



## Rapid one-pot synthesis of cycloheptatriene-phosphonium derivatives



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### ABSTRACT

The direct combination reaction of tropylium tetrafluoroborate with a range of mono- and bi-dentate phosphines in chlorinated solvents leads to the formation of a series of cycloheptatriene-phosphonium derivatives in excellent yields. Multi-nuclear NMR and single-crystal X-ray diffraction studies confirm the addition of the tropylium ligand to the phosphorous centre to form cycloheptatriene derivatives.

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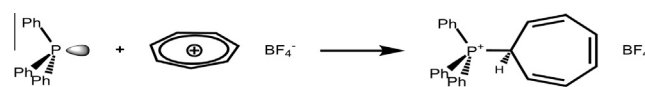
The ability to tune the electronic properties of coordination complexes is greatly enhanced by the large diversity of mono-, bi- and tri-dentate phosphine derivatives. These commercially available ligands may have a variety of aryl and alkyl substituents, variable bridge lengths and well-defined cone angles. The synthesis of coordination complexes with different phosphine ligands allows a systematic study of the structure–property relationships and the effect of the ligand on other material properties such as non-linear optical and catalytic effects. These compounds have increased electron density from the large aromatic systems that branch off of the phosphorous atoms, while the whole coordination complex has increased stability due to the chelating effect.

Although the phosphorous atoms are effective donor atoms with strong  $\sigma$ -donor properties, there have been fewer studies of alternate bonding motifs. Our group and others have shown that tropylium ( $C_7H_7^+$ ) and 1,3,5-cycloheptatriene (CHT) are effective ligands for coordination to palladium and other metals.<sup>1–5</sup> These complexes display unique coordination geometries in addition to catalytic activity. Conversion of a phosphorous ligand to the corresponding phosphonium group is a relatively straight-forward addition reaction. However, our literature search indicates that this has not been carried out systematically and although derivatives of a range of bidentate phosphonium derivatives are known, they

typically have not extended beyond the simplest tri-phenylalkyl phosphonium ( $Ph_3P^+R$ ) derivatives. Such derivatives are less capable of undergoing additional bonding interactions. Synthesis of a range of bis-quaternary phosphonium derivatives with the cycloheptatriene (CHT) group, would allow for additional haptic interactions, and lead to new ligands with unique properties.

Cycloheptatrienetriphenylphosphonium tetrafluoroborate [ $C_7H_7PPh_3$ ][ $BF_4^-$ ] (**1**) was successfully synthesized and characterized by Gilheany et al. as shown in Figure 1.<sup>6</sup> Subsequently a range of sandwich complexes incorporating a cationic tetrakis phosphonium ligand has been reported by several groups demonstrating that these complexes should possess the ability to coordinate to metal centres.<sup>7,8</sup> However, our literature search indicates that the systematic synthesis of analogous compounds from bidentate phosphines derivatives has not yet been reported. Herein we report the rapid synthesis of a series of cycloheptatriene phosphonium ligands.

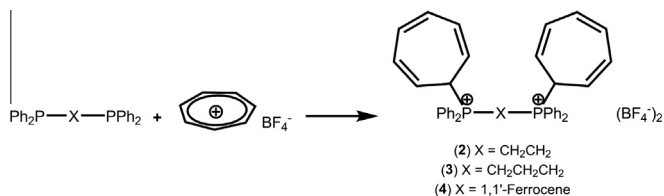
The reaction of one equivalent of bis-(diphenylphosphino) ethane (dppe) with two equivalents of [ $C_7H_7$ ][ $BF_4^-$ ] in either 1,2-dichloroethane or dichloromethane for 12 h at reflux gave [ $(C_7H_7PPh_2)_2CH_2CH_2$ ][ $(BF_4)_2$ ] (**2**), as an off-white solid (Scheme 1).



**Figure 1.** Synthesis of cycloheptatriene triphenylphosphonium tetrafluoroborate [ $C_7H_7PPh_3$ ][ $BF_4^-$ ] (**1**) by Gilheany and co-workers.

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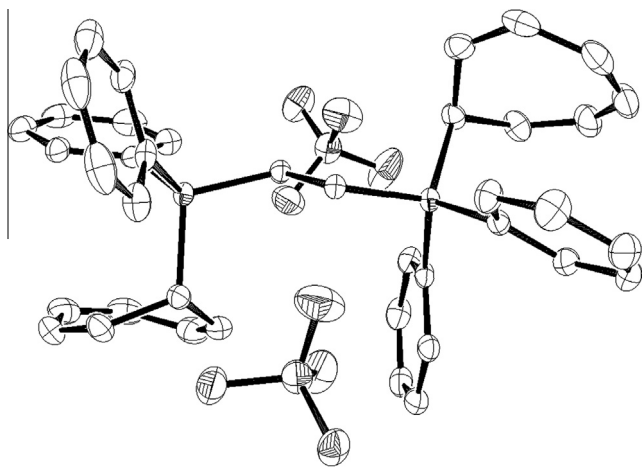
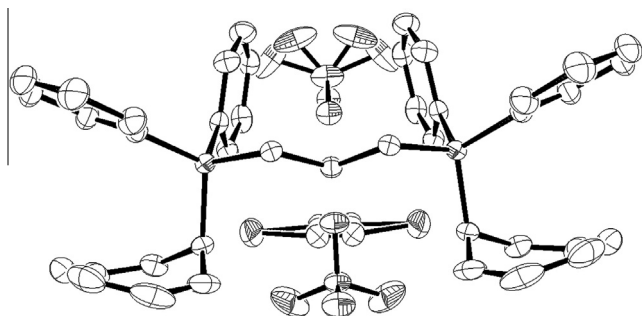
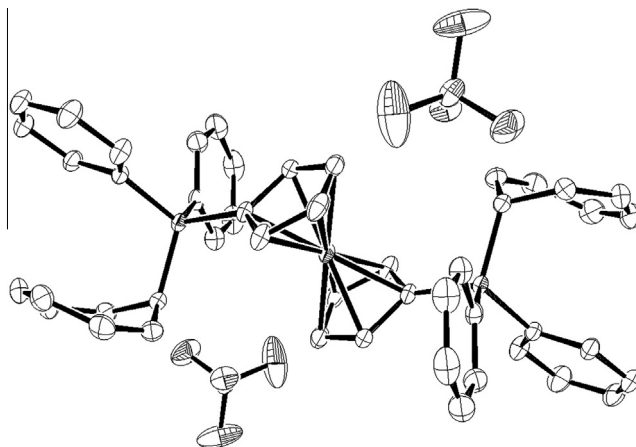
Scheme 1. Synthesis of compounds 2–4.

The reaction is carried out in a single flask and the product requires minimal purification. Analogous reactions with bis-(diphenylphosphino)propane (dppp) and bis-(diphenylphosphino)ferrocene (dppf) gave the di-substituted cycloheptatriene derivatives **3** and **4**, respectively in good yields, as a white and orange solid, respectively.

Recrystallization of **2–4** from chlorinated solvents and hexanes gave crystalline products in good yields. The crystals were relatively small and fragile, and synchrotron radiation was needed for data collection. Molecular structures of **2–4** as determined via single-crystal X-ray diffraction studies are shown in Figures 2–4, respectively.

The results of single crystal X-ray diffraction studies on compounds **2–4** are summarized in Table 1 and selected bond lengths and angles are collected in Table 2. Elemental analysis confirmed the expected molecular composition.

Analysis of the X-ray data of **2** confirmed that the two phosphorous atoms in each ligand were both coordinated to a CHT ring motif with the CHT moieties rotated away from each other. The

Figure 2. ORTEP plot of **2** at 50% probability with hydrogen atoms omitted.Figure 3. ORTEP plot of **3** at 50% probability with hydrogen atoms omitted. Image shown normal to the 001 plane with disordered anion and solvent molecule shown.Figure 4. ORTEP plot of **4** at 50% probability with hydrogen atoms omitted.Table 1  
Selected experimental data for **2–4**

|  | <b>2</b>  | <b>3</b>  | <b>4</b>  |
|--|---|---|---|
| Formula                                    | $\text{C}_{40}\text{H}_{38}\text{B}_2\text{F}_8\text{P}_2$        | $\text{C}_{43}\text{H}_{44}\text{B}_2\text{Cl}_2\text{F}_8\text{P}_2$                                 | $\text{C}_{48}\text{H}_{42}\text{B}_2\text{F}_8\text{FeP}_2$        |
| Moiety formula                             | $\text{C}_{40}\text{H}_{38}\text{P}_2^{2+}$<br>$2(\text{BF}_4)^-$ | $\text{C}_{40}\text{H}_{38}\text{P}_2^{2+}$<br>$2(\text{BF}_4)^-\cdot\text{C}_2\text{Cl}_2\text{H}_2$ | $\text{C}_{48}\text{H}_{42}\text{FeP}_2^{2+}$<br>$2(\text{BF}_4)^-$ |
| Fw   | 754.26  | 867.27  | 910.22  |
| Radiation type                             | Synchrotron,<br>0.77490 Å   | Synchrotron,<br>0.77490 Å   | Synchrotron,<br>0.77490 Å   |
| Space group                                | Orthorhombic,<br>Pbca   | Orthorhombic,<br>Cmc2 <sub>1</sub>  | Triclinic, P-1  |
| <i>a</i> (Å)                               | 13.8462(11)   | 22.860(2)   | 8.0308(6)   |
| <i>b</i> (Å)                               | 15.3234(12)   | 11.7003(8)  | 10.9214(8)  |
| <i>c</i> (Å)                               | 34.194(3)   | 15.6988(11)   | 13.6971(10)   |
| $\alpha$ (°)                               | 90  | 90  | 111.541(2)  |
| $\beta$ (°)                                | 90  | 90  | 106.715(2)  |
| $\gamma$ (°)                               | 90  | 90  | 92.889(2)   |
| <i>V</i> (Å <sup>3</sup> )                 | 7255.6(10)  | 4199.0(6)   | 1053.68(14)   |
| <i>Z</i>                                   | 8   | 4   | 1   |
| $\rho_{\text{calc}}$ (g cm <sup>-3</sup> ) | 1.381   | 1.327   | 1.434   |
| $\mu$ (mm <sup>-1</sup> )                  | 0.191   | 0.297   | 0.504   |
| <i>T</i> (K)                               | 150(2)  | 150(2)  | 150(2)  |
| Total rflns                                | 86849   | 24458   | 22040   |
| Unique rflns                               | 7465  | 4426  | 5250  |
|  | ( <i>R</i> <sub>int</sub> = 0.0669)                               | ( <i>R</i> <sub>int</sub> = 0.0320)   | ( <i>R</i> <sub>int</sub> = 0.0350)                                 |
| Final <i>R</i> Indices                     | <i>R</i> <sub>1</sub> = 0.0412                                    | <i>R</i> <sub>1</sub> = 0.0298  | <i>R</i> <sub>1</sub> = 0.0334                                      |
| ( <i>I</i> <sup>2</sup> > 2σ)              | <i>wR</i> <sub>2</sub> = 0.1034                                   | <i>wR</i> <sub>2</sub> = 0.0748   | <i>wR</i> <sub>2</sub> = 0.0837                                     |

Programs used: data collection and reduction: APEX2 and SAINT<sup>9</sup>; absorption correction: SADABS<sup>10</sup>; structure solution and refinement: SHELXTL and OLEX2.<sup>11,12</sup>

Table 2  
Selected bond lengths (Å) and angles (°) for **2–4**

|             | <b>2</b>   | <b>3</b> | <b>4</b>   |
|-------------|------------|----------|------------|
| P(1)–C(1)   | 1.8381(19) | 1.840(3) | 1.8343(15) |
| P(2)–C(22)  | 1.835(2)   |          |            |
| P(1)–C(8)   | 1.7920(19) | 1.786(2) | 1.7888(14) |
| P(2)–C(29)  | 1.7967(19) |          |            |
| P(1)–C(14)  | 1.7842(18) | 1.792(2) | 1.7909(15) |
| P(2)–C(35)  | 1.7849(18) |          |            |
| P(1)–C(20)  | 1.8162(18) | 1.796(2) | 1.7738(15) |
| P(2)–C(21)  | 1.8094(18) |          |            |
| C(20)–C(21) | 1.544(2)   | 1.527(3) | 1.435(2)   |

Programs used: data collection and reduction: APEX2 and SAINT<sup>9</sup>; absorption correction: SADABS<sup>10</sup>; structure solution and refinement: SHELXTL and OLEX2.

two phosphorous atoms in **2** are located in a slightly disordered tetrahedral environment with the bond distances and angles not significantly different between the two phosphorous centres. The P–C bond lengths in **2** are shorter in comparison with those

reported for the parent phosphine (dppe).<sup>13</sup> In addition there is a distortion in the tetrahedral geometry towards significantly larger angles upon coordination of the CHT ring. The structure is broadly similar to that reported by Gohlzadeh et al. for a dppe derivative with a triphenylphosphonium substitution pattern.<sup>14</sup> The presence of the two tetrafluoroborate anions was also confirmed.

In **3** the molecule lies on a mirror plane and the asymmetric unit is represented by a half-molecule. A molecule of 1,2-dichloroethane and both tetrafluoroborate anions are also located across this mirror plane. One of the tetrafluoroborate anions and the solvent molecule are disordered over two positions and use of a disorder model gave a final  $R_1$  value of 2.98%. The structure is broadly similar to that reported by Shi et al. for a related analogue, however interactions between the complex with the molybdate(VI) anion complex perturb the molecular geometry in that example.<sup>15</sup> In this example the CHT rings are oriented towards each other with a distance of 5.47 Å between the phosphorous atoms and 5.85 Å between the  $sp^3$  carbon atoms in the CHT rings. This distance is similar to that observed in related tropylium sandwich complexes, suggesting that **3** should be capable of binding metal atoms between the CHT ligands.

In **4** the iron atom lies on a crystallographic inversion centre akin to that of the parent phosphine (dppf).<sup>16</sup> The inversion centre causes the CHT rings to be oriented away from each other with a P–Fe distance of 3.47 Å, and a P–P distance of 6.94 Å. The bond between the phosphorous atom and the carbon on the cyclopentadienyl ring is significant shorter in **4** (1.774 Å) than in the unsubstituted parent complex (1.819 Å).<sup>16</sup> The bond distances between the phosphorous and carbon atom on the phenyl rings are also significantly shorter in **4** (1.788 and 1.791 Å) than in the parent complex (1.836 and 1.834 Å).

The bond distance from the phosphorous centre to the first bridging carbon atom (P(1)–C(20) 1.7738(15) Å) is shorter in **4** than in **2** or **3**, due to the difference in the nature of the bridging group.

The results of  $^1\text{H}$  and  $^{31}\text{P}$  NMR studies of the new complexes **2–4** are summarized in Table 3, with the resonance of the hydrogen atoms nearest the phosphonium cations displaying a steady progression to higher frequencies. This is not unexpected as electronic deshielding of the ligand groups is expected upon coordination of the CHT group. The  $^1\text{H}$  NMR spectra include a sharp set of peaks characteristic of the formation of a CHT derivative (5.20, 5.65, and 6.20 ppm) and no peaks characteristic of residual tropylium (9.27 ppm). A series of multiplets between 7.61 and 7.81 ppm typical of the phenyl rings in **2–4** were also observed. Signals characteristic of the bridging ethane (**2**), propane (**3**), and ferrocene (**4**) groups showed a slight but systematic shift downfield from those in the unsubstituted ligand (Table 3).

Examination of the  $^{31}\text{P}$  NMR also demonstrates a systematic downfield shift upon coordination of the CHT group as the electron density is perturbed by the conversion to a phosphonium centre. No  $^{31}\text{P}$ – $^{31}\text{P}$  interactions are observed across the bridging unit, and the  $^{19}\text{F}$  NMR confirmed the presence of the tetrafluoroborate anion (–150.4 ppm). The  $^{31}\text{P}$  NMR spectrum will be a sensitive probe of changes in the electronic environment if metal coordination is possible. UV–vis spectroscopy of **1–3** showed no significant features in the absorption spectra between 350 and 800 nm.

Complex **4** showed a broad absorption centred at 454 nm ( $\epsilon = 315 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), consistent with the presence of the ferrocene moiety. Complexes **2–4** were stable for extended periods of time in a variety of organic solvents including MeCN, acetone and chlorinated solvents. None of the complexes demonstrated any evidence of fluorescent properties.

Attempts to repeat the above reactions with bis-(diphenylphosphino)methane (dppm) gave an off-white material that was poorly soluble in chlorinated solvents.  $^{31}\text{P}$  NMR in  $d_3$ - $\text{CD}_3\text{CN}$  showed multiple signals at 24.0, 19.4, and –29 ppm, suggesting a mixture of unsubstituted, partially substituted, and fully substituted products. Significant unreacted tropylium was also observed (9.27 ppm) in the  $^1\text{H}$  NMR. Attempts to force the reaction to completion through the use of excess  $[\text{C}_7\text{H}_7][\text{BF}_4]$ , longer reflux times, and higher boiling point solvents were all unsuccessful in obtaining a single product. The success of the ethane bridged derivative (**2**) suggests that the shorter bridge length in dppm reduces the flexibility of the ligand between the phosphorous atoms, preventing efficient addition of the second tropylium moiety. Attempts to react  $\text{AsPh}_3$  and  $\text{SbPh}_3$  with  $[\text{C}_7\text{H}_7][\text{BF}_4]$  to form complexes analogous to **1** were also unsuccessful.

In conclusion, we have synthesized and characterized a new class of bis-quaternary phosphonium compounds. These novel ligands offer the opportunity for synthesizing new organometallic complexes where cooperative haptic interactions between the cycloheptatriene groups support metal centres in new molecular geometries. Intermolecular coordination of the cycloheptatriene groups may lead to new polymeric metal complexes. Reactivity studies with zero-valent metals are currently underway.

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## Supplementary data

Supplementary data (experimental details for the synthesis and characterization of **1–4**. The NMR and UV–vis spectra of **1–4** and details of the single crystal X-ray diffraction analysis in CIF format for **2–4**. The Crystallography Open Database (<http://www.crystallography.net/>) also contains the supporting crystallographic data for this paper) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2015.06.097>.

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**Table 3**  
Selected NMR data for **2–4** and parent phosphines complexes

|  | <b>2</b>   | <b>3</b>   | <b>4</b>   |
|--|------------|------------|------------|
| $^{31}\text{P}$ NMR shift of new complex | 23.2       | 23.5       | 23.7       |
| $^{31}\text{P}$ NMR of parent phosphine  | –12.6      | –17.5      | –17.3      |
| $^1\text{H}$ NMR of bridge               | 2.89, 2.90 | 3.20, 4.21 | 4.42, 4.84 |

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