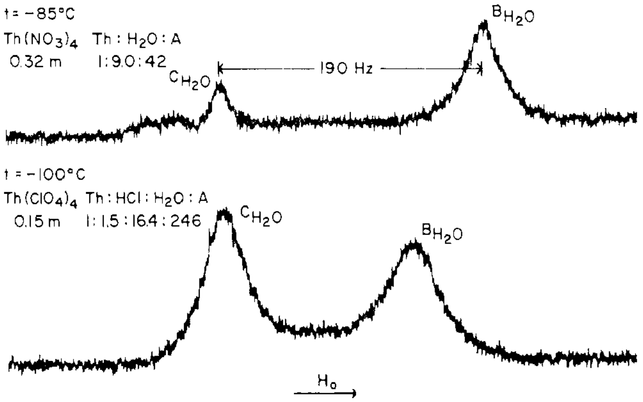

Figure 1.—The water pmr spectra of $Th(NO_3)_4$ and $Th(ClO_4)_4$ solutions in water–acetone mixtures, recorded on a Varian A-60 nmr spectrometer. The salt molalities, the mole ratios of all components, and the signals arising from bulk (B_{H_2O}) and complexed (C_{H_2O}) water molecules are shown in the diagram.

were attributed to complex formation and hydrolysis.[11] Since complex formation of these cations with perchlorate ion does not occur to any appreciable extent,[15,16] the present study was undertaken to obtain an estimate of their maximum hydration numbers.

The pmr measurements were carried out on a Varian A-60 and a Varian HA-100 nmr spectrometer, each equipped with a variable-temperature device for studies between −150 and +200°. The experimental method has been described in more detail elsewhere[3,6,7,11] and it involves cooling the example in the spectrometer probe until proton exchange has been slowed sufficiently to permit the observation of resonance signals for water molecules in the primary coordination shell of the cation and in bulk medium.

To assess the contribution of hydrolysis to the low hydration numbers found for the nitrate solutions of these cations, the same systems were studied in the presence of perchloric acid. Although the Y^{3+} and Th^{4+} hydration numbers remained unchanged in these experiments, the Sc^{3+} value increased from 3.9 to 5.1, a clear indication that a hydrolysis process was important in this solution. Since the mole ratio of H^+ to Sc^{3+} was varied from 0.7:1 to 1.1:1 in these experiments, it may be assumed that hydrolysis was completely repressed. The hydration number of 5.1 probably is still low, as a result of complex formation with nitrate ion.

Unacidified perchlorate solutions of these cations did not exhibit separate resonance signals for bound and bulk water molecules, since proton exchange was rapid even at −100°. This situation also prevailed for acidified $Sc(ClO_4)_3$ solutions and only broad, nonmeasurable signals were found for acidified $Y(ClO_4)_3$ solutions. However, as shown in Figure 1, acidified solutions of $Th(ClO_4)_4$ gave well-defined signals for bulk water and the cation solvation shell. The reason for this phenomenon cannot be stated without a knowledge of the proton-exchange mechanism.

From Figure 1, the spectra for solutions of $Th(NO_3)_4$ and $Th(ClO_4)_4$ in water–acetone can be compared. In contrast to the Th^{4+} hydration number of 2.9 previously found for the nitrate solution of Figure 1,[11] area measurements indicate that each Th^{4+} is hydrated by about 9.1 water molecules on the average in the perchlorate solution shown. This value was reproduced over an HCl to $Th(ClO_4)_4$ mole ratio range of about 0.8:1 to 1.5:1. These hydration numbers reflect the different complexing tendencies of nitrate and perchlorate ions. In the absence of appreciable complexing in the perchlorate solutions, each Th^{4+} can bind an average of nine water molecules in the first coordination shell, a value which must be close to the maximum for this ion.[17-22] Although the exact structure of the ionic species in the perchlorate solutions cannot be deduced solely from the pmr results, any future postulate must be consistent with this relatively large hydration number. Displacement of water molecules by nitrate ions reduces the average hydration number to about 3 in this system. This sharp reduction may indicate that a bidentate-type linkage between Th^{4+} and NO_3^- is occurring.

At the present time, studies of hydration and complex formation in solutions of Sn^{4+}, UO_2^{2+}, and Zn^{2+} are under way by this direct pmr method, and preliminary results indicate maximum solvation numbers of 6, 4, and 6, respectively, for these species.

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The Protonation of Zerovalent Nickel Complexes

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The formation of metal hydrides by the protonation of phosphine complexes of zerovalent platinum has been reported by Cariati, Ugo, and Bonati.[1] These authors

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[1] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

were unable to obtain analogous complexes of palladium and nickel. We wish to report evidence for the protonation of zerovalent nickel complexes in solution to give hydrides which differ from those of Cariati, *et al.*,[1] in being formally five-coordinate rather than four-coordinate.

The addition of strong acids to solutions of tetrakis(triethyl phosphite)nickel(0) in benzene, acetone, or chloroform leads to the appearance of a high-field proton magnetic resonance signal, as illustrated in Figure 1. The position of this resonance (14.3 ppm to high field of TMS in acetone and 14.5 ppm to high field of TMS in benzene and chloroform) is characteristic of and diagnostic for a proton directly bonded to a transition metal.[2] Such resonances have been observed with a number of strong acids, such as HCl, H_2SO_4, and CF_3COOH. Analogous nickel complexes of trimethyl phosphite and triphenyl phosphite give similar results. The high-field resonance using the triethyl phosphite complex has a quintet structure with $J = 26$ cps. This must be attributed to spin–spin interaction with four phosphorus atoms leading to the formulation of the reaction as

$$Ni[P(OC_2H_5)_3]_4 + HX \longrightarrow HNi[P(OC_2H_5)_3]_4^+ + X^- \quad (1)$$

Thus the hydride complex in this case is five-coordinate in contrast to the four-coordinate complexes $HPt(P(C_6H_5)_3)_3^+$ and $(P(C_6H_5)_3)_2PtHX$ reported by Cariati, *et al.* The fact that the nmr spectra are independent of the anions reported supports the formulation as a five- rather than a six-coordinate species.

Examination of the ^{31}P spectra provides confirmatory evidence for the hydride formation. Thus, in chloroform $Ni[P(OC_2H_5)_3]_4$ gives rise to a single resonance 159 ppm to low field of phosphoric acid. The resonance of the free ligand occurs 141 ppm to low field of phosphoric acid. On addition of trifluoroacetic acid to $Ni[P(OC_2H_5)_3]_4$, the original resonance disappears and a doublet, with $J \approx 26$ cps, is observed at -135 ppm. This must be attributed to the hydride.

Determinations of the intensity of the hydride resonance relative to that of the acidic proton have been made as a function of CF_3COOH concentration. These experiments showed that a limiting value of approximately one hydride hydrogen per $Ni[P(OC_2H_5)_3]_4$ molecule was reached in the presence of a large excess of acid. We deduce from this that a monohydride is formed (as indicated by the doublet structure of the ^{31}P resonance). The equilibrium constants for reaction 1 ($X^- = CF_3COO^-$) in $CDCl_3$ and CD_3CN are approximately 0.3. More accurate data on the equilibrium constants and kinetics of formation of nickel hydrides will be presented by other authors. The ^1H and ^{31}P nmr evidence could be interpreted to indicate that all four phosphorus atoms in the hydride molecule are equivalent, in which case a square-pyramidal geometry with the hydrogen at the apex would be indicated; however, we cannot eliminate the possibilities either that the chemical shifts and spin–spin coupling constants of a less symmetric structure (*e.g.*, a trigonal bipyramid) are fortuitously very similar or that there is a rate process which leads to fast exchange between nonequivalent phosphorus atoms. However, there is no broadening of the resonance on cooling to $-60°$.

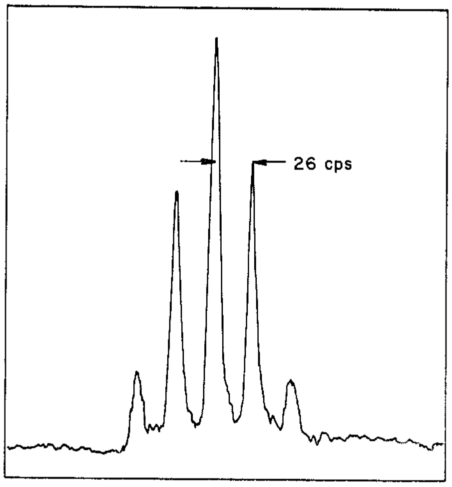

Figure 1.—Hydride resonance of $HNi[(OPC_2H_5)_3]_4^+$ at 60 Mcps. The $CDCl_3$ solution was acidified with CF_3COOH (three time averaging passes).

There are several references in the literature to spectroscopic evidence for nickel hydrides derived from phosphine systems of the form L_2NiX_2.[3-5]

It is likely that these are all species of the form L_2NiHX analogous to the Pt species described by Cariati, *et al.*[1] Quite recently a stable hydride of this type $[(C_6H_{11})_3P]_2NiHCl$ has been isolated as a crystalline solid.[6]

Up to the present time efforts to isolate five-coordinate nickel hydrides with phosphite ligands have been unsuccessful. However, analogous compounds containing chelating phosphine ligands have been prepared and are described in the following note.[7]

Contrary to molecular weight data in the literature,[8] the complex $Ni[P(OC_2H_5)_3]_4$ is not dissociated to any appreciable extent in benzene solution. This can be shown by a ^{31}P nmr study of solutions of the complex with and without added ligand. Free ligand resonances are observed for the solutions which have added ligand, but not for those which do not.

Extensive chemical and physical studies of these hydrides derived from nickel(0) phosphite complexes will be reported at a later date.

Experimental Section

Nmr spectra were obtained using a Varian HR 60 spectrometer for proton work and a 24.3-Mcps radiofrequency unit and probe for ^{31}P work. Nmr data are listed in Table I.

$Ni[P(OC_2H_5)_3]_4$ was prepared by stirring a mixture of 49.4 g of $NiCl_2 \cdot 6H_2O$ in 1 l. of acetonitrile for 2 hr at 25° and refluxing for

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TABLE I

Solvent	Acid	^{1}H chem shift[a]	^{31}P chem shift[b]	Coupling constant[c]
$(CD_3)_2CO$	CF_3COOH	14.3	−133	26
$CDCl_3$	CF_3COOH	14.5	−135	26
C_6D_6	CF_3COOH	14.4	−131	27
CD_3CN	CF_3COOH	14.5	−131	26
$CDCl_3$	H_2SO_4	14.4	−133	26

[a] Ppm from TMS. [b] Ppm from phosphoric acid. [c] From the proton spectrum. Values from the ^{31}P spectrum agree within experimental error.

10 min. The mixture was cooled to room temperature and 200 ml of triethyl phosphite was added. Rapid stirring for 45 sec was followed by the addition of 72 ml of diethylamine. This mixture was cooled in Dry Ice and filtered under nitrogen. The solid was washed with methanol and recrystallized from methanol under nitrogen. The product was dried under vacuum at 25°.

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Stable Nickel Hydride Complexes

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The addition of strong, nonaqueous acids to solutions of the nickel(0) complex $[(C_2H_5O)_3P]_4Ni$ leads to the formation of a nickel hydride cation[1] which has been well characterized in solution as $[(C_2H_5O)_3P]_4NiH^+$. However, attempts to isolate salts of this cation have been unsuccessful. The reaction of strong, aqueous acids with the tertiary phosphine–nickel(0) complexes $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Ni$ and $[(C_6H_5)_3P]_4Ni$ has been reported[2] to give hydrogen and nickel(II) salts only. This communication reports the addition of strong, nonaqueous acids to $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Ni$ to give stable, isolable nickel hydride complexes.

Experimental Section

All procedures were conducted either in an evacuated system or in an inert atmosphere. Solvents were dried on Linde molecular sieves except for tetrahydrofuran which was distilled from $LiAlH_4$. $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Ni$ was prepared by reduction of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiBr_2$ with $NaBH_4$.[3] Tetramethylsilane was used as an internal reference in recording the ^{1}H nmr spectra at 28°.

Preparation of $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiH\}AlCl_4$.—A 500-ml round-bottom flask was charged with $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Ni$ (5.0 g, 5.9 mmol) and 150 ml of toluene. Upon addition of sublimed $AlCl_3$ (0.8 g, 6.0 mmol), a dark brown oil formed. The mixture was degassed and anhydrous HCl (6.0 mmol) was condensed into the flask. The mixture was then stirred at 25° for 20 hr, and the orange precipitate was collected; no noncondensable gases were observed. The crude product was extracted with 90 ml of tetrahydrofuran and 90 ml of toluene was added to the orange-red, filtered extract. The solution was kept at −25° for 18 hr, and the orange prisms were collected, washed well with toluene, and dried at 25° (0.01 μ) 2 hr to give 3.9 g (65%) of $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiH\}[AlCl_4]$, mp 198–203°. *Anal.* Calcd for $C_{52}H_{49}AlCl_4NiP_4$: C, 60.9; H, 4.8; Al, 2.6; Cl, 13.8; Ni, 5.7; P, 12.1. Found: C, 60.7; H, 4.9; Al, 2.6; Cl, 13.8; Ni, 5.7; P 11.9.

The infrared spectrum of the crude product showed ν_{Ni-H} at 1950 cm^{-1} (Nujol mull) as a single absorption, but the recrystallized sample showed two bands at 1949 and 1916 cm^{-1}. Solution infrared spectra in $CHCl_3$ and tetrahydrofuran showed only one weak, broad absorption at 1950 cm^{-1}. The high-field proton nmr spectrum of the recrystallized sample showed τ_{Ni-H} at 22.95 in tetrahydrofuran, 23.07 in CD_2Cl_2, and 23.00 in CH_3OH. The fine structure was resolved only in CH_3OH as a quintet with $J_{P-H} = 6$ Hz.

Preparation of $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiH\}BF_4$.—A mixture of $AgBF_4$ (0.5 g, 2.6 mmol) and 20 ml of 1,2-dimethoxyethane was degassed under vacuum. Anhydrous HCl (3.0 mmol) was condensed into the flask and the mixture was stirred at 25° for 1 hr. This solution of HBF_4 was filtered (to remove AgCl) directly into a solution of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Ni$ (1.95 g, 2.3 mmol) in 50 ml of 1,2-dimethoxyethane. The yellow solution rapidly turned orange, and an orange, crystalline solid precipitated. After stirring the mixture at 25° for 1 hr, the crude product was collected and extracted with a total of 800 ml of hot tetrahydrofuran, and the filtered extract was concentrated to 100 ml under vacuum. After storage at −20° for 65 hr the solution was filtered, and the orange crystalline solid was washed with tetrahydrofuran and dried at 25° (0.01 μ) for 16 hr to give 1.1 g (51%) of $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiH\}BF_4$, mp 190°. *Anal.* Calcd for $C_{52}H_{49}BF_4NiP_4$: C, 66.2; H, 5.2; F, 8.1; Ni, 6.2; P, 13.1. Found: C, 65.9; H, 5.4; F, 7.7; Ni, 6.1; P, 13.9.

The infrared spectrum (Nujol mull) showed ν_{Ni-H} at 1950 (m) cm^{-1} in addition to bands characteristic of BF_4 and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; the ^{1}H nmr spectrum showed τ_{Ni-H} at 23.01 in CD_2Cl_2 solution; no fine structure was observed.

Preparation of $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiH\}(HCl_2)$.—Anhydrous HCl (16.5 mmol) was condensed into a degassed solution of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Ni$ (5.0 g, 5.9 mmol) in 150 ml of toluene. After being stirred at 25° for 3 hr the orange precipitate was collected, washed well with toluene, and dried at 25° (0.5 μ) 16 hr to give 5.3 g (96%) of orange $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiH\}(HCl_2)$, which darkens at 145° and decomposes at 190°. *Anal.* Calcd for $C_{52}H_{50}Cl_2NiP_4$: C, 67.3; H, 5.4; Cl, 7.6; Ni, 6.3; P, 13.3. Found: C, 66.6; H, 5.2; Cl, 8.2; Ni, 6.3; P, 13.3. Attempts to recrystallize this product led to decomposition.

The infrared spectrum (Nujol mull) showed ν_{Ni-H} at 1934 cm^{-1} in addition to bands characteristic of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$. In the ^{1}H nmr spectra of fresh CD_2Cl_2 solutions, the resonance observed at τ −3.22 (area 1) was assigned to the HCl_2^- anion[4–6] while the unresolved Ni–H resonance appeared at τ 23.02 (area 1).

Mixtures of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Ni$ and H_2SO_4 or CF_3COOH in acetone also showed high-field ^{1}H nmr resonances (τ 22.95 and 22.90, respectively) but no solid products were obtained.

Discussion

The addition of strong anhydrous acids to solutions of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2Ni$ produces the stable nickel hydride complexes $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiH\}^+X^-$ ($X^- = AlCl_4^-, BF_4^-, HCl_2^-$) in good yields. The complexes are high-melting, orange, crystalline solids that slowly decompose in air.

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