Poly-Onio Substituted Phosphorus Compounds

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Dedicated to Professor H. J. Bestmann

4-Dimethylaminopyridine reacts with phosphorus(III) and (V) halides to give formation of poly-onio substituted polycation salts. Their structures can be assigned on the basis of spectroscopic and analytical data and by anion exchange reactions.

4-Dimethylaminopyridine (DMAP),\(^1\) as a strong nucleophile, is known to react with a great variety of compounds containing positively polarized carbon centers with formation of pyridino-substituted onium salts.\(^2,3\)

We here report the first synthesis of per-onio substituted phosphorus compounds\(^4,5\) in the oxidation states + III and + V, containing DMAP as a ligand (L). Phosphorus(III) halides, when reacted with the triple amount of DMAP in ethyl acetate, readily form trispyridino-substituted complexes 1a–c according to Scheme 1 as colorless, 1a,b, or yellow, 1c, powders of poor solubility.

(Scheme 1). The \(^{31}\)P-NMR spectrum of 1d, as the only compound sufficiently soluble for \(^{31}\)P-NMR\(^2\) measurements, consists of a singlet at \(\delta = +121.7\) (with external 85% H\(_3\)PO\(_4\) as standard), which is in the typical range for highly deshielded three-coordinate phosphorus(III) compounds.\(^9\)

The anions in 1d can be exchanged by hexacyanoferrate(III) under mild conditions, giving the novel 1:1 electrolyte 1e.

Diphosphines, such as diphenylphosphine tetraiodide, can be poly-onio substituted likewise (Scheme 2):

(Scheme 2)

With quinuclidine, the sterically bulky salt 4, which is isostructural with 1d, results in good yield (Scheme 3):

(Scheme 3)

From 3 a 1:1 electrolyte analogous to 1e can be obtained by anion exchange with tetrabutylammonium hexacyanoferrate(III).

Extending the concept of poly-onio substitution to phosphorus(V) compounds leads to structurally novel derivatives of phosphoryl chloride and thiophosphoryl chloride (Scheme 4).

All anion exchange reactions mentioned for 1 and 3 can also be performed with 4 and 5. Electron-withdrawal in the P=X-bonds of 4 and 5 induced by the cationic ligands is not sufficient to make salts 4 and 5 X-transfer reagents\(^10\) (Scheme 4).

Coordination of five cationic ligands around a phosphorus(V) center by complete substitution of halogens in phosphorus(V) halides leads to the highly unusual pentacationic species 6 and 7 (Scheme 5). In the case of 6 the electrolyte type again is confirmed by quantitative formation of five equivalents of chlorotrimethylsilane (\(^1\)H-NMR scrutiny).
Table. Characteristic Data of Products 1a–e, 2–7

<table>
<thead>
<tr>
<th>Producta</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>1R (Nujol)b</th>
<th>¹H-NMRc (CD₂CN/TMS) δ, J (Hz)</th>
<th>³¹P-NMRd (CD₃NO₂), δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>24</td>
<td>98</td>
<td>3040 (m), 1640 (vs), 1560 (vs), 1400 (m), 1210 (m), 1070 (m), 1020 (m), 990 (w), 880 (m), 820 (m), 725 (w)</td>
<td>3.12 (3a, 18H), 7.40 (AA'BB', 12H)</td>
<td>–</td>
</tr>
<tr>
<td>1b</td>
<td>12</td>
<td>76</td>
<td>3080 (w), 1650 (vs), 1565 (vs), 1400 (m), 1220 (s), 1070 (w), 1000 (m), 810 (m), 750 (w), 725</td>
<td>3.23 (2a, 18H), 7.50 (AA'BB', 12H)</td>
<td>–</td>
</tr>
<tr>
<td>1c</td>
<td>12</td>
<td>85</td>
<td>3060 (s), 1650 (vs), 1560 (vs), 1390 (m), 1260 (w), 1205 (s), 1000 (s), 935 (m), 790 (s)</td>
<td>3.23 (2a, 12H), 7.57 (AA'BB', 12H)</td>
<td>–</td>
</tr>
<tr>
<td>1d</td>
<td>2</td>
<td>91</td>
<td>3100 (m), 1645 (vs), 1565 (vs), 1400 (m), 1260 (vs), 1210 (vs), 1155 (s), 1070 (m), 1050 (s), 1000 (s), 950 (w), 840 (m)</td>
<td>3.33 (2a, 18H), 7.55 (AA'BB', 12H)</td>
<td>+122.6</td>
</tr>
<tr>
<td>1e</td>
<td>3</td>
<td>51</td>
<td>3100 (w), 2130 (vs), 1650 (vs), 1540 (vs), 1400 (w), 1210 (m), 1120 (w), 1010 (w), 1000 (s), 820 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>89</td>
<td>3060 (s), 1635 (vs), 1560 (vs), 1400 (m), 1210 (vs), 1060 (m), 1000 (s), 960 (m), 830 (w), 800 (s), 725 (w)</td>
<td>3.23 (2a, 24H), 7.56 (AA'BB', 16H)</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>74</td>
<td>3060 (s), 2970 (s), 2900 (s), 2840 (m), 1500 (w), 1470 (s), 1435 (m), 1340 (w), 1270 (vs), 1155 (vs), 1020 (vs), 960 (m), 630 (s)</td>
<td>1.30 (m, 3H), 2.00 (m, 18H), 3.30 (m, 18H)</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>96</td>
<td>3040 (m), 1640 (vs), 1560 (vs), 1420 (m), 1210 (s), 1120 (m), 1100 (m), 1100 (m), 1080 (m), 1050 (s), 990 (m), 810 (s), 730 (w)</td>
<td>3.24 (2a, 18H), 7.59 (AA'BB', 12H)</td>
<td>–</td>
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<tr>
<td>5</td>
<td>12</td>
<td>99</td>
<td>3120 (w), 1640 (s), 1560 (vs), 1210 (s), 1170 (s), 1060 (m), 1000 (m), 940 (m), 890 (w), 810 (s), 770 (m), 720 (s)</td>
<td>3.20 (2a, 18H), 7.67 (AA'BB', 12H)</td>
<td>–</td>
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<tr>
<td>6</td>
<td>48</td>
<td>67</td>
<td>3100 (m), 1640 (vs), 1570 (s), 1410 (m), 1270 (vs), 1230 (vs), 1160 (s), 1090 (m), 1060 (m), 1040 (s), 1020 (s), 840 (m)</td>
<td>3.15 (s, 18H), 3.17 (s, 12H), 7.44 (2a AAB', 20H)</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>18</td>
<td>96</td>
<td>3100 (w), 1640 (vs), 1570 (s), 1410 (m), 1210 (m), 1060 (m), 1040 (s), 950 (w), 840 (m), 800 (m)</td>
<td>3.22 (2a, 18), 3.27 (s, 12H), 7.67 (2a AAB', 20H)</td>
<td>–</td>
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</tbody>
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* Satisfactory microanalyses obtained: C ± 0.34, H ± 0.36 (exceptions: 1c: –0.53, 1a: +0.56), N ± 0.39 (exception: 1b: +0.68).
* Measured on a Beckman Acculab 8 spectrophotometer.
* Recorded on a JEOI PMX 60 NMR spectrometer.
* Recorded on a JEOI GX 400 NMR spectrometer, with 85% H₃PO₄ as external standard.
* Paramagnetic.
* in KBr.

Due to a sphere of negative charge formed by the array of anions coordinated in the outer sphere of the polycation.

¹H-NMR spectra of 6 and 7 display two slightly different kinds of DMAP ligands. The integration ratio of 2:3 is consistent with the assumption of three equatorial and two axial ligands in a rigid arrangement. Ligand pseudorotation is frozen at 25°C measuring temperature. We assume steric and electrostatic effects induced by the five large counterions to be responsible for this. ³¹P-NMR signals lie in the typical range for highly deshielded pentacoordinate phosphorus(V) compounds (see Table).

According to preliminary studies with various reductants salts 6 and 7 behave as strong electron acceptors.

All preparations were carried out in oven-dried, N₂-flushed glassware. Solvents were dried by distillation from P₂O₅ or by dry-column chromatography over neutral aluminum oxide. Phosphorus halides were stored under N₂, all other commercially available reagents were used without further purification.

**Preparation of Poly-Oxo substituted Phosphorus Compounds; General Procedure:**

To a stirred solution of DMAP (611 mg, 5 mmol) in EtOAc (50 mL) the equivalent amount of phosphorus halide is slowly added. The mixture is stirred for 2–48 h then the product is filtered off and dried in an oil-pump vacuum at r.t. For preparation of triflate salts, DMAP is used together with the same amount of trimethylsilyl trifluoromethanesulfonate.

Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

Received: 28 June 1991
(2) Weiss, R.; Roth, R. Synthesis 1987, 870.