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°.

CONTRIBUTION NO. 1566 FROM THE CENTRAL RESEARCH
DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND COMPANY,
WILMINGTON, DELAWARE 19898

Stable Nickel Hydride Complexes

BY R. A. SCHUNN

Received April 21, 1969

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.

---

(1) W. C. Drinkard, D. R. Eaton, J. P. Jesson, and R. V. Lindsey, Jr., *Inorg. Chem.*, **9**, 392 (1970).

(2) F. Cariati, R. Ugo, and F. Bonati, *ibid.*, **5**, 1128 (1966).

(3) J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 2537 (1962).

(4) K. M. Harmon and R. R. Lake, *Inorg. Chem.*, **7**, 1921 (1968).

(5) L. W. Schroeder and J. A. Ibers, *J. Am. Chem. Soc.*, **88**, 2601 (1966).

(6) K. A. Hooten, *J. Chem. Soc.*, *A*, 680 (1969).

Solutions of the HCl_2^- salt are unstable and slowly decompose to give H_2 and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiCl_2$. The $AlCl_4^-$ and BF_4^- salts are soluble in polar organic solvents and are stable in the absence of air and water. The complexes are characterized as nickel hydride species on the basis of their infrared and ^1H nmr spectra.

The formation of these apparently five-coordinate nickel hydride complexes is analogous to the reaction of $[(C_2H_5O)_3P]_4Ni$ with strong acids described in the preceding note[1] and may be regarded either as an oxidative addition of a proton to Ni(0) to give a formally nickel(II) hydride complex or as a protonation of a Ni(0) complex. A stable four-coordinate nickel hydride complex $[(C_6H_{11})_3P]_2NiHCl$ was recently prepared[7] by treatment of a nickel(II) complex with $NaBH_4$ and spectroscopic evidence has been presented for analogous L_2NiHX complexes with L = $(C_2H_5)_3P$,[8] $(C_3H_7)_3P$,[9] and $(C_4H_9)_3P$.[10]

Triethyl phosphite reacted rapidly with $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2NiH\}AlCl_4$ in acetonitrile to give the free diphosphine ligand but no nickel complex was isolated. A ^1H nmr spectrum of a mixture of the $AlCl_4^-$ salt and a few drops of $(C_2H_5O)_3P$ showed new Ni–H resonances at τ 22.3 and 22.5 in addition to that of the original complex at τ 22.9. No fine structure was resolved on any of the resonances. The new hydride resonances probably arise from $[(C_2H_5O)_3P]_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]NiH^+$ and $[(C_2H_5O)_3P]_4NiH^+$ species formed by displacement of the diphosphine ligand. The low-field resonances arising from the phosphorus ligands were not recorded.

[7] M. L. H. Green and T. Saito, *Chem. Commun.*, 208 (1969).

[8] E. H. Brooks and F. Glockling, *J. Chem. Soc., A*, 1030 (1967).

[9] M. L. H. Green, C. N. Street, and G. Wilkinson, *Z. Naturforsch.*, **14b**, 738 (1959).

[10] M. L. H. Green, M. Nehmé, and G. Wilkinson, *Chem. Ind.* (London), 1136 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TEMPLE UNIVERSITY, PHILADELPHIA, PENNSYLVANIA 19122

Some Azido Complexes of Nickel(II), Palladium(II), and Platinum(II)

BY KRISTIN BOWMAN AND ZVI DORI

Received June 18, 1969

Although metal complexes containing the azide ion have been known for quite some time, it was only recently that an extensive investigation of the preparation and physical properties of azido complexes of transition metals had been carried out.[1] In this study, Beck and coworkers have prepared a variety of complexes of the general type $M(N_3)_4^{n-}$ and $M(N_3)_6^{n-}$. They have also shown that the azide ion can act as a bridging ligand, forming complexes such as $Pd_2(N_3)_6^{2-}$.

The nonlinearity of the metal–azide bond was first suggested by Staples and Tobe[2] on the basis of infrared measurements of some azido complexes of Co(III). Horrocks has reached the same conclusions from detailed infrared analysis of tetrahedral complexes of the type $M(N_3)_4^{2-}$ (M = Co(II), Zn(II)).[3] These conclusions were confirmed by several crystal structure investigations which were reported in recent years.[4–6]

Here we wish to report the synthesis and the physical properties of some azido complexes of Ni(II), Pd(II), and Pt(II).

Experimental Section

Microanalyses (Table I) were performed by Micro-Analysis, Inc., Wilmington, Del. 19808. Infrared spectra were taken in solution, in KBr pellets, and in Nujol mulls and were recorded on a Perkin-Elmer Model 225 spectrophotometer. Conductivity measurements were taken in chloroform and DMF solutions using an Industrial Instruments Model RC16B2 conductivity bridge. Electronic absorption spectra were recorded on a Cary 14 spectrophotometer. Proton nmr spectra were taken in chloroform-*d* solution and were recorded on a Varian A-60 spectrophotometer. X-Ray data were collected on Weissenberg and precession cameras using Mo Kα radiation.

The phosphine ligands used in this study were prepared by various published methods.[7]

Preparation of $LNi(N_3)_2$[8] (L = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (diphos), $(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ (vpp)).—In 75 ml of hot ethanol 1.0 g of $NiCl_2 \cdot 6H_2O$ (0.0042 mol) was dissolved and dehydrated with 2,2-dimethoxypropane. To this solution 0.0042 mol of the ligand in 50 ml of CH_2Cl_2 was added. The resulting orange precipitate was filtered and dissolved in 100 ml of DMF. A solution of 0.57 g of NaN_3 (0.009 mol) in 50 ml of methanol was added and the solution was stirred for 10 min. The desired complex was obtained by addition of methanol. The complex was recrystallized from a 1:1 by volume DMF–ether mixture to give an analytically pure sample.

Preparation of $L_2M(N_3)_2$ (L = $(C_6H_5)_2(CH_2{=}CH)P$, $(C_6H_5)_2CH_3P$, $(C_6H_5)_2(C_2H_5O)P$; M = Pd, Pt).—To a solution of 0.001 mol of K_2PtCl_4 or Na_2PdCl_4 in 50 ml of water was added a solution of 0.0025 mol of the ligand in 75 ml of ethanol under nitrogen. The solution was stirred for 10 min and the precipitate was isolated. The precipitate was then dissolved in 50 ml of hot DMF and 0.32 g of NaN_3 (0.0023 mol) in 50 ml of methanol was added under nitrogen. Concentration of the DMF solution to 20 ml and addition 100 ml of methanol caused the precipitation of the desired complex.

Preparation of $LPd(N_3)_2$ (L = diphos, vpp, bipy, *o*-phen), and $vppPt(N_3)_2$.—To a solution of 0.001 mol of K_2PtCl_4 or Na_2PdCl_4 in 50 ml of water was added a solution of 0.0025 mol of the ligand in 75 ml of ethanol under nitrogen. The solution was stirred for 10 min and the precipitate was isolated. The precipitate was then dissolved in 100 ml of hot DMF and 0.32 g of NaN_3 (0.0023 mol) in methanol was added under nitrogen. Concentration of the DMF solution to 20 ml and addition of 100 ml of methanol caused the precipitation of the desired complex.

Preparation of $LPt(N_3)_2$ (L = bipy, *o*-phen).—The chlorides were prepared according to the method of Morgan and Burstall[9]

---

[1] W. Beck, W. P. Fehlhammer, P. Pollmann, E. Schuierer, and K. Feldl, *Chem. Ber.*, **100**, 2335 (1967).

[2] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

[3] D. Forster and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1510 (1966).

[4] G. J. Palenik, *Acta Cryst.*, **17**, 360 (1964).

[5] Z. Dori, *Chem. Commun.*, 714 (1968).

[6] I. Agrell, *Acta Chem. Scand.*, **21**, 2647 (1967).

[7] Diphenylvinylphosphine: K. D. Berlin and G. B. Butler, *J. Org. Chem.*, **26**, 2537 (1961); monoethoxydiphenylphosphine: R. Rabinowitz and J. Pellon, *ibid.*, **26**, 4623 (1961); methyldiphenylphosphine: R. A. Zingaro and R. E. McClothlin, *J. Chem. Eng. Data*, **8**, 226 (1963); 1,2-vinylenebis-(diphenylphosphine): A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 2299 (1964).

[8] All the azide complexes reported here are not explosive and are stable when kept in the dark.

[9] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 965 (1934).