A Tetraphos Ligand with C_3 Symmetry

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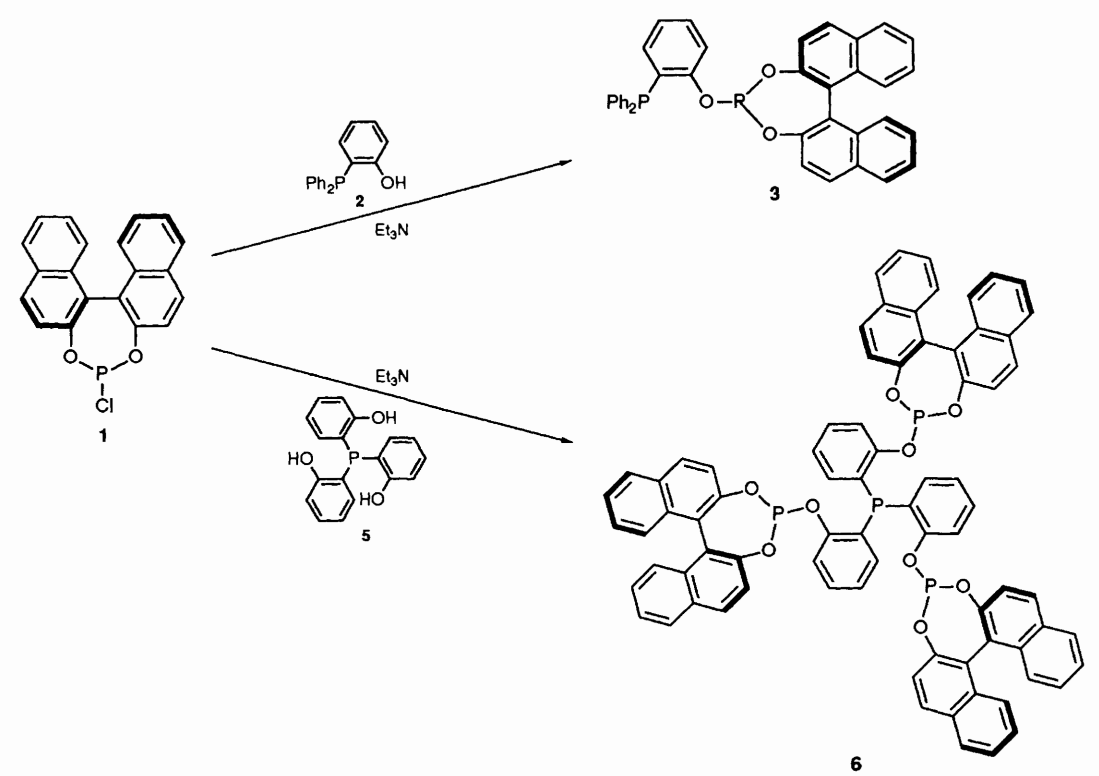
An optically active tetraphos ligand of C_3 symmetry and its platinum(0) coordination chemistry are described.

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 recently[2] little phosphite ligand development had taken place. We reported[3] 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, tetradentate ligand having C_3 symmetry. Ligands having C_3 symmetry have attracted much interest



Scheme 1

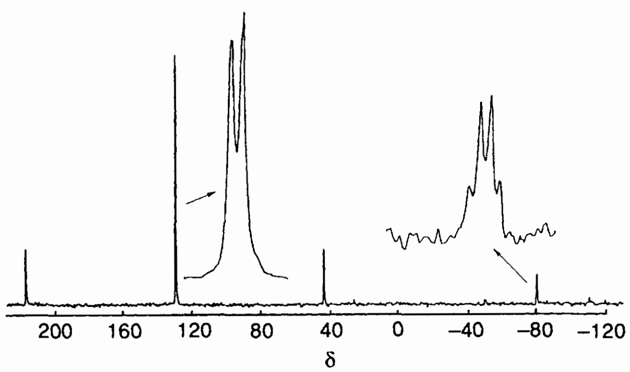
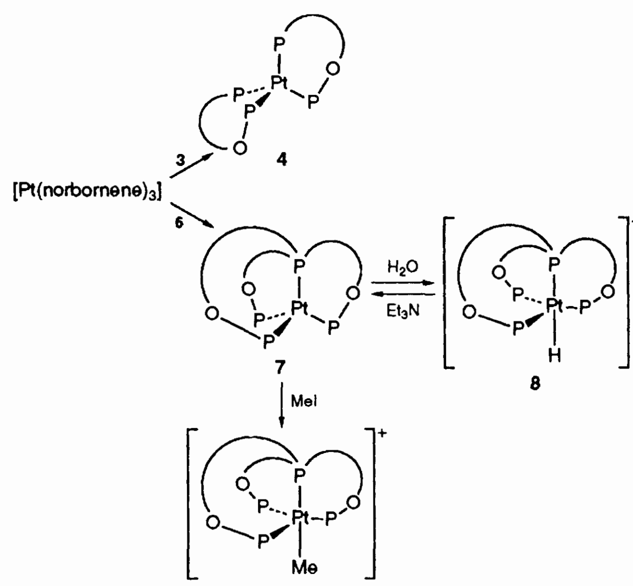


Fig. 1 $^{31}P\{^1H\}$ NMR spectrum (36.4 MHz, $CDCl_3$) of complex **7**

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 [Pt(norbornene)$_3$], forms the bis chelate platinum(0) complex **4** (Scheme 2). This prompted us to treat the phosphinotriphenol **5**[6] with 3 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 [Pt(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



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); $^{31}P\{^1H\}$ ($CDCl_3$): $\delta(P_A)$ 143.3 (d), $\delta(P_B)$ −15.7 (d), $^4J(PP)$ 15 Hz. For **4**: $^{31}P\{^1H\}$ ($CDCl_3$): $\delta(P_A)$ 135.8 (t), $^1J(PtP)$ 6335 Hz, $\delta(P_b)$ −8.0 (t), $^1J(PtP)$ 3120 Hz, $J(PP)$ 56 Hz. For **6**: $[\alpha]_D^{20}$ +335(17) (c = 1, THF); $^{31}P\{^1H\}$ ($CDCl_3$): $\delta(P_A)$ 143.8 (d), $\delta(P_B)$ −37.1 (q), $^4J(PP)$ 5 Hz. For **7**: $^{31}P\{^1H\}$ ($CDCl_3$): $\delta(P_A)$ 131.4 (d), $^1J(PtP)$ 6396 Hz, $\delta(P_B)$ −81.1 (q), $^1J(PtP)$ 2219 Hz, $^2J(PP)$ 12 Hz. $^{195}Pt\{^1H\}$ ($CDCl_3$): $\delta(Pt)$ −1025.2 (q × d) to high frequency of $\Xi(Pt)$ 21.4 MHz. For **8**: $^{31}P\{^1H\}$ (CD_2Cl_2): $\delta(P_A)$ 120.1 (d), $^1J(PtP)$ 4669 Hz, $\delta(P_B)$ −68.8 (q), $^1J(PtP)$ 1410 Hz, $^2J(PP)$ 49 Hz. ^1H (CD_2Cl_2): $\delta(PtH)$ −11.39 (d × q) $^2J(PH)$ 153.8, 2.5 Hz, $^1J(PtH)$ 641 Hz. For **9**: $^{31}P\{^1H\}$ (CD_2Cl_2): $\delta(P_A)$ 112.5 (d), $^1J(PtP)$ 4804 Hz, $\delta(P_B)$ −52.1 (q), $^1J(PtP)$ 1200 Hz, $^2J(PP)$ 46 Hz. ^1H (CD_2Cl_2): $\delta(PtCH_3)$ −0.67 (q × d) $^3J(PH)$ 11.1, 4.9 Hz, $^2J(PtH)$ 52.0 Hz.

‡ The tetraphosphine ligand $P(CH_2CH_2PPh_2)_3$ gives binuclear platinum(0) complexes in which the ligand bridges the metal centres; see ref. 7(*a*).

^1J(PtP) value of 2219 Hz for the central phosphino phosphorus in **7** is very small compared with the corresponding ^1J(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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