C(22)	−0.4066(8)	0.0081(9)	0.4076(4)	4.6(2)
C(23)	−0.5107(9)	−0.059(1)	0.4090(5)	6.8(3)
C(24)	−0.526(1)	−0.156(1)	0.3817(5)	6.5(3)
C(25)	−0.444(1)	−0.190(1)	0.3519(4)	6.2(3)
C(26)	−0.3405(9)	−0.1231(8)	0.3504(4)	4.9(3)
C(31)	−0.0102(9)	−0.2752(8)	0.4185(4)	4.7(3)
C(32)	−0.066(1)	−0.3757(9)	0.4312(5)	6.5(3)
C(33)	−0.002(1)	−0.4762(9)	0.4290(5)	7.6(4)
C(34)	0.107(1)	−0.478(1)	0.4138(6)	8.2(4)
C(35)	0.158(1)	−0.383(1)	0.4015(5)	7.5(4)
C(36)	0.101(1)	−0.2764(9)	0.4040(5)	5.9(3)
C(41)	0.490(2)	0.345(2)	0.4693(8)	13.2(6)*
C(42)	0.475(2)	0.417(2)	0.4283(7)	12.1(5)*
C(43)	0.552(2)	0.455(2)	0.3985(9)	15.3(7)*
C(44)	0.677(2)	0.394(2)	0.4176(8)	13.2(6)*
C(45)	0.680(1)	0.327(2)	0.4590(7)	11.3(5)*
C(46)	0.597(2)	0.294(2)	0.4867(9)	15.2(7)*
C(47)	0.397(2)	0.328(2)	0.502(1)	20(1)*

[a] e.s.d.s *in the least significant digits are given in parentheses.* Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. Starred atoms were refined isotropically.

The molecule of compound **2** shows several broad features that are similar to those of compound **1**, namely, two niobium atoms at a bonded distance from each other, with four terminal chlorine atoms, two bridging chlorine atoms and a bridging nitrene nitrogen atom. In this case, the remaining neutral, terminal ligands are different. On Nb(1) a SMe_2

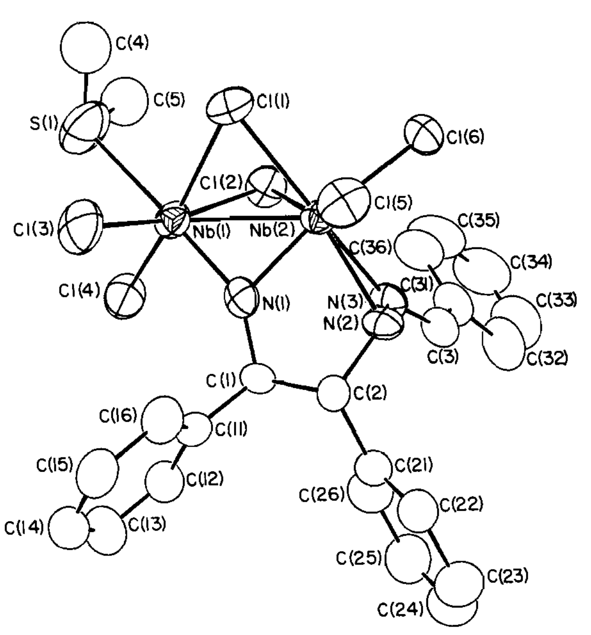


Fig. 2. An ORTEP drawing of the $Nb_2Cl_6(SMe_2)$(NCHPhCHPhNNCHPh) molecule which also defines the labeling scheme. The thermal ellipsoids enclose 40% cf electron density.

TABLE V. Table of Bond Distances (Å) for $Nb_2Cl_6(SMe_2)$(NCHPhCHPhHNNCHPh)$\cdot C_7H_8$[a]

Atom 1	Atom 2	Distance
Nb(1)	Nb(2)	2.681(1)
Nb(1)	Cl(1)	2.454(3)
Nb(1)	Cl(2)	2.511(3)
Nb(1)	Cl(3)	2.322(3)
Nb(1)	Cl(4)	2.351(3)
Nb(1)	S(1)	2.713(4)
Nb(1)	N(1)	1.932(8)
Nb(2)	Cl(1)	2.524(3)
Nb(2)	Cl(2)	2.551(3)
Nb(2)	Cl(5)	2.381(3)
Nb(2)	Cl(6)	2.474(3)
Nb(2)	N(1)	1.985(7)
Nb(2)	N(2)	2.191(7)
Nb(2)	N(3)	2.234(7)
S(1)	C(4)	1.61(3)
S(1)	C(5)	1.64(2)
N(1)	C(1)	1.46(1)
N(2)	N(3)	1.44(1)
N(2)	C(2)	1.51(1)
N(3)	C(3)	1.27(1)
C(1)	C(2)	1.54(1)
C(1)	C(11)	1.51(1)
C(2)	C(21)	1.51(1)
C(3)	C(31)	1.43(1)
C(11)	C(12)	1.39(1)
C(11)	C(16)	1.41(1)

(continued)

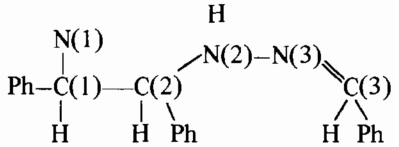
TABLE V. *(continued)*

Atom 1	Atom 2	Distance
C(12)	C(13)	1.40(1)
C(13)	C(14)	1.38(2)
C(14)	C(15)	1.43(2)
C(15)	C(16)	1.42(1)
C(21)	C(22)	1.38(1)
C(21)	C(26)	1.41(1)
C(22)	C(23)	1.44(2)
C(23)	C(24)	1.37(2)
C(24)	C(25)	1.40(2)
C(25)	C(26)	1.43(2)
C(31)	C(32)	1.43(2)
C(31)	C(36)	1.39(2)
C(32)	C(33)	1.41(2)
C(33)	C(34)	1.39(2)
C(34)	C(35)	1.35(2)
C(35)	C(36)	1.44(2)
C(41)	C(42)	1.39(3)
C(41)	C(46)	1.36(3)
C(41)	C(47)	1.52(4)
C(42)	C(43)	1.38(3)
C(43)	C(44)	1.59(3)
C(44)	C(45)	1.38(3)
C(45)	C(46)	1.38(3)

[a] e.s.d.s given in parentheses.

molecule is retained, while on Nb(2) there is an unusual dinitrogen ligand, which we shall now discuss in detail.

Since hydrogen atoms were not located in this structure we have to infer their presence indirectly; examination of bond angles and bond lengths provides virtually unambiguous indications of where they must be. In **II**, we present a schematic structure of the large ligand, including the four inferred hydrogen atoms. The reasoning on which this is based is as follows.



II

The sum of the three bond angles about N(1) is 357 ± 1°, thus identifying this as a nitrene type nitrogen with no attached hydrogen atom. The two N(1)–Nb distances, 1.932(8) and 1.985(7) Å, are also in accord with the sort of partial multiple nitrogen to metal bonding, shown in **I** and previously discussed for compound **1**.

Proceeding now to C(1), we see that all of the bond lengths are indicative of single bonds and the sum of the three bond angles is 331 ± 1°. Clearly, this is a tetrahedral carbon atom to which a hydrogen atom must be attached. Similarly, for C(2) the same

TABLE VI. Table of Angles (°) for $Nb_2Cl_6(SMe_2)(NCHPhCHPhHNNCHPh)\cdot C_7H_8$[a]

Atom 1	Atom 2	Atom 3	Angle
Nb(2)	Nb(1)	Cl(1)	58.69(7)
Nb(2)	Nb(1)	Cl(2)	58.75(7)
Nb(2)	Nb(1)	Cl(3)	118.2(1)
Nb(2)	Nb(1)	Cl(4)	124.50(8)
Nb(2)	Nb(1)	S(1)	134.47(8)
Nb(2)	Nb(1)	N(1)	47.6(2)
Cl(1)	Nb(1)	Cl(2)	77.33(9)
Cl(1)	Nb(1)	Cl(3)	91.0(1)
Cl(1)	Nb(1)	Cl(4)	161.0(1)
Cl(1)	Nb(1)	S(1)	85.6(1)
Cl(1)	Nb(1)	N(1)	101.2(2)
Cl(2)	Nb(1)	Cl(3)	167.7(1)
Cl(2)	Nb(1)	Cl(4)	88.95(9)
Cl(2)	Nb(1)	S(1)	88.4(1)
Cl(2)	Nb(1)	N(1)	86.1(2)
Cl(3)	Nb(1)	Cl(4)	101.5(1)
Cl(3)	Nb(1)	S(1)	86.9(1)
Cl(3)	Nb(1)	N(1)	100.1(2)
Cl(4)	Nb(1)	S(1)	80.9(1)
Cl(4)	Nb(1)	N(1)	90.7(2)
S(1)	Nb(1)	N(1)	170.0(2)
Nb(1)	Nb(2)	Cl(1)	56.15(7)
Nb(1)	Nb(2)	Cl(2)	57.29(6)
Nb(1)	Nb(2)	Cl(5)	109.71(7)
Nb(1)	Nb(2)	Cl(6)	135.95(7)
Nb(1)	Nb(2)	N(1)	46.0(2)
Nb(1)	Nb(2)	N(2)	121.0(2)
Nb(1)	Nb(2)	N(3)	117.6(2)
Cl(1)	Nb(2)	Cl(2)	75.35(9)
Cl(1)	Nb(2)	Cl(5)	81.3(1)
Cl(1)	Nb(2)	Cl(6)	93.11(9)
Cl(1)	Nb(2)	N(1)	97.4(2)
Cl(1)	Nb(2)	N(2)	158.0(2)
Cl(1)	Nb(2)	N(3)	163.6(2)
Cl(2)	Nb(2)	Cl(5)	156.63(9)
Cl(2)	Nb(2)	Cl(6)	86.86(9)
Cl(2)	Nb(2)	N(1)	83.9(2)
Cl(2)	Nb(2)	N(2)	123.2(2)
Cl(2)	Nb(2)	N(3)	88.6(2)
Cl(5)	Nb(2)	Cl(6)	93.42(9)
Cl(5)	Nb(2)	N(1)	100.4(2)
Cl(5)	Nb(2)	N(2)	79.9(2)
Cl(5)	Nb(2)	N(3)	114.6(2)
Cl(6)	Nb(2)	N(1)	163.8(2)
Cl(6)	Nb(2)	N(2)	99.2(2)
Cl(6)	Nb(2)	N(3)	82.4(2)
N(1)	Nb(2)	N(2)	75.1(3)
N(1)	Nb(2)	N(3)	84.0(3)
N(2)	Nb(2)	N(3)	37.9(3)
Nb(1)	Cl(1)	Nb(2)	65.15(7)
Nb(1)	Cl(2)	Nb(2)	63.96(7)
Nb(1)	S(1)	C(4)	110(1)
Nb(1)	S(1)	C(5)	109.8(9)
C(4)	S(1)	C(5)	93(1)
Nb(1)	N(1)	Nb(2)	86.4(3)
Nb(1)	N(1)	C(1)	145.5(6)
Nb(2)	N(1)	C(1)	124.7(6)

(continued)

TABLE VI. *(continued)*

Atom 1	Atom 2	Atom 3	Angle
Nb(2)	N(2)	N(3)	72.7(4)
Nb(2)	N(2)	C(2)	114.3(5)
N(3)	N(2)	C(2)	116.5(6)
Nb(2)	N(3)	N(2)	69.4(4)
Nb(2)	N(3)	C(3)	158.8(6)
N(2)	N(3)	C(3)	118.2(8)
N(1)	C(1)	C(2)	105.6(6)
N(1)	C(1)	C(11)	112.5(7)
C(2)	C(1)	C(11)	111.5(7)
N(2)	C(2)	C(1)	107.4(7)
N(2)	C(2)	C(21)	112.8(7)
C(1)	C(2)	C(21)	114.5(7)
N(3)	C(3)	C(31)	123(1)
C(1)	C(11)	C(12)	119.4(8)
C(1)	C(11)	C(16)	119.1(7)
C(12)	C(11)	C(16)	121.4(8)
C(11)	C(12)	C(13)	120(1)
C(12)	C(13)	C(14)	120(1)
C(13)	C(14)	C(15)	120(1)
C(14)	C(15)	C(16)	120(1)
C(11)	C(16)	C(15)	117.9(9)
C(2)	C(21)	C(22)	117.1(8)
C(2)	C(21)	C(26)	121.2(9)
C(22)	C(21)	C(26)	121.6(9)
C(21)	C(22)	C(23)	120(1)
C(22)	C(23)	C(24)	119(1)
C(23)	C(24)	C(25)	122(1)
C(24)	C(25)	C(26)	120(1)
C(21)	C(26)	C(25)	118(1)
C(3)	C(31)	C(32)	115(1)
C(3)	C(31)	C(36)	123.3(9)
C(32)	C(31)	C(36)	122(1)
C(31)	C(32)	C(33)	117(1)
C(32)	C(33)	C(34)	122(1)
C(33)	C(34)	C(35)	121(1)
C(34)	C(35)	C(36)	121(1)
C(31)	C(36)	C(35)	118(1)
C(42)	C(41)	C(46)	122(2)
C(42)	C(41)	C(47)	124(2)
C(46)	C(41)	C(47)	114(2)
C(41)	C(42)	C(43)	133(2)
C(42)	C(43)	C(44)	107(2)
C(43)	C(44)	C(45)	115(2)
C(44)	C(45)	C(46)	134(2)
C(41)	C(46)	C(45)	110(2)

[a] Numbers in parentheses are e.s.d.s in the least significant digits.

type of data (angles summing to 335 ± 1°) show that here too there is a hydrogen atom.

Turning to C(3), the N(3)–C(3) distance of 1.27 Å and the angle of 123° at C(3) leave no doubt that this is an sp^2 hybridized atom with only one hydrogen atom attached, as shown in **II**.

We now come to the question of the N(2)–N(3) unit. The N–N distance of 1.44 Å is indicative of a single bond and the sum of the observed bond angles about N(2) is 304 ± 1°. It seems clear, then, that there must be a hydrogen atom on N(2). For N(3), on the other hand, we conclude that there is no attached hydrogen atom, since N(3) is at the center of an N–N=C chain. In addition the sum of the observed bond angles is 346 ± 1°.

On the basis of the deduced picture, **II**, of the large ligand, we then draw the following conclusions about the molecule as a whole. The large ligand is a formally 2– ligand, as a result of its nitrene nitrogen atom, N(1), while the other two nitrogen atoms are neutral donors. This means that the niobium atoms are both Nb^{IV} and a single bond can be postulated to exist between them. While Nb(1) is six-coordinate (roughly octahedral), Nb(2) is seven-coordinate, with two of the seven ligand atoms, N(2) and N(3), being close to one of the sites expected for octahedral coordination. The entire molecule is thus quite similar to the face-sharing bioctahedron found in compound **1**.

The question of how the large tridentate ligand is formed from the starting material, PhHC=N–N=CHPh, is one we cannot even begin to answer. Whatever the mechanism, it is clear that no large activation energies are involved since the process occurs in a relatively short time at room temperature. A reasonable guess would be that the C(2)–N(2)–N(3)–C(3) chain with its attached phenyl groups and C–H bonds represents one of the original PhHC=N–N=CHPh molecules to which a PhHC=NH unit has added to generate the C(1)–C(2) bond, the nitrene nitrogen atom, N(1), and the N(2)–H bond.

Supplementary Material

Tables of structure factors and anisotropic thermal parameters are available from author F.A.C.

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