the atomic numbering scheme is defined as well. The arrangement of the ligands around the central tungsten atom closely defines a regular octahedron. The longest coordination sphere bond, W–P, has a length of 2.516 (2) Å while the average W–C bond distance is 2.01 [2] Å.[13] There are no significant differences among any of the W–C bond lengths, and, in particular, none between the axial one, 2.00 (1) Å, and the average of the four equatorial ones, 2.01 [2] Å. Considering the results obtained for some other $M(CO)_5L$ structures,[7] a difference of 0.02–0.05 Å might have been expected. Such a difference is, in fact, permitted within the uncertainties. The average C–O bond length is 1.16 [2] Å, and the W–C–O moieties are linear.

The trimethylphosphine ligand has normal bond distances and angles. The average P–C distance and C–P–C angle are 1.85 [1] Å and 102.7 [2.7]°, respectively, and are statistically identical with the dimensions observed for this ligand in *cis*-$Mo(CO)_4(PMe_3)_2$.[14] The refinement of this ligand indicated fairly high thermal activity, but it is reasonably well-behaved and there is no indication of rotational disorder.

The angles around the tungsten atom approximate closely to the expected octahedral angles of 90° and 180°. The P–W–C(5) angle is 179.3 (3)°, and the P–W–C(5) vector is essentially perpendicular to the equatorial carbonyl plane. The small observed deviation from a right angle is caused by the orientation of the PMe_3 ligand with respect to the cis CO groups. The C(7) methyl group points out over the C(1)–W–C(4) quadrant, slightly opening this angle to 91.7 (5)°. The two remaining methyl groups are located directly over carbonyl groups CO(2) and CO(3). The interaction produces P–W–C(2) and P–W–C(3) angles of 91.6 (3) and 91.3 (3)°, respectively. Conversely, the ligand groups CO(1) and CO(4) shift up toward methyl group C(7), giving a P–W–C(1) angle of 88.1 (3)° and a P–W–C (2) angle of 88.1 (3)°. The overall effect is to keep the W(1),C(1),C(2),C(3),C(4) unit totally planar but also to tilt this plane very slightly, thus reducing intramolecular contacts. These interactions are minor and we would not expect them to lengthen significantly the W–P bond distance. This type of interaction is also observable in the structures of the $M(CO)_5L$ (M = Mo, Cr; L = PPh_3, $P(CH_2CH_2CN)_3$) complexes.[7] The ligands in those complexes are also oriented in such a way as to yield two P–M–C angles greater than 90° and two that are slightly acute; as a whole, the equatorial unit is planar. However, in the $Mo(CO)_5(PPh_3)$ compound these deviations are much larger (P–M–C angles average 95 [1]° and 87.5 [2]° for the two sets) and may well imply a lengthening and weakening of the Mo–P bond as compared to a sterically unstressed bond.

There can be no doubt that such a steric factor causes the long W–P bond distance of 2.686 (4) Å in the structure of the $W(CO)_5[P(t\text{-}Bu)_3]$ complex. This $W\text{–}P(t\text{-}Bu)_3$ bond is 0.170 (6) Å longer than the $W\text{–}P(CH_3)_3$ bond. The steric crowding of the *tert*-butyl groups is also reflected in the large P–W–C angles, which average 96.6 [1.8]° for those three CO ligands most closely contacting the phosphine ligand. The similarities in the basicities of PMe_3 and $P(t\text{-}Bu)_3$ and the reported similarities in their (nonsteric) binding properties[15,16] would lead us to expect similar W–P bond lengths. Presumably, the large increase in the W–P bond length has decreased significantly the W–P bond strength, and we would predict, therefore, a greater lability of the phosphine ligand in $W(CO)_5[P(t\text{-}Bu)_3]$ than in $W(CO)_5(PMe_3)$.

Acknowledgment. We thank the Robert A. Welch Foundation for support of this work. D.J.D. thanks Tulane University for a sabbatical leave during the Spring semester of 1980 and B.W.S.K. is the recipient of a NATO Postdoctoral Fellowship administered by the Natural Sciences and Engineering Research Council of Canada.

Registry No. $W(CO)_5(PMe_3)$, 26555-11-3; $PPN[W(CO)_5Cl]$, 39048-34-5.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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Probable Fluxional Behavior in B_5H_{11}. A Theoretical Study Which Supports C_1 Symmetry

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Although the early X-ray diffraction study[1] assigned C_s symmetry to B_5H_{11} (Figure 1), the precision was insufficient to detect small distortions to C_1 (identity only) symmetry. Nor do the NMR results distinguish between C_s symmetry and two equivalent rapidly interconverting C_1 structures.[2] While a recent, much more precise, X-ray study shows C_1 symmetry, the question remains as to whether molecular crystal packing has induced this distortion.[3]

The most recent theoretical study[4] indicated that the C_s structure is the more stable, although the unique (endo) hydrogen on the apex boron could be displaced by as much as 10° at the cost of no more than about 1 kcal/mol. Inasmuch as this distortion converts a terminal, but weakly doubly bridged, hydrogen to a singly bridged hydrogen, correlation corrections, omitted from this earlier study, might be expected to favor the C_1 structure. This is indeed the case, as we now describe.

Recent work in this laboratory[5,6] has shown that geometry optimization at the double-ζ level followed by fixed geometry calculations including polarization or correlation can be combined to predict relative energies within a few kilocalories per mol. In the present study, we used the 3-21G basis to optimize the C_s and C_1 geometries of B_5H_{11}. The small number of Gaussian functions in this basis allows computational efficiency in calculating derivatives. All geometries were completely optimized within the assigned molecular symmetry.

The structure constrained to C_s symmetry was subjected[8] to 20 cycles of optimization, beginning with the symmetry-averaged structure of the X-ray diffraction study.[1] During the last four cycles of optimization the energy changed by only 0.3 kcal/mol.

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Table I. Comparison of Theoretical and Experimental Bond Distances (Å) for B_5H_{11}

interatomic dist[a]	theoretical[b] C_s	C_1	C_1[d]	exptl[c]
B_1B_2	1.8033	1.7574	1.7153	1.72
B_1B_3	1.8033	1.7569	1.7226	1.72
B_2B_3	1.8795	1.8455	1.7910	1.79
B_1B_4	1.9520	1.9326	1.8747	1.88
B_1B_5	1.9520	1.9145	1.8735	1.87
B_2B_4	1.7733	1.7534	1.7512	1.75
B_3B_5	1.7733	1.8463	1.7962	1.80
B_4B_5	3.0045	3.1093	3.0487	
$B_2H_bB_4$	1.2383/1.4465	1.2517/1.3970	1.2521/1.4331	1.19/1.30
$B_2H_bB_3$	1.3484/1.3484	1.3444/1.3214	1.3323/1.3084	1.28/1.25
$B_3H_bB_5$	1.2383/1.4465	1.2400/1.4676	1.2415/1.4303	1.19/1.34
$B_5H_bB_1$	1.9083/1.2212	1.5773/1.2276	1.5536/1.2259	1.55/1.07
B_1H_t	1.1785	1.1799	1.1800	1.07
B_2H_t	1.1769	1.1753	1.1752	1.10
B_3H_t	1.1769	1.1759	1.1758	1.06
B_4H_t	1.1817 (exo)	1.1838 (exo)	1.1838 (exo)	1.11
B_5H_t	1.1817 (exo)	1.1816 (exo)	1.1817 (exo)	1.06
B_4H_t	1.1812	1.1831	1.1840	1.12
B_5H_t	1.1812	1.1869	1.1870	1.11

[a] See Figure 1 for numbering. [b] Complete optimization at 3-21G level. [c] Reference 3. [d] Boron framework fixed to experimental distances in ref 3.

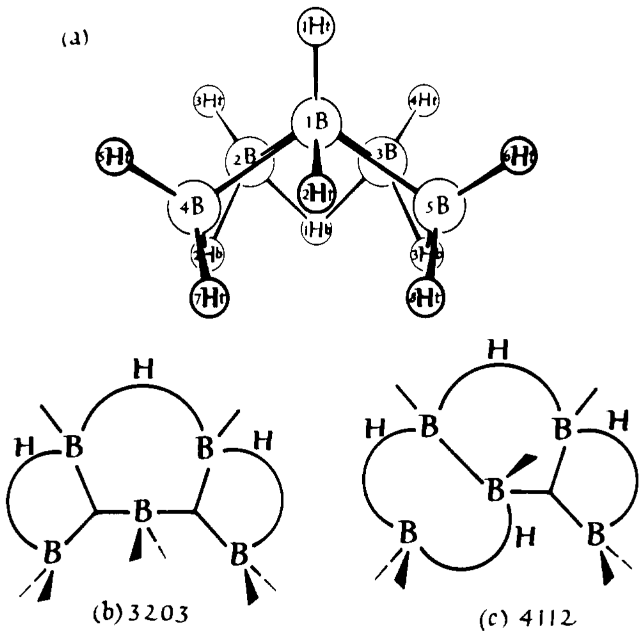

Figure 1.

The C_1 structure was considerably more difficult to optimize. We found, not to our surprise, that the use of internal coordinates presents difficulties for multicenter systems because bonding interactions cannot always be defined as stretch coordinates. For that reason we optimized the molecule in two stages. First, the boron framework was fixed to the positions of the C_1 structure as found in the X-ray diffraction study,[3] and only the hydrogen positions were optimized. Second, from these results, the molecular structure was then completely optimized.

Rather large changes, about 0.05 Å, in the boron–boron distances (Table I) lower the total energy by 1.2 kcal/mol (Table II). Thus the optimum geometries of boron hydrides are more difficult to predict than those of hydrocarbons. For example, displacement of one atom of a three-center bond usually involves a shift of electron density that compensates in the other interactions. Hence, the three-center bond is only slightly weakened. In a two-center bond, this reorganization does not occur so readily, and hence there is a more distinct minimum around the optimized bond length.

Table II. Relative Energies of B_5H_{11} (kcal/mol)

type of calcn	geometry C_s	C_1	C_1[a]
3-21G	0	0.10	1.27
6-31G	0	0.01	
MP2/6-31G	0.89	0	
6-31G*	0.80	0	
MP2/6-31G*[b]	1.70	0	

[a] Boron framework fixed; see text. [b] Estimated.

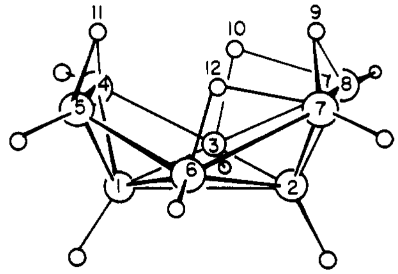

Figure 2.

With use of the 3-21G optimized geometries, single point calculations were made at the MP2/6-31G level[9] (200 000 molecular configurations) and the 6-31G* level[10] (10^7 integrals for C_1 symmetry). Relative energies were then corrected for the effect of correlation and polarization as shown in eq 1–3.

$$\Delta E = \text{6-31G}_{C_s} - \text{6-31G}_{C_1} + \Delta_{\text{pol}} + \Delta_{\text{CI}}$$

$$\Delta_{\text{pol}} = (\text{6-31G*}_{C_s} - \text{6-31G}_{C_s}) - (\text{6-31G*}_{C_1} - \text{6-31G}_{C_1})$$

$$\Delta_{\text{CI}} = (\text{MP2/6-31G}_{C_s} - \text{6-31G}_{C_s}) - (\text{MP2/6-31G}_{C_1} - \text{6-31G}_{C_1})$$

The C_s structure is only 0.01 kcal/mol more stable than the completely optimized C_1 structure at the 6-31G level (Table II). Both correlation and polarization favor the asymmetric structure, and after combination of the two effects at relative difference is predicted to be 1.7 kcal/mol in favor of the C_1 structure.

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(10) Including polarization (d orbitals) on all nonhydrogen atom.

The structure of B_8H_{12}[11] has two asymmetric hydrogen bridges, each of which is in a geometrical situation like that of the unique endo hydrogen atom of B_5H_{11}. Although hydrogen atoms H_{10} and H_{12} of B_8H_{12} would not be hindered in a terminal position (Figure 2), each one forms an asymmetric hydrogen bridge (1.493 Å/1.288 Å) not much different from that calculated for B_5H_{11} (1.577 Å/1.228 Å). Thus the C_1 geometry of B_5H_{11} is consistent in a general way with the C_s, rather than C_{2v}, structure of B_8H_{12}.

In summary, the most probable symmetry of B_5H_{11} is C_1, not C_s, and the low barrier for the C_1–C_s–C_1 process suggests a fluxional character for this molecule.

Acknowledgment. We thank the National Science Foundation (Grant CHE7719899) for support of this research. We also acknowledge Grant PCM77-11398 in support of the VAX Computer of the Chemistry Department.

Registry No. B_5H_{11}, 18433-84-6.

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Contribution from the Department of Chemistry,
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A New Mixed Tungsten–Nickel Carbonyl Cluster System: The $WNi_6(CO)_{17}^{2-}$ Ion[1]

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The first example of a mixed tungsten–nickel carbonyl cluster anion and the first example of a metal cluster system having a trigonal-bipyramidal arrangement of metal atoms was reported in 1971: the $W_2Ni_3(CO)_{16}^{2-}$ anion.[2]

Although not recognized at the time, a basic structural arrangement of nickel atoms (with respect to carbonylnickelate clusters) was found: the $[Ni(CO)_3(\mu\text{-}CO)_3]$ unit. This was elegantly demonstrated by the synthetic and structural studies of Chini and Dahl and their co-workers,[3-8] who showed that the carbonyl nickelate clusters $Ni_5(CO)_{12}^{2-}$, $Ni_6(CO)_{12}^{2-}$, $Ni_9(CO)_{18}^{2-}$, and $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 2–4) all contain a trigonal arrangement of three nickels atoms, three terminal carbonyl groups, and three bridging carbonyl groups. The nickel–nickel bond distances of the nickels in the trigonal array for the first three above and for the $W_2Ni_3(CO)_{10}^{2-}$ and $Mo_2Ni_3(CO)_{16}^{2-}$ ions are 2.36 ± 0.02 Å, suggesting a similarity in bonding. This appears to be especially true for the $M_2Ni_3(CO)_{16}^{2-}$ and $Ni_5(CO)_{12}^{2-}$ ions.[2,4,8] A qualitative discussion of the bonding in some of these species has suggested some basicity might be retained by the $Ni_6(CO)_{12}^{2-}$ ion. So that this could be checked, the ion was allowed to react with the Lewis acid species $W(CO)_5$.

The work of Chini and Dahl has also helped to clarify some of the earlier reports of clustered carbonylnickelate species such as $Ni_2(CO)_6^{2-}$,[9] $Ni_3(CO)_8^{2-}$,[10] $Ni_4(CO)_9^{2-}$, $Ni_4(CO)_9H^-$, and $Ni_5(CO)_9^{2-}$,[11,12] which were obtained by using various methods of reduction or disproportionation of $Ni(CO)_4$. The basis for assignment of these compositions were elemental analyses and in a few cases infrared spectra. Chini has shown, based on infrared spectra, that the material originally reported as $Ni_4(CO)_9^{2-}$ is most probably $Ni_6(CO)_{12}^{2-}$.[4] Thus some doubt as to the exact nature of the other earlier reported species still exists. The borohydride ion has been found to produce hydridic carbonyl species in the reduction with the group 6 metal carbonyls.[13] It was therefore of interest to determine whether similar results could be obtained with $Ni(CO)_4$.

Exprimental Section

Materials. All reagents were used as obtained from commercial sources. Methylene chloride was dried over molecular sieves, and tetrahydrofuran (THF) was distilled from sodium and benzophenone. All handling of nickel carbonyl was carried out in a vacuum line. All operations were performed in an inert atmosphere by using either Schlenk tube techniques or low-vacuum techniques.[14] *Caution*: $Ni(CO)_4$ is highly toxic and should be handled only in a vacuum line and/or a *good* fume hood.

Preparations of bis(triphenylphosphiniminium) chloride (hereafter referred to as (PPN)Cl)), $(PPN)_2W_2(CO)_{10}$, and $(PPN)_2W_2Ni_3(CO)_{16}$ were by the literature methods.[2,15]

Instrumental Characterization. (A) NMR Spectra. The ^{13}C NMR spectra were recorded with a JEOL PFT-100 spectrometer with Me_4Si as an external reference and acetone-d_6 as an internal lock. ^1H NMR spectra were obtained on a Varian model HA-100 spectrometer. All spectra were obtained at ambient temperature.

(B) Infrared Spectra. All spectra were obtained with a PE Model 621 spectrometer and calibrated with polystyrene or indene.

(C) Conductivity. Conductivities were determined as a function of concentration in nitromethane ($k = 9 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$) with use of Yellow Springs Instrument Co. Model 31 bridge and a cell with a cell constant of 0.1825 cm^{-1}.

(D) Analyses. Carbon, hydrogen, and nitrogen analyses were performed at the University of Georgia. Metal analyses were provided by Galbraith Laboratories, Inc.

Preparation of $(PPN)BH_4$. A 2.6-g sample of (PPN)Cl was dissolved in 20 mL of boiling water. This solution was added to 1.7 g of $NaBH_4$ dissolved in 50 mL of cold water. The precipitate which formed was immediately filtered. It was then dissolved in 50 mL of CH_2Cl_2, and the solution was dried with $MgSO_4$ and filtered again. The product was crystallized by the addition of 50 mL of diethyl ether, collected by filtration, and dried under vacuum at 100 °C. A yield of 2.25 g (90%) of product was obtained; mp 195–197 °C. Anal. Calcd: C, 69.6; H, 5.64; N, 2.19. Found: C, 69.4; H, 5.59; N, 2.10.

The IR spectrum of $(PPN)BH_4$ shows the expected B–H stretching frequencies in the 2100–2300-cm^{-1} region. $(PPN)BH_4$ is an air-stable, nonhydroscopic solid which is soluble in ethanol, methanol, dichloromethane, and acetonitrile but insoluble in THF, diethyl ether, and ethyl acetate.

Preparation of $(PPN)_2Ni_6(CO)_{12}$. To 50 mL of THF in a 250-mL flask was added 2.0 g of $NaBH_4$. After the flask was attached to the vacuum line and degassed, 5.0 mL (40 mmol) of $Ni(CO)_4$ was condensed into the reactor. The flask was allowed to warm, and a reflux condenser was attached. The mixture was refluxed under nitrogen. The mixture which was initially yellow turned dark red after 1 h. After 2 h at reflux, the solvent was removed under vacuum and the residue was dissolved in 100 mL of CH_2Cl_2 containing 2.0 g (3.5 nmol) of (PPN)Cl. This solution was filtered on Celite$^{\bullet}$, and 100 mL of ether was added to the filtrate. A 2.2-g sample (68% yield) of $(PPN)_2Ni_6(CO)_{12}$ was obtained; mp 194–196 °C. If extended

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