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# The coordination chemistry of phosphonites

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ABSTRACT

Transition metal complexes of phosphonites are of interest as catalysts because transition metal complexes of the closely related phosphines ($PR_3$), phosphinites ($PR_2XR$), and phosphites ($P(XR)_3$) have excellent catalytic properties for a variety of organic transformations. However, there has been surprisingly little research on the coordination chemistry of phosphonites. To help in remedying this deficiency, we have begun a study of the coordination chemistry of phosphonite ligands. In this project, seven new phosphonite ligands of the type RP(OR′O) (R = phenyl, 2-thienyl; ORO = 1,1′-bi-2-naphthoxy, 4-*tert*-butylphenoxy, and catechoxy) and their *cis*-$Mo(CO)_4$ complexes have been synthesized. The complexes have been characterized by $^{31}P$, $^{13}C$, and $^{1}H$ NMR spectroscopy, and X-ray crystal structures of four of the complexes have also been determined.

## 1. Introduction

Transition metal complexes with phosphorus-donor ligands are excellent catalysts for a variety of organic reactions [1–3]. The large majority of the phosphorus-donor ligands used in these catalysts are either phosphites, phosphinites or phosphines. More recently, transition metal complexes of phosphonites, the fourth class of phosphorus-donor ligands, have begun to be studied as catalysts and appear to exhibit interesting catalytic properties [4,5].

To realize the potential of transition metal complexes of phosphonites as catalysts, it is necessary to understand the coordination chemistry of these ligands and the factors that affect their steric and electron donor/acceptor properties. However, the coordination chemistry of these ligands is relatively unstudied with only three X-ray crystal structures of transition metal complexes of the ligands being reported [6–8]. The transition metal complexes in these structures are quite different, which limits any comparisons. In addition, all of the complexes have only a single ligand while many of the most interesting catalytically active complexes have two phosphonite ligands.

To provide insight into the coordination chemistry of phosphonite ligands, the seven phosphonite ligands shown in Fig. 1 were synthesized by the reactions of the appropriate $RPCl_2$ (R = phenyl, 2-thienyl) with one equivalent of a diol or two equivalents of an alcohol and were characterized by multinuclear NMR spectroscopy. Their *cis*-$Mo(CO)_4(\text{phosphonite})_2$ complexes were synthesized and purified by recrystallization [13]. The complexes were characterized using multinuclear NMR spectroscopy and also by X-ray crystallography when suitable crystals could be obtained.

## 2. Experimental

Tetrahydrofuran (THF) was first allowed to stand over magnesium sulfate before being distilled from $CaH_2$. It was then distilled from sodium metal/ benzophenone. Triethylamine ($Et_3N$) was first allowed to stand over KOH and then was distilled from benzophenone/sodium. Dichloromethane ($CH_2Cl_2$) was first allowed to stand over $CaH_2$ then distilled. All of the diols and alcohols used in the experiments were dried before use: 2,2′-biphenol was sublimed and 1,1′-binaphthol and 4-*t*-butylphenol were crystallized from toluene after the solution had been azeotropically dried. Dichlorophenylphosphine ($PhPCl_2$) was obtained from Aldrich Chemical Company and was distilled before use. Dichloro-2-thienylphosphine [9], $Mo(CO)_4(nbd)$ (nbd = [2.2.1]-bicyclohepta-2,5-diene) [10] and **3a** [11] were synthesized using literature methods. All reactions were carried out in a dry $N_2$ atmosphere using Schlenk techniques.

Nuclear magnetic resonance (NMR) spectra were taken of chloroform-*d* solutions of the ligands and complexes. The spectra were referenced either to internal tetramethylsilane ($^{1}H$ and $^{13}C$) or to external 85% phosphoric acid ($^{31}P$). The $^{31}P\{^{1}H\}$ NMR spectra were run on a Bruker DRX 400 MHz NMR spectrometer while the $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were run on a Bruker DPX 300 MHz NMR spectrometer, a Bruker DRX 400 MHz NMR spectrometer or on a Bruker Avance 700 MHz NMR spectrometer. In the cases where

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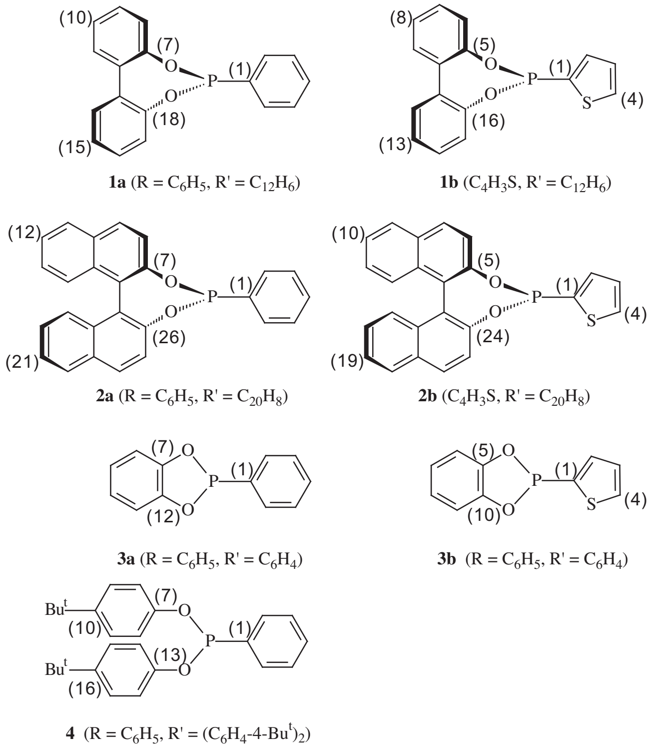

**1a** ($R = C_6H_5$, $R' = C_{12}H_6$) **1b** ($C_4H_3S$, $R' = C_{12}H_6$)

**2a** ($R = C_6H_5$, $R' = C_{20}H_8$) **2b** ($C_4H_3S$, $R' = C_{20}H_8$)

**3a** ($R = C_6H_5$, $R' = C_6H_4$) **3b** ($R = C_6H_5$, $R' = C_6H_4$)

**4** ($R = C_6H_5$, $R' = (C_6H_4\text{-}4\text{-}Bu^t)_2$)

**Fig. 1.** Monodentate phosphonite ligands, RP(OR′O) described in this work. The numbering scheme for the NMR spectral assignments of the carbon atoms is given by the numbers in parentheses.

the spectra were assigned, the assignment was made from a combination of DEPT 135, $^1H–^1H$ COSY, $^{13}C–^1H$ HMBC and $^{13}C–^1H$ HSQC experiments or by comparison with the assignments made for closely related compounds. For ligands **1a**, **1b**, **2a**, **2b**, **3a** and **3b** and their complexes, numbering was started at the carbon directly bonded to the phosphorus, continued around that ring, extended to one of the aromatic carbons bonded to an oxygen and finally continued around that aromatic ring ending with the carbon bonded to the other oxygen. For ligand **4** and its complex, numbering was started at the carbon directly bonded to the phosphorus and then continued around that ring. Equivalent carbons and hydrogens of the-$Bu^tC_6H_4O$ group were then given the same numbers starting with the carbon bonded to oxygen, next extending around the phenylene ring and finally ending on the Bu$^t$ group.

Compound purities were determined by C and H elemental analyses in most cases. The only exceptions to this were made for **5b** and **7b**. For both of these compounds, a batch of crystals containing an X-ray quality crystal was obtained from the relatively nonpolar solvent mixture dichloromethane/hexanes, and the $^{13}C$, $^1H$ and $^{31}P$ NMR resonances were completely assigned for the same batch of crystals. In this case, the elemental analysis does not provide any additional information because the only impurities would be organic compounds, which, if present, would have resonances in the NMR spectra. In addition, the $^{13}C$, $^1H$ and $^{31}P$ NMR spectral assignments for **5b** and **7b** are very similar to those of **5a** and **7a**, for which elemental analyses were obtained.

### 2.1. *(2,2′-$C_{12}H_8O_2$)P($C_6H_5$),* ***1a***

A solution of 0.635 g (3.42 mmol) of 2,2′-biphenol and 0.864 ml (6.84 mmol) of $Et_3N$ in 25 ml of THF was stirred as 0.61 g (3.4 mmol) of $PhPCl_2$ was added drop wise into the reaction mixture. This mixture was stirred for three hours and was then filtered to remove the triethylamine hydrochloride precipitate. The filtrate was evaporated under reduced pressure to yield 0.79 g (79%) of spectroscopically pure **1a** as a white solid. $^{31}P\{^1H\}$ NMR (162 MHz, chloroform-*d*): $\delta$ 186.01 (s).

### 2.2. *(2,2’-$C_{12}H_8O_2$)P($C_4H_3S$),* ***1b***

A solution of 5.09 ml (36.4 mmol) of $Et_3N$ and 3.38 g (18.2 mmol) of 2,2′-biphenol in 50 ml of THF and a solution of 3.36 g (18.2 mmol) of $(C_4H_3S)PCl_2$ in 50 ml of THF were added drop wise and simultaneously to 50 ml of THF over a period of 4 h with stirring. The reaction mixture was then filtered to remove the triethylamine hydrochloride precipitate. The filtrate was evaporated under reduced pressure to yield 5.23 g (96.3%) of a white solid. The solid was dissolved in a 1:4 mixture of dichloromethane/hexane and filtered through alumina, and the filtrate was evaporated to dryness to yield the spectroscopically pure ligand. $^{31}P\{^1H\}$ NMR (162 MHz, chloroform-*d*): $\delta$ 175.48 (s). $^1H$ NMR (300 MHz, chloroform-*d*): $\delta$ 7.72 (H2, 1H, ddd, $|^4J(H2H4)| = 1$ Hz, $|^3J(H2H3)| = 4$ Hz, $|^3J(H2P)| = 7$ Hz), 7.61 (H4, 1H, dd, $|^4J(H4H2)| = 1$ Hz, $|^3J(H4H3)| = 5$ Hz), 7.49 (H–$C_{12}H_8$, 2H, m), 7.31 (H–$C_{12}H_8$, 4H, m), 7.19 (H3, 1H, ddd, $|^4J(H3P)| = 1$ Hz, $|^3J(H3H2)| = 4$ Hz, $|^3J(H3H4)| = 5$ Hz), 7.00 (H–$C_{12}H_8$, 4H, m).

### 2.3. *(2,2′-$C_{20}H_{12}O_2$)P($C_6H_5$),* ***2a***

A solution of 5.11 g (17.8 mmol) of 1,1′-bi-2-naphthol and 4.97 mL (35.7 mmol) of $Et_3N$ in 50 mL of THF was added drop wise to a solution of 2.42 mL (17.8 mmol) of $PhPCl_2$ in 50 mL of THF over the course of one hour. The solution was then filtered through diatomaceous earth to remove the triethylammonium chloride precipitate, and the filtrate was filtered through 1 cm layers of both basic and neutral alumina in Schlenk funnels. The filtrate was evaporated to dryness to yield 6.83 g (98.0%) of spectroscopically pure **2a** as a white solid. $^{31}P\{^1H\}$ NMR (162 MHz, chloroform-*d*): $\delta$ 184.73 (s).

### 2.4. *(2,2′-$C_{20}H_{12}O_2$)P($C_4H_3S$),* ***2b***

A solution of 0.561 g (1.96 mmol) of 1,1′-bi-2-naphthol and 0.550 mL (3.95 mmol) of $Et_3N$ in 25 mL of THF was added drop wise to a solution of 0.371 g (2.00 mmol) of dichloro-2-thienylphosphine in 25 mL of THF over the course of one hour. The solution was then filtered through diatomaceous earth to remove the triethylammonium chloride byproduct, and the filtrate was evaporated to dryness to yield 0.780 g (100%) of crude product as a white solid. $^{31}P\{^1H\}$ NMR (162 MHz, chloroform-*d)*: $\delta$ 173.92 (s).

### 2.5. *(1,2-$C_6H_4O_2$)P($C_4H_3S$),* ***3b***

A solution of 4.21 g (38.0 mmol) of catechol and 10.6 mL (76.0 mmol) of $Et_3N$ in 50 mL of THF was stirred at room temperature as a solution of 7.07 g (38.0 mmol) of $(C_4H_3S)PCl_2$ in 40 mL of THF was added drop wise over a period of one hour. Then the reaction mixture was filtered through diatomaceous earth to remove the triethylammonium chloride byproduct, and the filtrate was evaporated to dryness to yield a colorless oil. A $^{31}P\{^1H\}$ NMR spectrum of this oil indicated that numerous impurities were present in addition to the desired product. The oil was distilled under a vacuum of 200 mtorr. The first fraction, which distilled at 112 °C, contained product with a small amount of oxidation/hydrolysis byproduct and weighed 0.880 g (10.4%). $^{31}P\{^1H\}$ NMR (162 MHz, chloroform-*d*): $\delta$ 164.60 (s).