metal centers. The dissimilarity of the spectra of the two forms is consistent with form II being six-coordinate. The most striking difference between the spectra of the two forms is in the PO_2 stretching region where form I has two strong bands and form II has three. The two bands observed for form I are quite readily assigned to the antisymmetric and symmetric PO_2 stretches.[7] The intensity and position of the three bands in form II's spectra are characteristic of PO_2 stretching vibrations, but for C_{2v} or C_s symmetry of the phosphinate anion only two strong PO_2 stretching bands are expected. It may well be that form II contains more than one structural type of phosphinate.

The thermograms for both forms were recorded by dsc, and the results are given in Table I. The temperatures of the transitions were found to vary with the thermal history of the sample as well as its size and heating rate, so that the values given are only approximate. The transition temperatures and energies of form I are in the range of those previously observed for $Zn[OP(C_8H_{17})_2O]_2$[8] which is isomorphous with form I. The assignment for the endothermic transformation at 54° for form I is based on that made for the isomorphous $Zn[OP(C_8H_{17})_2O]_2$ polymers, whereas the assignment of the transition at 111° was made after a careful study with a light polarizing microscope. The higher temperature transition for $Zn[OP(C_8H_{17})_2O]_2$ was previously assigned as a melting. However, even well above 170° birefringence was observed for both $Co[OP(C_8H_{17})_2O]_2$ and $Zn[OP(C_8H_{17})_2O]_2$. Thus the high temperature transition is most probably a transition from a crystalline form to a paracrystalline form, similar to that described for other zinc and cobalt phosphinates.[2] The thermogram of form II shows one transition which corresponds to its conversion to form I and which was found to be irreversible.

TABLE I

DSC ENDOTHERMS FOR $Co[OP(C_8H_{17})_2O]_2$

Form	Approx transition temp, °C	ΔH, cal/g	Assignment
I	54	5.1	Solid state transition from one crystalline form to another
	111	5.8	Transition from crystalline form to paracrystalline form
II	68	24.9	Transition from form II to form I

Although both forms are soluble in nonpolar solvents, infrared spectra indicate that form II converts irreversibly to form I upon dissolution and consequently no molecular weight data could be obtained for form II. Form II is crystalline with a considerably different X-ray powder pattern than form I which can be either crystalline or amorphous. The *d* spacings for both forms are given in Table II.

This appears to be the first example of a poly(metal phosphinate) which exists both in four- and six-coordinate forms. However the two isomers have some similarities to the well known α and β forms of $Co(py)_2Cl_2$.[9] In both systems the six-coordinate form converts to the four-coordinate form on heating or dissolution; on the other hand, the conversion in the $Co(py)_2Cl_2$ system is reversible, whereas in the $Co(OP(C_8H_{17})_2O)_2$ system it is not.

TABLE II

X-RAY POWDER PATTERNS OF $Co[OP(C_8H_{17})_2]O_2$[a]

Form I		Form II	
d, Å	*I*[b]	*d*, Å	*I*[b]
16.07	100	14.04	100
10.07	40	10.32	30
9.10	30	8.81	80
8.42	100	4.71	60
7.09	30	4.35	90
6.24	10	4.06	20
4.94	60	3.63	50
4.58	5		
4.27	50		

[a] Cu Kα radiation was used. [b] Relative intensities estimated visually.

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Ab Initio Self-Consistent Field Calculation of the Energies of Formation of B_2H_6 and $B_2H_7^-$

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Accurate binding energies cannot usually be obtained from Hartree–Fock (HF) calculations because the changes in correlation energy are often of the same orders of magnitude as the corresponding changes in the HF energy.[1] The HF binding energies are still of interest, however, when some estimate of the sign and magnitude of the correlation energy changes can be made. We report in this note *ab initio* self-consistent field (SCF) calculations[2] of the energies of formation, ΔE_f, for B_2H_6 and $B_2H_7^-$.

An extensive calculation of the ΔE_f for the reaction

$$2BH_3(g) \longrightarrow B_2H_6(g) \qquad (1)$$

has been reported by Gelus, Ahlrichs, Staemmler, and Kutzelnigg (GASK).[3] This calculation employed a large Gaussian basis set and the correlation energy corrections were estimated using the independent electron pair approximation.[3,4] The total ΔE_f was estimated to be -36.0 ± 5 kcal/mol. These authors attributed -11.5 kcal to the HF energy changes, and -24.5 kcal to changes in the correlation energy; these values included estimates of -3.0 kcal/mol and -7.7

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kcal/mol, respectively, for supposed inadequacies in the basis set.

Our calculation of the ΔE_f for B_2H_6 employed the experimental geometry for B_2H_6,[5] and an optimized geometry for BH_3. The B–H distance in BH_3, 1.19 Å, is the same as that found previously[6] from a minimum basis set. An extended basis was used (exponents in parentheses) for both BH_3 and B_2H_6, described by Laws, Stevens, and Lipscomb (LSL):[7] H 1s (1.449), H 2s (1.0205), H 2p (1.952), B 1s (7.338), B 1s (3.996), B 2s (1.724), B 2s (1.110), B 3s (4.796), B 2p (4.558), B 2p (1.753), B 2p (0.931), B 3d (1.490). The total energy for B_2H_6 is given by LSL as -52.8331 au, and our new total energy for BH_3, calculated using the LSL basis, is -26.4014 au. From these energies we find that the near-Hartree–Fock limit of ΔE_f is -19.0 kcal/mol, in contrast to GASK's calculated value of -8.5 kcal/mol and their estimate of the Hartree–Fock limit of -11.5 kcal/mol.

Experimental values of ΔH_f for B_2H_6 range from -25 to -38 kcal/mol for kinetic measurements and from -39 to -59 kcal/mol for mass spectrometric results.[8] A recent kinetic value, consistent with several reactions, is -35.5 kcal/mol,[9] corresponding to a ΔE_f of -34.9 kcal/mol.

However, the estimated Hartree–Fock limit of -19.0 kcal/mol is not in the most favorable range of experimental values, probably largely because of change in the correlation energy in the formation of B_2H_6 from $2BH_3$. GASK's calculated value of this correlation energy is -16.8 kcal/mol, but they add -7.7 kcal/mol as an estimate of the effect of inadequacy of their basis set on the correlation part. The result, -24.5 kcal/mol, is not necessarily the appropriate value to be added to our near-Hartree–Fock limit. Indeed, we suspect that GASK have overestimated the magnitude of the correlation correction, and we observe that their *calculated* correlation energy is about the difference between our near-Hartree–Fock limit and the most probable experimental value. However, we have not computed the correlation correction to our near-Hartree–Fock wave function, but such a procedure would give the most appropriate correlation correction to our value of -19.0 kcal/mol.[10]

The molar energy of formation for the reaction

$$BH_4^-(g) + BH_3(g) \longrightarrow B_2H_7^-(g) \qquad (2)$$

was calculated using optimized minimum basis sets of BH_4^-,[11] BH_3,[12] and $B_2H_7^-$. The geometry of $B_2H_7^-$ has not been determined experimentally, but the proposed structure[13] consists of two BH_3 groups connected by a linear B–H–B three-center bond. The nmr spectra[14] indicate the presence of two BH_3 groups, but nothing about the nature of the B–H–B linkage could be determined. In particular, the possible asymmetry of the B–H–B bond could not be established or disproved.

We have calculated a geometry for staggered $B_2H_7^-$ from a minimum basis set of Slater-type orbitals, using a program previously described.[15] The starting geometry and exponents were taken from the calculation on diborane.[16] The geometry and exponents were optimized until a convergence of 10^{-3} au in the energy was achieved. All calculations were made at the self-consistent field method, except for the optimization of the H_tBH_t angle by the PRDDO method.[17] However, all final results on $B_2H_7^-$ were obtained by the SCF method. In Table I we present optimized bond distances, exponents, and the energy analysis. Although the B–H_t bond distance of 1.223 Å is longer than B–H_t distances usually found in boron hydrides,[18] this distance is exactly the average of the B–H distances in BH_4^- (1.255 Å)[19] and BH_3 (1.19 Å).[6] The B–H_b distance of 1.309 Å is shorter in $B_2H_7^-$ than in B_2H_6, but the smaller bridge hydrogen exponent indicates that the electron density associated with the B–H–B bond is more "spread out" in $B_2H_7^-$ than in B_2H_6. The same trend is also seen in the H_t exponents, as one might expect for a negative ion. Our SCF calculations on other negative ions[20] also indicate that the bond distances are longer and the exponents smaller than in neutral molecules. The bridge hydrogen position was also optimized by moving the hydrogen atom relative to the two borons. To within the accuracy of our basis set, the B–H–B bond is symmetrical, and a nonlinear BH_bB structure is less stable.

TABLE I

$B_2H_7^-$ OPTIMIZED EXPONENTS, BOND DISTANCES, AND ENERGY ANALYSIS

	Exponents[a]	Parameters (D_{3d})	Energy analysis[a]	
H_t	1.066	B–H_t 1.223 Å	Electronic energy	-84.8603
H_b	1.138	B–H_b 1.309 Å	Nuclear repulsion energy	31.5433
B 1s	4.690	H_tBH_t 113.8°	Total energy	-53.3170
B 2s	1.472	H_tBH_b 104.7°	Ionization potential	0.243
B 2p	1.466	BH_bB 180.0°	$-E/T$	0.9988

[a] All quantities in these columns are in au.

For $B_2H_7^-$, the calculated ΔE_f is -25.1 kcal/mol. This value is in good agreement with the experimental ΔH_f of -31.0 ± 8 kcal/mol.[21] We can guess the sign and magnitude of the correlation energy by noting that the correlation energy should increase with the number of three-center bonds or, equivalently, that the correlation energy should increase with the number of next neighbor bond interactions. Since the number of three-center bonds (and next neighbor interactions)

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increases in both reactions, the calculated energies of formation should be higher (less negative) than the experimental values. Also, the correlation correction to the HF ΔE_f should be smaller for $B_2H_7^-$ than for B_2H_6.

Our results are summarized in Table II.

TABLE II

SUMMARY OF ΔH_f CALCULATIONS

	Total energies, au	H_f, kcal/mol
BH_3	−26.4014	−19.0[a]
B_2H_6	−52.8331[c]	
BH_3	−26.3533[d]	
BH_4^-	−26.9232[e]	−25.4[b]
$B_2H_7^-$	−53.3170	

[a] For reaction 1. [b] For reaction 2. [c] Reference 7. [d] Reference 12. [e] Reference 11.

We believe that the basis set for B_2H_6 is of such quality that our value for the energy of formation is essentially a Hartree–Fock value. In view of the reasonable agreement with experiment for the calculated energy of formation of $B_2H_7^-$, we predict that the B–H–B bond is symmetric in the gas phase. However, in the crystal phase, forces could conceivably be sufficient to produce some asymmetry.[22]

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(22) NOTE ADDED IN Proof.—Inclusion of all 14 single and 210 double excitations from the valence shells of minimum Slater basis SCF wave functions for BH_3, B_2H_6, and possible transition states has yielded the following results. This correlation correction is −10.6 kcal for reaction 1. Further studies with expanded basis sets will give a more appropriate correlation correction to be added to the HF value of −19.0 kcal for reaction 1. The best transition state discovered so far is centrosymmetric, of C_{2h} symmetry, having two very unsymmetrical hydrogen bridges and a B · · · B distance of 3.0 Å, and is less stable than $2BH_3$ by 2.6 kcal (study in progress by I. M. Pepperberg, D. A. Dixon, and W. N. Lipscomb).

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Electronic Effects of Phosphorus Ligands on the Protonation of NiL_4 Complexes

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Novel cationic nickel hydride complexes formed by protonation of $Ni[P(OEt)_3]_4$[1] and $Ni[Ph_2PCH_2CH_2PPh_2]_2$[2] by strong acids have been reported recently. Solutions of $HNi[P(OEt)_3]_4^+$ are catalytically active in the coupling of butadiene and ethylene to form hexadienes[3] and in olefin isomerization.[4] We now wish to report that a wide range of similar complexes of the type $HNiL_4^+$ can be formed by these protonation reactions. Equilibrium constants for reaction 1 using H_2SO_4 in

$$H^+ + NiL_4 \overset{K}{\rightleftharpoons} HNiL_4^+ \qquad (1)$$

CH_3OH are shown to depend on the electron donor–acceptor character of the phosphorus ligands L.

Addition of strong acids like H_2SO_4 to solutions of zerovalent nickel complexes of the type NiL_4 forms $HNiL_4^+$, as shown by the appearance of a symmetrical quintet[1,5] at high field in the proton nmr spectra (Table I). Though the chemical shift shows no systematic variation, the value of J_{PH} increases quite regularly as the electron-withdrawing ability of the phosphorus ligands increases, judging from the carbonyl stretching frequencies measured for $Ni(CO)_3L$ complexes.[6]

TABLE I

^1H NMR DATA ON $HNiL_4^+$ COMPOUNDS[a]

Ligand	J_{PH},[c] Hz	τ[b]	Solvent
$P(O\text{-}p\text{-}C_6H_4OCH_3)_3$	35 ± 2	23.1	CD_2Cl_2
$P(O\text{-}p\text{-tolyl})_3$	33 ± 2	23.2	CD_2Cl_2
$P(OMe)_3$	29.5	24.0	CD_2Cl_2
$P(OCH_2CH_2Cl)_3$	28.0	23.9	$CDCl_3$
$P(OEt)_3$[d]	26.5	24.3	CD_2Cl_2
$PPh(OEt)_2$	22.5	23.4	$CDCl_3$
$Ph_2PCH_2CH_2PPh_2$[e]	5.5	22.9	CD_2Cl_2
PMe_3	4.5	27.2	CD_3CN

[a] Formed *in situ* by the addition of H_2SO_4 to solutions of NiL_4. The latter were prepared as described by C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970). [b] Measured at −20° with respect to internal tetramethylsilane using a Varian HA-100 spectrometer. [c] Uncertainty ±0.5 Hz, unless noted otherwise. [d] Hydride first reported in ref 1. [e] Hydride first reported in ref 2.

Equilibrium constants for hydride formation (eq 1) with selected compounds were measured spectrophotometrically using H_2SO_4 in CH_3OH at 0°, as described earlier for $Ni[P(OEt)_3]_4$.[7] The results are shown in Table II and Figure 1. The value of K for $Ni[Ph_2PCH_2CH_2PPh_2]_2$ is most uncertain because of the extremely low solubility of the complex in CH_3OH ($\sim 10^{-4}$ M). The hydride formed was, however, exceedingly stable.

TABLE II

HYDRIDE FORMATION CONSTANTS WITH H_2SO_4 IN CH_3OH AT 0°

No.	L	K, M^{-1}	$\nu_{CO}(A_1)$ of $Ni(CO)_3L$,[a] cm^{-1}
1	$Ph_2PCH_2CH_2PPh_2$	410 ± 120[b]	2066.7[f]
2	$PPh(OEt)_2$	107 ± 13[b,c]	2074.2
3	$P(OEt)_3$	33 ± 3[c,d]	2076.3
4	$P(OMe)_3$	35 ± 2[c]	2079.5
5	$P(OCH_2CH_2Cl)_3$	1.2 ± 0.2[c]	2084.0
6	$P(OCH_2CCl_3)_3$	<0.1[b,e]	2091.7

[a] Infrared data from ref 6. [b] Determined at ambient temperature. [c] 0.1 M L added. See ref 7. [d] Reported earlier in ref 7. [e] No change in uv spectrum on adding 1 M H_2SO_4. [f] Value for PPh_2Et.

As expected, the equilibrium constant decreases as the phosphorus ligands remove more electron density from the metal. With $Ni[P(OCH_2CCl_3)_3]_4$, the complex with the most strongly electron-withdrawing ligands of

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