Niobium Complexes with Terdentate Diphosphino- and Diamino-amido Ligands. Crystal Structure of $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]\cdot C_6H_5Me$†

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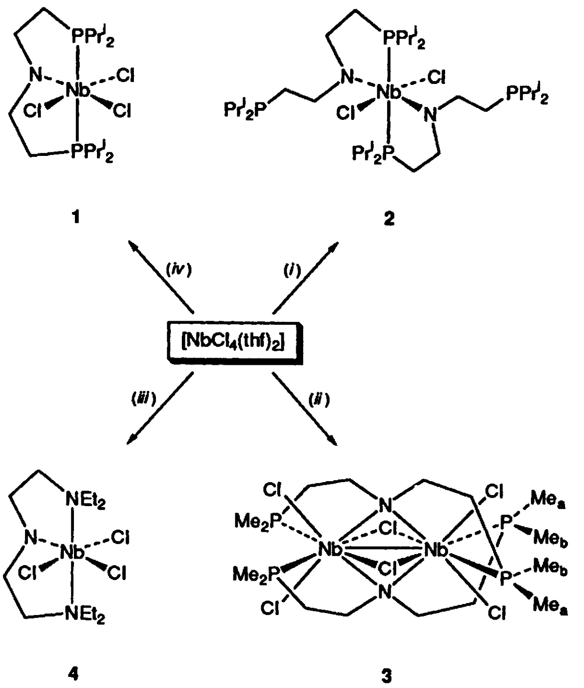
The reaction of $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran) with bis(tertiary phosphinoethyl)amides $Li[N(CH_2CH_2PR_2)_2]$ (R = Me or Pr^i) resulted in the formation of new niobium dialkylamides. The specific complexes generated depend on the stoichiometry of the reaction and the bulk of the tertiary phosphine substituents. Thus, with the bulky diisopropylphosphino function, monomeric paramagnetic mono- and bis-ligand complexes are obtained, $[NbCl_3\{N(CH_2CH_2PPr^i_2)_2\}]$ and $[NbCl_2\{N(CH_2CH_2PPr^i_2)_2\}_2]$. However with the less sterically encumbered dimethylphosphino function only the diamagnetic dinuclear complex, $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]$, can be isolated; its crystal structure shows equivalent bridging terdentate amide ligands with two bridging chlorides for each dimeric unit resulting in eight-co-ordinate niobium atoms. In contrast, the bis(2-diethylaminoethyl)amide $Li[N(CH_2CH_2NEt_2)_2]$, an analogue of the smaller phosphine, again only gave rise to paramagnetic monomeric derivatives.

Since ternary dialkylamido complexes of electropositive metals are not readily available without kinetic stabilisation by bulky ligands, we have undertaken a study of the co-ordination properties of flexible and versatile chelating amides. As part of this we have reported on the use of a terdentate diaminoamide in the stabilisation of amido halide derivatives of niobium[1] and have demonstrated that the chelating ability of such ligands enables kinetic stabilisation of partially substituted halide complexes that have otherwise been inaccessible. In this paper we investigate relative differences in the co-ordination behaviour of these compounds as a function of variations in the donor atom and bulk of the substituents. Thus, together with stoichiometric and steric control, new classes of dialkylamidoniobium complexes have been prepared and characterised spectroscopically, analytically and in one case crystallographically.

Results and Discussion

The new compounds reported herein are represented in Scheme 1.

Bis(tertiary phosphinoethyl)amido Complexes.—The reaction of $[NbCl_4(thf)_2]$ with 1 mole equivalent of $Li[N(CH_2CH_2PPr^i_2)_2]$ in toluene gives rise to pale brown solutions from which green-yellow prisms of complex **1** were isolated and for which analytical and mass spectroscopic data indicate the stoichiometry $[NbCl_3\{N(CH_2CH_2PPr^i_2)_2\}]$. Treatment of a toluene suspension of freshly prepared $[NbCl_4(thf)_2]$ with 2 equivalents of the lithium amide gave a brown oil from which **2** was obtained as feathery yellow crystals by recrystallisation from light petroleum (b.p. 40–60 °C). Analytical and mass spectroscopic data are consistent with the formula $[NbCl_2\{N(CH_2CH_2PPr^i_2)_2\}_2]$. Both compounds **1** and **2** are paramagnetic (μ_{eff} = 1.70 and 1.71 μ_B respectively) consistent with d^1 Nb^{IV}. In frozen toluene solution they give rise to 10-line ESR spectra with the expected hyperfine structure arising from coupling to the ^{92}Nb nucleus ($I = \frac{9}{2}$); no superhyperfine coupling to either nitrogen or phosphorus was observed.



Scheme 1 Reactions of $[NbCl_4(thf)_2]$ (thf = tetrahydrofuran) with $Li[N(CH_2CH_2PR_2)_2]$ and $Li[N(CH_2CH_2NEt_2)_2]$ reagents. Note that the diastereotopic methyl substituents in **3** are indicated for one half of the molecule. (*i*) $2Li[N(CH_2CH_2PPr^i_2)_2]$; (*ii*) $Li[N(CH_2CH_2PMe_2)_2]$; (*iii*) $Li[N(CH_2CH_2NEt_2)_2]$; (*iv*) $Li[N(CH_2CH_2PPr^i_2)_2]$

This behaviour is similar to that previously observed for the diaminoamido analogue of **2**, *i.e.* $[NbCl_2\{N(CH_2CH_2NEt_2)_2\}_2]$.[1] The reaction of $[NbCl_4(thf)_2]$ with 1 mole equivalent of $Li[N(CH_2CH_2PMe_2)_2]$ in toluene gives rise to orange diamagnetic prisms of **3**, $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]\cdot C_6H_5Me$.

The identity of complex **3** was confirmed analytically and spectroscopically. In addition its dimeric nature was established by a single-crystal structure determination (see below). Although **1** and **2** are air- and moisture-sensitive, they are thermally stable in both the solid and solution states under an

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

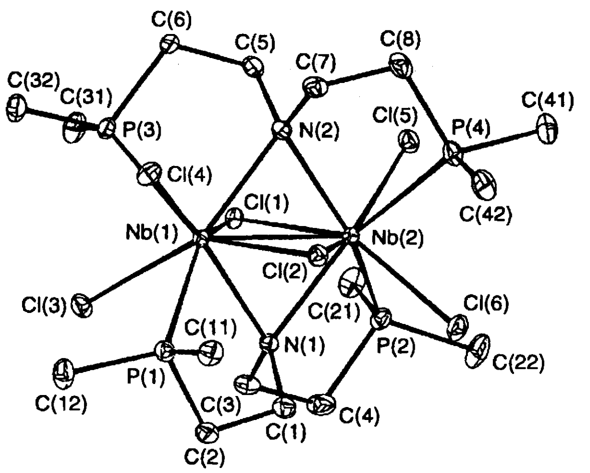

Fig. 1 The molecular structure (30% probability ellipsoids) of $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]$ and atom numbering scheme

inert atmosphere up to 100 °C. In contrast, a toluene solution of **3** is thermally unstable at above 70 °C. Thermal decomposition in hot toluene gave an unidentified toluene-insoluble yellow solid. Solid **3** can, however, be handled for a moderate period in air. As would be expected, the bis(ligand) complex, **2**, is very soluble in light petroleum whilst the monoligand complexes, **1** and **3**, are sparingly soluble in aliphatic hydrocarbons but soluble in aromatic solvents (*e.g.* toluene), **3** being the least soluble. The apparent enhanced solubility of **1** and **2** compared with **3** may be due to the influence of the bulky phosphine substituents.

The stereochemistries of complexes **1** and **2** in solution are undetermined, although they may well be similar to the structures of $[ZrCl_3\{N(SiMe_2CH_2PPr^i{}_2)_2\}]$[2] and $[ZrCl_2\{N(SiMe_2CH_2PMe_2)_2\}_2]$.[3] Complexes **1** and **2** are sufficiently volatile for informative mass spectra to be obtained. Although the parent ions of both compounds were observed, the molecular ion of **2**, [m/z = 771 (1%)] had a lower intensity compared with that of **1** [m/z = 503 (32%)]; this may be due to the relative volatility or thermal instability of **2** under mass-spectroscopic conditions. In both cases the base peak (100%) is assigned to $[CH_2CH_2PPr^i{}_2]^+$. Fragmentation with possible migration of Pr^i or $PPr^i{}_2$ groups to the niobium atom was observed. For **1**, this is demonstrated by the observation of a cluster of peaks at around m/z 439, 368, 360 and 322 which are assigned to $[NbPr^i{}_2Cl_2\{N(CH_2CH_2PPr^i{}_2)_2\} - PPr^i{}_2]^+$ (5%), $[NbPr^i{}_2\{N(CH_2CH_2PPr^i{}_2)_2\} - PPr^i{}_2]^+$ (1%), $[NbCl(Pr^i)\{N(CH_2CH_2PPr^i{}_2)_2\} - PPr^i{}_2]^+$ (4%) and $[NbPr^i\{N(CH_2CH_2PPr^i{}_2)_2\} - PPr^i{}_2]^+$ (2%) respectively. Similar group-transfer reactions are observed for **2**. This observation may suggest that organometallic complexes containing chloride as well as terdentate amide ligands can be synthesised and isolated. Peaks between m/z 306 and 41 are the same as those observed in the mass spectrum of the free amide. In the mass spectrum of **3** there are no niobium-containing fragments corresponding to dimeric ions, however a cluster of peaks with the highest mass observed at m/z 390 (6.1%) may be assigned to $[NbCl_3\{N(CH_2CH_2PMe_2)_2\}]^+$. The fragmentation indicated loss of Cl, Me, PMe and PMe_2 groups; peaks between m/z 194 and 45 were similar to those observed in the spectrum of the free amine $NH(CH_2CH_2PMe_2)_2$.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of dinuclear complex **3** contains a singlet at δ +21.64 indicating magnetically equivalent co-ordinated phosphorus donors. The ^1H NMR spectrum also shows equivalent NCH_2 groups (δ 4.8) which appear as a broad triplet and PCH_2 groups (δ 3.30) as a complex multiplet. The PCH_3 resonances appear as two equally intense doublets (δ 1.47, 1.35; $^2J_{PH}$ = 7.5 Hz) indicating that the methyl groups are diastereotopic. In addition, toluene of solvation is observed. Thus both $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra are consistent with a symmetrical dimeric structure with terdentate chelating ligands and bridging amido nitrogens in solution.

The IR spectra of $Nb(NEt_2)_4$ and $Nb(NMe_2)_4$[4] show bands at 587 and 540 cm^{-1} respectively which were assigned to the Nb–N stretching mode. By comparison, bands observed at 590 and 580 cm^{-1} in the spectra of **1** and **2** respectively may be attributed to ν(Nb–N). The band observed at 510 cm^{-1} is probably due to ν(Nb–P).[5] Also by comparison with assignments reported for a series of niobium chloro complexes,[6] bands observed at 300, 290 and 265 cm^{-1} for **1** and 310 and 270 cm^{-1} for **2** may be assigned to Nb–Cl stretching frequencies. In contrast to the monomeric compounds **1** and **2** where only one ν(Nb–N) band was observed in each case, two bands were observed in the region assignable to ν(Nb–N) for **3** at 595 and 580 cm^{-1}, presumably due to bridging Nb–N–Nb stretching modes. More bands were also apparent in the region expected for ν(Nb–Cl) (350, 320, 280, 260 and 250 cm^{-1}) and these may be attributed to the presence of both bridging and terminal chlorides. In addition, the weak bands at 490 and 470 cm^{-1} may be assigned to ν(Nb–P).[5b]

Bis(tertiary aminoethyl)amido Complexes.—We have previously described the bis(amido) complex $[NbCl_2\{N(CH_2CH_2NEt_2)_2\}_2]$ which was prepared by the reaction of $[NbCl_4(thf)_2]$ with 2 mol of the lithium amide in thf.[1] Treatment of a $[NbCl_4(thf)_2]$ suspension in toluene with an equimolar amount of the lithium amide in toluene at −78 °C gave a dark brownish red slurry from which $[NbCl_3\{N(CH_2CH_2NEt_2)_2\}]$ **4** can be isolated. The compound can be crystallised from cold toluene as small orange paramagnetic prisms. The mass spectrum also indicates this stoichiometry, the principal features being: (*i*) a very weak (0.5%) parent-ion cluster around m/z 414, (*ii*) the most intense niobium-containing peak observed at m/z 320 (2%) is due to $[NbCl_2\{N(CH_2CH_2NEt_2)_2\} - Et_2]^+$ and (*iii*) the base peak at m/z 74 (100%) corresponds to $[NEt_2]^+$. The ESR spectrum of **4** in frozen toluene shows a 10-line pattern coupled to $^{93}Nb^{IV}$. Again, there is no observed nitrogen superhyperfine structure; such featureless ESR spectra have been reported for other niobium(IV) amides and the bis(amido) complex, $[NbCl_2\{N(CH_2CH_2NEt_2)_2\}_2]$, behaves similarly.[1] The six ligand bonds to niobium are probably arranged in the same way as those in the crystallographically characterised $[ZrCl_3\{N(SiMe_2CH_2PPr^i{}_2)_2\}]$,[2] and presumably also resembles that for compound **3** (see below).

Crystal Structure of $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]\cdot C_6H_5Me$ **3**.—The crystal structure of compound **3** consists of discrete molecules of the dimeric niobium core and toluene. A view of the molecular structure and the atom numbering scheme is shown in Fig. 1. The complex has three approximate two-fold symmetry axes and each niobium atom is eight-co-ordinate. The two equivalent bridging terdentate ligands span the Nb–Nb axis symmetrically in a helical fashion such that the bridging amido-nitrogen atoms are approximately tetrahedral and sit on an axis orthogonal to that of two bridging chlorides. The overall geometry of the dimeric unit can be viewed as two square-antiprismatic units sharing a rhombically distorted square N_2Cl_2 face. Bridging $N(CH_2CH_2PR_2)_2$ (R = Me or Pr^i) ligands are precedented[7] as is the overall co-ordination geometry in **3** by the analogous phosphido complex $[Zr_2Cl_6(Cl)H\{P(CH_2CH_2PMe_2)_2\}_2]$.[8] Selected interatomic distances and angles are listed in Table 1, fractional atomic coordinates in Table 2 and comparative data for a range of similar compounds in Table 3.

The niobium–phosphorus bond distances are similar within experimental error; the average [2.647(4) Å] falls within the range of 2.61–2.71 Å observed in several niobium–chloride derivatives of tertiary phosphine ligands despite variations in oxidation states and co-ordination numbers of the metal centre.

Table 1 Selected bond lengths (Å) and angles (°) for $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]\cdot C_6H_5Me$

Nb(2)–Nb(1)	2.724(4)	Cl(1)–Nb(1)	2.514(4)	C(11)–P(1)	1.825(7)	C(12)–P(1)	1.811(7)
Cl(2)–Nb(1)	2.497(3)	Cl(3)–Nb(1)	2.533(4)	C(4)–P(2)	1.829(7)	C(21)–P(2)	1.826(7)
Cl(4)–Nb(1)	2.530(4)	P(1)–Nb(1)	2.652(4)	C(22)–P(2)	1.808(7)	C(6)–P(3)	1.831(6)
P(3)–Nb(1)	2.644(4)	N(1)–Nb(1)	2.310(5)	C(31)–P(3)	1.835(7)	C(32)–P(3)	1.815(7)
N(2)–Nb(1)	2.337(5)	Cl(1)–Nb(2)	2.503(4)	C(8)–P(4)	1.821(7)	C(41)–P(4)	1.822(7)
Cl(2)–Nb(2)	2.500(4)	Cl(5)–Nb(2)	2.528(4)	C(42)–P(4)	1.831(7)	C(1)–N(1)	1.504(8)
Cl(6)–Nb(2)	2.533(4)	P(2)–Nb(2)	2.650(4)	C(3)–N(1)	1.506(7)	C(5)–N(2)	1.506(7)
P(4)–Nb(2)	2.640(4)	N(1)–Nb(2)	2.329(6)	C(7)–N(2)	1.505(7)		
N(2)–Nb(2)	2.324(5)	C(2)–P(1)	1.819(7)				
Cl(1)–Nb(1)–Nb(2)	56.9(2)	Cl(2)–Nb(1)–Nb(2)	57.0(2)	Cl(6)–Nb(2)–Nb(1)	126.1(2)	Cl(6)–Nb(2)–Cl(1)	144.6(3)
Cl(2)–Nb(1)–Cl(1)	113.9(2)	Cl(3)–Nb(1)–Nb(2)	128.5(4)	Cl(6)–Nb(2)–Cl(2)	80.2(4)	Cl(6)–Nb(2)–Cl(5)	107.0(2)
Cl(3)–Nb(1)–Cl(1)	82.7(3)	Cl(3)–Nb(1)–Cl(2)	144.0(2)	P(2)–Nb(2)–Nb(1)	117.4(4)	P(2)–Nb(2)–Cl(1)	75.2(2)
Cl(4)–Nb(1)–Nb(2)	127.3(1)	Cl(4)–Nb(1)–Cl(1)	144.1(5)	P(2)–Nb(2)–Cl(2)	139.1(1)	P(2)–Nb(2)–Cl(5)	75.4(1)
Cl(4)–Nb(1)–Cl(2)	81.3(1)	Cl(4)–Nb(1)–Cl(3)	104.2(1)	P(2)–Nb(2)–Cl(6)	73.8(3)	P(4)–Nb(2)–Nb(1)	117.2(2)
P(1)–Nb(1)–Nb(2)	116.1(1)	P(1)–Nb(1)–Cl(1)	140.0(1)	P(4)–Nb(2)–Cl(1)	139.6(1)	P(4)–Nb(2)–Cl(2)	74.6(1)
P(1)–Nb(1)–Cl(2)	73.5(1)	P(1)–Nb(1)–Cl(3)	73.9(1)	P(4)–Nb(2)–Cl(5)	73.4(1)	P(4)–Nb(2)–Cl(6)	74.1(2)
P(1)–Nb(1)–Cl(4)	74.4(3)	P(3)–Nb(1)–Nb(2)	117.0(1)	P(4)–Nb(2)–P(2)	125.3(2)	N(1)–Nb(2)–Nb(1)	53.7(2)
P(3)–Nb(1)–Cl(1)	74.2(2)	P(3)–Nb(1)–Cl(2)	139.9(3)	N(1)–Nb(2)–Cl(1)	71.0(2)	N(1)–Nb(2)–Cl(2)	71.7(2)
P(3)–Nb(1)–Cl(3)	73.9(1)	P(3)–Nb(1)–Cl(4)	74.1(3)	N(1)–Nb(2)–Cl(5)	143.3(1)	N(1)–Nb(2)–Cl(6)	84.8(2)
P(3)–Nb(1)–P(1)	126.9(1)	N(1)–Nb(1)–Nb(2)	54.4(2)	N(1)–Nb(2)–P(2)	74.9(2)	N(1)–Nb(2)–P(4)	142.7(1)
N(1)–Nb(1)–Cl(1)	71.1(2)	N(1)–Nb(1)–Cl(2)	72.1(2)	N(2)–Nb(2)–Nb(1)	54.5(2)	N(2)–Nb(2)–Cl(1)	71.5(2)
N(1)–Nb(1)–Cl(3)	84.9(2)	N(1)–Nb(1)–Cl(4)	143.8(1)	N(2)–Nb(2)–Cl(2)	71.5(2)	N(2)–Nb(2)–Cl(5)	83.7(2)
N(1)–Nb(1)–P(1)	74.8(2)	N(1)–Nb(1)–P(3)	141.2(1)	N(2)–Nb(2)–Cl(6)	142.6(1)	N(2)–Nb(2)–P(2)	143.0(1)
N(2)–Nb(1)–Nb(2)	54.0(2)	N(2)–Nb(1)–Cl(1)	71.1(2)	N(2)–Nb(2)–P(4)	75.1(2)	N(2)–Nb(2)–N(1)	108.2(2)
N(2)–Nb(1)–Cl(2)	71.3(2)	N(2)–Nb(1)–Cl(3)	143.9(1)	Nb(2)–N(1)–Nb(1)	71.9(2)	C(1)–N(1)–Nb(1)	118.0(4)
N(2)–Nb(1)–Cl(4)	84.9(2)	N(2)–Nb(1)–P(1)	141.3(1)	C(1)–N(1)–Nb(2)	122.7(4)	C(3)–N(1)–Nb(1)	122.3(4)
N(2)–Nb(1)–P(3)	75.3(2)	N(2)–Nb(1)–N(1)	108.4(2)	C(3)–N(1)–Nb(2)	117.7(4)	C(3)–N(1)–C(1)	103.3(4)
Cl(1)–Nb(2)–Nb(1)	57.3(3)	Cl(2)–Nb(2)–Nb(1)	56.9(1)	Nb(2)–N(2)–Nb(1)	71.5(2)	C(5)–N(2)–Nb(1)	116.6(3)
Cl(2)–Nb(2)–Cl(1)	114.2(3)	Cl(5)–Nb(2)–Nb(1)	126.8(1)	C(5)–N(2)–Nb(2)	123.9(4)	C(7)–N(2)–Nb(1)	123.8(4)
Cl(5)–Nb(2)–Cl(1)	80.9(3)	Cl(5)–Nb(2)–Cl(2)	143.5(1)	C(7)–N(2)–Nb(2)	117.3(4)	C(7)–N(2)–C(5)	103.0(4)

Table 2 Fractional atomic coordinates (× 10^4) for non-hydrogen atoms in $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]\cdot C_6H_5Me$

Atom	*x*	*y*	*z*
Nb(1)	95.9(4)	1338.4(3)	1691.8(1)
Nb(2)	718.5(4)	2486.8(4)	1021.1(1)
Cl(1)	−1476(1)	2907(1)	1301.2(3)
Cl(2)	2287(1)	935(1)	1411.3(3)
Cl(3)	−2160(1)	344(1)	1819.2(3)
Cl(4)	1675(1)	1012(1)	2331.8(3)
Cl(5)	412(1)	4816(1)	840.6(3)
Cl(6)	1763(1)	1417(1)	464.7(3)
P(1)	546(1)	−1152(1)	1744.5(3)
P(2)	−1211(1)	2507(1)	400.1(3)
P(3)	−879(1)	2811(1)	2219.9(3)
P(4)	3212(1)	3456(1)	1039.6(3)
N(1)	−464(4)	573(3)	1056(1)
N(2)	1259(3)	3273(3)	1659(1)
C(1)	125(5)	−691(4)	956(1)
C(2)	−191(5)	−1705(4)	1257(1)
C(3)	−1927(4)	511(5)	857(1)
C(4)	−2002(6)	935(5)	426(1)
C(11)	2310(5)	−1747(5)	1792(2)
C(12)	−186(5)	−2099(5)	2109(2)
C(21)	−2637(5)	3634(5)	387(2)
C(22)	−787(6)	2688(6)	−97(1)
C(5)	594(5)	4431(4)	1814(1)
C(6)	252(5)	4203(4)	2235(1)
C(7)	2759(4)	3457(4)	1810(1)
C(8)	3451(5)	4266(5)	1516(1)
C(31)	−2610(5)	3495(5)	2109(2)
C(32)	−906(5)	2276(5)	2725(1)
C(41)	3575(5)	4574(5)	658(2)
C(42)	4699(5)	2389(5)	1064(2)
C(1S)	3765(5)	2937(4)	9035(1)
C(2S)	4792(5)	2178(5)	8908(1)
C(3S)	5493(5)	1292(5)	9156(2)
C(4S)	5193(5)	1139(5)	9536(2)
C(5S)	4173(6)	1879(5)	9670(2)
C(6S)	3466(5)	2774(5)	9421(2)
C(7S)	3012(5)	3919(5)	8766(2)

The average Nb–N bond distances are very close [average 2.325(5) Å] to those observed in the complexes $[\{NbCl_2(\mu\text{-}S)(NCMe)_2\}_2]\cdot n$MeCN ($n$ = 1 or 2)[6b] which have an identical average length. In addition, the Nb–N bond lengths are similar within experimental error and all atoms in the Nb_2N_2 framework are coplanar, forming a rhombus.

An interesting feature of the structure of complex **3** is the marked shortness of the average bridging chloride–niobium bond lengths [Nb–Cl_b 2.503(4) Å] compared to the average terminal chloride–niobium bond lengths [Nb–Cl_t 2.533(4) Å]. This is unexpected since, almost invariably, bridging chloride–metal distances are longer than terminal within the same transition-metal complex[18] suggesting that the short Nb–Cl_b distances in the present compound are of significance. It is possible that the unexpectedly short bridge Nb–Cl_b bonds are due to delocalisation of electron density into p_π orbitals of equatorial bridging chlorides as has been suggested for $NbCl_4\cdot 2L$ complexes (L = pyridine or substituted pyridines) on the basis of molecular-orbital calculations.[14a] This electron delocalisation into ligands described as weak π acceptors may be enhanced by the presence of good electron-donating ligands about the metal centres and the presence of π acceptors in equatorial[14] bridging positions.

The Nb–Nb single bond length of 2.724(4) Å observed in compound **3** is very close to that found in the partially resolved structure of $[\{NbCl_3[N(CH_2CH_2AsMe_2)_2]\}_2]$.[9] Despite the differences in the oxidation states and the ionic radii between the formally d^1 Nb^{IV} in **3** and in d^2 niobium(III) complexes such as $[\{NbCl_3(dppe)\}_2]$[11] and $[\{NbCl_3(dppm)\}_2]$[12] [where Nb=Nb double bonds are presumed; dppe = 1,2-bis(diphenylphosphino)ethane, dppm = bis(diphenylphosphino)methane], the Nb–Nb separations are almost identical within experimental error. The Nb–Nb bond distance in **3** is shorter than the corresponding distances observed in the two chloride-bridged niobium(IV) adducts of monodentate tertiary phosphine ligands, $[Nb_2Cl_8(PR_3)_4]$[15] [for PR_3 = PMe_3, Nb–Nb 2.833(1) Å; for PMe_2Ph, Nb–Nb 2.837(1) Å], although the Nb atoms in all of these niobium(IV) complexes have the same oxidation

Table 3 Comparison of some geometrical parameters (lengths in Å, angles in °)* of selected niobium complexes

Compound	Oxidation state	Nb–Nb	Nb–P	Nb–N	Nb–Cl_b	Nb–Cl_t	Cl_b–Nb–Cl_b	Nb–Cl_b–Nb	Chelate angle	Ref.
$[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]$	+4	2.724(4)	2.645(5)	2.324(5)	2.506(4)	2.532(4)	114.05(3)	66.0(1)	75.2(2)	This work
$[\{NbCl_3[N(CH_2CH_2AsMe_2)_2]\}_2]$	+4	2.70(2)		2.28(2)	2.540(6)	2.500(6)			75.0(5)	9
$[\{NbCl_2[P(CH_2CH_2PMe_2)_2]\}_2]$	+3	3.116(4)	2.623(6)			2.461(4)			72.57(2)	10
$[\{NbCl_3(dppe)\}_2]$	+3	2.730(3)	2.679(4)		2.450(4)	2.397(4)	112.3(1)	67.7(1)	77.7(1)	11
$[\{NbCl_3(dppm)\}_2]$	+3	2.696(1)	2.662(2)		2.454(2)	2.400(2)	113.35(5)	66.65(5)		12
$[\{NbCl_2(\mu\text{-}S)(NCMe)_2\}_2]\cdot n MeCN$	+4	2.869(3)		2.310(26)		2.385(5)				6*b*
$[NbCl_4(NCMe)_2]$	+4			2.220(13)		2.340(6)				6*b*
$[\{NbCl_4(PMe_2Ph)_2\}_2]$	+3	2.838(1)	2.700(1)		2.541(1)	2.484(1)	112.1(3)			13
Nb_2Cl_{10}	+5	3.951(2)			2.555(6)	2.284(6)	78.7(4)	101.3(3)		14*b*
$[\{NbCl_4(PMe_3)_2\}_2]$	+4	2.833(1)	2.671(1)		2.541(1)	2.502(1)	112.25(4)	67.75(4)		15
$Nb(NMe_3)_5$	+5			2.010(17)						16
$[NbOCl_3(PMe_3)_3]$	+5		2.641(3)			2.506(3)				5*c*
$[NbSCl_3(PMe_3)_3]$	+5		2.644(3)			2.492(2)				5*c*
$[NbCl_4(PMe_3)_3]$	+4		2.651(6)			2.442(13)				17

* Averaged values are given for compounds with multiple values in each category.

state and radii. Although it is very reasonable to consider the niobium atoms in **3** as singly bonded, these data suggest that the extent of metal–metal bonding cannot be solely based on geometrical parameters especially in view of the behaviour of similar complexes with bridging linear terdentate diphosphinophosphido ligands $P(CH_2CH_2PMe_2)_2$ where diamagnetism may well arise from antiferromagnetic spin coupling *via* the bridge. The relative shortness of the Nb–Nb interaction in **3** may be due to several influences including (*i*) the electron-rich donor environment around Nb enabling an efficient d–d interaction for niobium–niobium bond formation as has been previously suggested,[19] (*ii*) the small N bridging atoms drawing the metals together and (*iii*) constraints due to the unique arrangement of the bridging terdentate amidophosphine ligands where two chelates are fused at a common bridging atom. The chelating angle subtended at niobium in **3** (75°) falls within the range observed in the structures of $[\{Nb^{III}Cl_2[P(CH_2CH_2PMe_2)_2]\}_2]$[10] and $[\{Nb^{III}Cl_3(dppe)\}_2]$ (75–78°). This narrow range of values appears to be preferred for five-membered chelate rings, regardless of the oxidation state and ionic radius of the metal centre and the nature of the donor groups involved. In order to achieve such a chelating angle, the terdentate ligand may exert a pressure on the metal centres to move closer to each other than would otherwise be expected so as to reduce any strain in the chelating ring, since in the observed bridging configuration the chelate rings would have to open out if the metal–metal distance was increased. It is presumably this third influence which causes the analogous complex **4** to remain monomeric, since the relatively shorter niobium–tertiary donor bonds would exert significant strain in the chelate rings if the ligand were forced into a symmetrical linear terdentate bridging configuration similar to that in **3**. It is interesting that although the ligand $N(CH_2CH_2NEt_2)_2$ is known to form terdentate monomeric complexes of Ti^{III} and V^{III},[1] there are no reported examples of it bridging.

Experimental

All reagents and solvents were obtained from commercial sources except for $[NbCl_4(thf)_2]$,[20] $Me_2(S)PP(S)Me_2$,[21] $PHMe_2$,[22] $Li[PPr^i_2]$,[23] $ClP(Pr^i)_2$ and $PHPr^i_2$,[24] $NH(CH_2CH_2PR_2)_2$,[25] $Li[N(CH_2CH_2PR_2)_2]$[26] (R = Me or Pr^i) and $Li[N(CH_2CH_2NEt_2)_2]$[1] which were prepared according to published methods. The use of freshly prepared $[NbCl_4(thf)_2]$ was important for the success of some of the following reactions. Reactions involving secondary phosphines and nitrogen mustards were carried out in a well ventilated fume cupboard. All solvents were rigorously dried over an appropriate reagent, degassed and distilled under high-purity dinitrogen prior to use. Manipulations were by standard Schlenk-type procedures or in inert-atmosphere glove-boxes. Yields quoted are for the analytically pure isolated material based on the metal halides used unless otherwise stated.

Instruments.—Infrared spectra were obtained from Nujol mulls on a 577 Perkin-Elmer grating spectrophotometer (4000–200 cm^{-1}), and referenced to polystyrene (1601 cm^{-1}). Mass spectra were recorded on a VG Mass Lab. instrument at the SERC Mass Spectrometry Centre, Swansea; samples were introduced as solids. The quoted molecular weight refers to the strongest peak in the parent-ion cluster (only the most intense peak is recorded for each isotopometric cluster of ions). Melting and decomposition points were measured in sealed capillary tubes under dinitrogen by using a Gallenkamp apparatus and are uncorrected. The ESR spectra were obtained on a Varian E109 X-band instrument at ≈9.4 GHz at low temperature (120 K) using a quartz-glass tube. Solid-state magnetic susceptibilities were measured on a Johnson-Matthey magnetic susceptibility balance at ambient temperature and standardised against mercury tetrathiocyanatocobaltate(II). Proton and ^{13}C NMR spectra were obtained on a Bruker WM-360 spectrometer (360 MHz, ^1H; 90 MHz, ^{13}C) in C_6D_6 and were referenced to residual protic impurity (^1H, δ 7.27) or the solvent carbon (^{13}C, δ 128.8). The $^{31}P-\{^1H\}$ NMR spectra were obtained on a JEOL FX90Q spectrometer (36.23 MHz) and referenced to external H_3PO_4 (85%, δ 0) and are positive to low field. Elemental analyses were by CHN Analysis (Leicester, UK).

Preparations.—*[Bis(2-diisopropylphosphinoethyl)amido]trichloroniobium*(IV), $[NbCl_3\{N(CH_2CH_2PPr^i_2)_2\}]$ **1**. The complex $[NbCl_4(thf)_2]$ (1 g, 2.64 mmol) was suspended in toluene (80 cm^3). To this was slowly added a solution of $Li[N(CH_2CH_2PPr^i_2)_2]$ (0.82 g, 2.64 mmol) in toluene (30 cm^3) and stirring continued for 15 min at −78 °C. The reaction mixture was allowed to warm slowly to ambient temperature and stirred for 72 h. After filtration a pale brown solution was obtained which was evaporated to dryness under reduced pressure and the resultant solid washed with cold (−70 °C) diethyl ether (3 × 10 cm^3). The remaining solid was extracted into toluene (2 × 40 cm^3) and filtered. The filtrate was concentrated until saturated and cooled (−10 °C). The small pale greenish yellow prisms were collected, washed with cold (−70 °C) Et_2O (2 × 20 cm^3) and dried *in vacuo*. The mother-liquor was concentrated and cooled as before to give a second crop of prisms. The combined yield was 0.8 g (60%); m.p. 140 °C (Found: C, 38.8; H, 7.2; N, 2.7. Calc. for $C_{16}H_{36}Cl_3NNbP_2$: C, 38.2; H, 7.2; N, 2.8%). IR: 1455vs, 1405m, 1375s, 1360(sh), 1340(sh), 1295m, 1250s, 1215m, 1195m, 1140m, 1110(sh), 1065s, 1015(sh), 650s, 630m, 610m, 590m, 510s, 450s, 380m(br), 300(sh), 290vs and 265s cm^{-1}. $\mu = 1.7\ \mu_B$. Mass spectrum: *m/z* 503, M^+, 32; 467, $[M - Cl]^+$, 61; 462 $[M - Pr^i]^+$, 1; 439, $[NbPr^i_2Cl_2\{N(CH_2CH_2PPr^i_2)_2\} - PPr^i_2]^+$, 5; 426, $[M - (Cl + Pr^i)]^+$, 7; 392, $[M - (2Cl + Pr^i)]^+$, 5; 368, $[NbPr^i_2\{N(CH_2CH_2PPr^i_2)_2\} - PPr^i_2]^+$, 1; 360, $[NbCl(Pr^i)\{N(CH_2CH_2PPr^i_2)_2\} - PPr^i_2]^+$, 4; 340, $[M - (Cl + 3Pr^i)]^+$, 3; 322, $[NbPr^i\{N(CH_2CH_2PPr^i_2)_2\} - PPr^i_2]^+$, 2; 306, $[N(CH_2CH_2PPr^i_2)_2]^+$, 64; 262, $[N(CH_2CH_2PPr^i_2)_2 - Pr^i]^+$, 28; 220, $[N(CH_2CH_2PPr^i_2)_2 - 2Pr^i]^+$, 4; 188, $[N(CH_2CH_2PPr^i_2)_2 - PPr^i_2]^+$, 56; 174, $[N(CH_2CH_2PPr^i_2)_2 - CH_2PPr^i_2]^+$, 17; 162, $[N(CH_2CH_2PPr^i_2)_2 - CH_2CH_2PPr^i_2]^+$, 2; 145, $[CH_2CH_2PPr^i_2]^+$, 100; 131, $[CH_2PPr^i_2]^+$, 3; 117, $[PPr^i_2]^+$, 27; 103, $[CH_2NCH_2CH_2PPr^i]^+$, 5; 89, $[CH_2NCH_2CH_2P]^+$, 2; 75, $[PPr^i]^+$, 9; 62, $[C_4N]^+$, 1; 57, $[PC_2H_2]^+$, 3; and 41, $[Pr^i - 2H]^+$, 17%.

Bis[bis(2-diisopropylphosphinoethyl)amido]dichloroniobium(IV), $[NbCl_2\{N(CH_2CH_2PPr^i_2)_2\}_2]$ **2**. To a cold (−78 °C) stirred suspension of $[NbCl_4(thf)_2]$ (1 g, 2.64 mmol) in toluene (80 cm^3) was added a solution of the lithium amide (1.6 g, 5.00 mmol) in toluene (30 cm^3) dropwise with stirring. The mixture was stirred for 20 min at −78 °C and then allowed to warm to ambient temperature. After 3 d the solvent was removed under vacuum and the residue was extracted with light petroleum. The brown oily residue obtained by evaporation of the light petroleum was held under vacuum for 3 d and then washed with cold (−70 °C) light petroleum (2 × 5 cm^3). The solid residue crystallised as feathery yellow crystals from cold (−30 °C) light petroleum, yield 0.4 g (20%); m.p. 74 °C (Found: C, 50.5; H, 9.2; N, 3.4. Calc. for $C_{32}H_{72}Cl_2N_2NbP_4$: C, 49.8; H, 9.4; N, 3.6%). IR: 1455vs, 1400m, 1380(sh), 1370s, 1360(sh), 1290m, 1250(sh), 1240s, 1210m, 1180s, 1150m(br), 1090(sh), 710s, 695s, 650m, 640(sh), 605s, 580m, 510m, 455s, 380m(br), 310vs and 270m cm^{-1}. $\mu = 1.71\ \mu_B$. Mass spectrum: *m/z* 771, $[M]^+$, 1; 769, $[M - 2H]^+$, 2.5; 652, $[M - (Cl + 2Pr^i)]^+$, 0.5; 640 $[M - (2H + 3Pr^i)]^+$, 0.1; 520, $[NbClPr^i_2\{N(CH_2CH_2PPr^i_2)_2\}]^+$, 0.2; 467, $[M - N(CH_2CH_2PPr^i_2)_2]^+$, 0.8; 448, $[NbCl(Pr^i)(PPr^i_2)(NCH_2CH_2PPr^i_2)]^+$, 0.1; 439, $[NbPr^i\{N(CH_2CH_2PPr^i_2)_2\}]^+$, 0.3; 330, $[NbCl(Pr^i)(NCH_2CH_2PPr^i_2)]^+$, 1.9; 322, $[NbCl_2Pr^i_2\{N(CH_2CH_2)\}_2]^+$, 1.9; 306, $[N(CH_2CH_2PPr^i_2)_2]^+$, 23.8; 262, $[N(CH_2CH_2PPr^i_2)_2 - Pr^i]^+$, 58.9; 220, $[N(CH_2CH_2PPr^i_2)_2 - 2Pr^i]^+$, 3.0; 188, $[N(CH_2CH_2PPr^i_2)_2 - PPr^i_2]^+$, 87.9; 174, $[N(CH_2CH_2PPr^i_2)_2 - CH_2PPr^i_2]^+$, 24.2; 145, $[CH_2CH_2PPr^i_2]^+$, 100.0; 133, $[CH_2PPr^i_2]^+$, 11.0; 102, $[CH_2NCH_2CH_2PPr^i]^+$, 16.8; 89, $[CH_2NCH_2CH_2P]^+$, 12.8; 75, $[PPr^i]^+$, 40.9; 61, $[PPr^i - CH_2]^+$, 14.9; and 43, $[Pr^i]^+$, 70.4%.

Bis[bis(2-dimethylphosphinoethyl)amido]hexachlorodiniobium(IV) (Nb–Nb), $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]\cdot C_6H_5Me$ **3**. A suspension of $[NbCl_4(thf)_2]$ (1 g, 2.64 mmol) in toluene (80 cm^3) was slowly treated with an equimolar amount of $Li[N(CH_2CH_2PMe_2)_2]$ (0.525 g, 2.64 mmol) in toluene (30 cm^3) with vigorous stirring at −78 °C. After being stirred for 15 min at −78 °C, the reaction mixture was allowed to warm to ambient temperature and stirred for 3 d. The brown-orange slurry obtained was filtered and the filtrate evaporated to dryness in vacuum. The residue was triturated with Et_2O (50 cm^3), filtered and extracted with toluene (3 × 20 cm^3) (heating at this stage diminishes yield). On standing at −20 °C during 3 d lustrous brown-orange prisms separated which become dull and opaque upon exposure to vacuum. Concentration and cooling of the filtrate affords a second crop of prisms. Overall yield 0.31 g (30%). An analytical sample was washed with light petroleum and dried in vacuum to remove toluene of solvation, m.p. (decomp.) 195 °C (Found: C, 25.1; H, 5.0; N, 3.2; Calc. for $C_8H_{20}Cl_3NNbP_2$: C, 24.6; H, 5.2; N, 3.6%). IR: 2000vw, 1735w, 1470vs, 1410s, 1380s, 1340m, 1325w, 1295m, 1280vs, 1270(sh), 1190s, 1160vw, 1030m(br), 1020(sh), 1010s, 985(sh), 930vs, 905(sh), 840m(br), 805m(br), 770m, 730s, 700(sh), 655m, 595m, 580w, 490vw, 470vw, 420m, 350vs, 320s, 280vs, 260m and 250m cm^{-1}. NMR (C_6D_6, 22 °C): ^{31}P-$\{^1H\}$, δ +21.64 (s); ^1H, δ 4.8 (8 H, br t, NCH_2), 3.30 (8 H, m, PCH_2, 2.12 (3 H, s, $C_6H_5CH_3$), 1.47 (12 H, d, J_{PH} = 7.5, PCH_3) and 1.35 (12 H, d, J_{PH} = 7.5 Hz, PCH_3). Mass spectrum: *m/z* 390, M^+, 6.1; 355, $[M - Cl]^+$, 7.6; 327, $[M - (Cl + 2Me)]^+$, 1.4; 266 $[M - (Cl + 2Me + PMe_2)]^+$, 5.0; 238, $[M - (3Cl + PMe)]^+$, 1.5; 194, $[N(CH_2CH_2PMe_2)_2]^+$, 4.7; 178, $[N(CH_2CH_2PMe_2)_2 - Me]^+$, 25.1; 132, $[N(CH_2CH_2PMe_2)_2 - PMe_2]^+$, 10.0; 122, $[Me_2P\text{–}PMe_2]^+$, 17.3; 118, $[CH_2NCH_2CH_2PMe_2]^+$, 8.2; 107, $[Me_2P\text{–}PMe]^+$, 17.2; 91, $[CH_2CH_2PMe_2]^+$, 3.2; 75, $[CH_2PMe_2]^+$, 20.6; 61, $[PMe_2]^+$, 60.6; and 45, $[PCH_2]^+$, 28.7%.

[*Bis(2-diethylaminoethyl)amido*]*trichloroniobium*(IV), $[NbCl_3\{N(CH_2CH_2NEt_2)_2\}]$ **4**. To $[NbCl_4(thf)_2]$ (1 g, 2.637 mmol) in toluene (100 cm^3) was added a toluene solution of $Li[N(CH_2CH_2NEt_2)_2]$ (0.583 g, 2.637 mmol, 30 cm^3) with stirring at −30 °C; this temperature was maintained for 30 min. The resultant deep red slurry was allowed to warm slowly to ambient temperature. After 48 h the solvent was evaporated *in vacuo* and the residue washed with Et_2O (2 × 10 cm^3). The brownish red solid was extracted into toluene (3 × 20 cm^3), filtered, evaporated until saturated and cooled (−10 °C) to give small orange prisms (0.11 g, 10%), m.p. 150 °C (Found: C, 34.6; H, 6.7; N, 9.9. Calc. for $C_{12}H_{28}Cl_3N_3Nb$: C, 34.8; H, 6.8; N, 10.2%). $\mu = 1.68\ \mu_B$. Mass spectrum: *m/z* 414, M^+, 0.5; 393, $[M^+ - 21]$, 1; 357 $[NbCl_3\{N(CH_2CH_2NEt_2)_2\} - Et_2)]^+$, 0.4; 348, $[NbCl_2\{N(CH_2CH_2NEt_2)_2\} - Et]^+$, 0.5; 320 $[NbCl_2\{N(CH_2CH_2NEt_2)_2\} - Et_2]^+$, 2; 228, $[NbCl\{N(CH_2CH_2NEt_2)_2\} - CH_2CH_2NEt_2]^+$, 1; 216, $[N(CH_2CH_2NEt_2)_2]^+$, 35; 188, $[N(CH_2CH_2NEt_2)_2 - Et]^+$, 8; 173, $[N(CH_2CH_2NEt_2)_2 - (Et + CH_2)]^+$, 1; 156, $[N(CH_2CH_2NEt_2)_2 - CH_2NEt]^+$, 1; 143, $[N(CH_2CH_2NEt_2)_2 - NEt_2]^+$, 7; 129, $[N(CH_2CH_2NEt_2)_2 - CH_2NEt_2]^+$, 8; 117, $[N(CH_2CH_2NEt_2)_2 - CH_2CH_2NEt_2]^+$, 3; 102, $[N(CH_2CH_2NEt_2)_2 - NCH_2CH_2NEt_2]^+$, 17; 86, $[H_2CNEt_2]^+$, 30; 74, $[NEt_2]^+$, 100; 58, $[H_2CNEt]^+$, 34; and 46, $[H_2NEt]^+$, 57%.

Single-crystal Structure Analysis of $[\{NbCl_3[N(CH_2CH_2PMe_2)_2]\}_2]\cdot C_6H_5Me$ **3**.—Brownish orange irregular crystals suitable for X-ray diffraction were obtained from toluene–light petroleum (20:1 v/v) held at −10 °C for 3 d. A single well developed crystal of approximate dimensions 0.25 × 0.15 × 0.10 mm was mounted in a thin-walled glass capillary sealed under oxygen-free dry dinitrogen gas and used for X-ray data collection.

Crystal data. $C_{23}H_{48}Cl_6N_2Nb_2P_4$, M_r = 875.07, monoclinic, space group $P2_1/n$, a = 9.799(5), b = 10.491(2), c = 34.122(5) Å, β = 97.46(2)°, U = 3477.08 Å^3, Z = 4, D_c = 1.672 g cm^{-3}, μ_{calc} = 12.97 cm^{-1}, $F(000)$ = 1776.

The lattice parameters and intensity data were recorded at 150 K using a Delft Instruments FAST area detector diffractometer positioned at the window of a rotating-anode generator and Mo-Kα radiation (λ = 0.710 69 Å) by following previously described procedures.[27] 17 238 Reflections were measured ($2.03 < \theta < 28.12°$, index ranges $-12 \leqslant h \leqslant 8$, $-12 \leqslant k \leqslant 9$, $-42 \leqslant l \leqslant 41$) and processed to yield 6854 unique reflections (R_{int} = 0.073); of these 5811 were considered observed $[F_o > 3\sigma(F_o)]$ and used in the refinement. The data were also corrected for absorption effects[28] (maximum and minimum correction factors = 1.176 and 0.893 respectively).

The structure was solved by direct methods[29] followed by Fourier-difference syntheses and refined on F using full-matrix least squares.[30] All non-hydrogen atoms were treated anisotropically; the hydrogen atoms were included in calculated positions with a common U_{iso} being refined for all. Unit weights were used which gave satisfactory agreement analyses. Final $R\ [= \Sigma(\Delta F)/\Sigma(F_o)]$ and $R'\ \{= [\Sigma w(\Delta F)^2/\Sigma(F_o{}^2)]^{\frac{1}{2}}\}$ were 0.0328 and 0.0408 respectively for 362 parameters and 5811 observed data [ρ_{min}, ρ_{max} in the final difference map = −0.80, +0.52 e Å^{-3}; $(\Delta/\sigma)_{max}$ = 0.34]. All calculations were done on a 486DX2/66 personal computer. Sources of scattering factor data were as in ref. 28.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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