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A Microwave Investigation of the Structure of Trimethylamine–Trimethylborane[1]

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The microwave spectra of eight isotopic species of $(CH_3)_3N{\cdot}B(CH_3)_3$ have been studied. These gave the following structural parameters when methyl group parameters were assumed: $d(BN) = 1.698 \pm 0.01$ Å, $d(NC) = 1.470 \pm 0.01$ Å, $d(BC) = 1.69 \pm 0.04$ Å, $\angle NBC = 108.0 \pm 1.5°$, $\angle BNC = 111.6 \pm 0.5°$. A comparison of these parameters indicates that geminal nonbonded distances vary over a small range for the acid and base moieties in a number of B–N adducts. Boron–carbon single bond distances vary over a range of about 0.17 Å and this can be roughly correlated with the nominal hybridization about boron and carbon. It is suggested that the difference in the BN dative bond energies of $Me_3N{\cdot}BMe_3$ vs. $Me_3N{\cdot}BF_3$ is likely to be correlated with the difference in their heats of dissociation and is a major factor in the lower stability of $Me_3N{\cdot}BMe_3$.

We have reinvestigated the microwave spectrum of the weak adduct trimethylamine–trimethylborane (TMA·TMB). Our aims were to obtain an accurate value for the B–N distance and reasonable estimates for the remaining structural parameters and to gain further insight into the relative importance of steric factors, reorganization energies, and donor–acceptor bond energies in determining both the structure and strength of such adducts. Additional motivation was provided because no accurate structural studies exist for such complexes involving trimethylborane.

Lide et al.[2] first examined the microwave spectrum of TMA·TMB. They showed that at pressures of about 0.2 mmHg broad absorption bands could be observed ($\Delta\nu_{1/2} = 40$ MHz) which fit a symmetric top formula. From the rotational constant determined from the peak maximum and assumptions for $r(CN) = 1.47$ Å, $r(CB) = 1.56$ Å, and tetrahedral bond angles, they estimated a BN distance of 1.80 ± 0.15 Å with the large uncertainty arising from varying the initial assumptions over a plausible range. Several other workers[3–5] have speculated that the true BN distance should lie at values ranging from 1.62 to 1.81 Å.

We have succeeded in resolving this ambiguity by determining the ^{10}B–^{11}B and ^{14}N–^{15}N isotope shifts. This leads to a value of $r_s(BN) = 1.698 \pm 0.01$ Å. Using this datum and isotopic data from $(CD_3)_3N{\cdot}B(CH_3)_3$ and $(^{13}CH_3)_3N{\cdot}B(CH_3)_3$, it is possible to estimate other structural parameters with similar or somewhat poorer precision.

Experimental Section

Samples. Trimethylborane and $^{15}NH_4Cl$ (95% ^{15}N) were kindly donated by D. F. Shriver and R. C. Taylor, respectively. $(CH_3)_3{}^{15}N$ was prepared from $^{15}NH_4Cl$ and paraformaldehyde, $(CH_2O)_3$, as outlined by Clippard.[6a] $(^{13}CH_3)_3N$ was liberated for use from a previously prepared[17] sample of $(^{13}CH_3)_3NBF_3$ via base-displacement employing 1,4-diaza[2.2.2]bicyclooctane (DABCO).[6b] The original preparation of the trimethylamine utilized $(^{13}CH_2O)_3$ (90 atom % ^{13}C) obtained from Merck. $(CD_3)_3N$ was liberated from $(CD_3)_3N{\cdot}HCl$, also from Merck (99% D). Using standard high vacuum line procedures[7] the TMA·TMB adducts were prepared by condensing $(CH_3)_3B$ with a slight excess of amine into a Pyrex tube and allowing the tube to warm to −45 °C. Volatiles remaining at this temperature were removed by pumping through a −196 °C trap.

Spectrometer. A Hewlett-Packard 8460A microwave spectrometer[8] was used in the region 26.5–40.0 GHz. Pressures between 0.05 and 0.15 mmHg and absorption cell temperatures between 23 and −20 °C were employed. Temperature-dependent studies were made by placing dry ice around the cell and observing the intensity across an absorption band until the compound condensed on the cell walls.

Spectra. All the isotopically distinct species gave broad absorption bands whose peak maxima occurred at regular intervals of $2B(J + 1)$ as expected for a symmetric top. A typical band is illustrated in Figure 1. The width of the CH_3OH impurity line in the figure indicates that the breadths of the bands are not due solely to pressure broadening but arise from numerous overlapping transitions. Some structure was apparent on the bands, especially on the high-frequency side. However, efforts to resolve the spectra further by lowering temperature and pressure produced significant improvements only on the high-frequency end of the band. Presumably, this rich structure is associated with the overlapping of a large number of transitions arising from the ground vibrational state and excited low-frequency vibrational states split by centrifugal distortion and vibration–rotation interactions typical of degenerate modes in symmetric tops and possibly even complicated by a low barrier to internal rotation. However, attempts at fitting the distinct transitions to standard formulas for such interactions proved futile.

Efforts to identify the region of the band corresponding to the ground vibrational state by observing a relative increase in intensity upon lowering the temperature were unsuccessful. These attempts were frustrated by the total decrease in intensity of the whole band due to sample condensation. Consequently, we estimated the ground-state rotational constants for the ^{11}B isotopic species by measuring the band maximum and attaching an uncertainty that encompassed the band's half-width. It seems unlikely that the ground-state values would fall outside this region since symmetric tops with methyl groups usually have excited vibrational states shifted to both higher and lower frequency from the ground state. These rotational constants and moments of inertia are listed in Tables I and II, respectively.

It was possible to determine ^{10}B–^{11}B isotope shifts for each band despite the fact that the predicted isotope shift was only about twice the band's half-width and not completely resolvable. This was achieved by noting that the prominent, much sharper structure on the high-frequency side had a similar satellite pattern shifted by a nearly constant amount to still higher frequency. Examples of two particularly prominent transitions are labeled in Figure 1 as the ^{11}B and ^{10}B doublets. These satellite lines have the correct intensity and temperature dependence to be arising from ^{11}B and ^{10}B isotopic species. Measurements of these pairs of lines along with several others readily observed at longer time constants led to the isotope shifts listed in Table III and the estimates for I_0 for the ^{10}B species listed in Table II. These transitions also provide a check on the ^{15}N, ^{13}C, and D_9 isotope shifts measured from the band maxima. Although the detailed assignment of the transitions used to measure these isotope shifts is unclear, this procedure should lead to fairly precise estimates of the correct ground-state isotope shifts.

Structure Determination. The structural parameters were estimated from the moments in Table II using standard procedures. The BN distance was estimated using Kraitchman's equation[9] which has the form $I_s - I_p = \mu z_s^2$ where I_s and I_p are the moments of inertia of the substituted and parent isotopic species, μ is a reduced mass calculated from the known masses, and z_s is the coordinate of the substituted atom in the principal-axis system of the parent isotopic species. The calculations of boron and nitrogen coordinates and the BN distance in four different coordinate systems are listed in Table IV. The calculations of the BN distance are nicely consistent. This parameter can be reliably estimated in spite of the ambiguities in assigning spectra since the Kraitchman procedure depends on differences between moments. Thus, a large degree of cancellation of systematic errors in estimating the ground-state moments will occur. A r_s value of 1.698 ± 0.01 Å is obtained with an uncertainty sufficient to cover remaining ambiguities in the moments.

The remaining structural parameters were estimated by fitting the eight moments of inertia in Table II using a least-squares fitting

Table I. Frequencies for Band Maxima and Rotational Constants in MHz for $(CH_3)_3{}^{11}B{\cdot}N(CH_3)_3$ Isotopic Species

	normal[a]		^{15}N		$(CD_3)_3N$		$(^{13}CH_3)_3N$	
$J \rightarrow J+1$	ν_0	B_0	ν_0	B_0	ν_0	B_0	ν_0	B_0
10 → 11	34 636	1574.4	34 565	1571.1	30 913	1405.1	33 767	1534.9
11 → 12	37 782	1574.3	37 708	1571.2	33 725	1405.2	36 840	1535.0

[a] Additional band maxima for the normal isotopic species were measured: 18 884 (1573.7), 22 035 (1573.9), 25 180 (1573.7), 31 490 (1574.5).

Table II. Estimated Ground-State Moments of Inertia (u Å^2)

$(CH_3)_3{}^{11}B{\cdot}{}^{14}N(CH_3)_3$	321.02 ± 0.80
$(CH_3)_3{}^{10}B{\cdot}{}^{14}N(CH_3)_3$	320.20 ± 0.80
$(CH_3)_3{}^{11}B{\cdot}{}^{15}N(CH_3)_3$	321.67 ± 0.80
$(CH_3)_3{}^{10}B{\cdot}{}^{15}N(CH_3)_3$	320.88 ± 0.80
$(CH_3)_3{}^{11}B{\cdot}{}^{14}N(CD_3)_3$	359.65 ± 0.85
$(CH_3)_3{}^{10}B{\cdot}{}^{14}N(CD_3)_3$	358.68 ± 0.85
$(CH_3)_3{}^{11}B{\cdot}{}^{14}N(^{13}CH_3)_3$	329.26 ± 0.85
$(CH_3)_3{}^{10}B{\cdot}{}^{15}N(^{13}CH_3)_3$	328.52 ± 0.85

Table III. The Isotope Shift between ^{10}B and ^{11}B Transitions: $\Delta\nu$ (MHz) = $\nu(^{10}B) - \nu(^{11}B)$

	normal	^{15}N	$(CD_3)_3N$	$(^{13}CH_3)_3N$
$J \rightarrow J+1$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
10 → 11	85.0		85.2	87.0
11 → 12	92.8	93.9		95.3

Table IV. Boron and Nitrogen Substitution Coordinates and r(BN) in Å

parent	$\lvert z_B \rvert$	$\lvert z_N \rvert$	r(BN)
^{11}B-^{14}N	0.880	0.818	1.698
^{11}B-^{15}N	0.887	0.810	1.698
^{10}B-^{14}N	0.888	0.810	1.698
^{10}B-^{15}N	0.895	0.803	1.698

Table V. Structural Parameters from Fitting Moments of Inertia

Assumed
d(CH) = 1.09 ± 0.01 Å, d(BN) = 1.698 Å
<HCH = <HCB = <HCN = 109°28′

Derived

	calcd I[a]	calcd II[b]	best estimate
d(BC), Å	1.706 ± 0.015	1.677 ± 0.015	1.69 ± 0.04
d(NC), Å	1.472 ± 0.007	1.469 ∓ 0.007	1.470 ± 0.01
<NBC, deg	107.7 ± 0.3	108.4 ± 0.4	108.0 ± 1.5
<BNC, deg	111.4 ± 0.1	111.9 ± 0.1	111.6 ± 0.5

[a] Moments in Table II uncorrected. [b] Moments corrected for a shortening of 0.005 Å upon deuteration.

program.[10] The overall fit was within 0.02%. The results labeled calcd I in Table V were obtained when the following was assumed: d(CH) = 1.09 Å, d(BN) = 1.6982 Å, and tetrahedral angles for methyl groups. The uncertainties are sufficient to cover the divergence obtained if d(CH) is varied by ±0.01 Å or if the moments are varied over the range indicated in Table II. The results labeled calcd II in Table V were obtained using the same procedure except that the moments for the $(CD_3)_3N{\cdot}B(CH_3)_3$ species were changed by an amount sufficient to cover a shortening of 0.005 Å of the average CH bond upon deuteration.[11] It is clear that the isotopic data fix the parameters of the C_3NB framework reasonably well while the $B(CH_3)_3$ moiety and CH parameters are coupled through the moments and, therefore, are less reliably fixed. As different assumptions for the methyl group geometries are made, most of this variation will be taken up by r(BC) and ∠CBC. The column labeled "best estimate" in Table V gives the midrange values for calcd I and II with uncertainties that should be sufficient to include the various methyl group geometries that can be assumed and the uncertainties in the ground-state moments of inertia. The values derived in Table V correspond to the so-called r_0 parameters.[10,11]

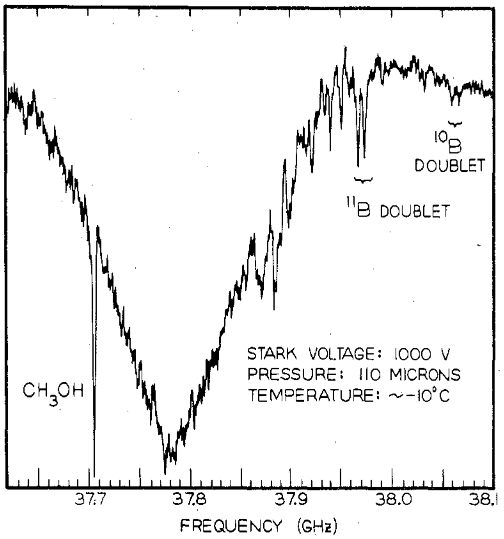

Figure 1. The $J = 11 \rightarrow J = 12$ transition region for $(CH_3)_3B{\cdot}N(CH_3)_3$.

Discussion

Structural parameters for four TMA·BX_3 adducts recently studied in this laboratory are summarized in Table VI. The TMA·TMB adduct is the least stable as judged by known heats of dissociation and the fact that it is the only species extensively dissociated at room temperature. The longer length of the BN bond readily correlates with this instability. From such structural data, we have attempted to assess the relative contributions that reorganization energies and donor–acceptor bond energies make in determining adduct stability using the energy partitioning suggested by Coyle and Stone.[12] The donor–acceptor interaction might be further interpreted as a boron–nitrogen bonding interaction opposed by a steric contribution, or F strain employing Brown's classic analysis,[13] while the reorganization step includes a contribution from B

Table VI. Structural Parameters for Trimethylamine-BX_3 Adducts[a]

$Me_3N{\cdot}BX_3$	r(BN), Å	r(NC), Å	<CNC, deg	<XBX, deg	ΔH_{diss}[b]
$Me_3N{\cdot}BH_3$[c]	1.638 ± 0.01	1.483 ± 0.01	109.0 ± 1	113.1 ± 0.2	32.1–47.4[e]
$Me_3N{\cdot}BH_2F$[d]	1.633 ± 0.006	1.494 ± 0.016	109.5 ± 1	113.5 ± 3.5	
$Me_3N{\cdot}BF_3$[e]	1.636 ± 0.004	1.476 ± 0.005	108.6 ± 0.2	112.4 ± 0.2	26.6[f]
$Me_3N{\cdot}BMe_3$	1.698 ± 0.01	1.470 ± 0.01	107.3 ± 0.5	110.9 ± 1	17.6[g]
Me_3N[h]		1.451 ± 0.003	110.9 ± 0.6		

[a] All results are from microwave spectra. See ref 22 for other determinations. [b] In kcal/mol for the reaction $Me_3N{\cdot}BX_3(g) \rightarrow Me_3N(g) + BX_3(g)$. [c] P. Cassoux, R. L. Kuczkowski, P. S. Bryan, and R. C. Taylor, *Inorg. Chem.*, **14**, 126 (1975). [d] P. Cassoux, R. L. Kuczkowski, G. Fong, and R. A. Geanangel, *J. Mol. Struct.*, in press. [e] Reference 17. [f] R. C. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, 78, 2061 (1956). [g] Reference 13b. [h] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **51**, 1580 (1969).

Table VII. Nonbonded XX Distances (Å) in BX_3 and Their Adducts

X···X	F···F	Cl···Cl	Br···Br	I···I	C···C
BX_3	2.27 (1)[a]	3.01 (1)[f]	3.28 (1)[g]	3.66 (1)[h]	2.73 (1)[i]
$Me_3N{\cdot}BX_3$	2.30 (1)[b]	3.03 (1)[j]	3.26 (1)[k]	3.67 (1)[k]	2.78 (8)
$CH_3CN{\cdot}BX_3$	2.25 (2)[c]	3.02 (1)[c]			
$H_3P{\cdot}BF_3$	2.28 (1)[d]				
$H_3N{\cdot}BF_3$	2.27 (3)[e]				
$Me_3P{\cdot}BX_3$		3.07 (2)[l]	3.32 (2)[l]	3.71 (3)[l]	

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Table VIII. Nonbonded CC Distances (Å) in $(CH_3)_3E{\cdot}BX_3$ (E = N, P, As) Adducts

	N	P	As
Me_3E	2.39 (1)[a]	2.80 (1)[h]	2.91 (5)[l]
$Me_3E{\cdot}BH_3$	2.42 (3)[b]	2.89 (2)[i]	3.09 (3)[m]
$Me_3E{\cdot}BF_3$	2.40 (1)[c]		
$Me_3E{\cdot}BCl_3$	2.43 (1)[d]	2.93 (2)[j]	
$Me_3E{\cdot}BBr_3$	2.40 (3)[e]	2.92 (2)[j]	
$Me_3E{\cdot}BI_3$	2.39 (4)[e]	2.98 (4)[j]	
$Me_3N{\cdot}BMe_3$	2.37 (3)		
$Me_3N{\cdot}AlH_3$	2.42 (1)[f]		
$Me_3N{\cdot}AlMe_3$	2.41 (1)[g]		
Me_3EO		2.85 (2)[k]	3.10 (3)[k]
Me_3ES		2.87 (1)[k]	3.08 (2)[k]

[a] Table VI, ref *h*. [b] Table VI, ref *c*. [c] Reference 17. [d] Reference 5. [e] Reference 22e. [f] A. Almenningen, G. Gundersen, T. Haugen, and A. Haaland, *Acta Chem. Scand.*, **26**, 3928 (1972). [g] G. A. Anderson, F. R. Forgaard, and A. Haaland, *ibid.*, **26**, 1947 (1972). [h] P. S. Bryan and R. L. Kuczkowski, *J. Chem. Phys.*, **55**, 3049 (1971). [i] P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, 11, 553 (1972). [j] Table VII, ref *l*. [k] C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen, and K. Hedberg, *J. Am. Chem. Soc.*, 97, 6352 (1975). [l] D. R. Lide, Jr., *Spectrochim. Acta*, **15**, 473 (1959). [m] J. R. Durig, B. A. Hudgens, and J. Odom, *Inorg. Chem.*, 13, 2306 (1974).

Table IX. B–C Bond Lengths (Å) as a Function of Nominal Orbital Hybridization

	hybrid orbitals		
molecule	B	C	length
$Me_3N{\cdot}BMe_3$	sp^3	sp^3	1.69 (4)
$Me_2N{\cdot}BMe_2$	sp^2	sp^3	1.65 (2)[a]
$BMeF_2$	sp^2	sp^3	1.60 (3)[b,c]
BMe_3	sp^2	sp^3	1.57 (1)[d]
Me_2BOBMe_2	sp^2	sp^3	1.573 (4)[e]
$MeSBMe_2$	sp^2	sp^3	1.570 (4)[f]
$H_3CNC{\cdot}BH_3$	sp^3	sp	1.566 (4)[g]
BMe_2F	sp^2	sp^3	1.55 (2)[c]
$OC{\cdot}BH_3$	sp^3	sp	1.534 (10)[h]
H_2CCHBF_2	sp^2	sp^2	1.533 (8)[i]
$HCCBF_2$	sp^2	sp	1.513 (5)[j]

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strain. This has led to several empirical correlations involving structural data which shall be discussed first.

It is interesting to observe in Table VII that the nonbonded XX distances in BX_3 and their adducts vary over only a small range. This suggests that the geminal interactions (B strain) are similar although the vicinal interactions (F strain) should vary markedly for these adducts. A similar observation can be made regarding the amine C···C distances in Table VIII while the C···C distances in Me_3P and Me_3As are more variable. These observations correlate well with Bartell's suggestion[14] that nonbonded interatomic distances are often rather constant about small central atoms like N and, therefore, may lead to the breakdown of VSEPR rationalizations when correlating changes in structural parameters. This latter suggestion can certainly apply to the well-documentated observation that *d*(CN) lengthens and ∠CNC decreases for amines upon complexation in contrast to the opposite behavior for Me_3P. There is also some hint from the data in the tables that F strain contributes to the weakness of the TMA·TMB adduct since the amine C···C distance is slightly shorter than in most other complexes and the Me_3B moiety is appreciably distorted in spite of the longer BN bond length. In the isoelectronic hexamethylethane steric effects have been proposed to account for the long central CC distance ($r_g = 1.582 \pm 0.01$ Å)[4] and angle deformations.

Another interesting correlation arose from efforts to place into perspective the BC bond length of 1.69 ± 0.04 Å in TMA·TMB which appears to be the longest yet reported. The correlation is summarized in Table IX where known BC bond lengths are listed along with the nominal hybridization on boron and carbon. This correlation is similar to the well-known effect[15] whereby CC single bonds vary over about 0.12 Å depending upon the number of groups attached to the carbon atoms. However, it is apparent from the data in Table IX that a simple linear or nearly linear function which depends only on the number of attached groups to boron and carbon will not adequetely represent the data, unlike the case for carbon–carbon bonds.[15,16] A combination of several effects may be forwarded to rationalize the correlation including covalent radii characteristic of the hydridization state, electron delocalization, steric effects, and electronegativity/bond ionicity.[16] The observed correlation may be useful for estimating BC bond distances in systems lacking in experimental data and lends support to the long BC distance obtained from our analysis.

The highly dissociated nature of TMA·TMB in the gas phase at room temperature compared with TMA·BH_3 and TMA·BF_3 was pointed out earlier. A discussion[17] of the relative stabilities of the latter two adducts in terms of the borane reorganization energies and BN dative bond energies led to the inference that the higher reorganization energy of BF_3 (ΔH_R = 27.9 kcal vs. 15.1 kcal for BH_3) accounts for a major contribution to the stability difference. If BMe_3 is assumed to have a similar reorganization energy, between 15.1 and 27.9 kcal, then the ΔH_{diss} for the TMA·TMB and TMA·BF_3 adducts (Table VI) dictates that the donor–acceptor bond energy will be from 9 to 22 kcal stronger for the BF_3 adduct.[18,19] This difference will only decrease as ΔH_R for BMe_3 increases above 27.9 kcal which seems unreasonable given the increased π bonding in planar BF_3.[20] Hence, it appears that a major contribution to the decrease in stability for the BMe_3 adduct vs. the BF_3 adduct arises from a weaker donor–acceptor bond energy, presumably in part from steric effects. This conclusion and the energy estimates are similar to those for the acetonitrile adducts of BCl_3 and BF_3 in which the BN bond was found to be 0.07 Å longer in the BF_3 complex.[21] In that example a difference in BN bond energies was estimated between 8 and 16 kcal/mol using an extrapolated bond energy–bond length correlation and 18 kcal based on a force constant extrapolation. Reorganization energy calculations for BMe_3 of comparable quality to those performed for BH_3 and BF_3[17] could provide further support for the above analysis.

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Registry No. $(CH_3)_3{}^{11}B\cdot N(CH_3)_3$, 66750-72-9; $(CH_3)_3{}^{10}B\cdot N(CH_3)_3$, 66769-47-9; $(CH_3)_3{}^{11}B\cdot{}^{15}N(CH_3)_3$, 66750-71-8; $(CH_3)_3{}^{10}B\cdot{}^{15}N(CH_3)_3$, 66750-70-7; $(CH_3)_3{}^{11}B\cdot N(CD_3)_3$, 66750-69-4; $(CH_3)_3{}^{10}B\cdot N(CD_3)_3$, 66750-68-3; $(CH_3)_3{}^{11}B\cdot N({}^{13}CH_3)_3$, 66750-67-2; $(CH_3)_3{}^{10}B\cdot N({}^{13}CH_3)_3$, 66750-65-0; $Me_3N\cdot BMe_3$, 1704-27-4.

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(18) This reasoning also assumes that the reorganization energies for the Me_3N moieties can be neglected. The small differences in their structures (Table VI) should not seriously vitiate the argument.

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Notes

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Preparation and Molecular Structure of $[(\eta\text{-}C_5H_5)_2Ta(Me_2PC_2H_4PMe_2)]Cl\cdot CH_3CN$

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Despite the stability of organometallic compounds of vanadium(II) and vanadium(0) (e.g., $(\eta\text{-}C_5H_5)_2V$[3] and $V(CO)_6$[4]), no reports of the isolation of di- or zerovalent tantalum or niobium complexes have appeared,[5] excepting $(LiPh)_4MPh_2(ether)_{3.5}$ (M = Nb, Ta)[6]. We recently reported the preparation of $TaCl_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane), a well-characterized molecular Ta(II) complex.[7] The availability of this material led us to explore its chemistry with nucleophilic reagents in an attempt to find simple metathetical reactions leading to organometallic compounds of Ta(II). We report the reaction of $TaCl_2(dmpe)_2$ with cyclopentadienide ion, which apparently proceeds by disproportionation, and the crystal structure of $[(\eta\text{-}C_5H_5)_2Ta(dmpe)]Cl\cdot CH_3CN$.

Experimental Section

Solvent purification, manipulations, and instrumental measurements were performed as previously described.[7] $Na(C_5H_5)\cdot DME$[8] (DME = dimethoxyethane) and $TaCl_2(dmpe)_2$[7] were prepared by literature methods. A positive ^{31}P chemical shift represents a resonance at lower field than 85% H_3PO_4.

$[(\eta\text{-}C_5H_5)_2Ta(dmpe)]Cl$. A 10-mm Pyrex tube, fitted with a stopcock, was charged with 1.00 g (1.81 mmol) of $TaCl_2(dmpe)_2$ and 0.700 g (3.98 mmol) of $Na(C_5H_5)\cdot DME$. The tube was evacuated and cooled to −196 °C, and ca. 5 mL of THF condensed onto the solids. After being sealed in vacuo and heated to 100 °C overnight, the vessel was opened and the solids were collected by filtration. Extraction of the residue with CH_2Cl_2 and evaporation of the solvent afforded 0.44 g (0.89 mmol, 49%) of the crude product. An analytical sample was recrystallized from CH_2Cl_2–heptane at −78 °C: ^1H NMR (CD_2Cl_2) τ 5.07 (t, J_{PH} = 2.2 Hz, 10 H), 8.4 (br, m, 16 H)—dmpe methyl and methylene resonances are overlapping and poorly resolved; $^{31}P\{^1H\}$ NMR (CD_3CN) 14.0 ppm (s). Anal. Calcd for $C_{16}H_{26}ClP_2Ta$: C, 38.69; H, 5.28. Found: C, 38.44; H, 5.18.

Extraction of the reaction mixture with CH_3CN or recrystallization of the purified product from CH_3CN gave the acetonitrile adduct $[(\eta\text{-}C_5H_5)Ta(dmpe)]Cl\cdot CH_3CN$ (vide infra).

$[(\eta\text{-}C_5H_5)Ta(dmpe)_2Cl]Cl$. A mixture of 1.50 g (2.73 mmol) of $TaCl_2(dmpe)_2$ and g 0.96 (5.46 mmol) of $Na(C_5H_5)\cdot DME$ was reacted similarly, except that the sealed tube was allowed to stand for 24 h at room temperature. An identical workup gave 0.85 g (1.38 mmol, 51%) of yellow crystals: ^1H NMR (CD_3CN) τ 5.55 (quintet, J_{PH} = 3.2 Hz, 5 H), 8.5 (br, m, 32 H)—dmpe methyl and methylene resonances are overlapping and poorly resolved; $^{31}P\{^1H\}$ NMR (CD_3CN) 5.78 ppm (s). Anal. Calcd for $C_{17}H_{37}Cl_2P_4Ta$: C, 33.08;

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