(Grant No. RR-01077 from the Division of Research Resources). We thank Professor Malcolm H. Chisholm for kindly providing us with a preprint of ref 24.

Registry No. A, 83801-91-6; B, 83801-93-8; $W_2Cl_4(\mu\text{-O-}n\text{-Pr})_2[Me_2C(O)C(O)Me_2]_2$, 83801-92-7; $W_2Cl_2(\mu\text{-OEt})_2(OEt)_2[Me\text{-}n\text{-PrC(O)C(O)Me-}n\text{-Pr}]$, 90913-78-3; $W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(EtOH)_2$, 78350-74-0; $W_2Cl_4(\mu\text{-OEt})_2(O\text{-}i\text{-Pr})_2(i\text{-PrOH})_2$, 85202-62-6; $W_2Cl_4(\mu\text{-O-}n\text{-Pr})_2(O\text{-}n\text{-Pr})_2(n\text{-PrOH})_2$, 83801-94-9; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; 2-pentanone, 107-87-9; tungsten, 7440-33-7.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters (20 pages). Ordering information is given on any current masthead page.

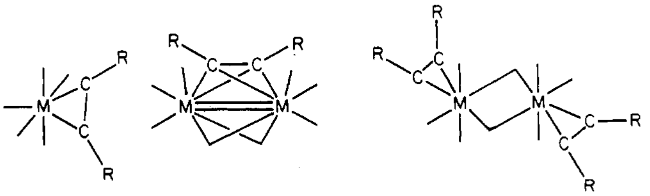
A New Double Bond Metathesis Reaction: Conversion of an Nb=Nb and an N=N Bond into Two Nb=N Bonds

F. Albert Cotton,* Stan A. Duraj, and Wieslaw J. Roth

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. *Received December 21, 1983*

Abstract: $Nb_2Cl_6(Me_2S)_3$ reacts readily with azobenzene, $C_6H_5N{=}NC_6H_5$, to afford a red crystalline product, $[NbCl_2(Me_2S)(NC_6H_5)]_2(\mu\text{-Cl})_2$, in 50–60% yields. This compound has been characterized by NMR, IR, mass spectrometry, and X-ray crystallography. It is a centrosymmetric molecule in which each of two niobium(V) atoms have distorted octahedral coordination, with the ligand set consisting of two bridging Cl atoms, with one normal (2.462 (2) Å) and one long (2.762 (2) Å) bond, two mutually cis terminal chlorine atoms with Nb–Cl distances of 2.325 (3) Å and 2.344 (3) Å, one $Nb\text{–}SMe_2$ bond, 2.654 (3) Å, and one $Nb{=}NC_6H_5$ bond, 1.733 (7) Å. The long Nb–Cl bridge bond is trans to the $Nb{=}NC_6H_5$ bond. The dinuclear molecule can be regarded as the product of an inorganic double bond metathesis reaction in which Nb=Nb and N=N bonds react to yield two Nb=N bonds. The Nb=N—C group is practically linear, 175.1 (7)°. The compound crystallizes in space group $C2/c$ with unit cell dimensions of $a = 20.736$ (4) Å, $b = 7.671$ (1) Å, $c = 16.780$ (3) Å, $\beta = 96.86$ (2)°, $V = 2650$ (2) Å^3, and $Z = 4$. Refinement, using a data to parameter ratio of 9.4, converged with an unweighted discrepancy index of 4.89%.

Metal–metal multiple bonds constitute a source of remarkable reactivity.[1] In the case of the chemistry of doubly bonded niobium and tantalum, in their oxidation states of III, this extensive reactivity is perhaps best demonstrated by the reactions of the $Cl_2(R_2S)M(\mu\text{-Cl})_2(\mu\text{-}R_2S)M(R_2S)Cl_2$ molecules (where R_2S represents tetrahydrothiophene or dimethyl sulfide) with unsaturated organic molecules such as isocyanides,[2] nitriles,[3-5] and acetylenes.[6-9] With *tert*-butyl isocyanide, $Nb_2Cl_6(SMe_2)_3$ has been shown to afford two novel complexes,[2] $Nb_3Cl_8(t\text{-BuNC})_5$ and $Nb_2Cl_6(t\text{-BuNC})_6$, whereas with nitriles, the $M_2Cl_6(SC_4H_8)_3$ compounds reductively couple two molecules of the nitrile with concomitant oxidation of the metal atoms.[3-5] The reactivity of our dinuclear, doubly bonded M^{III} starting materials towards acetylenes is manifested in several ways, which include (1) the formation of complexes of the following general types



(2) dimerization to give molecules with new carbon–carbon bonds which further react with the metal to form unusual structures containing metallocycles, (3) oligomerization to substituted benzenes, or (4) polymerization to substituted, high molecular weight polyolefins.

We now wish to report a new and unprecedented form of chemical behavior for the niobium–niobium double bond, namely, a double bond metathesis reaction with azobenzene, $C_6H_5N{=}NC_6H_5$, whereby Nb=Nb + N=N affords 2Nb=N, i.e., a product containing metal–imide linkages.

Experimental Section

All operations were performed under an atmosphere of argon by using standard Schlenk techniques and a double-manifold vacuum line. Toluene and hexane were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless cannulae and/or syringes. Azobenzene was deaerated under vacuum at 25 °C. $Nb_2Cl_6(SMe_2)_3$ was prepared according to the published procedure[10] for $Nb_2Cl_6(THT)_3$ by using dimethyl sulfide instead of tetrahydrothiophene. The ^1H NMR spectrum was obtained on a Varian XL 200 spectrometer. The IR spectrum was recorded on a Perkin-Elmer 783 spectrophotometer. Mass spectra were measured (direct insertion probe, 70 eV; the probe temperature increased steadily from 25 to 230 °C) on a Hewlett-Packard 5980A mass spectrometer equipped with a 5933A data system.

$[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-Cl})_2$. A solution of $Nb_2Cl_6(SMe_2)_3$ (0.50 g, 0.85 mmol) in 20 mL of benzene was filtered and to the filtrate azobenzene (0.25 g, 1.4 mmol) was added. Upon stirring, the color of the reaction mixture changed from purple to red within several minutes. Stirring of the mixture was continued at room temperature for 12 h, after which it was filtered into a flask, leaving a red solid behind. A total of 60 mL of hexane was carefully added on top of this filtrate and the flask was placed in a refrigerator. After a period of 1–2 days, a red crystalline solid was obtained. The red solids were combined and washed 3 times with 10 mL of fresh hexane. Yield: 58%, 0.35 g. ^1H NMR (C_6D_6): δ 1.73 (s, 12 H), 7.13 (m, 10 H). IR (Nujol), cm^{-1}: 1320 (m), 1300 (w), 1278 (w), 1255 (w), 1165 (w), 1153 (w), 1090 (w), 1065 (m), 1030 (m), 1020 (m), 1000 (w), 982 (m), 975 (m), 915 (vw), 910 (w), 832 (w), 760

---

[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982**, *29*, 1. See also Figure 9–11 in: Cotton, F. A. *J. Chem. Educ.* **1983**, *60*, 713.

[2] Cotton, F. A.; Roth, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 3734.

[3] Finn, P. A.; Schaefer, K. M.; Kelty, P. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 220.

[4] Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525.

[5] Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094.

[6] Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2352, 2354.

[7] Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1981**, *20*, 1285.

[8] Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233.

[9] Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Organometallics* **1982**, *1*, 1640.

[10] Maas, E. T.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1096.

0002-7863/84/1506-4749$01.50/0

Table I. Crystallographic Data

formula	$Nb_2C_{16}H_{22}Cl_6S_2N_2$
formula weight	705.03
space group	$C2/c$
systematic absences	hkl, $h + k \neq 2n$ $h0l$, $l \neq 2n$
a, Å	20.736 (4)
b, Å	7.671 (1)
c, Å	16.780 (3)
β, deg	96.86 (2)
V, Å^3	2650 (2)
Z	4
d_{calcd}, g/cm^3	1.767
crystal size, mm	0.45 × 0.25 × 0.50
μ(Mo Kα), cm^{-1}	15.988
data collection instrument	CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation reflections, number, range (2θ)	25, 16.06 ≤ 2θ ≤ 27.72
temp, °C	22
scan method	ω–2θ
data collection range, 2θ, deg	5 ≤ 2θ ≤ 50
no. of unique data, total	1579
with $F_o^2 > 3\sigma(F_o^2)$	1190
no. of parameters refined	127
R^a	0.0489
R_w^b	0.0553
quality-of-fit indicator^c	1.289
largest shift/esd, final cycle	0.001
largest peak, e/Å^3	0.607

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

(vs), 737 (m), 720 (m), 685 (s). MS, m/e (relative intensity): 289 (100) $Nb^{35}Cl_3NC_6H_5$, 198 (96.3) $Nb^{35}Cl_3$, 154 (25.4) $Nb^{35}Cl_2$, 128 (11.9) $Nb^{35}Cl$, 93 (13.6) Nb, 91 (3.2) NC_6H_5, 62 (2.9) SMe_2. The expected isotopic envelopes were observed; for example, for $NbCl_3NC_6H_5$ the following pattern was seen: 289 ($Nb^{35}Cl_3NC_6H_5$) 100, 291 ($Nb^{35}Cl_2{}^{37}ClNC_6H_5$) 98.4, 293 ($Nb^{35}Cl^{37}Cl_2NC_6H_5$) 31.8, and 295 ($Nb^{37}Cl_3NC_6H_5$) 3.7, which is consistent with the theoretical expectation of $1:1:{}^1/_3:{}^1/_{27}$.

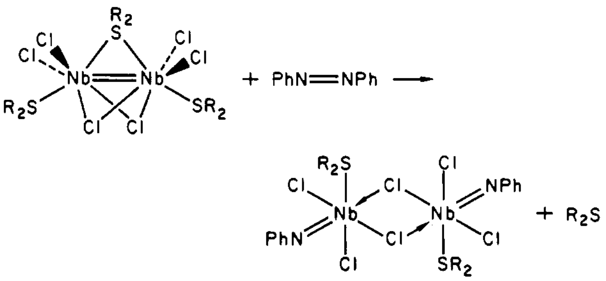
Crystallographic quality crystals can be prepared by a slightly modified procedure. The solution of $Nb_2Cl_6(SMe_2)_3$ in benzene (20 mL) is carefully covered with a layer of PhNNPh in hexane (20 mL) in a Schlenk tube, and the reaction mixture is allowed to stand undisturbed. Large, blocklike, red crystals of $[NbCl_2(SMe_2)(NPh)]_2(\mu\text{-}Cl)_2$ are formed upon mixing of the solutions within 2–3 weeks (yield: 41%, 0.25 g). The IR spectrum of these crystals is identical with the IR spectrum obtained above.

X-ray Crystallography. General procedures have already been described elsewhere.[11] Information about data collection and structure refinement for $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$ is given in Table I. The intensity data were corrected for Lorentz and polarization effects.

The niobium atoms were located by Patterson synthesis. Full-matrix least-squares refinement and difference Fourier calculations were used to locate the remaining non-hydrogen atoms. All 14 atoms were refined anisotropically to convergence. Tables of structure factors and anisotropic thermal parameters are available as supplementary material.

Results and Discussion

Synthesis and Spectral Characterization. The reaction between $[NbCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$ and azobenzene in benzene affords red crystals, proved by X-ray crystallography to contain $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$ molecules. The structural details will be discussed fully below. This compound, a Nb(V) dimer, results from a reaction that can be represented by eq 1. This reaction could be described as an oxidative addition of the N═N bond to the dinuclear niobium(III) compound, and this point of view has the merit of emphasizing the fact that the reaction converts niobium(III) to niobium(V). An alternative description, which we prefer to emphasize, is that the reaction is a kind of olefin metathesis in which neither of the "olefins" contains C═C bonds. Thus, in formal terms we would write eq 2.



(1)

$$\mathrm{Nb{=}Nb + {-}N{=}N{-} \rightarrow 2Nb{=}N{-}} \qquad (2)$$

This is the first example of any such reaction of a metal–metal double bond, none having been seen as yet with other metals or with $R_2C{=}CR_2$ compounds. With triple bonds there are some interesting and important reactions that are formally comparable, namely those of Schrock and co-workers[12] shown schematically in eq 3.

$$\mathrm{M{\equiv}M + {-}C{\equiv}C{-} \rightarrow 2M{\equiv}C{-}} \qquad (3a)$$

$$\mathrm{M{\equiv}M + {-}C{\equiv}N \rightarrow M{\equiv}C{-} + M{\equiv}N} \qquad (3b)$$

The cleavage of N═N bonds by metal atoms to yield M═N bonds under any circumstances is a highly unusual process, and only two prior examples appear to have been reported. These involve the use of rather special azo compounds, viz., CF_3NNCF_3[13] and $Me_3SiNNSiMe_3$.[14] There is one report of the reaction of azobenzene in which cleavage of the N═N bond occurs, but the product contains a bridging PhN group as well as a bridging PhNNPh molecule.[15]

The ^1H NMR spectrum of $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$ has a very normal appearance, consistent with a diamagnetic Nb(d^0) species.

The IR spectrum can be interpreted by comparison with the spectra of the reactants, $Nb_2Cl_6(SMe_2)_3$[16] and PhNNPh.[17] In the region 950–1400 cm^{-1} there are several bands which match those observed in $[NbCl_2(SMe_2)]_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)$, viz., 1320 m, 1300 w, 1255 w, 1090 w, 1030 m, 1020 m, 982 m, 975 m cm^{-1}. The remaining bands in this region are weak, except for one at 1065 cm^{-1}. On the basis of assignments made for PhNNPh they can be attributed to vibrations within the NPh group. Literature data indicate that the metal imide, Nb═N, vibration, which is expected to appear between 900 and 1200 cm^{-1}, is notoriously difficult to assign with certainty.[18] We cannot do it unequivocally in this case, but we suggest that the band at 1065 cm^{-1} may be due to the Nb═N stretch. It coincides with a band found for azobenzene (CC and CCH modes) but it is much more prominent than other NPh vibrations. Since for pure PhNNPh most bands in the region 950–1400 cm^{-1} have comparable intensity, it seems unlikely that coordination to a metal would selectively enhance one ligand vibration (the observed relative enhancement is roughly 5-fold).

The fragmentation pattern observed in the mass spectrum confirms the major structural units of $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$. Thus, ions of the following fragments are observed: $NbCl_3NC_6H_5$, $NbCl_3$, $NbCl_2$, NbCl, Nb, NC_6H_5, and SMe_2, which was evolved first as the temperature started to increase. Although no molecular ion (702 for $^{93}Nb_2{}^{35}Cl_6{}^{32}SMe_2{}^{14}N^{12}C_6H_5$) was observed, the highest detected ion (516) clearly suggests a more than monomeric structure. The

---

(11) See for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(12) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

(13) Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1805.

(14) Wiberg, N.; Haring, W.; Schubert, U. *Z. Naturforsch., B* **1978**, *B33*, 1365.

(15) Gambarotta, S.; Floriani, C.; Chiese-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 1015.

(16) (a) Allen, A. D.; Naito, S. *Can. J. Chem.* **1976**, *54*, 2948. (b) Tsunoda, M.; Hubert-Pfalzgraf, L. G. *Inorg. Synth.* **1982**, *21*, 16.

(17) (a) Klima, M. I.; Kotov, A. V.; Gribov, L. A. *J. Struct. Chem. (Engl. Transl.)* **1972**, *13*, 1060. (b) "The Aldrich Library of Infrared Spectra"; Pouchert, C. J.; Aldrich Chemical Co., Inc., 1970.

(18) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

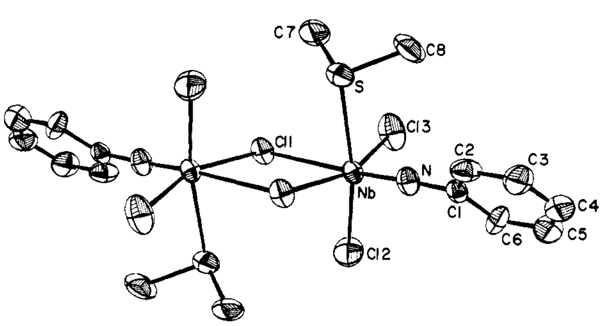


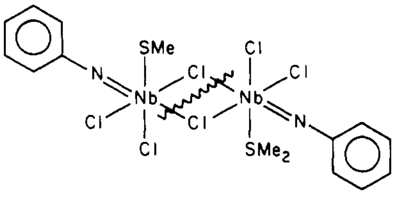
Figure 1. ORTEP drawing of the $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$ complex, which also defines the labeling scheme. The thermal ellispoids enclose 50% of electron density.

Table II. Positional and Isotropic Equivalent Thermal Parameters for $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Nb	−0.08929 (4)	0.0470 (1)	0.03615 (5)	2.52 (2)
Cl(1)	−0.0236 (1)	−0.1483 (3)	−0.0665 (1)	3.10 (5)
Cl(2)	−0.1125 (2)	0.2440 (5)	−0.0702 (2)	4.95 (8)
Cl(3)	−0.1756 (1)	−0.1420 (5)	0.0006 (2)	5.22 (8)
S	−0.0474 (2)	−0.1940 (4)	0.1435 (2)	3.98 (7)
N	−0.1203 (4)	0.162 (1)	0.1119 (5)	3.1 (2)
C(1)	−0.1498 (4)	0.260 (1)	0.1685 (6)	2.5 (2)
C(2)	−0.1220 (6)	0.266 (1)	0.2479 (6)	3.6 (3)
C(3)	−0.1527 (6)	0.359 (1)	0.3030 (6)	4.2 (3)
C(4)	−0.2107 (6)	0.439 (2)	0.2801 (7)	4.6 (3)
C(5)	−0.2392 (6)	0.434 (2)	0.1996 (7)	4.8 (3)
C(6)	−0.2092 (5)	0.343 (1)	0.1428 (6)	3.5 (2)
C(7)	−0.0493 (7)	−0.407 (1)	0.0970 (8)	6.3 (3)
C(8)	−0.1144 (6)	−0.218 (2)	0.2037 (7)	5.4 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

ion $NbCl_3NC_6H_5$ arises from splitting the dimer, following loss of both SMe_2 ligands, into two halves presumably by severing the weaker Nb–Cl(1) bonds (vide infra).



Molecular Structure of $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$. Crystals of this molecule consist of an ordered array of discrete molecules which reside on centers of inversion. An ORTEP drawing of the entire molecule unit is shown in Figure 1, which also defines the numbering scheme. The positional parameters are listed in Table II and the bond lengths and bond angles are given in Tables III and IV, respectively. Very broadly speaking the structure can be described as two octahedra sharing an edge. However, there are several large and interesting distortions from that idealization. First, the structure is elongated in the Nb···Nb direction, as would be expected since there can be no bonding between the two niobium(V) atoms. The Nb···Nb distance here is 4.096 (2) Å, which is even greater than that found in the Nb_2Cl_{10} molecule[19] where the corresponding distance is 3.951 (2) Å. The greater separation in this case may be attributed to the fact that two of the Nb–Cl bridge bonds are especially long and weak because of the strong trans-weakening influence of the Nb═N bonds. Thus, the $Nb(\mu\text{-}Cl)_2Nb$ parallelogram has two Nb–Cl edges that compare favorably with normal distances of that sort, e.g., with the length of the equivalent bridge bonds in Nb_2Cl_{10}, 2.555 (6) Å, whereas the other two Nb–Cl bridge bonds are very much longer, 2.762 (2) Å.

Table III. Bond Lengths (Å) for $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$[a]

Nb–Nb′	4.096 (2)[b]	S–C(8)	1.823 (11)
Nb–Cl(1)	2.762 (2)	N–C(1)	1.407 (11)
Nb–Cl(1)′	2.462 (2)	C(1)–C(2)	1.388 (12)
Nb–Cl(2)	2.344 (3)	C(1)–C(6)	1.408 (12)
Nb–Cl(3)	2.325 (3)	C(2)–C(3)	1.381 (14)
Nb–S	2.654 (3)	C(3)–C(4)	1.365 (15)
Nb–N	1.733 (7)	C(4)–C(5)	1.408 (14)
S–C(7)	1.809 (11)	C(5)–C(6)	1.388 (14)

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

Table IV. Bond Angles (deg) for $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$[a]

Cl(1)–Nb–Cl(1)′	76.87 (8)	S–Nb–N	88.7 (3)
Cl(1)–Nb–Cl(2)	86.94 (9)	Nb–Cl(1)–Nb′	103.13 (8)
Cl(1)–Nb–Cl(3)	85.60 (9)	Nb–S–C(7)	110.3 (4)
Cl(1)–Nb–S	84.24 (8)	Nb–S–C(8)	103.8 (4)
Cl(1)–Nb–N	170.9 (3)	C(7)–S–C(8)	99.6 (6)
Cl(1)′–Nb–Cl(2)	93.3 (1)	Nb–N–C(1)	175.1 (7)
Cl(1)′–Nb–Cl(3)	159.0 (1)	N–C(1)–C(2)	120.2 (8)
Cl(1)′–Nb–S	81.54 (9)	N–C(1)–C(6)	118.0 (8)
Cl(1)′–Nb–N	96.5 (2)	C(2)–C(1)–C(6)	121.7 (9)
Cl(2)–Nb–Cl(3)	97.2 (1)	C(1)–C(2)–C(3)	119 (1)
Cl(2)–Nb–S	170.6 (1)	C(2)–C(3)–C(4)	120 (1)
Cl(2)–Nb–N	99.8 (3)	C(3)–C(4)–C(5)	121 (1)
Cl(3)–Nb–S	85.4 (1)	C(4)–C(5)–C(6)	120 (1)
Cl(3)–Nb–N	99.5 (3)	C(1)–C(6)–C(5)	117.7 (9)

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

The terminal Nb–Cl bond lengths, 2.325 (3) and 2.344 (3) Å, are comparable to those found in Nb_2Cl_{10}, viz., 2.250 (6) and 2.302 (5) Å. The Nb–SMe_2 distance of 2.654 (3) Å is comparable to such distances in the $M_2X_6(R_2S)_3$ molecules, viz., ca. 2.63 Å in those with X = Br, R_2S = THT, and M = Nb or Ta and 2.635 (3) and 2.618 (5) Å for the compounds with M = Ta and X = Cl containing THT and Me_2S, respectively.[20,21]

The Nb═NC_6H_5 bonding is of special interest. This bond is extemely short and the Nb═N—C chain is practically linear, with an angle of 175.1 (7)°. The bond length here, 1.733 (7) Å, can be compared with the other reported imido–niobium bond lengths, namely 1.783 (3) Å in $Nb(S_2CNEt_2)_3(NC_6H_4CH_3)$[18] and 1.752 (6) Å in the $[Nb_2Cl_8(CH_3CN)_2C_4H_6N_2]^{2-}$ ion.[3] It seems clear that in our new compound we have a case where the Nb to N bond order is appreciably greater than 2.0 as a result of Nπ to Nb dative π bonding. The importance of such interactions has been recognized and discussed by Nugent and Haymore.[18]

Acknowledgment. We thank Dr. J. Efimenko of this department for the mass spectral measurements. We are grateful to the National Science Foundation for support.

Registry No. $[NbCl_2(SMe_2)(NC_6H_5)]_2(\mu\text{-}Cl)_2$, 91054-06-7; $Nb_2Cl_6(SMe_2)_3$, 61069-51-0; PhN═NPh, 103-33-3.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

---

(19) Zalkin, A.; Sands, D. E. *Acta Crystallogr.* **1958**, *11*, 615.

(20) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981**, *20*, 2716.

(21) Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263.