Electrophilic ring-opening of $[(RP)_nAs]^-$ anions; a simple route to functionalised neutral phosphines of the type $[(Bu^tP)(Bu^tRP)_2]$

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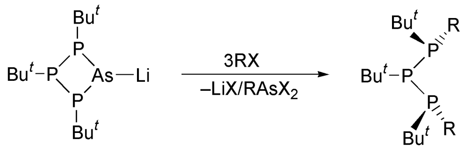
Ring opening of the cyclic $[(Bu^tP)_3As]^-$ anion results from reactions with electrophiles (RX = H_2O, MeI, $CH_2{=}CHCH_2I$, $PhCH_2Br$), providing a simple and general approach to triphosphine ligands of the type $[(Bu^tP)(Bu^tRP)_2]$.

We found recently that heterocyclic anions of the type $[(RP)_nE]^-$ (n = 3 or 4; E = As, Sb; R = Bu^t, 1-adamantyl, cyclohexyl) can be prepared in a single step by the reactions of alkali metal primary phosphides with $E(NMe_2)_3$ (E = As, Sb).[1] Our particular interest in these species stems from their potential to act as sources of group 15 atoms, as suggested by the isolation of Zintl compounds from the same reaction systems at higher temperatures.[1] These heterocyclic anions exhibit unusual reactivity with transition metal metallocenes, the reaction of the Lewis base complex $[\{(Bu^tP)_3As\}Li\cdot 2DABCO\cdot thf]$ **1** [DABCO = $N(CH_2CH_2)_3N$] with $[CpM(CO)_3Cl]$ (M = Mo, W) leading to addition of the $[(Bu^tP)_3As]^-$ anion to the Cp ring rather than displacement of the metal-bonded Cl ligand.[2] Here we show that $[(RP)_nAs]^-$ anions are useful synthons of the corresponding $(RP)_n^{2-}$ dianions, as illustrated by the reactions of $[(Bu^tP)_3As]^-$ with electrophiles which provides direct access to a large range of terminally substituted triphosphine ligands.

The reactions of **1** with a range of electrophiles (1:3 equiv., respectively) occur smoothly at −78 °C in thf–toluene giving insoluble precipitates of HAsO(OH) (in the case of H_2O) or organo-arsenic dihalides $[RAsX_2]$ (with organic halides as electrophiles) which are readily removed by filtration (Scheme 1). Removal of the solvent under vacuum gives 72–98% yields of the terminally substituted triphosphines $[(Bu^tP)(Bu^tRP)_2]$ (R = H **2**, Me **3**, $CH_2{=}CHCH_2$ **4**, $PhCH_2$ **5**).† The high purity of the materials obtained *directly* by this procedure is confirmed by their room-temperature ^1H and ^{31}P NMR spectra, which show little or no impurities. The ^{31}P NMR spectra of **2**–**5** are consistent with those of previously reported triphosphines,[3] **2** (*meso* and *racemic* isomers), **4** and **5** appearing as characteristic A_2M multiplets and **3** as a more complex eight line A_2B multiplet (*i.e.* $\Delta\delta \approx \Delta J$). A further feature of the ^1H NMR spectra of **3** and **5** is the appearance of the Me and benzyl methylene protons as deceptively simple triplets.[4] Model *ab initio* calculations reveal that the reactions producing **2**–**5** are highly thermodynamically favourable. For example, the gas-phase reaction of 3MeI with $[\{Bu^tP\}_3AsLi]$ is exothermic by 57.4 kcal mol^{-1} (at the B3LYP/6-311G** level).‡ This reaction becomes even more favourable (−66.2 kcal mol^{-1}) once solution effects are included. Calculations of the reactions involving $[\{RP\}_3AsLi]$ (R = H, Me, Bu^t) also reveal that these reactions are enthalpically driven (with negligible entropy changes being associated in solution).



X= OH, R= H **2**; X= Br, I, R = Me **3**, $PhCH_2$ **4**, $CH_2{=}CHCH_2$ **5**

Scheme 1

A limited number of terminally substituted triphosphines of the type $[(RP)(RR'P)_2]$ have been prepared previously by reactions of $[(RP)_3M_2]$ (M = alkali metal) with electrophiles.[3] These salts can be generated either by cleavage of $(RP)_n$ with an alkali metal (giving the salt as a mixture with other homologues)[5] or by reaction of $[(RP)(RHP)_2]$ (prepared by reduction of terminal halides $[(RP)(RXP)_2]$) with alkali metals.[3a] Importantly, although often efficient these procedures involve several steps starting from the simple dihalides $RPCl_2$, with extensive manipulation and purification at each stage. The electrophilic ring-opening reaction described here provides the potential means by which any primary phosphine (from which **1** and related heterocycles are prepared in a single step in crystalline form) can be converted selectively into a broad range of terminally substituted triphosphines. The closest related approach utilises $[Cp_2Zr(PPh)_3]$ as a source of $[PhP]_3^-$ in the synthesis of the cyclic compounds $[PhP]_4$ and $[(PhP)_3SnBu^t_2]$.[6]

Owing presumably to the involved and specialised synthetic methods previously required in the synthesis of tri- and tetra-phosphines, to our knowledge, no studies of their coordination chemistry have been reported. The few structurally characterised examples of coordination compounds of this type are transition metal complexes in which the tri- or tetra-phosphine frameworks have been assembled at the transition metal centre.[7] However, these reactions do not appear to be selective in terms of the chain length of the phosphine incorporated, with the chain length of the phosphines being dependent on the organic substituents[7a,b] as well as the reaction conditions.[8] An illustration that these ligands can indeed be transferred *intact* to a transition metal centre is provided in this study by the synthesis† and structural characterisation§ of $[W(CO_4)\text{-}\{(Bu^tP)(Bu^tHP)_2\}]$ **6** (Fig. 1). The structural features of **6** are similar to those of $[W(CO)_4\{(Bu^tP)(Me_2P)_2\}]$, the only other complex previously characterised in which a chelating triphosphine ligand is present.[7a] The presence of only one isomer of the triphosphine (the symmetric *meso* form) at the W centres of **6** is of some interest. Previous NMR studies (consistent with those presented in the current work†) have shown that this is the predominant isomer in solutions of free **2**.[3a] The fact that the isomer of **6** incorporating a *racemic* form of the triphosphine is not produced in this reaction may be due to steric factors, leading to the selection of the *meso* form in the complex.

In summary, the new, high yielding method of preparing terminally substituted non-symmetric, triphosphines should allow systematic investigation of the coordination chemistry of

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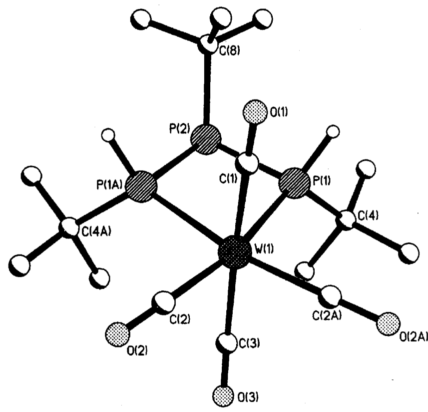

Fig. 1 Structure of **6**; H-atoms (except those attached to the P atoms) have been omitted for clarity. Key bond lengths (Å) and angles (°): W(1)–P(1) 2.512(1), W(1)–C(2) 1.990(5), W(1)–C(3) 2.017(7), P(1)–P(2) 2.215(2); P(1)–W(1)–P(1A) 72.96(5), P(2)–P(1)–W(1) 101.09(5), P(1)–P(2)–P(1A) 84.78(7).

this class of ligands. This should be of particular importance in relation to the widespread application of ligand frameworks such as $(CH_2)_n(PPh_2)_2$ (n = 1 or 2) and the growth of interest in ligand systems with well defined bite, steric and stereochemical characteristics in the field of homogeneous catalysis. Significantly, preliminary studies of the reactions of the heterocyclic anion $[\{CyP\}_4As]^-$ with electrophiles (RX) suggest that analogous tetraphosphines of the type $[(CyP)_2(CyRP)_2]$ are generated.[9]

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Notes and references

† *Syntheses* of **2**–**5**: the electrophiles (1.5 mmol) were added dropwise to a solution of **1** (0.64 g, 0.5 mmol) in thf (1 ml)–toluene (20 ml) at −78 °C over a 10 min period. The reactions were allowed to warm to room temperature and stirred for 1 h. For **3**–**5**, white precipitates of the organo-arsenic dihalides in colourless or faint yellow solutions were formed. The precipitates were removed by filtration and the filtrates reduced under vacuum to give crystalline or semi-crystalline solids. For **2**, a yellow solution was produced which was reduced under vacuum to give the triphosphine as a liquid. **2**: 0.13 g (98%); δ_H(+25 °C, d_8-toluene, 400.13 MHz): *meso isomer*, 3.41 (d, P–H, $^1J_{PH}$ 203 Hz), 1.38 (d, Bu^{t}P(2), J 12.9 Hz), 1.30 [d, Bu^{t}P(1,3), J 12.5 Hz]; *racemic isomer*, 3.30 (d, P–H, $^1J_{PH}$ 205 Hz), 1.52 (d, Bu^{t}P(2), J 12.5 Hz), 1.33 [d, Bu^{t}P(1,3), J 12.5 Hz] (ratio of isomer A : B *ca.* 2 : 1); δ_P(+25 °C, d_8-toluene, 161.975 MHz): *meso isomer*, −12.84 [dd, P(1) and P(3)], −46.33 [dd, P(2)] ($^1J_{P(2)P(1,3)}$ 231.5 Hz); *racemic isomer*, −14.0 [dd, P(1) and P(3)], −39.19 [dd, P(2)] ($^1J_{P(2)P(1,3)}$ 207.3 Hz). **3**: yield 0.12 g (82%); δ_H(+25 °C, d_8-toluene, 400.13 MHz) 1.44 (t, 4H, CH_2, av. J 9.7 Hz, Me), 1.25–1.18 (m, 27H, Bu^{t}P); δ_P(+25 °C, d_8-toluene, 161.975 MHz) −40.5 [P(1) and P(3)], −41.8 [P(2)] (8 line multiplet, $^1J_{P(2)P(1,3)}$ 231.0 Hz). **4**: yield 0.14 g (82%); δ_H(+25 °C, d_8-toluene, 400.13 MHz) 5.95 (m, 4H, $C\mathit{H}_2$=CH–), 4.95 (dd, 2H, CH_2=C*H*CH_2) 2.75 [q. (overlapped dt), 4H, CH_2=CHCH_2, J 7.6 Hz], 1.24 [d, 9H, Bu^{t}P(2), J 12.5 Hz], 1.22 [d, 18H, Bu^{t}P(1,3), J 12.9 Hz]; δ_P(+25 °C, d_8-toluene, 161.975 MHz) −38.3 [dd, P(1) and P(3)], −47.7 [dd, P(2)] ($^1J_{P(2)P(1,3)}$ 232.6 Hz). **5**: yield 0.16 g (72%); δ_H(+25 °C, d_8-toluene, 400.13 MHz) 7.2–6.9 (m, 10H, Ph), 2.27 (t, 4H, CH_2, av. J 6.7 Hz), 1.25 [d, 9H, Bu^{t}P(2), J 12.9 Hz], 1.11 [d, 18H, Bu^{t}P(1,3), J 13.6 Hz]; δ_P(+25 °C, d_8-toluene, 161.975 MHz) −39.5 [dd, P(1) and P(3)], −46.6 [dd, P(2)] ($^1J_{P(2)P(1,3)}$ 233.4 Hz).

Synthesis of **6**: the complex was prepared by the 1 : 1 reaction of **2** with $[W(CO)_5(thf)]$ in toluene–thf. IR(CH_2Cl_2) ν_{max} = 2015s (*cis* to P), 1913s (sh), 1899vs, 1874s (*trans* to P). δ_H(+25 °C, 400.13 MHz, $CDCl_3$) 4.06 (d, J_{PH} 154 Hz), 1.35 [d, 9H, Bu^{t}P(2), J_{PH} 14 Hz], 1.27 [d, 18H, Bu^{t}P(1,3), J_{PH} 16.5 Hz]. δ_P(+25 °C, $CDCl_3$, 161.975 MHz) 121.1 (t, J 156 Hz), −67.0 [d, 156 Hz (dd, dec. $^1J_{PH}$ 154, $^3J_{PH}$ 16.5 Hz)]. Correct C, H analysis were obtained.

‡ Ab initio *MO calculations*: all calculations were performed using Gaussian 98[11] at the B3LYP/6-311G** level. The solvent effects were incorporated using the PCM[12] model in Gaussian 98. Iodine basis set was obtained from the PNL basis set database.[13] Absolute energies of gas-phase species, solution-phase absolute energies are in parentheses (units E_h): MeI −6959.45606284 (−6959.457283), LiI 6927.13495426 (−6927.158942), $[MeAsI_2]$ 16114.9342294 (−16114.935814), $[\{HP\}_3AsLi]$ −3269.38038964 (−3269.392137), $[\{HP\}_3Me_2]$ −1105.79309134 (−1105.794835), $[\{MeP\}_3AsLi]$ −3387.37832745 (−3387.389669), $[\{MeP\}_3Me_2]$ −1223.78389534 (−1223.786033), $[\{Bu^tP\}_3AsLi]$ −3741.2815255, $[\{Bu^tP\}_3Me_2]$ −15577.67467541. $\Delta H(g)_{reaction}$, for $[\{RP\}_3AsLi]$, $\Delta H(solv)_{reaction}$ and $\Delta G(solv)_{reaction}$ (respectively) are in parentheses (units kcal mol^{-1}): R = H, −71.3 (−79.0, 78.5); R = Me, −66.9 (75.1, 74.6); R = Bu^t, −57.4 (−66.2, 63.5).

§ *Crystal data* for **6**; $C_{16}H_{29}O_4P_3W$, M = 562.15, orthorhombic, space group *Pnma*, Z = 4, a = 17.3386(7), b = 13.7599(5), c = 9.4610(4) Å, V = 2257.2(2) Å^3, μ(Mo-Kα) = 5.345 mm^{-1}, T = 180(2) K. Data were collected using a Nonius Kappa CCD diffractometer. Of a total of 21678 reflections collected, 2087 were independent (R_{int} = 0.082). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[10] Final $R1$ = 0.027 [$I > 2\sigma(I)$] and $wR2$ = 0.066 (all data). CCDC 182/1837. See http://www.rsc.org/suppdata/cc/b0/b007553l/ for crystallographic files in .cif format.

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