

A Tetrachlorophosphite Ligand with C_3 Symmetry

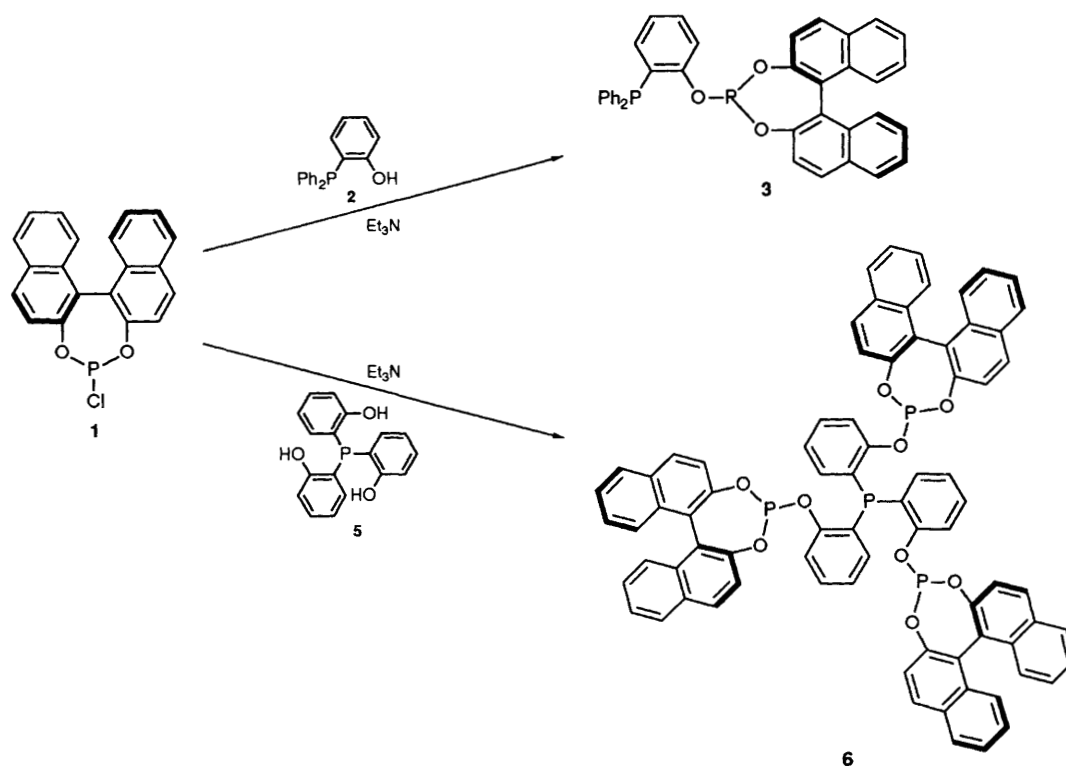
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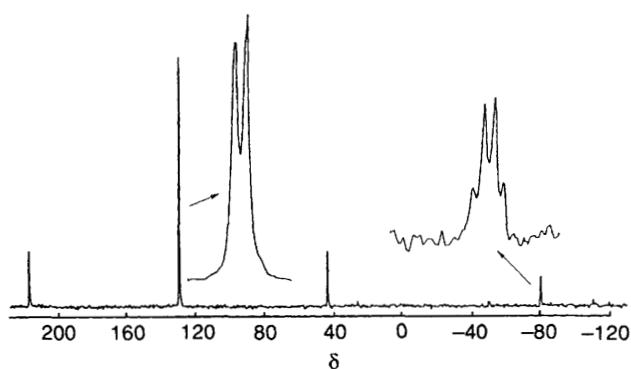
An optically active tetrachlorophosphite ligand of C_3 symmetry and its platinum(0) coordination chemistry are described.

Metal-phosphites have a distinctly different chemistry from metal-phosphines and are known to have superior catalytic activity for hydroformylation and hydrocyanation of alkenes.¹ Despite this, until recently² little phosphite ligand development had taken place. We reported³ that access to optically

active monophosphites is easily achieved *via* the readily available chlorophosphite **1** (*S*-configuration). We now report a simple, one-step procedure from **1** for the synthesis of an optically active, tetrachlorophosphite ligand having C_3 symmetry. Ligands having C_3 symmetry have attracted much interest

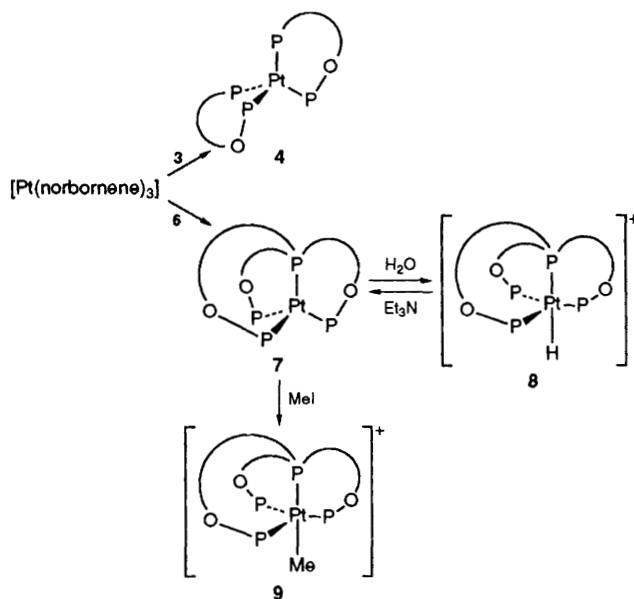


Scheme 1

Fig. 1 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (36.4 MHz, CDCl_3) of complex 7

recently because of their great potential in asymmetric catalysis.⁴

The phosphinophenol **2**⁵ reacts with chlorophosphite **1** in the presence of Et_3N to give the optically active bidentate ligand **3**[†] (Scheme 1) which, upon addition of $[\text{Pt}(\text{norbornene})_3]$, forms the bis chelate platinum(0) complex **4** (Scheme 2). This prompted us to treat the phosphinotriphenol **5**⁶ with **3**



Scheme 2

[†] All new compounds have been isolated and satisfactory elemental analyses obtained. *Selected data:* for **3**: $[\alpha]_D^{20} +155(8)$ ($c = 1$, THF) (THF = tetrahydrofuran); $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3): $\delta(\text{P}_A)$ 143.3 (d), $\delta(\text{P}_B)$ -15.7 (d), $^4J(\text{PP})$ 15 Hz. For **4**: $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3): $\delta(\text{P}_A)$ 135.8 (t), $^1J(\text{PtP})$ 6335 Hz, $\delta(\text{P}_B)$ -8.0 (t), $^1J(\text{PtP})$ 3120 Hz, $^2J(\text{PP})$ 56 Hz. For **6**: $[\alpha]_D^{20} +335(17)$ ($c = 1$, THF); $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3): $\delta(\text{P}_A)$ 143.8 (d), $\delta(\text{P}_B)$ -37.1 (q), $^4J(\text{PP})$ 5 Hz. For **7**: $^{31}\text{P}\{^1\text{H}\}$ (CDCl_3): $\delta(\text{P}_A)$ 131.4 (d), $^1J(\text{PtP})$ 6396 Hz, $\delta(\text{P}_B)$ -81.1 (q), $^1J(\text{PtP})$ 2219 Hz, $^2J(\text{PP})$ 12 Hz. $^{195}\text{Pt}\{^1\text{H}\}$ (CDCl_3): $\delta(\text{Pt})$ -1025.2 (q \times d) to high frequency of $\Xi(\text{Pt})$ 21.4 MHz. For **8**: $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2): $\delta(\text{P}_A)$ 120.1 (d), $^1J(\text{PtP})$ 4669 Hz, $\delta(\text{P}_B)$ -68.8 (q), $^1J(\text{PtP})$ 1410 Hz, $^2J(\text{PP})$ 49 Hz. ^1H (CD_2Cl_2): $\delta(\text{PtH})$ -11.39 (d \times q) $^2J(\text{PH})$ 153.8, 2.5 Hz, $^1J(\text{PtH})$ 641 Hz. For **9**: $^{31}\text{P}\{^1\text{H}\}$ (CD_2Cl_2): $\delta(\text{P}_A)$ 112.5 (d), $^1J(\text{PtP})$ 4804 Hz, $\delta(\text{P}_B)$ -52.1 (q), $^1J(\text{PtP})$ 1200 Hz, $^2J(\text{PP})$ 46 Hz. ^1H (CD_2Cl_2): $\delta(\text{PtCH}_3)$ -0.67 (q \times d) $^3J(\text{PH})$ 11.1, 4.9 Hz, $^2J(\text{PtH})$ 52.0 Hz.

equiv. of **1** in the hope of obtaining the tetradentate ligand **6**. Indeed, **6** was readily formed in this way, isolated in good yield (70%) and fully characterised.

Ligand **6** reacts smoothly with $[\text{Pt}(\text{norbornene})_3]$ to give the mononuclear species **7**, as is unambiguously established from the doublet and quartet in the ^{31}P NMR spectrum (see Fig. 1) and the quartet of doublets in the ^{195}Pt NMR spectrum. No previous examples of a tetradentate ligand encapsulating a tetrahedral platinum(0) centre have been reported.[‡] The

[‡] The tetraphosphine ligand $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ gives binuclear platinum(0) complexes in which the ligand bridges the metal centres; see ref. 7(a).

$^1J(\text{PtP})$ value of 2219 Hz for the central phosphino phosphorus in **7** is very small compared with the corresponding $^1J(\text{PtP})$ value of 3120 Hz in **4** reflecting the strain present in the fused tricyclic structure of **7**.

Complex **7** is protonated by water or HBF_4 to give the cationic hydrido complex **8** and addition of Et_3N to **8** regenerates the neutral **7** (Scheme 2). Hence, **8** is an unusual example of an optically active Brønsted acid. Complex **7** also reacts with an excess of MeI to give the methyl complex **9**. In complexes **8** and **9**, the ligand **6** is behaving like other tripodal tetradentate ligands in stabilising trigonal bipyramidal geometry at platinum(II)⁷ but their unique feature is that they are optically active and have C_3 symmetry.

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