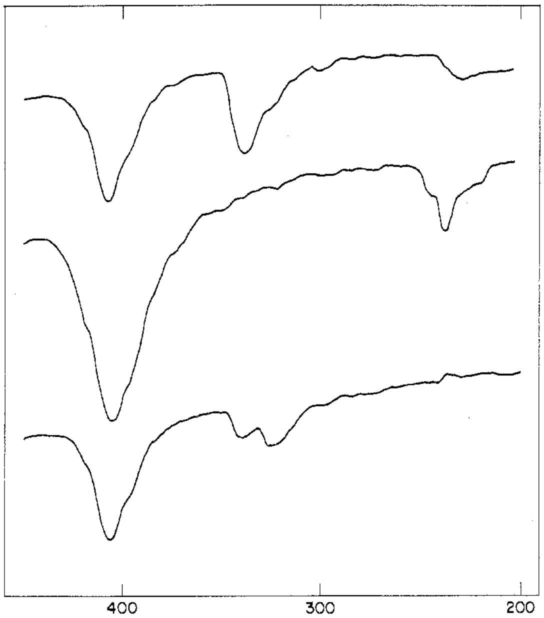

Figure 1. Far-infrared spectra of *trans*-$K_2Pt(CN)_4Cl_2$ (top trace), *trans*-$K_2Pt(CN)_4Br_2$ (middle trace), and *trans*-$K_2Pt(CN)_4BrCl$ (bottom trace).

are further disordered by the random occupancy with chloride (~32%) and bromide (~32%). Through variation of the ratios of **3** and **4** in eq 1, **2** can be synthesized with variable halogen stoichiometries, i.e., $K_2Pt(CN)_4Cl_xBr_{0.3-x}\cdot 3H_2O$. Furthermore, the ramifications of the introduced additional disorder associated with **2** (with respect to **1**) can be studied.

As part of the study of **2** the aqueous equimolar reaction product of **3** and **4** was reevaluated to determine if it was a simple mixture of **3** and **4** or *trans*-$Pt^{IV}(CN)_4BrCl^{2-}$, **5**. The mixed-halogen complex **5** was prepared from a minimum amount of warm water[16] and has been a postulated intermediate in the halide-assisted anation of Pt(IV) complexes.[17] The infrared spectra (in a polyethylene pellet) of **3–5** in the ν_{CN} and ν_{Pt-X} regions were obtained. In the ν_{CN} region sharp singlets at 2172, 2162, and 2169 cm^{-1} were observed for **3–5**, respectively. In contrast to the ν_{Pt-Cl} and ν_{Pt-Br} absorption frequencies at 338 and 258 cm^{-1} for **3** and **4**, respectively, **5** lacked these absorptions and exhibited ν_{Pt-X} at 324 and 340 cm^{-1}, Figure 1. Furthermore, the x-ray powder diffraction pattern of **5** cannot be decomposed into the powder patterns of **3** and **4**. Thus, **5**[18] is a unique phase.

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Registry No. *trans*-$K_2Pt(CN)_4Cl_2$, 12072-77-4; *trans*-$K_2Pt(CN)_4Br_2$, 12072-67-2; *trans*-$K_2Pt(CN)_4BrCl$, 63765-22-0; $K_2Pt(CN)_4$, 562-76-5; bromine, 7726-95-6; chlorine, 7782-50-5.

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o-Diphenylphosphinophenol and Its Coordination Compounds

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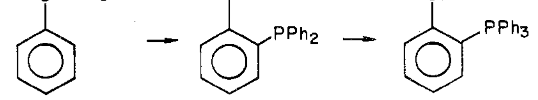
Transition metal complexes of phosphinoanisoles have been recently reported with attention to their lability,[1] oxidative additions,[2] and *o*-dealkylation.[3] The latter study also describes metal complexes formally derived from the previously unknown class of ligands, *o*-diorganophosphinophenols. Herein we describe a convenient synthesis for *o*-diphenylphosphinophenol from phenol itself; furthermore we describe several of its metal complexes.

Results and Discussion

o-Diphenylphosphinophenol is prepared from phenol in three steps: first the phenol is protected and activated, next the diphenylphosphino group is attached, and finally the hydroxyl group is deprotected. Methoxymethyl phenyl ether is easily prepared on a large scale by the reaction of phenol with sodium hydride followed by treatment with chloromethyl methyl ether. The metalation of methoxymethyl phenyl ether[4,5] by butyllithium yields the *o*-lithio derivative which, when reacted in situ with chlorodiphenylphosphine, yields **1**. Similar orthometalations have been used by us to prepare other phosphorus chelates.[1] **1** exhibits the chemical and spectroscopic characteristics expected for a tertiary arylphosphine. Acid catalyzed methanolysis of **1** cleanly gives the desired phenol (**2**), PPhOH, in 42% overall yield. **2** is easily sublimable, shows a broad absorption in the infrared at 3400 cm^{-1}, and has a proton resonance absorption at δ 6.15 which disappears upon



1 2

Table I. Analytical and Related Data for New Compounds

Compd	Color	Mp	Found (calcd) % C	% H	% P	Mol wt
(1) $Ph_2P(o\text{-}PhOCH_2OCH_3)$	Colorless	122–121	74.35 (74.53)	6.06 (5.90)	9.22 (9.62)	322[a] (322)
(2) $Ph_2P(o\text{-}PhOH)$	Colorless	164–165	77.54 (77.70)	5.51 (5.40)	11.09 (11.1)	278[a] (278)
(3) $(Ph_2P(o\text{-}PhO))_2Ni$	Orange	>300	70.28 (70.4)	4.94 (4.57)	10.24 (10.1)	643[b] (609)
(4) $(Ph_2P(o\text{-}PhO))_2Pd$	Yellow	>300	65.17 (65.5)	4.28 (4.24)	9.13 (9.40)	668[b] (660)
(5) $(Ph_2P(o\text{-}PhO))(Ph_2Pt(o\text{-}PhOH))PtCl$	Yellow[c]	230	54.89 (54.89)	3.44 (3.68)	7.32 (7.90)	806[b] (790)
(6) $(Ph_2P(o\text{-}PhO))NiC_5H_5$	Orange	~ 240 dec	68.69 (68.9)	4.74 (4.74)	7.79 (7.74)	383[b] (391)
(7) $Ph_2P(o\text{-}PhO)Tl$	Colorless	243–247	44.38 (44.90)	3.22 (2.91)	5.75 (6.40)	

[a] By mass spectrometry. [b] By osmometry in CH_2Cl_2. [c] % Cl: 5.08 (4.50).

deuteration. Shaw et al. have reported *o*-di-*tert*-butylphosphinophenol which they characterized by its ^1H NMR spectrum.[6]

2 reacts with divalent metal salts of nickel, palladium, and platinum to afford orange, yellow, and colorless complexes $M(PPhO)_2$, respectively. Shaw, who prepared the platinum complex by dealkylation of $Pt(Ph_2P(o\text{-}PhOCH_3))_2Cl_2$, argues for the cis geometry based on the magnitude of J_{PPt}.[3] Since the infrared spectra of the Ni and Pd complexes are very similar to the platinum one, we assume that their geometry is the same. Theoretically one should be able to differentiate cis and trans by the multiplicity of the intense ν_{C-O} absorbances in the 1250–1350-cm^{-1} region; however, these assignments are ambiguous.

In the synthesis of $Pt(PPhO)_2$, we also isolated a yellow complex formulated Pt(PPhO)(PPhOH)Cl (**5**) based on elemental analysis and spectral characteristics. The ^1H NMR of **5** shows a sharp absorption 10.06 ppm downfield of TMS of the expected integrated intensity relative to the phenyl region (1:28). Furthermore the infrared spectrum of **5** has a broad absorbance centered at 3350 cm^{-1} unlike the other $M(PPhO)_2$ complexes. Reaction of **5** with base cleanly converts it to colorless $Pt(PPhO)_2$ as judged by chromatography, the color change, and the infrared spectrum of the product. Compound **5** represents an unusual case of a platinum(II) complex which contains two different phosphines[7] and we sought to determine its stereochemistry by measurement of J_{PtP}. The 60 MHz ^{31}P NMR spectrum shows two lines at 800 and 850 Hz upfield of H_3PO_4 which are the absorbances in the absence of ^{195}Pt coupling; however, a search in the region 2500 to 4500 Hz upfield from this "doublet" showed no ^{195}Pt satellites.[8]

PPhOH also reacts with nickelocene in hot benzene to afford η^5-CpNiPPhO (**6**) which was purified by preparative thick-layer chromatography. **6** is air stable in solution and has a ^1H NMR spectrum characteristic of both a symmetric $^5\eta$-Cp group (τ 4.65) and PPhO (τ 2.2–3.7).

PPhOH reacts with thallium ethoxide in THF to afford TlPPhO (**7**) in quantitative yield, a reaction characteristic of phenols. Compound **7** reacts with a variety of metal halides and consequently will prove to be a valuable intermediate in exploring the coordination chemistry of PPhOH.

Experimental Section

The following instruments were used in the characterization of the new compounds described: Varian HA.100 ^1H NMR spectrometer, Varian MS-9 mass spectrometer, Perkin-Elmer IR.457 infrared spectrophotometer. Analyses and molecular weights were determined by the Research School of Chemistry Analytical Services.

Methoxymethyl *o*-Diphenylphosphinophenyl Ether (1). A solution containing 55 mL of 2 M BuLi and 12 g of *N,N,N′,N′*-tetramethylethylenediamine in 50 mL of petroleum ether (bp <50 °C) was added to an ice-cooled solution of 13.8 g (0.1 mol) of methoxymethyl phenyl ether in 200 mL of petroleum ether (bp <50 °C). The solution became yellow and a pale precipitate formed after 12 h. The solution was cooled in ice and chlorodiphenylphosphine, 22 g (0.1 mol), in petroleum ether was added slowly. The resultant solution was stirred 12 h and evaporated. The residue was extracted with Et_2O and $CHCl_3$ and the combined organic phase was washed with 1 M Na_2HPO_4, concentrated to an oil, and diluted with 75 mL of MeOH. After cooling 30 min the crystals were collected and recrystallized from CH_2Cl_2–MeOH to yield 17.6 g (54% yield) of the phosphine ether.

***o*-Diphenylphosphinophenol (2).** **1**, 5.0 g, was dissolved in 500 mL of anhydrous MeOH. This solution was saturated with anhydrous HCl gas and allowed to stand 24 h. The solution was filtered and concentrated to an oil which was then dissolved in 50 mL of boiling MeOH; H_2O (~150 mL) was slowly added during boiling until the cloud point was reached. The solution was then stirred while cooling. After filtration the solid was dried in vacuo over silica gel. The yield is 3.7 g (79%). A small portion was sublimed at 135–140 °C at 0.5 mm to yield an analytically pure sample.

Bis(*o*-diphenylphosphinophenolato)nickel and -palladium (3 and 4). These complexes were prepared by the addition of 2 equiv of the ligand to methanolic solutions of $NiCl_2 \cdot 6H_2O$ or Na_2PdCl_4 followed by the addition of 2 equiv of triethylamine after evaporation of the solutions. Recrystallization from CH_2Cl_2–MeOH yielded crystals of analytical purity.

Chloro(*o*-diphenylphosphinophenolato)(*o*-diphenylphosphinophenol)platinum(II) (5). $PtCl_2$ (66.2 mg) and **2** (138 mg) were heated under reflux in $CHCl_3$ for 27 h. After filtration the pale yellow solution was concentrated to 3 mL and diluted with hexane to yield 79.3 mg of white $Pt(PPhO)_2$ whose properties were consistent with Shaw's formulation. The yellow solution was concentrated and diluted with MeOH to give 87 mg of **5**. Addition of 1 drop of 20% NaOH to a CH_2Cl_2 solution of **6** caused rapid decolorization. The chromatographic behavior of the product was identical with that of $Pt(PPhO)_2$.

Cyclopentadienyl(*o*-diphenylphosphino)phenolatonickel(II) (6). Nickelocene, 188 mg, and **1**, 278 mg, were heated in benzene for 5 min and evaporated. Preparative thin-layer chromatography of the product on silica gel eluting with 1:10 acetone–$CHCl_3$ yielded an orange band ($R_f \approx 0.5$) which was extracted with acetone and crystallized from hexane.

***o*-Diphenylphosphinophenolatothallium(I) (7).** TlOEt (35 μL) was added to **2** (139 mg) in 10 mL of dry THF. After 4 h the crystals were collected and vacuum dried. Yield 240 mg (100%).

Registry No. **1**, 62815-32-1; **2**, 60254-10-6; **3**, 62816-21-1; **4**, 61004-47-5; **5**, 62851-12-1; **6**, 62816-20-0; **7**, 62816-19-7; methoxymethyl phenyl ether, 824-91-9; chlorodiphenylphosphine, 1079-66-9; nickelocene, 1271-28-9.

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(8) The "doublet" observed in the ^{31}P NMR spectrum of **3** probably represents the center lines of an AB quartet. A computer calculation in cases of $J_{PP'}$ = 300–500 Hz and $\Delta\delta_{PP'}$ = 2–3 ppm shows that the intensities of the outer lines will be less than those of the inner pair by a factor of 50.

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Reactions of Ethylenediamine-*N,N'*-diacetatodiaquo Complexes of Cobalt(III). 3. A Kinetic Study of the β-*cis*-Co(EDDA)(OH$_2$)$_2^+$ $\rightleftharpoons$ α-*cis*-Co(EDDA)(OH$_2$)$_2^+$ Isomerization Reaction

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In earlier papers we have described the oxalate anation of α-*cis*-Co(EDDA)(OH$_2$)$_2^+$ in both highly[1] and slightly[2] acidic aqueous media. Recently, the preparation of the β-*cis*-Co(EDDA)(OH$_2$)$_2^+$ isomer[3] has been reported.[4] In studying the reaction between oxalate species and the β-*cis*-diaquo isomer it soon became apparent that the β-*cis*-Co(EDDA)(OH$_2$)$_2^+$ $\rightleftharpoons$ α-*cis*-Co(EDDA)(OH$_2$)$_2^+$ isomerization reaction was very important in the chosen pH and temperature ranges. We wish to report here our characterization of the above isomerization reaction in the ranges $40 \leq T \leq 60$ °C and $1.47 \times 10^{-4} \leq [\mathrm{H}^+] \leq 5.00 \times 10^{-2}$ M.

Experimental Section

Ethylenediamine-*N,N'*-diacetic acid was used as received from Pfaltz and Bauer, Inc. All other chemicals were reagent quality. Distilled water was used throughout.

α-*cis*-[Co(EDDA)(OH$_2$)$_2$]ClO$_4$ was prepared as previously described.[2] β-*cis*-[Co(EDDA)(OH$_2$)$_2$]ClO$_4$ was prepared by a method similar to that of Garnett and Watts.[4] Elution of the β-cis isomer was accomplished in a cooled (3 °C) column using 0.40 M HClO$_4$. Further, to be sure that the β-*cis*-[Co(EDDA)(OH$_2$)$_2$]ClO$_4$ complex was as free of any contamination as possible, it was recycled through the ion exchange and crystallization procedures before being used in characterization or kinetic studies. After filtration of the solid, washing with acetone yielded a nicely crystalline product. Elemental analysis was performed by Galbraith Laboratories, Inc. Anal. Calcd for β-*cis*-[Co(EDDA)(OH$_2$)$_2$]ClO$_4$ (CoC$_6$H$_{14}$O$_{10}$N$_2$Cl): C, 19.55; H, 3.83; N, 7.60. Found: C, 19.56; H, 3.94; N, 7.50.

Kinetic studies were made using a Coleman Perkin-Elmer Model 46 spectrophotometer equipped as previously described.[2] Rate constants were determined at 383 nm. This corresponds closely to a peak position as well as a large molar absorptivity difference position for α- and β-*cis*-Co(EDDA)(OH$_2$)$_2^+$. "Infinite" absorbance measurements were made after 9–12 half-lives and were checked intermittently for constancy. The complex concentration was 5.00×10^{-3} M in all of the experiments reported.

The procedure for a typical kinetic run is outlined as follows. Aliquots of stock solutions containing the proper amounts of HNO$_3$ (by dilution of standarized HNO$_3$) and NaNO$_3$ (by weight, μ = 0.50) were brought to the desired temperature in a water bath. The reaction was initiated by adding solid complex (β-cis isomer) to the solution with rapid stirring. A portion of the solution was then transferred to a dry, equilibrated 1-cm cell and the absorbance followed as a function of time. The reference cell contained H$_2$O.

The equilibrium constant for the isomerization reaction was determined from the equilibrium spectrum at 387 nm after 10 half-lives.

Results and Discussion

Peak positions and molar absorptivities for our samples of β-*cis*-[Co(EDDA)(OH$_2$)$_2$]ClO$_4$ are λ 384 nm, ϵ_{384} 133 cm^{-1} M^{-1}, and λ 520 nm, ϵ_{520} 171 cm^{-1} M^{-1}. Those reported by Garnett and Watts[4] are λ 383 nm, ϵ_{383} 137 cm^{-1} M^{-1}, and λ 515 nm, ϵ_{515} 180 cm^{-1} M^{-1}. Repeated ion exchange chromatography of our β-*cis*-Co(EDDA)(OH$_2$)$_2^+$ samples indicated no impurities in our preparations and further, numerous crystallization operations gave reproducible peak positions and molar absorptivities. Our samples of α-*cis*-[Co(EDDA)(OH$_2$)$_2$]ClO$_4$ gave molar absorptivities identical with those reported by Kuroda and Watanabe[5] and by Garnett and Watts.[4]

The equilibrium constant for the isomerization reaction was determined under two different sets of conditions: (1) [H$^+$] = 5.2×10^{-4} M, T = 45.0 °C, and (2) [H$^+$] = 4.77×10^{-2} M (HNO$_3$), T = 55 °C. Defining $K_{\mathrm{eq}} = [\alpha\text{-}cis\text{-Co(EDDA)(OH}_2)_2^+]/[\beta\text{-}cis\text{-Co(EDDA)(OH}_2)_2^+]$ we report $K_{\mathrm{eq}} = 25 \pm 4$ as determined from the equilibrium spectrum after 10 half-lives under the above conditions. Within experimental error (mainly associated with uncertainties, ±1 unit, in the molar absorptivities) there appears to be no temperature or pH dependence in this range. No attempt was made to further refine K_{eq} because the above value was sufficient for direction in the following kinetic study.

An aqueous solution of red β-*cis*-Co(EDDA)(OH$_2$)$_2^+$ slowly changes in color to the purple associated with α-*cis*-Co(EDDA)(OH$_2$)$_2^+$. The rate of this change depends on the acidity of the solution as well as T. Ion-exchange chromatography (Dowex 50W-X8, 100–200 mesh, H$^+$ form) of equilibrated solutions initially containing pure β-cis isomer showed the presence of only two +1 charged species. These were subsequently identified as the α-*cis*- and β-*cis*-Co(EDDA)(OH$_2$)$_2^+$ isomers, respectively. Band size indicated the formation of the α-cis isomer was strongly favored at equilibrium. Ion-exchange chromatography of an equilibrated solution initially containing pure α-*cis*-Co(EDDA)(OH$_2$)$_2^+$ gave results identical with the above. In acidic solution, repetitive spectral scanning between 600 and 350 nm (Cary 14) showed the expected isosbestic point at λ 553 nm indicating a simple interconversion between the isomers.

A series of kinetic runs was made systematically varying T and [H$^+$] in the ranges $1.47 \times 10^{-4} \leq [\mathrm{H}^+] \leq 5.00 \times 10^{-2}$ M and $40 \leq T \leq 60$ °C. [H$^+$] was adjusted using HNO$_3$ and the ionic strength was held constant at μ = 0.50 using NaNO$_3$. At the lower hydrogen ion concentrations the pH was found to remain constant within ±0.04 pH unit during the first 2–4 half-lives of the reaction. The isomerization reaction was followed for at least 2 half-lives and plots of $-\log (A_t - A_\infty)$ vs. time were linear during this period.

The observed rate constant, k_{obsd}, is the sum of the rate constants for the interconversions β-cis $\rightarrow$ α-cis (k_β) and α-cis $\rightarrow$ β-cis (k_α). The value of K_{eq}, however, establishes that k_α is ~4% of k_β in the ranges studied, and hence to an adequate approximation $k_{\mathrm{obsd}} \simeq k_\beta$.

Table I lists the various values of k_{obsd} obtained as a function of total hydrogen ion concentration and temperature. Duplicate runs generally gave k_{obsd} values that agreed within 3% of the original. Hydrogen ion concentration affects k_{obsd} in an inverse fashion. In the ranges $50 \leq T \leq 60$ °C and $[\mathrm{H}^+] > 1.0 \times 10^{-3}$ M, plots of k_{obsd} vs. $[\mathrm{H}^+]^{-1}$ are linear with a positive temperature-dependent intercept. Here $[\mathrm{H}^+] \simeq C_{\mathrm{HNO_3}}$, i.e., acid dissociation of β-*cis*-Co(EDDA)(OH$_2$)$_2^+$ does not contribute to total [H$^+$]. This is not surprising since Garnett's measured pK_β (pK_1 for β-*cis*-Co(EDDA)(OH$_2$)$_2^+$) is 6.0 at 20 °C.[6] Although some temperature dependence is