contrast, $FeC_7H_8^+$ is the only product ion formed from the reaction of Fe^+–benzyne. Once again, the dramatic change of reactivity upon going from $FeC_6H_4^+$ to $Fe_2C_6H_4^+$ indicates the important role of the metal center and suggests, therefore, that the reaction is probably initiated by the metal center, and is not simply between the ligands themselves. The type of product ions observed suggests that the cluster center inserts into both C–C and C–H bonds of propene.

In conclusion, the reactivity of Fe_2^+–benzyne is much different from that of Fe_2^+ and Fe^+–benzyne. The enhanced reactivity toward alkanes of $Fe_2C_6H_4^+$ with respect to that of bare Fe_2^+ probably arises due to two effects. First, in analogy to the Co_2CO^+ case discussed above, the ligand polarizes or in some way changes the electronic structure of the metal center to permit oxidative addition. Second, the coordination of the highly unsaturated benzyne ligand provides a very efficient pathway for further steps following initial metal center oxidative insertion, with the high exothermicity gained from partially saturating the C–C triple bond of the benzyne ligand to a double bond providing a significant driving force. Unlike Fe^+–benzyne, its dinuclear metal counterpart does not polymerize chlorobenzene around the metal center. In the reaction with small alkanes, the dinuclear benzyne complex ion seems to prefer C–H insertion over C–C insertion, resulting in the predominant formation of the hydrogenation product ion, Fe_2^+–benzene, while Fe^+–benzyne generates significantly more product ions corresponding to C–C bond insertion.

Acknowledgment is made to the Division of Chemical Sciences, Office of Basic Sciences, U.S. Department of Energy (Grant DE-FG02-87ER13766), for supporting this research and to the National Science Foundation (Grant CHE-8612234) for continued support of the FTMS.

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X-ray Study of $Ta(CHCMe_3)(S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3)_3(SEt_2)$ Suggests Why It Is Inactive for Metathesis of Ordinary Olefins

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Tantalum alkylidene complexes of the type $Ta(CHCMe_3)(DIPP)_3(THF)$ (DIPP = $O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) will react readily with terminal olefins or ethylene to give "base-free" tantalacyclobutane complexes (e.g., with styrene to give $Ta[CH(Ph)CH(t\text{-}Bu)CH_2](DIPP)_3$) or new alkylidene complexes (e.g., with vinyltrimethylsilane to give $Ta(CHSiMe_3)(DIPP)_3(THF)$).[1] They are quite active catalysts (several hundred turnovers) for the metathesis of ordinary internal olefins such as *cis*-2-pentene, although longevity is limited by instability of one or more intermediates, most likely alkylidene complexes in which a β proton is present. (No example has yet been observed.) In contrast, $Ta(CHCMe_3)(TIPT)_3(THF)$ (TIPT = $S\text{-}2,4,6\text{-}C_6H_2\text{-}i\text{-}Pr_3$) does not react with ordinary olefins and will not metathesize them. $Ta(CHCMe_3)(TIPT)_3(py)$ *will* react with norbornene to give *stable* $Ta\{[CH(C_5H_8)CH]_xCHCMe_3\}(TIPT)_3(py)$, in which a β proton is present. Base-free (five-coordinate) tantalacyclobutane complexes made from norbornene are observed when DIPP ligands are present, but not when TIPT ligands are present.

We speculated that the structures of $Ta(CHR)(TIPT)_3(base)$ complexes differ fundamentally from those of the type $Ta(CHR)(DIPP)_3(base)$ and that this is at least part of the reason for the strikingly different chemistry of the two types of complexes. A structure of a complex of the latter type, a vinylalkylidene complex, $Ta[C(Me)C(Me)CHCMe_3](DIPP)_3(py)$, prepared by adding pyridine to a metallacyclobutene complex prepared from $Ta(CHCMe_3)(DIPP)_3(THF)$ and 2-butyne, showed it to be approximately a trigonal bipyramid containing an η^1-vinylalkylidene ligand in an equatorial position and a pyridine ligand in an axial position.[2] One can propose that the axial pyridine ligand in $Ta[C(Me)C(Me)CHCMe_3](DIPP)_3(py)$ occupies the same position that an incoming olefin would occupy and that formation of an "axial/equatorial" tantalacyclobutane ring could take place readily. We have now prepared a suitably crystalline $Ta(CHCMe_3)(TIPT)_3(base)$ derivative (base = diethyl sulfide) and have determined its structure. The structure is, in fact, significantly different from that of the DIPP relative and goes a long way toward explaining the different catalytic behavior of the TIPT versus the DIPP complexes.

Experimental Section

Preparation of $Ta(CHCMe_3)(TIPT)_3(SEt_2)$. Diethyl sulfide (94 μL, 0.87 mmol) was added via syringe to a stirring solution of $Ta(CHCMe_3)(TIPT)_3(THF)$[1] (0.300 g, 0.29 mmol) in ether (10 mL) at room temperature. The color of the solution remained orange. After 15 min the solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The resulting orange-red solid was dissolved in pentane, and the solution was cooled to –30 °C to give large orange crystals (0.203 g, 66%). ^{1}H NMR: δ 7.15 (s, C_m), 3.93 (septet, 6, ortho $C\mathit{H}Me_2$), 2.83 (para $C\mathit{H}Me_2$), 2.47 (q, 4, $CH_3C\mathit{H}_2S$), 1.36 (d, 36, ortho $CH\mathit{Me}_2$), 1.25 (d, 18, para $CH\mathit{Me}_2$), 1.02 (t, 6, $C\mathit{H}_2CH_2S$), 0.83 (s, 9, $CHC\mathit{Me}_3$). ^{13}C NMR: δ 262 (broad, J_{CH} unresolved, $\mathit{C}HCMe_3$), 151.1, 149.1, and 134.2 (C_{ipso}, C_o, and C_p), 121.7 (C_m), 48.0 ($CH\mathit{C}Me_3$), 34.6 (para $\mathit{C}HMe_2$), 33.0 (ortho $\mathit{C}HMe_2$), 32.4 ($CHC\mathit{Me}_3$), 27.6 (broad t, $CH_3\mathit{C}H_2S$), 24.5 (para $CH\mathit{Me}_2$), 24.0 (ortho $CH\mathit{Me}_2$), 15.1 (CH_3CH_2S). (Routine multiplicities are not listed.) The alkylidene proton resonance is assumed to be found in the complex region around 4 ppm, as it is in the analogous pyridine adduct.[1] Ligand exchange leads to broadening of the resonance at 25 °C, and spectra were too complex at all temperatures to locate the resonance difinitively. The situation in the case of the THF adduct is analogous.[1] Elemental analyses were low for C, H, and S, we presume because of the lability of the diethyl sulfide ligand.

X-ray Study. A yellow plate of $Ta(CHCMe_3)(TIPT)_3(SEt_2)$ having approximate dimensions 0.150 × 0.350 × 0.350 mm was mounted on a glass fiber that was transferred to the diffractometer in a cold stream of dinitrogen. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation and a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $22.00° < 2\theta < 32.00°$, corresponded to a triclinic cell with dimensions a = 17.458 (3) Å, b = 19.109 (4) Å, c = 10.096 (2) Å, α = 90.77 (2)°, β = 102.41 (2)°, γ = 116.65 (1), V = 2917 (3) Å^3, and Z = 2. For a fw = 1047.48, the calculated density is 1.192 g/cm^3. The space group was determined to be $P\bar{1}$ (No. 2). Data were collected at a temperature of –70 ± 1 °C by using the ω-scan technique to a maximum 2θ value of 55.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26°. Scans of $(1.09 + 0.35 \tan \theta)°$ were made at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of two rescans), and the counts were accumulated to ensure good counting statistics. Stationary-background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

Of the 13 850 reflections collected, 13 410 were unique (R_{int} = 0.038); equivalent reflections were merged. The intensities of three representative reflections that were measured after every 197 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo Kα is 20.3 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.77 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by the Patterson method.[3] The non-hydrogen atoms were refined either anisotropically or isotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d_{C-H} = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the B_{equiv} values of the atoms to

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(1) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964.

(2) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.

(3) Walker, N.; Stuart, D. *Acta Crystal.* **1983**, *A39*, 158.

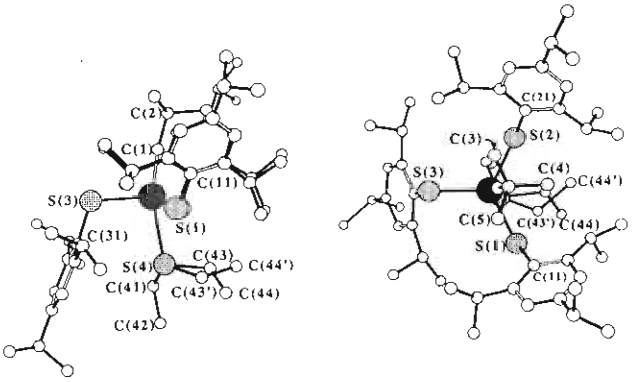

Figure 1. Two views of Ta(CHCMe$_3$)(S-2,4,6-C$_6$H$_2$-*i*-Pr$_3$)$_3$(SEt$_2$). (Disordered ethyl group (43,44; 43′,44′) is shown in both views.)

Table I. Selected Bond Distances (Å) and Angles (deg) in Ta(CHCMe$_3$)(TIPT)$_3$(SEt$_2$)

Ta–C(1)	1.894 (6)	S(1)–Ta–S(4)	71.01 (6)
Ta–S(1)	2.394 (2)	S(1)–Ta–C(1)	98.8 (2)
Ta–S(2)	2.391 (2)	S(2)–Ta–C(1)	98.0 (2)
Ta–S(3)	2.391 (2)	S(2)–Ta–S(4)	77.22 (6)
Ta–S(4)	2.750 (2)	S(3)–Ta–C(1)	101.3 (2)
Ta–S(1)–C(11)	116.9 (2)	S(3)–Ta–S(4)	96.25 (6)
Ta–S(2)–C(21)	116.7 (2)	S(4)–Ta–C(1)	162.2 (2)
Ta–S(3)–C(31)	110.8 (2)	Ta–C(1)–C(2)	172.8 (5)
S(1)–Ta–S(2)	123.92 (6)	Ta–S(4)–C(43)	104.8 (4)
S(1)–Ta–S(3)	114.41 (6)	Ta–S(4)–C(43′)	118.8 (8)
S(2)–Ta–S(3)	113.96 (6)	Ta–S(4)–C(41)	112.4 (3)

which they were bonded. The initial cycle of full-matrix least-squares refinement[4] was based on 10690 observed reflections ($I > 3.00\sigma(I)$) and 530 variable parameters and converged (largest parameter shift was 0.01 times its esd) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.047$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.068$.

The standard deviation of an observation of unit weight[5] was 1.67. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.11 and −1.22 e/Å^3, respectively.

One ethyl group of the coordinated diethyl sulfide would not refine. The problem was satisfactorily solved by treating the ethyl group (C(43) and C(44)) as disordered over two positions of equal occupancy. This disorder precluded refinement of these carbon atoms as anisotropic scatterers. No other problems were encountered.

Neutral-atom scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in F_c;[7] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[8] All calculations were performed with the TEXSAN[9] crystallographic software package of the Molecular Structure Corp.

Results

Two views of Ta(CHCMe$_3$)(TIPT)$_3$(SEt$_2$) are shown in Figure 1, and selected bond distances and angles are given in Table I.

The geometry overall can be described as a distorted trigonal bipyramid containing three thiolate ligands in equatorial positions. The phenyl rings of two of the thiolate ligands point up around the neopentylidene ligand, while the third points down toward the diethyl sulfide ligand. In all structurally characterized examples of TBP complexes that contain three bulky arenethiolate ligands, the thiolates are found in equatorial positions with one pointed toward one axial ligand and two toward the other axial ligand ("two up, one down") with M–S–C angles of ~110°,[10] so it is not surprising to find a similar result here. The distortion from ideal TBP geometry could be explained by repulsion between the neopentylidene group and the two thiolate ligands that point up toward it and by repulsion between the third thiolate ligand and the diethyl sulfide ligand. The angle between the alkylidene ligand and the coordinated diethyl sulfide is the largest interligand angle in the complex (S(4)–Ta–C(1) = 162.2 (2)°). The neopentylidene and diethyl sulfide ligands are effectively trans to one another. The Ta–S bond lengths are normal, while the Ta–S(4) bond length is rather long (2.750 (2) Å), consistent with the observed lability of the diethyl sulfide ligand.

The neopentylidene ligand falls into the category of a highly "distorted" variety[11] that contains an "agostic"[12] α-hydrogen atom, as evidenced from the shorter than expected[11] Ta–C(1) bond and essentially linear Ta–C(1)–C(2) angle. Since the *tert*-butyl group is bent toward the space between S(2) and S(1), the C–H$_\alpha$ bond presumably lies in the same plane as the Ta–S(3) bond, and the Ta–C(1)–H$_\alpha$ bond angle is <90°. The value of J_{CH} in such a circumstance (it can be as low as 75 Hz[11,12]) is much smaller than expected in "normal" alkylidene ligands (~130 Hz). However, in this circumstance a small value for J_{CH} could not be confirmed because of the breadth of the C$_\alpha$ resonance that probably results from loss of diethyl sulfide on the NMR time scale and because of equilibration with C$_\alpha$ in hypothetical monomeric Ta(CHCMe$_3$)(TIPT)$_3$ before it dimerizes to give [Ta(CHCMe$_3$)(TIPT)$_3$]$_2$.[11] The J_{CH} values could be determined for the related THF adduct (J_{CH} = 76 Hz in THF-d_8) and pyridine adduct (J_{CH} = 94 Hz in C$_6$D$_6$),[11] so there is little doubt that J_{CH} is also low in Ta(CHCMe$_3$)(TIPT)$_3$(SEt$_2$). Alkylidene ligands appear to be most distorted when the d-electron count is low, and other ligands in the complex are relatively poor π donors (e.g., chlorides and alkyls).[11]

Discussion

The structure of Ta(CHCMe$_3$)(TIPT)$_3$(SEt$_2$) is similar to that of [Ta(DIPT)$_3$(THF)]$_2$(μ-N$_2$) (DIPT = 2,6-diisopropylbenzenethiolate[10f]) in which the dinitrogen ligand is in an axial position with THF trans to it. In contrast, the structures of [Ta(DIPP)$_3$(THF)]$_2$(μ-N$_2$)[10f] and Ta[CMeCMeCH(*t*-Bu)](DIPP)$_3$(py) both contain the multiply bound ligand in an "equatorial" position (if they are called distorted trigonal bipyramids) with the base (THF or py) in a cis axial position. (In Ta(CMeCMeCHCMe$_3$)(DIPP)$_3$(py) the C$_\alpha$–Ta–N angle is 92°.) The emerging pattern seems to be that bases in phenoxide complexes can bind in a position cis to the multiply bound ligand while those in bulky benzenethiolate complexes bind trans to the multiply bound ligand.

The above findings suggest why Ta(CHCMe$_3$)(TIPT)$_3$(SEt$_2$) is a poor catalyst for the metathesis of ordinary olefins; the incoming olefin most likely must bind trans to the alkylidene ligand.

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(4) Least squares function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/(Lp)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, and p = p factor.

(5) Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

(6) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(7) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(8) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(9) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp.: Woodlands, TX, 1985.

(10) (a) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1533. (b) Bishop, P. T.; Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1986**, 967. (c) Dilworth, J. R.; Hutchinson, J.; Zubieta, J. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1034. (d) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 3362. (e) Davison, A.; de Vries, N.; Dewan, J.; Jones, A. *Inorg. Chim. Acta* **1986**, *120*, L15. (f) Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.* **1988**, *27*, 2050. (g) Walborsky, E. C.; Wigley, D. E.; Roland, E., Dewan, J. C.; Schrock, R. R. *Inorg. Chem.* **1987**, *26*, 1615. (h) De Vries, N.; Dewan, J. C.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 1574. (i) Bishop, P. T.; Dilworth, J. R.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2535. (j) de Vries, N.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3728.

(11) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986.

(12) (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

Note that norbornene and 2-butyne *will* react with Ta($CHCMe_3$)($TIPT)_3$(SEt_2), so *if* they also bind trans to the alkylidene ligand, the lifetime of the olefin or acetylene complex must be sufficiently long to permit rearrangement of the initial adduct to one in which the alkylidene ligand is cis to the substrate, in order that a metallacycle can form. (We should note that again there is no proof that the mechanisms of reactions between Ta($CHCMe_3$)($TIPT)_3$(SEt_2) and a variety of substrates are all fundamentally the same.) A similar conclusion was arrived at in order to explain the inactivity of alkylidyne complexes containing bulky arenethiolate ligands for the metathesis of internal acetylenes.[13]

An important question is whether the metal is significantly less electrophilic in the thiolate complexes than it is in analogous phenoxide complexes. One could intuit that σ donation by a thiolate ligand should be greater than that in a phenoxide ligand and may overpower what appears to be a reduced amount of π donation to yield a more electron-rich metal overall.[13] However, there are virtually no data in the literature that bear on this important point. Another unknown is the exact nature of the initial metal/olefin interaction. It is assumed at this stage to have primarily σ character, but a component of π character cannot be discounted a priori. Under these circumstances attribution of a lower reactivity for the thiolate alkylidene complexes to a reduced metal electrophilicity, as was stated with more certainty in the case of the alkylidyne complexes,[13] is unjustified.

Acknowledgment. R.R.S. thanks the National Science Foundation (Grant CHE 88-22508) for support, and K.C.W. thanks the Central Research Department of DOW Chemical Co. for a predoctoral fellowship. We also thank the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER 75292).

Supplementary Material Available: An ORTEP drawing and a fully labeled drawing of Ta(CH-*t*-Bu)($TIPT)_3$(SEt_2) and a table of final positional and thermal parameters (8 pages); a listing of final observed and calculated structure factors (90 pages). Ordering information is given on any current masthead page.

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(13) Murdzek, J. S.; Blum, L.; Schrock, R. R. *Organometallics* **1988**, *7*, 436.

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Formation of the Dihydrogenphosphide–Bis[tetraborane(8)] Anion. Protic Acid Behavior of Phosphine–Tetraborane(8)

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The reactions of $BH_3\cdot PH_3$ and $B_3H_7\cdot PH_3$ with $NaBH_4$ have been reported in the literature.[1,2] These phosphine adducts behaved as protic acids and produced the $PH_2\cdot 2BH_3^-$ and $B_3H_7\cdot PH_2\cdot BH_3^-$ anions, respectively, when reacted with $NaBH_4$. The reaction of $B_3H_7\cdot PH_3$ was faster than that of $BH_3\cdot PH_3$. This reactivity difference was attributed to the stronger borane activity of the B_3H_7 fragment compared to the BH_3 fragment. The tetraborane(8) (B_4H_8) fragment being a stronger borane acid than B_3H_7,[3] the protic acid character of the recently reported $B_4H_8\cdot PH_3$[4] was expected to be stronger than that of $B_3H_7\cdot PH_3$. The reaction of $B_4H_8\cdot PH_3$ with $NaBH_4$ was studied, and the results are described in this note.

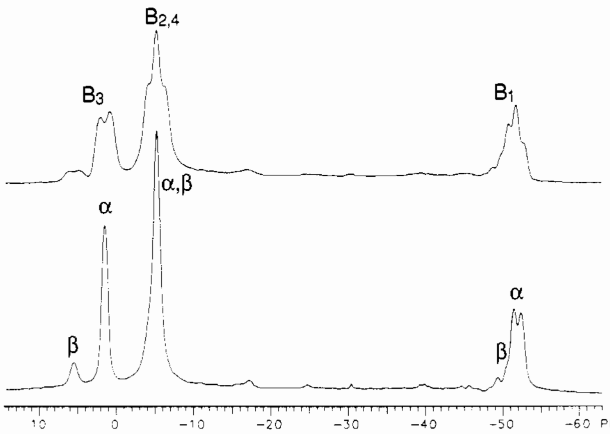

Figure 1. ^{11}B NMR (96.2 MHz) spectra of the $PH_2\cdot 2B_4H_8^-$ ion: upper spectrum, normal; lower spectrum, proton-spin decoupled.

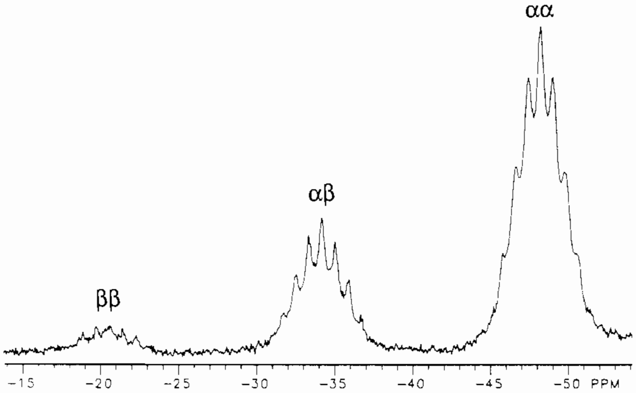

Figure 2. ^{31}P NMR (121.4 MHz) spectrum of the $PH_2\cdot 2B_4H_8^-$ ion, proton-spin decoupled.

Table I. NMR Data for the $PH_2\cdot 2B_4H_8^-$ Ion:[a] Shift, ppm (J_{XY}, Hz)

Boron-11[b]

α form			β form		
B_3	$B_{2,4}$	B_1	B_3	$B_{2,4}$	B_1
+1.4 (J_{BH} = 119)	−5.3 (J_{BH} = 105)	−52.0 (J_{BH} = 93) (J_{BP} = 90)	+5.4 (J_{BH} = 108)		−50.0 (J_{BH} = 107) (J_{BP} = 102)

Phosphorus-31[c]

αα form	αβ form	ββ form
−48.3 (J_{BP} = 95)	−34.2 (J_{BP} = 100)	−20.6

[a] Solvent: diethyl ether. [b] At −10 °C. Shift reference: $BF_3\cdot O(C_2H_5)_2$; external. [c] At −20 °C. Shift reference: 85% orthophosphoric acid; external.

Results

Reaction of $B_4H_8\cdot PH_3$ with $NaBH_4$. Phosphine–tetraborane(8) reacted with sodium borohydride in tetrahydrofuran, slowly at −80 °C and rapidly at −45 °C, according to the equation

$$2B_4H_8\cdot PH_3 + Na^+BH_4^- + THF \xrightarrow[\text{in THF}]{-80\ °C} Na^+[PH_2\cdot 2B_4H_8]^- + H_2 + PH_3 + BH_3\cdot THF \quad (1)$$

Although $BH_3\cdot THF$ was the major adduct product of BH_3, the $B_2H_7^-$ anion and $BH_3\cdot PH_3$ were present in small quantities in the reaction solution. The product salt, $Na[PH_2\cdot 2B_4H_8]$, was soluble in tetrahydrofuran and diethyl ether and could be isolated as a white solid that was unstable at room temperature.

NMR Spectra of $PH_2\cdot 2B_4H_8^-$. The ^{11}B and ^{31}P NMR spectra of the anion are shown in Figures 1 and 2, respectively, and the chemical shift data are listed in Table I. The adducts of B_4H_8 are considered to exist in two isomeric forms: endo and exo with respect to the position of the ligand relative to the hinge-shaped

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(1) Mayer, E.; Laubengayer, A. W. *Monatsh. Chem.* **1970**, *101*, 1138.
(2) DePoy, R. E.; Kodama, G. *Inorg. Chem.* **1988**, *27*, 4077.
(3) Edwards, L. J.; Parry, R. W. *J. Am. Chem. Soc.* **1959**, *81*, 3554.
(4) Jock, C. P.; Kodama, G. *Inorg. Chem.* **1988**, *27*, 3431.

0020-1669/90/1329-1106$02.50/0