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Synthesis and Electronic Structures of Tetrakis Complexes of Phenyldialkoxyphophines with d^{10} Metals

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Tetrakis complexes of d^{10} metals with $PhP(OR)_2$ ($R = CH_3$, C_2H_5) are prepared by reduction of anhydrous metal(II) halides in absolute ROH using an excess ol ligand. The new complexes characterized here are $Ni[PhP(OR)_2]_4$, $Pd[PhP(OR)_2]_4$, and $Cu[PhP(OR)_2]_4Cl$. The Pd^0 and Cu^I complexes are much more air sensitive than the Ni^0 complexes, which are relatively stable. The absorption spectrum of each of the complexes shows a band at lower energy than the first system exhibited by the free ligand; assuming approximate tetrahedral stereochemistry, this band is assigned to the metal to ligand transitions $d(2e, 3t_2) \rightarrow \pi^*PhP(OR)_2$.

Introduction

The first tetrakis complex of Ni^0 with a phosphorus donor ligand was made by reacting nickel carbonyl with PCl_3,[2] giving $Ni(PCl_3)_4$. The complexes $Ni(PB_3)_4$ and $Ni(PF_3)_4$ may be prepared by substitution with PBr_3 and PF_3, respectively.[3] Nickel carbonyl has also been fully substituted with phosphorus triisocyanate and triisothiocyanate,[4] diphosphines such as $o\text{-}C_6H_4\text{-}[P(C_2H_5)_2]_2$,[5] and triethylphosphite.[6] Alternative routes to Ni^0 complexes include the reaction of metallic nickel with CH_3PCl_2[7] and aromatic diphosphines,[5] and the reduction of nickelocene using phosphites such as $P(OPh)_3$.[8]

Vinal and Reynolds have demostrated that Ni^{II} halides are reduced by trialkyl phosphites in the presence of an amine.[9] This is a very simple and convenient synthetic procedure, but the resultant Ni^0 complexes are not very stable. In the course of our investigations[10] of the coordination chemistry of phosphorus-donor ligands, we have found that Ni^{II} halides are readily reduced by phenyldialkoxyphosphines to stable Ni^0 complexes. Furthermore, the reaction may be extended to Cu^{II} and Pd^{II} halides. The present paper reports the preparation and characterization of Ni^0, Pd^0, and Cu^I complexes of the ligands $PhP(OCH_3)_2$ and $PhP(OC_2H_5)_2$. The electronic spectra of these complexes are discussed and certain preliminary electronic structural conclusions are reached.

Experimental Section

Chemicals. The methyl and ethyl diesters of phenyl phosphonous acid were prepared according to the method of Rabinowitz and Pellon.[11] $Nickel^{II}$ bromide, $palladium^{II}$ chloride, and $copper^{II}$ chloride were obtained as anhydrous salts and used as received. Reagent grade $nickel^{II}$ chloride hexahydrate was made anhydrous by reaction with 2,2-dimethoxypropane.[12]

Preparations. *$Ni[PhP(OC_2H_5)_2]_4$.* 1.30 g. (0.01 mole) of anhydrous $NiCl_2$ (or equivalent amount of $NiBr_2$) and 10 g (0.05 mole) of $PhP(OC_2H_5)_2$ were placed in 100 ml of absolute ethanol and refluxed for 3 hrs. Upon slow cooling, yellow crystals separated out of solution. The crystals were filtered, washed with absolute ethanol, and vacuum dried. Concentration of the mother liquor to 30 ml yielded additional crystals. Yield, 97%. *Anal.* Calcd. for $Ni[PhP(OC_2H_5)_2]_4$: C, 56.51; H, 7.11; P, 14.60. Found: C, 56.27; H, 7.17; P, 14.54.

$Ni[PhP(OCH_3)_2]_4$. 0.55 g $NiBr_2$ (0.0025 mole) and 3.4 g $PhP(OCH_3)_2$ (0.020 mole) were placed in 50 ml absolute methanol under nitrogen and refluxed for 5 hr. Upon cooling the solution, pale yellow crystals separated out. These were filtered, washed with methanol, and vacuum dried. Yield, 70%. *Anal.* calcd. for $Ni[PhP(OCH_3)_2]_4$: C, 51.98; H, 5.99. Found: C, 50.75; H, 5.86.

$Pd[PhP(OC_2H_5)_2]_4$. 2 g (0.0113 mole) of anhydrous $PdCl_2$ and 13.5 g (0.067 mole) of $PhP(OC_2H_5)_2$ were placed in 100 ml of absolute ethanol and refluxed for 3 hr under nitrogen. The $PdCl_2$ dissolved and the color of the solution became pale yellow. The solution was slowly cooled and after one day yellow crystals separated out. The crystals were filtered and dried under vacuum in a glove box under nitrogen.

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On exposure to air or moisture, the complex decomposes, developing a dark coloration in a few minutes. When stored in a vial under nitrogen, the crystals are more stable; however, they melt to yellow viscous liquid in a few days. Three weeks after the initial preparation, we were able to recover some more crystals by concentration of the mother liquor. Yield, 64%. *Anal.* Calcd. for Pd[PhP($OC_2H_5)_2]_4$: C, 53.43; H, 6.72; P, 13.77. Found: C, 52.60; H, 6.27; P, 12.93.

Pd[PhP($OCH_3)_2]_4$. 0. 85 g $PdCl_2$ (0.005 mole) and 5.1 g PhP($OCH_3)_2$ (0.030 mole) were placed in 100 ml absolute methanol under nitrogen and refluxed for 20 hr. Upon cooling the solution, colorless crystals separated out. The crystals were filtered and washed in a glove box under nitrogen; they decompose very rapidly upon exposure to air or moisture. *Anal.* Calcd. for Pd[PhP($OCH_3)_2]_4$: C, 48.83; H, 5.63. Found: C, 48.10; H, 5.43.

Cu[Ph($POC_2H_5)_2]_4Cl$. 1.36 g (0.01 mole) of $CuCl_2$ and 12 g (0.06 mole) of PhP($OC_2H_5)_2$ were placed in 100 ml absolute methanol under nitrogen and refluxed for 20 hr. Upon cooling the solution, no crystals were observed. The solution was allowed to stand under nitrogen for three days in a refrigerator (–20°C) and colorless needles grew. These were washed with ethanol and dried under vacuum. Yield, 35%. *Anal.* Calcd. for Cu[PhP($OC_2H_5)_2]_4Cl$: C, 53.75; 6.76; P, 13.86. Found: C, 53.19; H, 6.52; P, 13.63.

Cu[PhP($OCH_3)_2]_4Cl$. 0.34 g $CuCl_2$ (0.0025 mole) and 3.4 g PhP($OCH_3)_2$ (0.020 mole) were placed in 50 ml absolute methanol under nitrogen and refluxed for 20 hr. Upon cooling the solution, only a few tiny crystals were observed. The solution was allowed to stand under nitrogen for three days, and large colorless crystals grew. These were washed with methanol and dried. *Anal.* Calcd. for Cu[PhP($OCH_3)_2]_4Cl$: C, 49.30; H, 5.68; Cl, 4.55. Found: C, 48.09; H, 5.98; Cl, 4.39.

Physical Measurements. Electronic spectra were measured on a Cary Model 14 recording spectrophotometer. Spectral grade solvents were used. Magnetic susceptibility measurements were made on solid samples by the Gouy method using Hg[Co($NCS)_4$] as calibrant.[13]

Results and Discussion

All of the complexes reported here are diamagnetic. The Ni^0 and Pd^0 complexes are quite soluble in nonpolar solvents such as cyclohexane; the Cu^I complexes are soluble in polar organic solvents such as acetonitrile. The Pd^0 complexes are extremely sensitive to air or moisture. Even in a sealed bottle under nitrogen the colorless crystals gradually become grey-brown, indicating the probable presence of metallic Pd. The Cu^I complexes are somewhat more stable, but over a period of a few weeks a liquid appears at the surface of the crystals, indicating some decomposition.

In contrast to these observations, the two Ni^0 complexes appear to be relatively stable, even in air. Samples kept in stoppered vials for several months still showed the same electronic spectra and gave no visible evidence of decomposition. This is especially interesting when compared with the instability of Ni[P($OC_2H_5)_3]_4$; our sample of colorless crystals of this complex prepared by the method of Vinal and Reynolds[9] began to decompose to a green Ni^{II} complex after several days in air. The much greater air stability of Ni[PhP($OC_2H_5)_2]_4$ relative to Ni[P($OC_2H_5)_3]_4$ in the solid state led to an investigation of solutions containing these complexes.

Solutions of Ni[P($OC_2H_5)_3]_4$, P($OC_2H_5)_3$, Ni[PhP($OC_2H_5)_2]_4$, and PhP($OC_2H_5)_2$ were prepared in cyclohexane and acetonitrile. Ultraviolet spectra were taken of each solution and of mixtures of complex and ligand. The intensity of the first absorption system of Ni[P($OC_2H_5)_3]_4$, with a maximum at 42,000 cm^{-1}, increases on adding PhP($OC_2H_5)_2$. The spectral change indicates that replacement of P($OC_2H_5)_3$ ligands is occurring. In sharp contrast, the lowest absorption system in Ni[PhP($OC_2H_5)_2]_4$, at about 30,000 cm^{-1}, which obeys Beer's law, is not as significantly affected on addition of P($OC_2H_5)_3$ and allowing the solutions to come to equilibrium. Thus, with respect to the solutions studied, it appears that Ni[PhP($OC_2H_5)_2]_4$ is more stable than is Ni[P($OC_2H_5)_3]_4$.

Electronic Structures and Spectra. In order to facilitate discussion of the electronic structures of the d^{10} complexes, a qualitative molecular orbital level scheme has been estimated for a model complex Ni[$PR_3]_4$ of T_d symmetry; it is reasonable to assume an approximate tetrahedral geometry for the d^{10} metal complexes under consideration. The orbitals of probable importance in bonding for the model complex are the σ, π, and π^* levels of PR_3 and the 3d, 4s, and 4p orbitals of Ni. The energy levels shown in Figure 1 reflect the expected orders $\pi^* > \sigma > \pi$ and $4p > 4s > 3d$.

The predicted ground state electronic configuration for the T_d model is $\ldots(2e)^4\ (3t_2)^6 = {}^1A_1$; this is in agreement with the diamagnetism measured for all the d^{10} complexes in this study. The 2e and $3t_2$ levels are the usual ligand field d-orbital levels.

For the T_d model complex, electronic transitions are allowed to ${}^1T_2$ excited states. The two lowest energy ${}^1T_2$ excited states should be derived from the metal to ligand transitions $3t_2 \rightarrow 4t_2$ and $2e \rightarrow 4t_2$, respectively. Since the splitting of $3t_2$ and 2e is probably small (<5000 cm^{-1}), these two ${}^1T_2$ states may be expected to appear very close together.

The solution electronic spectra of the various d^{10} complexes are given in Table I. For reference, it should be noted that P($OC_2H_5)_3$ does not have any absorption maxima below 45,000 cm^{-1}, whereas PhP($OC_2H_5)_2$ absorbs strongly in the 40,000 cm^{-1} region. The broad band at 42,000 cm^{-1} ($\varepsilon = 22{,}000$) in Ni[P($OC_2H_5)_3]_4$ is significantly lower than ligand absorption and is assigned as a combination of $3t_2 \rightarrow 4t_2$ and $2e \rightarrow 4t_2$. Bands analogous to the 42,000 cm^{-1} band in Ni[P($OC_2H_5)_3]_4$ appear at 30,000 cm^{-1} ($\varepsilon = 17{,}500$) in Ni[PhP($OC_2H_5)_2]_4$, 36,800 cm^{-1} ($\varepsilon = 8000$) in Cu[PhP($OC_2H_5)_2]_4^+$, and 32,300 cm^{-1}

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Table I. Electronic Absorption Spetra of Tetrakis Complexes of d^{10} Metals with $P(OC_2H_5)_3$ and $PhP(OC_2H_5)_2$ Ligands

Complex	Solvent	Band maxima, cm^{-1} [a]
$Ni[P(OC_2H_5)_3]_4$	cyclohexane	42,000 (22,000)
$Ni[PhP(OC_2H_5)_2]_4$	cyclohexane	30,000 (17,500) 40,200 (22,000)
	EPA	30,000 (17,500) 40,600 (22,000)
$Pd[PhP(OC_2H_5)_2]_4$	3:2 methylcyclohexane/ 2-methyl-butane	32,300 (17,000) [b]
$Cu[PhP(OC_2H_5)_2]_4Cl$	4:1 ethanol/methanol	36,800 (8,000) sh 4,000 (13,500)

[a] Spectra measured at 300°K; molar extinction coefficient in parentheses. [b] The spectrum of this complex in the region of ligand absorption (>35,000 cm^{-1}) exhibits vibrational structure leading to a principal maximum at 42,500 cm^{-1} (ε = 24,000).

(ε = 17,000) in $Pd[PhP(OC_2H_5)_2]_4$. Because the presence of a phenyl group in the ligand makes the use of the model energy levels (Figure 1) incorrect in a strict sense, we shall adopt the notation d(2e, $3t_2$) $\rightarrow$ $\rightarrow \pi^*PhP(OC_2H_5)_2$ for the assignment of the lowest electronic transitions in the d^{10} $PhP(OC_2H_5)_2$ complexes.

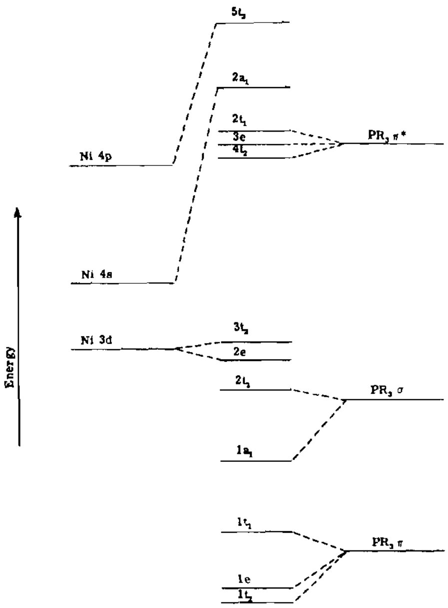

Figure 1. Estimated relative energies of some molecular orbitals for a model $Ni(PR_3)_4$ complex of T_d symmetry. Only the principal correlation lines are shown.

The fact that the first band peaks at higher energy in the Cu^I than in the Ni^0 complex is strong evidence in favor of the metal to ligand type assignment.

The small difference in the energies of the d(2e, $3t_2$) $\rightarrow$ $\pi^*PhP(OC_2H_5)_2$ transitions in the Ni^0 and Pd^0 complexes contrasts sharply with the very large difference observed for the lowest d $\rightarrow$ π^*CN transition in the d^8 square planar complexes $Ni(CN)_4^{2-}$ and $Pd(CN)_4^{2-}$.[14] This contrast dramatizes the large role played by the metal p valence orbital of a_{2u} symmetry in the square planar cases. Presumably, the metal p orbitals are not as involved in the lowest transitions in the tetrahedral complexes, because of their strong involvement in σ bonding.

The much lower energy of d $\rightarrow$ π^* transitions in $Ni[PhP(OC_2H_5)_2]_4$ than in $Ni[P(OC_2H_5)_3]_4$ requires comment. It might have been expected that excitations to π^* would be lower energy for $P(OC_2H_5)_3$ than for $PhP(OC_2H_5)_2$, because of the electron withdrawing nature of $-OC_2H_5$ groups. However, it appears that electron repulsion in the excited configuration $d^9(\pi^*)^1$ is a very important additional factor. We suggest that the repulsion of the π^* electron with the nonbonding pairs on oxygen is much more severe for three $-OC_2H_5$ groups than for two, leading to lower energy for d $\rightarrow$ π^* transitions in $PhP(OC_2H_5)_2$ complexes.

The above interpretation can be extended to shed some light on the more general question of the extent of M $\rightarrow$ P π-bonding in the ground state. The experimental spectra show that it requires less energy to promote an electron from Ni^0 to the π^* level of $PhP(OC_2H_5)_2$ than to $\pi^*P(OC_2H_5)_3$; thus it is probable that d $\rightarrow$ π^* bonding is more extensive in complexes containing the former ligand. The fact that our present studies have shown that $Ni[PhP(OC_2H_5)_2]_4$ is more stable than $Ni[P(OC_2H_5)_3]_4$ may reflect the stronger π-acceptor character of $PhP(OC_2H_5)_2$.

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