Solutions of the HCl_2^- salt are unstable and slowly decompose to give H_2 and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$-$NiCl_2$. 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 $\{[(C_6H_5)_2$-$PCH_2CH_2P(C_6H_5)_2]_2NiH\}AlCl_4$ 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 $[(C_2H_5$-$O)_3P]_2[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]NiH^+$ and $[(C_2H_5$-$O)_3P]_4NiH^+$ 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).

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

BY KRISTIN BOWMAN AND ZVI DORI

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 $Pd_2(N_3)_6^{2-}$.

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

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 $K\alpha$ 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 $NiCl_2\cdot6H_2O$ (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 $L_2M(N_3)_2$ ($L = (C_6H_5)_2(CH_2{=}CH)P$, $(C_6H_5)_2$-CH_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]

(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).

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(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).

Compound	Color	% C		% H		% N		% P	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Ni(diphos)(N₃)₂	Red	57.75	57.75	4.65	4.74	15.53	16.14	11.44	11.28
Ni(vpp)(N₃)₂	Red-orange	57.90	57.09	4.12	5.48				
Pd(diphos)(N₃)₂	Yellow	53.00	52.30	4.11	4.26	14.27	14.27	10.53	10.72
Pd(vvp)(N₃)₂	Yellow	53.19	53.11	3.78	3.93	14.32	11.47	10.57	11.39
Pd(phen)(N₃)₂	Gold	38.87	39.13	2.17	2.47	30.23	30.48		
Pd(bipy)(N₃)₂	Gold	34.59	35.87	2.32	2.38	32.31	31.00		
Pd[(C₆H₅)₃P]₂(N₃)₂	Orange	60.42	60.70	4.23	4.17	11.75	12.01		
Pt(diphos)(N₃)₂	White	46.22	46.42	3.57	3.58	12.40	12.22	9.15	9.16
Pt(bipy)(N₃)₂	Gold	27.57	27.79	1.85	1.82	25.73	25.66		
Pt(phen)(N₃)₂	Gold	31.38	32.01	1.75	1.59				

and then treated as described above for the preparation of the Pd complexes.

Preparation of diphosPt(N₃)₂.—The chloride was prepared according to the method of Westland[10] and treated as described above for the corresponding Pd complexes.

Results and Discussion

The compounds Ni(diphos)(N₃)₂ and Ni(vpp)(N₃)₂ are red diamagnetic solids which exhibit one electronic absorption maximum in the visible region at 21,950 and 22,200 cm⁻¹, respectively. These complexes are nonelectrolytes in a variety of organic solvents and their electronic absorption spectra in solution are very similar to the ones observed in the solid state. Thus, it is reasonable to suggest that these complexes are square planar both in solution and in the solid state.

Based on the electronic absorption spectra of the nickel complexes it appears that the ligand vpp exerts a somewhat stronger ligand field on the metal ion. The same observation was recently reported by Meek[11] for similar complexes of Ni(II).

The palladium complexes are all light yellow to orange. They are nonelectrolytes in organic solvents such as CHCl₃ and DMF and their electronic absorption spectra in solution and in the solid state are essentially the same. The possibility of formation of complexes such as [L₂M][M(N₃)₄] with the ligands bipy and *o*-phen is ruled out on the basis of the observed electronic absorption spectra.

The nmr absorption pattern of the methyl groups of the complex ((C₆H₅)₂CH₃P)₂Pd(N₃)₂ consists of a 1:2:1 triplet (centered at τ 8.1) suggesting that this complex has the *trans* configuration.[12] No signal due to the *cis* isomer is observed. The similarity between the physical properties of this complex and the other Pd(II) complexes containing the monodentate phosphine ligand suggests that these complexes also have the *trans* configuration.

In contrast to the palladium complexes, the azido complexes of platinum with phosphine ligands are colorless and are insoluble in nonpolar solvents indicative of *cis* configuration.[13] The nmr spectrum of the methyl protons of the complex ((C₆H₅)₂CH₃P)₂Pt(N₃)₂ consists of three symmetrical doublets centered at τ 8.1.[12] No resonance due to the *trans* isomer is observed.

(10) A. D. Westland, *J. Chem. Soc.*, 3060 (1965).
(11) C. A. McAuliffe and D. W. Meek, *Inorg. Chem.*, **8**, 904 (1969).
(12) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc., A*, 770 (1966).
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TABLE II
ASYMMETRIC STRETCHING BANDS FOR THE AZIDE MOIETY

Compound	ν_{as}, cm⁻¹	
	Mull	Soln
Ni(diphos)(N₃)₂	2030 w,[c] 2047	2041 w, 2056[a]
Ni(vpp)(N₃)₂	2042, 2062	2042, 2057[a]
Pd(diphos)(N₃)₂	2035, 2060 sh[c]	2040 sh, 2075[a]
Pd(vpp)(N₃)₂	2033, 2046	2032, 2043[a]
Pd(phen)(N₃)₂	2018 w, 2058	2035 sh, 2045[b]
Pd(bipy)(N₃)₂	2018 w, 2055	2045, 2060 sh[b]
Pd[(C₆H₅)₃P]₂(N₃)₂	2035	2032, 2046[a]
Pd[(C₆H₅)₂(C₂H₅O)P]₂(N₃)₂	2027, 2044 w	2031 sh, 2044[a]
Pd[(C₆H₅)₂CH₃P]₂(N₃)₂	2020 w, 2044	2032 w, 2045[a]
Pt(diphos)(N₃)₂	2038 w, 2048	2057[a]
Pt(vpp)(N₃)₂	2049	2055[a]
Pt(phen)(N₃)₂	2035, 2053	2044[b]
Pt(bipy)(N₃)₂	2036 w, 2080	2049, 2058[b]
Pt[(C₆H₅)₃P]₂(N₃)₂	2036, 2054 w	2044, 2058[a]
Pt[(C₆H₅)₂CH₃P]₂(N₂)₂	2032 w, 2058	2045 sh, 2060[a]
Pt[(C₆H₅)₂(CH₂=CH)P]₂(N₃)₂	2036, 2058	2045 sh, 2060[a]

[a] In CH₂Cl. [b] In DMF. [c] Abbreviations: w, weak; sh, shoulder.

Of particular interest are the infrared data obtained for these complexes (Table II). The complex ((C₆H₅)₃P)₂Pd(N₃)₂ exhibits a sharp absorption band at 2030 cm⁻¹ which is attributed to the azide asymmetric stretch. This band splits into two peaks of approximately equal intensity in methylene chloride and DMF solutions. All other complexes reported here exhibit this two-peak pattern both in solution and in the solid state.

To understand this behavior better, we have undertaken a study of the crystal and molecular structure of the complex ((C₆H₅)₃P)₂Pd(N₃)₂. The complex crystallizes in the triclinic system in a cell of dimensions $a = 10.27 \pm 0.02$ Å, $b = 9.22 \pm 0.02$ Å, $c = 9.87 \pm 0.02$ Å, $\alpha = 74.51 \pm 0.02°$, $\beta = 111.53 \pm 0.02°$, $\gamma = 88.02 \pm 0.02°$, and $V = 828.1$ Å³. The experimental density of 1.43 g/cm³ obtained by flotation in CCl₄–benzene solution agrees well with a calculated density of 1.42 g/cm³ for one molecule in the unit cell. Preliminary results suggest that the space group is P1̄ with the palladium atom occupying the (0, 0, 0) special position of the space group. Thus, in the solid state the two azide moieties are equivalent, resulting in one sharp band for the azide asymmetric stretch. This result also suggests that in solution the complex ((C₆H₅)₃P)₂Pd(N₃)₂ is not centrosymmetric and that the two azide

groups are not equivalent to one another. To further elucidate this problem, we are currently investigating the crystal and molecular structure of the complex Pd-(diphos)(N$_3$)$_2$.

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Electron Spin Resonance in Molybdenum(V) and Tungsten(V) Compounds

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Continuing work in our laboratories has involved the preparation and characterization of transition metal alkoxides.[1-8] Particular emphasis has been placed on d^1 systems whose paramagnetism has subsequently led to the prediction of bonding properties.[7,9] For example, evidence points to more covalency in the b$_2$ and b$_1$ molecular orbitals whereas the e molecular orbital becomes more ionic from $^-OCH_3$ to $^-OC_4H_9$ in V(OR)Cl$_5^{2-}$.[7]

Other workers,[10-13] including our group,[14] have studied the effect of changing F$^-$ to Cl$^-$ to Br$^-$ in MoOX$_5^{2-}$. A substantial change was found for the $g_\parallel$ value. The $g_\perp$ values also changed, but less drastically.

As yet, no study has involved the selective change of ligands on the c_{4v} axis of symmetry. Our purpose is to illustrate the g-value variation between W(OR)-Cl$_5^-$ and W(OR)$_2$Cl$_4^-$. We will also compare magnetic tensor values for Mo(OR)$_2$Cl$_4^-$, MoOCl$_4^-$, and Mo-OCl$_5^{2-}$.

Experimental Section

Compounds.—Molybdenum(V) and tungsten(V) complexes were described previously.[5,8]

Spectroscopic Measurements.—X-Band esr spectra were recorded at 298 and 78°K on a Varian V-4502-04 spectrophotometer. First-derivative absorptions were recorded on an X-Y recorder with the X axis proportional to the magnetic field strength. A Hall probe was used as field sensor. Markings, which were placed on the recorded spectra by means of a Hew-

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(2) R. A. D. Wentworth and C. H. Brubaker, Jr., *ibid.*, **3**, 47 (1964).
(3) D. A. McClung, L. R. Dalton, and C. H. Brubaker, Jr., *ibid.*, **5**, 1985 (1966).
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(5) D. P. Rillema, W. J. Reagan, and C. H. Brubaker, Jr., *ibid.*, **8**, 587 (1969).
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(11) K. DeArmond, B. B. Garett, and H. S. Gutowski, *J. Chem. Phys.*, **42**, 1019 (1965).
(12) H. Kon and N. E. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).
(13) P. T. Monoharan and M. T. Rogers, *J. Chem. Phys.*, **49**, 5510 (1968).
(14) L. A. Dalton, R. D. Bereman, and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 2477 (1969).

lett-Packard 524-C frequency counter, allowed calibration of the magnetic field. This data enabled calculation of hyperfine splittings. The g values were calculated from the measured magnetic field and klystron frequency.

In conversion of hyperfine values from gauss into reciprocal centimeters, the experimental g values were used in the equation $\nu = g\beta H/h$.

Results and Discussion

The spin Hamiltonian which accounts for an electron spin resonance spectrum of a compound with axial symmetry in a frozen solution is

$$H = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y)$$

where $S = \frac{1}{2}$, $I(^{95}Mo, 15.8\%; ^{97}Mo, 9.6\%) = \frac{5}{2}$, and $I(^{183}W, 14.2\%) = \frac{1}{2}$.

At room temperature the anisotropies add to zero and the Hamiltonian becomes

$$H = \langle g \rangle \beta H \cdot S + \langle a \rangle I \cdot S$$

$$\langle g \rangle = \frac{1}{3}(g_\parallel + g_\perp)$$

$$\langle a \rangle = \frac{1}{3}(A + 2B)$$

The high-field approximation cannot be applied rigorously because hyperfine splittings are 50 G or more in width. The eigenvalues which lead to a second-order perturbation correction of $h\nu = g\beta H_0$ are: for isotropic g

$$H_0 = H_m + \langle a \rangle m_I + \langle a \rangle^2 [I(I + 1) - m_I^2]/2H_m$$

for $g_\parallel$

$$H_0 = H_m + A m_I + B^2 [I(I + 1) - m_I^2]/2H_m$$

for $g_\perp$

$$H_0 = H_m + B m_I + (A^2 + B^2)[I(I + 1) - m_I^2]/4H_m$$

where H_m is the magnetic field position of the esr line due to the component m_I of the nuclear spin I. In previous equations ν is the klystron frequency and A and B are the nuclear hyperfine splitting constants. These corrections were reiterative, were performed with a program designed for this purpose,[15] and were carried out on the MSU control data 3600 computer. Five iterations were carried through. The program also contained a plot routine. The simulated spectrum was then changed by altering the magnetic tensor values until a match was obtained between the computed and experimental spectra.

Electron spin resonance spectra were obtained on powdered samples and on various solutions at 78 and 297°K. The ^{95}Mo–^{97}Mo hyperfine spectrum was observed.

An absorption in an experimental spectrum of tungsten was thought to be hyperfine structure from ^{183}W. Since no hyperfine structure could be duplicated by the computer, the absorption may have been due to a rhombic distortion or an impurity. The ^{183}W hyperfine structure is thought to be masked by the broad absorption of the isotopes with $I = 0$ becuase the half-width is approximately 100 G.

(15) P. T. Monoharan and T. Krigas, EPRSIG 3 program.