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 $\Delta E_f$ should be smaller for $B_2H_7^-$ than for $B_2H_6$.

Our results are summarized in Table II.

TABLE II

SUMMARY OF $\Delta H_f$ 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

BY CHADWICK A. TOLMAN

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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

$$H^+ + NiL_4 \overset{K}{\rightleftharpoons} HNiL_4^+ \tag{1}$$

$CH_3OH$ 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 | $\tau$[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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(5) The appearance of the NiH resonance as a quintet is attributed to rapid intramolecular ligand exchange in these labile presumably trigonal-bipyramidal five-coordinate complexes. The phenomenon has recently been studied in detail in $HM(PF_3)_4$ complexes by P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *ibid.*, **93**, 1797 (1971).

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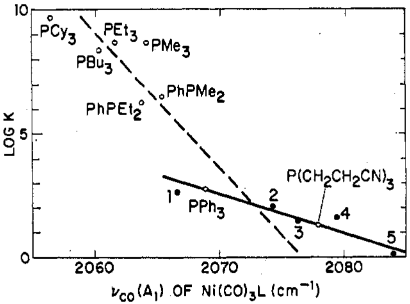

Figure 1.—Variation of protonation equilibrium constant with $\nu_{CO}(A_1)$ of $Ni(CO)_3L$ from ref 6. The solid line and closed circles refer to the $NiL_4$ complexes listed in Table II. The dashed line and open circles refer to the free phosphines.[10]

those tested, the extent of protonation was below the level of detection in 1 $M$ $H_2SO_4$. The equation of the solid line in Figure 1 is $\log K = 0.16(2086 - \nu_{CO})$. Using this equation it is possible to calculate[8] an approximate hydride formation constant for $HNi(CO)_4^+$ of $\sim10^{-7}\ M^{-1}$, which explains why the hydride has not so far been observed although nickel hydrides have been proposed as intermediates in acetylene carbonylation reactions using $Ni(CO)_4$.[9]

One interesting aspect of our results is the comparison of $NiL_4$ basicities with those of the free ligands L. Some phosphine $pK_a$ values measured by potentiometric titration[10] in nitromethane are also plotted in Figure 1. The equation of the dashed line is $\log K = 0.55(2076.6 - \nu_{CO})$. Though our data and those of Streuli[10] were measured in different solvents, two facts clearly emerge from Figure 1. Protonation on nickel in the $NiL_4$ complexes is only about 0.3 times as sensitive to changes of substituents on phosphorus as is direct protonation of the free phosphine. A greater sensitivity of the electron density on phosphorus to changes in substituents is chemically reasonable and is also indicated by recent ESCA measurements[11] of P $2p^3/_2$ and Ni $2p^3/_2$ binding energies in these complexes. As the substituents become more electron withdrawing, it becomes easier to protonate the $NiL_4$ complex than the free phosphine. This is why we were able to add excess ligand in the cases of complexes **2**–**5** without interference in determining $K$'s for these complexes. In a mixture of $PMe_3$ and $Ni(PMe_3)_4$ we anticipate preferential protonation of the phosphine.

The subject of transition metal basicity towards Lewis acids has recently been reviewed by Shriver,[12] who pointed out that metal basicity is expected to increase for more electron-donating ligands. This expectation was based primarily on the effect of replacing CO by $PPh_3$, as in the series $[Co(CO)_{4-n}(PPh_3)_n]^-$, and has now been confirmed for these $NiL_4$ complexes. Enhanced basicity is one factor favoring catalytic activity of these complexes for olefin coupling[3] and isomerization[4] reactions, both of which involve formation of $HNiL_4^+$ as a first step, and is also expected to favor oxidative addition reactions of the conventional type involving cleavage of XY bonds.

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[8] The calculation is based on a value of 2128 cm$^{-1}$ for the Raman-active $\nu_{CO}(A_1)$ mode of $Ni(CO)_4$ reported by H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, **35**, 2168 (1961).

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## Titanium(III) Chloride in Methanol with Small Amounts of Water

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Very little information concerning the solvation of titanium(III) ions in solution is available in the literature. This information is of interest in the study of corrosion[1] as well as in the chemistry of transition metal ions. As part of some spectroscopic and electrochemical studies of titanium,[2,3] the electron spin resonance (esr) spectra of $TiCl_3$ in methanol–water systems were investigated. We wish to report here the results of an esr investigation of $TiCl_3$ in methanol-*O-d* containing 0–0.1 $M$ $D_2O$.

Titanium(III) chloride has been found to form stable complexes which contain chlorides and alcohols, ethers, nitriles, ketones, or amines as ligands. Those complexes containing 2-propanol and *sec*-butyl alcohol[4] have been assigned the structure $[TiCl_2(alcohol)_4]^+Cl^-$.[5] Complexes with methanol that have been isolated or detected in solution include $[TiCl_n(CH_3OH)_{6-n}]^{3-n}$ where $n$ is 0–6 and also several seven- and eight-ligand complexes.[6]

The solvation of titanium(III) has been investigated in acetonitrile,[7] methanol,[8] and water.[8,9] Using nuclear magnetic resonance spectroscopy (nmr), Chmelnick and Fiat[8] found that the average coordination number of methanol on titanium chloride in methanol is 4, which suggests a complex of the form $[TiCl_2(CH_3OH)_4]^+$. These nmr measurements required fairly high concentrations of $TiCl_3$.

In order to investigate the nature of titanium(III) in dilute methanol solutions, esr spectroscopy was selected due to its high sensitivity. Methanol solutions containing from 0.5 to 40 m$M$ $TiCl_3$ and from 10 to 100 m$M$ $D_2O$ were investigated. Esr studies of titanium(III) complexes in solutions that have been reported include titanium(III) chelates[10] in aqueous

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