# ChemComm

This article is part of the

## Frontiers in Molecular Main Group Chemistry web themed issue

Guest editors: Manfred Scheer and Richard Layfield

All articles in this issue will be gathered together online at

www.rsc.org/cc/maingroup



Cite this: Chem. Commun., 2012, 48, 7359-7361

### COMMUNICATION

## **P–P Menschutkin preparation of prototypical phosphinophosphonium** salts<sup>†</sup>‡

Saurabh S. Chitnis,<sup>a</sup> Elizabeth MacDonald,<sup>b</sup> Neil Burford,<sup>\*ab</sup> Ulrike Werner-Zwanziger<sup>b</sup> and Robert McDonald<sup>c</sup>

*Received 29th April 2012, Accepted 31st May 2012* DOI: 10.1039/c2cc33082b

Reactions of Me<sub>3</sub>P with alkyl- or arylchlorophosphines yield phosphinophosphonium salts in quantitative yields, demonstrating a Menschutkin P–P methodology that has potentially broad application for element–element bond formation.

The classical Menschutkin reaction<sup>1</sup> yields an alkylammonium salt from an alkyl halide and an amine, representing a Lewis basic nitrogen center interacting with a Lewis acidic carbon center to eliminate a halide anion. The reaction offers a facile approach to N–C bond formation, but should be generally applicable between atomic centers that offer sufficient basicity and centers that participate in a bond that involves a sufficiently effective leaving group. For example, specific imines displace a chloride ion from a chloroaminophosphine to give an oniophosphine, represented by 1.<sup>2</sup> Moreover, NMR spectroscopic data and elemental analytical data indicate Pn–Pn' bond formation (Pn = P, As, Sb) in reactions of pnictines with halopnictines.<sup>3–7</sup>



We now provide definitive confirmation of a homoatomic P–P Menschutkin reaction and demonstrate that Me<sub>2</sub>PCl and Ph<sub>2</sub>PCl are both sufficiently Lewis acidic to engage methylated phosphines as donors to form P–P bonds in phosphinophosphonium **2** frameworks. We have used the reaction to prepare the chloride salt of the prototypical phosphinophosphonium cation  $[Me_3PPMe_2]^+$ , **3**, which has been comprehensively characterized and compared with salts formed from chlorophosphines that have been activated to phosphenium cations by halide abstraction.<sup>8,9</sup>

Table 1 lists the products identified by P-31 NMR spectroscopy from mixtures of  $R_3P$  (R = Me, Ph) with  $R'_nPCl_{3-n}$ (R' = Me, Ph; n = 0, 1, 2) or dmpe (dimethylphosphinoethane, Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>) as illustrated in Schemes 1 and 2. Me<sub>3</sub>P reacts with Me<sub>2</sub>PCl or MePCl<sub>2</sub> on contact (white powders formed from the gas phase) to give compounds 3 and 4, respectively, and dmpe reacts with Me<sub>2</sub>PCl or MePCl<sub>2</sub> on contact to give compounds 5 and 6, respectively. All reactions proceed quantitatively according on the stoichiometry of the mixture. The reactions also occur in acetonitrile with immediate precipitation of the products. Reactions of Me<sub>3</sub>P or dmpe with Ph<sub>2</sub>PCl and PhPCl<sub>2</sub> in dichloromethane give the analogous mono- and dicationic products 7-10. Product 8 is partially converted to Me<sub>3</sub>PCl<sub>2</sub> and cyclo-P<sub>4</sub>Ph<sub>4</sub> over several weeks at room temperature. Reaction of Me<sub>3</sub>P with PCl<sub>3</sub> yielded a mixture of insoluble polymeric material, Me<sub>3</sub>PCl<sub>2</sub> and 11, identified by comparison of P-31 chemical shifts and coupling constants with those of known triphosphenium cations.<sup>10</sup> The composition of products 3-10 was established by elemental analysis and P-31 NMR spectroscopy and their ionic structure was confirmed by comparison of chemical shifts with those of the previously reported [O<sub>3</sub>SCF<sub>3</sub>]<sup>-</sup> salts of phosphinophosphonium cations (Table 1).



Although the solubility of compounds **3–6**, **8**, and **10** is too low to obtain solution P-31 NMR data, P-31 CP/MAS NMR spectra for the solids provides definitive data, as shown for example in Fig. 1 for the precipitate from the reaction between Me<sub>3</sub>P and Me<sub>2</sub>PCl. The distinctive pattern of two doublets (one in the phosphine region and the other in the phosphonium region) is consistent with that observed for [Me<sub>3</sub>PPMe<sub>2</sub>][O<sub>3</sub>SCF<sub>3</sub>].<sup>11</sup> In contrast to reactions of PMe<sub>3</sub> or dmpe, P-31 NMR spectra of mixtures involving PPh<sub>3</sub> with Me<sub>2</sub>PCl, MePCl<sub>2</sub>, Ph<sub>2</sub>PCl, PhPCl<sub>2</sub>,

<sup>&</sup>lt;sup>a</sup> Department of Chemistry, University of Victoria, Victoria, BC V8W3V6, Canada. E-mail: nburford@uvic.ca;

Fax: + 1 250 721 7147; Tel: + 1 250 721 7150

<sup>&</sup>lt;sup>b</sup> Department of Chemistry, Dalhousie University, Halifax, NS B3H4J3, Canada

<sup>&</sup>lt;sup>c</sup> X-ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G2G2, Canada

<sup>†</sup> This article is part of the *ChemComm* 'Frontiers in Molecular Main Group Chemistry' web themed issue.

<sup>‡</sup> Electronic supplementary information (ESI) available: CCDC 879397–879400. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc33082b

Table 1 P-31 NMR chemical shifts,  ${}^{1}J_{P-P}$  coupling constants and spin systems for phosphinophosphonium cations as chloride and triflate salts (NMR data obtained for solutions, unless denoted by CP/MAS)

$\Delta\delta$ (ppm); <sup>1</sup> J <sub>P-P</sub> (Hz, ±15); spin system		
Cation	Counterion = $[Cl]^-$	Counterion = $[O_3SCF_3]^-$
$  \frac{\left[(Me_{3}PPMe_{2}]^{+} (3)\right]}{\left[(Me_{3}P)_{2}PMe_{1}^{2^{+}} (4)\right]} \\ \left[dmpe(PMe_{2})_{2}\right]^{2^{+}} (5) \\ \left[dmpePMe_{1}^{2^{+}} (6)\right] \\ \left[(Me_{3}PPPh_{2}]^{+} (7)\right] \\ \left[(Me_{3}P)_{2}PPh_{1}^{2^{+}} (8)\right] \\ \left[dmpe(PPh_{2})_{2}\right]^{2^{+}} (9) \\ \left[dmpePPh_{1}^{2^{+}} (10)\right] \\ \left[(Me_{3}P)_{2}P_{1}^{+} (11)\right] $	20, -66 (CP/MAS); 249; AX 20, -63 (CP/MAS); broad; AXX' 30, -75 (CP/MAS); 272; AX 50, -86 (CP/MAS); 296, 271; AXX' 15, -24; broad; AX <sup>a</sup> 97, <sup>b</sup> -51, 31,2; broad; A, A, AX 19, -15; broad; AX 48, -77 (CP/MAS); broad; AX <sub>2</sub> 18, -146 (CP/MAS); 434; AX <sub>2</sub>	18, -59; 274; AX <sup>11</sup> 25, -63; 285, 295; AXX' <sup>19</sup> 24, -58; broad; AX; (This work) 53, -88; 278, 283; AXX'; (This work) 15, -23; 289; AX <sup>11</sup> 24, -46; 286, 298; AXX' <sup>19</sup> 21, -21; 300; AX <sup>18</sup> 53, -68; 277, 275; AXX'; (This work) 15, -156; 439, 438; AXX'; (This work)

<sup>a</sup> Me<sub>3</sub>PCl<sub>2</sub>, ref. 20. <sup>b</sup> cyclo-P<sub>4</sub>Ph<sub>4</sub>, ref. 21.







and PCl<sub>3</sub> show only signals corresponding to starting materials, even after prolonged heating.

Crystals of  $[Me_3PPMe_2][Cl]$  (**3**[Cl]) have been obtained from a dilute CH<sub>3</sub>CN solution, and characterized by X-ray crystallography as an ionic compound, as shown in Fig. 2. The crystals and the powder do not melt, but both sublime in the same temperature range. In the solid state, **3** adopts a staggered conformation about the P–P bond. The closest interion P–Cl distance (3.614 Å) occurs at P2 and *trans* to P1 on the P1–P2 axis, but is significantly larger than the sum of the van der Waals' radii of P and Cl (3.55 Å). Each chloride ion is stabilized by five Cl–H contacts (2.760–2.860 Å) involving the methyl groups from three adjacent cations. The observed conformation, bond lengths, and angles of **3** are in good agreement with the



Fig. 2 Thermal ellipsoid plot (50% probability) of  $[Me_3PPMe_2](3)[Cl]$ in the solid state. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): X-ray: P1–P2 = 2.1767(6), P1–C1 = 1.790(2), P1–C2/ C2' = 1.7855(15), P2–C3/C3' = 1.8329(15), C1–P1–C2/C2' = 108.9, C2–P1–C2' = 106.3, C3–P2–C3' = 100.7, P1–P2–C3/C3' = 98.2, P1–P2–C12 = 178.4, C1–P1–P2–C3/C3' = 51.1; *cf.* Calc. gas phase (MP2/cc-pVTZ): P1–P2 = 2.190, P1–C1 = 1.808, P1–C2/C2' = 1.805, P2–C3/C3' = 1.843, C1–P1–C2/C2' = 108.2, C2–P1–C2' = 108.4, C3–P2–C3' = 100.9, P1–P2–C3/C3' = 98.2. C1–P1–P2–C3/C3' = 51.2.

calculated (MP2/cc-pVTZ) gas-phase structure of the cation (Fig. 2 caption).

While the P-P bond length in 3 [2.1767(6) Å, 2.190 Å (MP2)] is predictably shorter than that in the neutral Me<sub>2</sub>PPMe<sub>2</sub> [2.212(1) Å,<sup>12</sup> 2.213 Å (MP2)], it is surprisingly shorter than that in the dication [Me<sub>3</sub>PPMe<sub>3</sub>][OTf]<sub>2</sub> [2.198(2) Å,<sup>11</sup> 2.227 Å (MP2)], although the differences are small. On the other hand, comparisons of the P-C distances can be understood in terms of the increasing cationic charge affecting a small but significant shortening of the P-C bonds at the phosphonium centers. The similarity of the P-C bonds in P<sub>2</sub>Me<sub>4</sub> with those at P2 in 3, and the fact that P-P distance is independent of charge suggests that the cationic charge is accommodated by the P-C bonds at the phosphonium centers. The effect is replicated in the calculated structures of Me<sub>2</sub>PPMe<sub>2</sub>,  $[Me_3PPMe_2]^+$  and  $[Me_3PPMe_3]^{2+}$  (see Supporting Information). The nearly linear P1-P2-Cl2 angle (178.4°) in the solid state structure of 3[Cl] models the finale of the S<sub>N</sub>2 mechanism envisaged for a Menschutkin process, featuring a disphenoidal acceptor site (P2) with the incoming phosphine and the outgoing halide on the same axis, analogous to the trigonal bipyramidal acceptor carbon centre in the C-N Menschutkin reaction.<sup>13</sup>

The Born-Fajans-Haber cycle for the formation of  $[Me_3PPMe_2]$ -[Cl] from Me<sub>2</sub>PCl and Me<sub>3</sub>P shown in Fig. 3 has been constructed using experimentally measured<sup>14</sup> enthalpies of vaporization ( $\Delta H_{vap}$ ), a calculated value for the chloride-ion-affinity of  $[Me_2P]^+$ 



**Fig. 3** Born-Haber-Fajans cycle for the formation of  $[Me_3PP-Me_2](3)[Cl]$  from Me<sub>2</sub>PCl and Me<sub>3</sub>P (all values in kJ mol<sup>-1</sup>).



**Fig. 4** Pictorial representation of the LUMOs in (i) Me<sub>2</sub>PCl, (ii) Ph<sub>2</sub>PCl at the MP2/cc-pVTZ level. View perpendicular to the  $\sigma_v$  plane of symmetry. H-atoms omitted for clarity. See also Supporting Information.

 $(\Delta H_{\text{CIA}})^{15}$  a calculated value for the P–P bond strength in  $[Me_3PPMe_2]^+$  ( $\Delta H_{P-P}$ ), and a Volume-Based-Thermodynamics<sup>16</sup> calculation for the value of the lattice enthalpy  $(\Delta H_{\text{lat}})$ , to give the overall reaction an exothermicity  $(\Delta H_{\text{rxn}})$ of 14.2 kJ mol<sup>-1</sup>. The  $\Delta H_{P-P}$  value (356 kJ mol<sup>-1</sup>) for  $[Me_3PPMe_2]^+$  is dramatically larger than that calculated for  $P_2Me_4$  (256 kJ mol<sup>-1</sup>, G3 level).<sup>17</sup> The small magnitude of  $\Delta H_{\rm rxn}$  renders the overall thermodynamics sensitive to small changes in  $\Delta H_{P-P}$  and  $\Delta H_{lat}$  and we speculate that these variations are the reason that previous reports of reaction mixtures containing longer-chained trialkylphosphines (triethyl-, tri-n-butyl-, and tri-n-octyl-) and alkyl- or arylhalophosphines described thermally unstable adducts and redox decomposition products.<sup>3–5</sup> In particular, the inverse relationship between  $\Delta H_{\text{lat}}$  and the volume of the interacting ions makes  $\Delta H_{\rm rxn}$  less negative for larger trialkylphosphines The inclusion of a strong Lewis acid into the mixture of Me<sub>2</sub>PCl and Me<sub>3</sub>P as a halide abstractor will render  $\Delta H_{\rm rxn}$  more negative as the positive  $\Delta H_{\text{CIA}}$  of  $[\text{Me}_2\text{P}]^+$  will be compensated by the negative  $\Delta H_{\text{CIA}}$ of the abstractor (e.g. -321 kJ mol<sup>-1</sup> for AlCl<sub>3</sub>).<sup>22</sup>

The large value of  $\Delta H_{\text{CIA}}$  for  $[\text{Me}_2\text{P}]^+$  (770 kJ mol<sup>-1</sup>) precludes heterolytic dissociation of Me<sub>2</sub>PCl as a plausible step prior to P–P bond formation. *Ab initio* calculations indicate that the LUMO for both Me<sub>2</sub>PCl and Ph<sub>2</sub>PCl is the P–Cl  $\sigma^*$ -antibonding orbital (Fig. 4). On this basis, we

interpret the reaction as a bimolecular Menschutkin process, driven by the  $\Delta H_{P-P}$  and  $\Delta H_{lat}$  of the phosphinophosphonium salt and facilitated by the occupation of the P–Cl  $\sigma^*$ -MO in the acceptor. We envisage that appropriate consideration of these parameters will lead to broader application of the Menschutkin approach to element–element bond formation.

In summary, formation of the prototypical phosphinophosphonium chloride salt by direct combination of a phosphine and a chlorophosphine demonstrates the P–P Menschutkin reaction, which has potentially broad applicability.

We thank the Natural Sciences and Engineering Research Council of Canada, the Canada Research Chairs Program, the Canada Foundation for Innovation and the Nova Scotia Research and Innovation Trust Fund for funding and NMR-3 for use of instrumentation.

#### Notes and references

- 1 N. Menschutkin, Z. Physik. Chem., 1890, 5, 589.
- 2 R. Reed, R. Reau, F. Dahan and G. Bertrand, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 399–401.
- 3 W. Seidel, Z. Anorg. Allg. Chem., 1964, 8, 141-150.
- 4 S. F. Spangenberg and H. H. Sisler, *Inorg. Chem.*, 1969, 8, 1006–1010.
- 5 J. C. Summers and H. H. Sisler, *Inorg. Chem.*, 1970, 9, 862–869.
- 6 J. A. Boon, H. L. Byers, K. B. Dillon, A. E. Goeta and
- D. A. Longbottom, *Heteroat. Chem.*, 3000, **11**, 226–231.
- 7 K. B. Dillon and P. K. Monks, *Dalton Trans.*, 2007, 1420–1424.
- 8 N. Burford and P. J. Ragogna, J. Chem. Soc., Dalton Trans., 2002, 4307–4315.
- 9 C. A. Dyker and N. Burford, Chem.-Asian J., 2008, 3, 28-36.
- 10 A. Schmidpeter, S. Loschmidt and W. S. Sheldrick, Angew. Chem., Int. Ed. Engl., 2003, 24, 226–227.
- 11 J. J. Weigand, S. D. Riegel, N. Burford and A. Decken, J. Am. Chem. Soc., 2007, 129, 7969–7976.
- 12 O. Mundt, H. Riffel, G. Becker and A. Simon, Z. Naturforsch. Teil B., 1988, 43, 952.
- 13 S. Shaik, A. Ioffe, A. C. Reddy and A. Pross, J. Am. Chem. Soc., 1994, 116, 262–273.
- 14 Me<sub>2</sub>PCI: A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, 1958, **80**, 1107–1109Me<sub>3</sub>P: L. H. Long and J. H. Sackman, *Trans. Faraday Soc.*, 1957, **53**, 1606–1611.
- 15  $\Delta H_{\text{CIA}}$  for  $[\text{Me}_2\text{P}]^+$  was calculated using the experimentally known  $\Delta H_{\text{CIA}}$  for AlCl<sub>3</sub> as a reference enthalpy. See Supporting Information.
- 16 H. D. B. Jenkins and L. Glasser, J. Chem. Eng. Data, 2011, 568, 874–880.
- 17 K. B. Borisenko and D. W. H. Rankin, J. Chem. Soc., Dalton Trans., 2002, 3135–3141.
- 18 N. Burford, P. J. Ragogna, R. MacDonald and M. J. Ferguson, *Chem. Commun.*, 2003, 2066–2067.
- 19 D. Knackstedt, Investigations of Phosphenium insertion into Phosphorus-Phosphorus Bonds, M.Sc. Dissertation, Dalhousie University, Halifax, NS, 2011.
- 20 K. George, A. L. Hector, W. Levason, G. Reid, G. Sanderson, M. Webster and W. Zhang, *Dalton Trans.*, 2011, 40, 1584–1593.
- 21 M. Baudler, B. Carlsohn, W. Bohm and D. Reuschbach, Z. Naturforsch. Teil B, 1976, 31, 558.
- 22 Y. U. Pervova, M. V. Korobov and L. N. Sidorov, *Russ. J. Phys. Chem.*, 1992, **66**, 635.