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Preparation of Hydridonickel Phosphites

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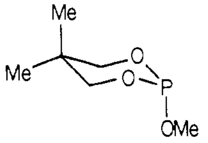
Direct protonation of $Ni(phosphite)_4$ compounds containing acyclic, monocyclic, and bicyclic phosphite ligands has been achieved using H_2SO_4, CF_3COOH, and FSO_3H. The pale yellow solutions, containing $HNi(phosphite)_4^+$ species, are extremely air sensitive and thermally decompose even at room temperature; hence these hydrido complexes have only been characterized in solution using a combination of ^1H and ^{31}P nmr spectroscopy. However, protonation of a tetrakis(bicyclic phosphite)nickel(0) derivative with HCl, HBF_4, or HPF_6 has led to the isolation of solid hydridonickel phosphite complexes of the type $HNi(bicyclic\ phosphite)_4{}^+X^-$ ($X^- = HCl_2^-, BF_4^-, PF_6^-$). The cream powders are stable for many days at room temperature under vacuum and they have been identified by both analysis and ir spectroscopy. Further characterization was not possible since the compounds were not soluble in any common solvents. The variation in the ease of protonation of the $Ni(phosphite)_4$ derivatives and the trend in P-H coupling constants in the $HNi(phosphite)_4^+$ species suggested that the basicity order of the $Ni(phosphite)_4$ complexes, and hence the basicity of the coordinated phosphite ligands, is acyclic $\geqslant$ monocyclic > bicyclic. An ir study of the corresponding $Ni(CO)_3(phosphite)$ derivatives supported this sequence.

Introduction

Recently, Schunn[2] succeeded in preparing hydrido complexes by direct protonation of zerovalent nickel phosphine species. Drinkard[3] and more recently Tolman[4] have applied this procedure to the preparation of acyclic phosphite derivatives, and although they were unable to isolate any solid compounds, they did obtain spectroscopic evidence for the formation of hydrido moieties according to the equation

$$Ni[P(OC_2H_5)_3]_4 + H_2SO_4 \xrightarrow{\text{ether}} HNi[P(OC_2H_5)_3]_4{}^+HSO_4^- \qquad (1)$$

The present work describes the preparation of hydridonickel complexes containing the constrained phosphites **1** and **2**.



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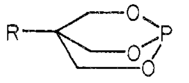

2a, R = Me
b, R = n-C_6H_{13}

Experimental Section

All reactions were performed in a dry nitrogen atmosphere using Schlenk-tube techniques. Infrared spectra of the hydride complexes were obtained on Nujol mulls using a Beckman IR-12 spectrometer. The carbonyl spectrum of $Ni(CO)_3(1)$ was obtained using a Perkin-Elmer 337 spectrometer fitted with a Beckman scale expansion unit calibrated against gaseous carbon monoxide. Proton nmr spectra were recorded on Varian HA-100 or Hitachi Perkin-Elmer R20B spectrometers. ^{31}P nmr spectra were obtained on a Bruker HX-90 spectrometer operating in the Fourier transform mode.

Ligands. The monocyclic ligand **1**[5] and the bicyclic ligand **2a**[6] were prepared as described in the literature.

1,3,7-Trioxa-2-phospha-5-*n*-hexylbicyclo[2.2.2]octane (2b). Under a dry nitrogen atmosphere, 19.0 g (0.1 mol) of the hexyl triol[7] was dissolved in 300 ml of dry tetrahydrofuran containing 30.4 g (0.3 mol) of dry triethylamine. This mixture was added dropwise to a mechanically stirred solution of 13.7 g (0.1 mol) of phosphorus trichloride dissolved in 200 ml of tetrahydrofuran. The resultant mixture was filtered (to remove triethylamine hydrochloride) and the filtrate was concentrated under vacuum to an oil. The oil was diluted with an equal volume of ether and then heptane was added to the cloud point and the solution was vigorously shaken. The emulsion was filtered through alumina and the clarified solution was concentrated under vacuum at 80-90° for several hours to give 17.4 g (80%) of **2b** as a colorless mobile oil. The product was characterized by its proton nmr spectrum in $CDCl_3$ ($\delta(CH_2)$, 3.96 (6 H) doublet; $^3J(POCH_2) = 2$ Hz; δ(hexyl), 1.21 (10 H), 0.91 (3 H) multiplets).

Tetrakis(phosphite)nickel(0) Complexes. $Ni(1)_4$ was prepared from anhydrous NiI_2 according to the method described by Vinal and Reynolds[8] using acetonitrile as solvent. However, unlike most other derivatives, which precipitate directly from the reaction mixture, the $Ni(1)_4$ remains in solution and so necessitated the following isolation procedure. After performing a reaction using 3.13 g (10 mmol) of NiI_2, the acetonitrile solution was concentrated to a volume of about 5 ml and 30 ml of benzene and 60 ml of ether were added. After filtration of the precipitated alkylammonium iodide, the filtrate was concentrated to dryness under vacuum and the residue was warmed to 80° to remove any unreacted ligand. The pale orange powder was extracted several times with warm hexane which, when concentrated under vacuum, yielded a white crystalline solid. The solid was redissolved in 1:1 hexane-benzene and chromatographed on alumina using the same solvent. The resulting eluent was pumped to dryness giving 5.0 g (70%) of white crystals. The solid appears to be stable indefinitely when kept under nitrogen and stable to the atmosphere for 1 week or more. A proton nmr spectrum indicated that the compound was a benzene adduct, and analysis confirmed this. *Anal.* Calcd for $Ni(C_6H_{13}O_3P)_4\cdot 0.25C_6H_6$: C, 41.8; H, 7.3; P, 16.9. Found: C, 41.7; H, 7.2; P, 16.7.

$Ni(2a)_4$, $Ni(2b)_4$, and $Ni[P(OC_2H_5)_3]_4$ were prepared from anhydrous NiI_2 *via* the method of Vinal and Reynolds[8] using acetonitrile as solvent or from nickel tetrafluoroborate as described by Verkade.[9] The bicyclic complexes were purified by chromatography on alumina using dichloromethane as solvent and eluent. The $Ni(2a)_4$ and $Ni(2b)_4$ complexes are indefinitely stable under nitrogen and do not appear to deteriorate when exposed to the atmosphere for 1 month or more. $Ni(2a)_4$ has been characterized previously.[10] $Ni(2b)_4$ was obtained in 30% yield. *Anal.* Calcd for $Ni(C_{10}H_{19}PO_3)_4$: C, 51.5; H, 8.2; P, 13.3. Found: C, 51.3; H, 8.5; P, 12.9.

Hydridotetrakis(phosphite)nickel(II) Salts. Phosphite 1-HSO_4^-. This was prepared following the procedure described by Tolman[4] for the $P(OC_2H_5)_3$ derivative. The product was an air sensitive, thermally unstable pale yellow oil.

Phosphite 1-, 2a-, and 2b-CF_3COO^-. These complexes were prepared at room temperature *in situ* by adding an excess of trifluoroacetic acid (about 0.5 ml) to a chloroform or dichloromethane solution or suspension (1-2 ml of solvent) containing approximately 300 mg (0.5 mmol) of the appropriate NiL_4 derivative. In each case an air-sensitive pale yellow solution was produced.

Phosphite 2a- and 2b-SO_3F^-. About 200 mg (0.3 mmol) of NiL_4 was carefully dissolved in about 2 ml of fluorosulfonic acid contained in a 10-mm diameter nmr tube cooled to −78° and maintained

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(1) NSF Undergraduate Research Participant.

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under a nitrogen atmosphere. The pale yellow hydride solutions decompose above −20°, so nmr spectra were obtained by inserting the samples into the probe precooled to −40°.

Phosphite 2a-HCl$_2^-$. Ni(2a)$_4$, 400 mg (0.6 mmol), was dissolved in 80 ml of dry, nitrogen-saturated benzene and the solution warmed to 50°. A steady stream of dry HCl was then passed into the solution and an immediate pale cream precipitate formed. After bubbling the HCl for 15 min, the solution was allowed to cool under nitrogen. The solid was then filtered off and washed with warm benzene to give 180 mg (45%) of the cream solid hydrido complex. The product is stable for about 1 week under nitrogen and can be handled in the air for short periods. *Anal.* Calcd for $[HNi(C_5H_9PO_3)_4]HCl_2$: C, 33.2; H, 5.3; P, 17.2; Cl, 9.80. Found: C, 33.3; H, 5.5; P, 16.1; Cl, 9.41.

Phosphite 2a-BF$_4^-$ and -PF$_6^-$. To a solution of 1.5 g (23 mmol) of Ni(2a)$_4$ in 180 ml of nitrogen-saturated dichloromethane was added the stoichiometric amount of HBF_4 or HPF_6 (prepared from Ag-BF_4 or $AgPF_6$ plus gaseous HCl in 15 ml of $LiAlH_4$-dried glyme). An immediate cream precipitate was produced and the reaction mixture was stirred for an additional 5 hr. The solid was then filtered off, washed with dichloromethane, and dried under vacuum. The yield in each case was about 1.0 g (55%). The cream solids are stable for months under vacuum at room temperature and can be handled in air for brief periods. *Anal.* Calcd for $[HNi(C_5H_9PO_3)_4]BF_4$: C, 32.5; H, 5.0; P, 16.8. Found: C, 32.3; H, 5.0; P, 15.6. Calcd for $[HNi(C_5H_9PO_3)_4]PF_6$: C, 30.1; H, 4.7; P, 19.5. Found: C, 29.9; H, 4.7; P, 19.1.

Tricarbonyl(ligand 1)nickel(0). To 340 mg (2 mmol) of $Ni(CO)_4$ dissolved in 20 ml of ice-cold nitrogen-saturated dichloromethane was added dropwise 330 mg (2 mmol) of neat ligand **1**. After being stirred for 15 min the solution was allowed to warm to room temperature and an infrared spectrum was taken: ν(CO), $A_1 = 2082 \pm 1$, $E = 2010 \pm 5$ cm^{-1}.

Results

Solution Studies. When complexes of the type Ni(**2a**)$_4$ or Ni(**2b**)$_4$ are dissolved in fluorosulfonic acid or when trifluoroacetic acid is added to a chloroform or dichloromethane solution of the appropriate Ni(phosphite)$_4$ complex, a pale yellow solution is immediately produced. Both proton and phosphorus nmr spectroscopy (see Table I) confirm that protonation of the NiL_4 complex has occurred, and the results are most readily interpreted in terms of a $HNiL_4^+$ species formed according to eq 1.

The equivalence of all four phosphorus atoms (as indicated by the hydride quintet) suggests the $HNiL_4^+$ cation might be a rigid arrangement having a square-pyramidal structure with the proton in the apical position. Alternatively the cation could be conformationally mobile, in which case either a fluxional trigonal bipyramid or a structure retaining the tetrahedrally disposed phosphite ligands with the hydrogen atom rapidly traversing all four faces could be envisaged. The latter "proton tunneling" mechanism has recently been discussed by Jesson[11] with regard to five-coordinate rhodium and six-coordinate iron and ruthenium phosphite hydrides.

The pale yellow solutions are extremely air sensitive and upon exposure to the atmosphere almost instantly become deep yellow. As with the acyclic derivatives, solutions of these hydride complexes are thermally unstable and tend to decompose over a period of 1 hr or so even when maintained under a nitrogen atmosphere.

In $CHCl_3$ or CH_2Cl_2 protonation of both $Ni[P(OC_2H_5)_3]_4$ and Ni(**1**)$_4$ is essentially complete, as indicated by the total disappearance of the ^{31}P nmr singlet peak of NiL_4 which is replaced by the doublet of $HNiL_4^+$ at higher field. In contrast, the Ni(**2a**)$_4$ and Ni(**2b**)$_4$ complexes only partially protonate according to the equilibrium

$$H^+(\text{solvated}) + NiL_4 \overset{K}{\rightleftarrows} HNiL_4^+ + \text{solvent} \qquad (2)$$

Table I. Nmr Parameters for Nickel Complexes

$HNiL_4^+X^-$						
L	X^-	$\tau(^1H)$ quintet	^2J-(PH),[a] Hz	$\delta(^{31}P)$[b] doublet	NiL_4, $\delta(^{31}P)$[b] singlet	Solvent
$P(OEt)_3$	HSO_4^-	24.3[c]	26.5[c]	−135[c]	−161[c,d]	CH_2Cl_2
	HSO_4^-	24.4	26.5			CH_2Cl_2
	CF_3COO^-		26.6	−132	−159	$CDCl_3$
1	HSO_4^-	23.4	34			CH_2Cl_2
	CF_3COO^-	23.3	33	−133	−151	$CDCl_3$
2a	CF_3COO^-	23.7	41	−118	−128	$CDCl_3$
	SO_3F^-		42	−117	−135	HSO_3F
2b	CF_3COO^-	23.7	40	−120	−128	$CDCl_3$
	SO_3F^-		44	−117	−135	HSO_3F

[a] Data from both ^1H and ^{31}P nmr spectra were essentially identical. [b] Ppm relative to external 85% H_3PO_4 (estimated to ±1ppm). [c] As reported by Tolman.[4] [d] Solvent for the ^{31}P nmr spectrum was CH_3-OH.

Thus the ^{31}P spectrum of an acidified solution of Ni(**2a**)$_4$ or Ni(**2b**)$_4$ shows both the singlet peak due to nonprotonated complexes and the doublet due to $HNiL_4^+$. The relative integration of the two peaks suggests that, in trifluoracetic acid, the nickel complex is approximately 90% protonated and in neat fluorosulfonic acid it is about 96% protonated. Similar behavior was observed when the protonation was conducted with ethereal H_2SO_4: the acyclic and monocyclic phosphite derivatives yield $HNiL_4^+HSO_4^-$ complexes as pale yellow oils while the bicyclic phosphite complexes failed to react. These observations can be explained by considering eq 2 to be an acid–base equilibrium. The less basic Ni(**2a**)$_4$ and Ni(**2b**)$_4$ complexes are only partially protonated in $CHCl_3$-CH_2Cl_2 whereas in ether they are weaker bases than the solvent. Hence the addition of acid to the system merely protonates the ether in preference to the nickel complex.

Solid Complexes. Using suitable reaction conditions it has been possible to isolate, for the first time, solid hydridonickel phosphite derivatives. Gaseous HCl reacted immediately with Ni(**2a**)$_4$ dissolved in benzene to give a cream precipitate which exhibited a rather weak infrared band assigned to ν(Ni-H) at 2020 cm^{-1}. Analysis indicated the solid product was $[HNi(\mathbf{2a})_4]HCl_2$.

Solutions of HBF_4 or HPF_6 in glyme reacted with Ni(**2a**)$_4$ dissolved in CH_2Cl_2 to give immediate cream precipitates which also showed weak ν(Ni-H) absorptions at 2013 and 2011 cm^{-1}, respectively. Analysis of the products indicated reaction had occurred to produce complexes of the type $[HNi(\mathbf{2a})_4]X$ ($X^- = BF_4^-, PF_6^-$).

Unfortunately none of these solid hydrido complexes are soluble in any common organic solvents: the HCl_2^- salt, although soluble in CH_2Cl_2, dissolves with decomposition to release gaseous HCl regenerating Ni(**2a**)$_4$. None of the complexes react with CCl_4 at room temperature. This result is not so surprising, since Schunn[12] cited instances where known hydride complexes dissolve without decomposition in CCl_4. On the other hand, the complexes do react with water to produce acidic solutions and precipitate Ni(**2a**)$_4$.

Discussion

The essentially complete protonation of the acyclic and monocyclic NiL_4 derivatives contrasts with the partial protonation of Ni(**2a**)$_4$ and Ni(**2b**)$_4$ and suggests that the former complexes are stronger bases than the latter. This conclusion is supported by recent work of Tolman,[13] who suggested that the value of ^2J(PH) in the $HNiL_4^+$ cations was propor-

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Table II. Comparison of Nmr, Ir, and Equilibrium Data

L	$\tau(^1H)^c$	^2J(PH),^{c} Hz	ν(CO)-(A_1),^{d} cm^{-1}	$K(CH_3OH$ at 0°),^{c} M^{-1}
dppe	22.9	5.5	2067	410
$P(OEt)_3$	24.4	26.5	2076	33
1	23.3^a	34^a	2082^a	(4.4)^b
$P(OCH_2CH_2Cl)_3$	23.9	28	2084	1.2
2a, 2b	23.7^a	41^a	2087	(0.6)^b
$P(OCH_2CCl_3)_3$	*e*	*e*	2092	<0.1

[a] This work; all other data from ref 13 and C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970). [b] Interpolated from ref 13. [c] Data on $HNiL_4^+$ complexes. [d] Data on $Ni(CO)_3L$ complexes. [e] Not observed.

tional to the basicity of the coordinated ligands. Indeed Table II clearly indicates that as the basicity of the ligand decreases, ^2J(PH) increases. This difference in basicity must be directly related to the differing basicities of the ligands attached to the nickel atom. As noted by Shriver,[14] the more electron donating the ligand, the more basic the metal. The relative basicities of a series of ligands can be deduced by comparing the change in carbonyl stretching frequency as the ligand is varied. Table II lists the carbonyl stretching frequencies of the A_1 mode in the corresponding $Ni(CO)_3L$ series as the P donor is changed.[15] The trend in basicities is reasonably consistent with the trend deduced from ^2J(PH) values.

From an extensive spectrophotometric study of the protonation of acyclic nickel phosphites, Tolman[13] deduced an empirical relation between log *K* (the equilibrium constant for the protonation reaction 2, measured at 0° in CH_3OH) and the frequency of the A_1 mode in the corresponding $Ni(CO)_3L$ complex. Using the observed frequency for this mode we have interpolated *K* values for the protonation of the $Ni(\mathbf{1})_4$, $Ni(\mathbf{2a})_4$, and $Ni(\mathbf{2b})_4$ complexes and they are listed in Table II. The fact that *K* for the monocyclic complex is almost one order of magnitude greater than that of the bicyclic derivatives accords with the ready observation of the monocyclic phosphite nickel hydride and the difficulty in detecting the bicyclic phosphite nickel hydride.

Finally, we note that both the protonation behavior and the infrared data suggest the basicity order for unsubstituted phosphites is acyclic ⩾ monocyclic > bicyclic. This sequence has recently been suggested by one of us[16] where it was rationalized in terms of changes in hybridization at the phosphite oxygen stemming from molecular constraint.

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Registry No. $HNi(P(OEt)_3)_4^+CF_3COO^-$, 25512-94-1; $HNi(\mathbf{1})_4^+$-HSO_4^-, 52699-29-3; $HNi(\mathbf{1})_4^+CF_3COO^-$, 52731-26-7; $HNi(\mathbf{2a})_4^+CF_3$-COO^-, 52699-31-7; $HNi(\mathbf{2a})_4^+SO_3F^-$, 52699-32-8; $HNi(\mathbf{2b})_4^+CF_3$-COO^-, 52699-34-0; $HNi(\mathbf{2b})_4^+SO_3F^-$, 52699-35-1; $Ni(\mathbf{1})_4$, 52748-20-6; $Ni(\mathbf{2a})_4$, 14730-03-1; $Ni(\mathbf{2b})_4$, 52731-25-6; **2b**, 52698-99-4; HNi-$(\mathbf{2a})_4^+HCl_2^-$, 52699-36-2; $HNi(\mathbf{2a})_4^+BF_4^-$, 52699-37-3; $HNi(\mathbf{2a})_4^+PF_6^-$, 52699-39-5; $Ni(CO)_3(\mathbf{1})$, 52699-40-8.

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Displacement Reactions on Donor-Haloalanes. Some Novel Four-Coordinate Chelated Aminedihydroaluminum(1+) Salts

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Iodide salts of two novel four-coordinate aluminum cations *N,N,N',N'*-tetramethylethylenediaminedihydroaluminum(1+) and sparteinedihydroaluminum(1+) have been prepared by nucleophilic displacement reactions on trimethylamine-iodoalane and characterized by infrared absorption and conductivity measurements. Trimethylamine-bromoiodoalane has been prepared along with *N,N,N',N'*-tetramethylethylenediamine complexes of AlH_2Br and $AlHBr_2$. The reaction with the monobromoalane yields the bromide salt of the chelated aluminum(1+) ion, while with the dibromoalane, the product appears to be a molecular complex containing five-coordinate aluminum.

Introduction

The preparation and characterization of electrolytes containing four-coordinate boron cations of the type $LL'BH_2^+$ where L and L' denote neutral electron-donor molecules have been described,[1-4] and although numerous four-coordinate aluminum salts have been prepared,[5-7] analogous dihydro $L_2AlH_2^+$ species have not been reported. We have employed a method similar to one utilized in the synthesis of dihydroboron cations,[8,9] involving the reaction of trimethylamine-iodoalane with the bidentate nitrogen bases *N,N,N',N'*-tetramethylethylenediamine (TMED) and sparteine to prepare, *via* nucleophilic displacement of iodide ion and transamination, salts containing the corresponding chelated aminedihydroaluminum(1+) ions. Reactions of TMED with $(CH_3)_3N\cdot AlH_2Br$ and $(CH_3)_3N\cdot AlHBr_2$, respectively, lead to a species which in solution appears to correspond to the bromide salt of the $TMED\text{-}AlH_2^+$ ion and to a chelated complex which may contain five-coordinate aluminum.

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