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Base-Induced 1,3-Sigmatropic Rearrangement of Mesitylphosphonium Salts

CLUSTER ISSUE

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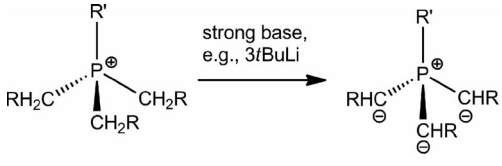
Attempted synthesis of the ylide dianion [2,4,6-$Me_3C_6H_2P$-$(CHR)_3]^{2-}$ (2,4,6-$Me_3C_6H_2$ = mesityl, R = H or Me) by the reaction of mesitylphosphonium iodides [2,4,6-$Me_3C_6H_2PR_3]^+I^-$ (R = Me, **1**; R = Et, **2**) with *t*BuLi at reflux does not result in the anticipated deprotonation of the phosphorus-bonded R groups. Instead, quantitative 1,3-sigmatropic rearrangement occurs to give new benzylic phosphonium salts [(3,5-$Me_2C_6H_3)CH_2PR_3]^+I^-$ (R = Me, **6**; R = Et, **7**), in which the phosphonium centre, the R_3P group, is transferred to an *ortho*-CH_3 group. In situ ^{31}P NMR spectroscopic studies show that the reaction is base-activated and stoichiometric with respect to *t*BuLi. DFT calculations support the conclusion that the rearrangement is thermodynamically favourable in the gas phase and in THF and show that the rearrangement is enthalpically driven.

Introduction

Applications of phosphorus ylides as ligands in inorganic chemistry were first introduced by Schmidbaur, opening up a rich area of transition and main group metal coordination chemistry.[1,2] Our interest in this area has recently focused on the triple deprotonation of the phosphonium salts $[R'P(CH_2R)_3]^+X^-$ (X = a halide ion) to give ylides of the type $[R'P(CHR)_3]^{2-}$ (Scheme 1).[3] Previously, we were able to structurally authenticate the first (and currently the only) example of this type of organometallic ligand, present in the lithiate $[\{PhP(CH_2)_3\}_2(Li{\cdot}THF)_4]$.[3] We also showed that the $[PhP(CH_2)_3]^{2-}$ dianion of the latter can be transferred smoothly to other metal centres.[4] The metal-exchange reaction with $FeBr_2$ afforded the unusual hydride complex $[\{PhP(CH_2)_3Fe\}_4(\mu_4\text{-}H)]^-$, composed of a tetrahedron of Fe^{II} atoms with a μ_4-H at the centre of the cluster.



Scheme 1. Deprotonation of phosphonium cations $[R'P(CH_2R)_3]^+$ to give tripodal ylide ligands of the type $[R'P(CHR)_3]^{2-}$.

Encouraged by these results, we have begun to synthesise a range of phosphonium salts containing various bridgehead (R′) and pendant (R) groups, aiming to improve the solubility and the donor/acceptor character of the tripodal ylide frameworks obtained on deprotonation. We note that, apart from our own studies, almost nothing is known about the reactivity of these key precursors. Relevant to the current work, the synthesis of phosphonium salt [2,4,6-$Me_3C_6H_2PMe_3]^+I^-$ (**1**) was first reported around 80 years ago but,[5] to the best of our knowledge, it has never been explored further. In this paper we show that the bridgehead (R′) group is not merely a spectator but that its choice is highly important to the formation of stable tripodal ylide ligands. Specifically, the presence of the mesityl functionality gives rise to a rearrangement, previously unknown in phosphonium chemistry, in which the phosphonium centre of the ligand is transferred quantitatively onto the *ortho*-CH position in the presence of *t*BuLi.

Results and Discussion

A particular issue with the previously investigated $[PhP(CH_2)_3]^{2-}$ ligand is the low solubility of the lithiate $[\{PhP(CH_2)_3\}_2(Li{\cdot}THF)]$ and the metal complexes formed in metal–ligand exchange reactions.[6] This drawback has thwarted further exploration of the coordination chemistry of the $[PhP(CH_2)_3]^{2-}$ ligand by us to date. The starting point in the current studies was therefore to provide related lithiates containing a broader range of $[R'P(CHR)_3]^{2-}$ ligands that have greater solubility, making them more useful precursors for metal-exchange reactions (particularly with regard to obtaining crystalline products). This can be achieved by modifying the bridgehead (R′) or pendant (R) groups. In order not to crowd the ligands sterically in the

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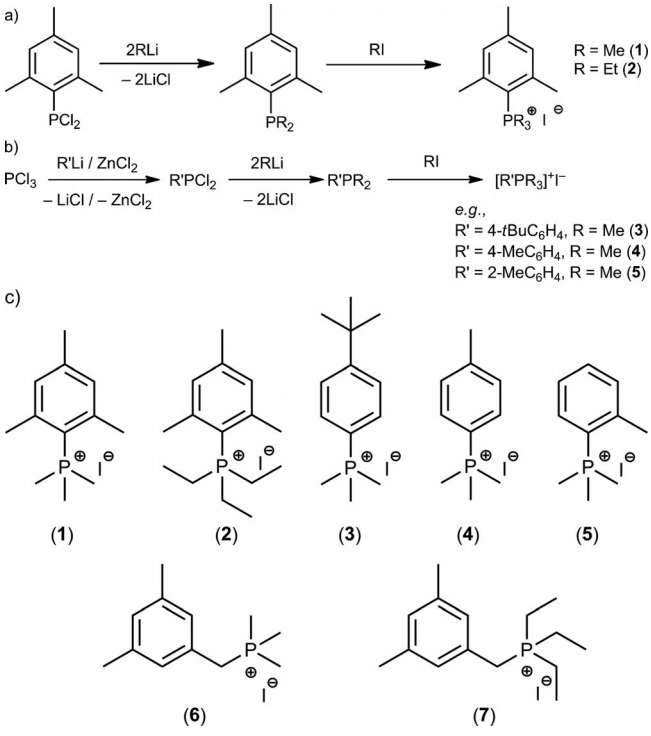
domain of the three anionic C atoms, we elected to focus on the bridgehead position. Mesityl derivative [2,4,6-$Me_3C_6H_2P(CH_2)_3]^{2-}$ was one obvious target since the mesityl group has long been employed to increase solubility and aid crystallisation in ligand chemistry.

Phosphonium salt [2,4,6-$Me_3C_6H_2P(CH_3)_3]^+I^-$ (**1**) was easily obtained by a modification of the procedure outlined in the literature[5] in which 2,4,6-$Me_3C_6H_2PCl_2$ is reacted with MeLi (2 equiv.) in Et_2O, the LiCl produced is filtered off, and the filtrate is reacted directly with MeI (1 equiv.) (Scheme 2a). It was obtained in 59% yield by crystallisation of the residue from anhydrous methanol (see Exp. Sect.). This procedure is also readily applicable to the modifications of the pendant (R) groups, as shown by the synthesis of [2,4,6-$Me_3C_6H_2PEt_3]^+I^-$ (**2**) (80% crystalline yield) by using EtLi and EtI in place of MeLi and MeI (see Supporting Information). The 2,4,6-$Me_3C_6H_2PCl_2$ starting material is easily prepared by the reaction of 2,4,6-$Me_3C_6H_2Li$ with PCl_3 according to the method of Oshikawa et al.[7] However, the monosubstitution reaction cannot easily be controlled where less sterically bulky groups are involved. In these cases we have found that the reactions of R′ZnCl (generated in situ from $ZnCl_2$ and R′Li at –78 °C) with PCl_3 offers a general route to the precursors $R'PCl_2$, which can be used in an identical way, as previously mentioned, to give phosphonium salts $[R'PR_3]^+I^-$. (Scheme 2b).[8] Phosphonium salts [(4-*t*BuC_6H_4)$PMe_3]^+I^-$ (**3**), [(4-MeC_6H_4)-$PMe_3]^+I^-$ (**4**) and [(2-MeC_6H_4)$PMe_3]^+I^-$ (**5**) were prepared in this way (see Supporting Information).



Scheme 2. (a) Synthesis of **1** and **2**, (b) general approach to phosphonium salts of the type $[R'P(R)_3]^+I^-$, starting from PCl_3 (full experimental details on the syntheses and characterisation of **1**, **2**, **3**, **4** and **5** are found in the Supporting Information) and (c) all phosphonium salts synthesised and the rearranged products.

Phosphonium salts **1** and **2** were fully characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and C, H elemental analysis. The H-coupled ^{31}P NMR spectrum of **1** is particularly diagnostic, showing a 10-line binomial multiplet at δ = 20.1 ($^2J_{H-P}$ = 13.7 Hz) ppm, while the spectrum of **2** consists of a broad multiplet at δ = 39.0 ppm. In addition, the single-crystal X-ray analyses of both **1** and **2** were obtained in order to provide further, unequivocal support for their structures prior to studies of their rearrangement with *t*BuLi. The structure of **1** shows no unexpected features and is presented in Figure 1.[9] The structure of **2** can be seen in the Supporting Information.

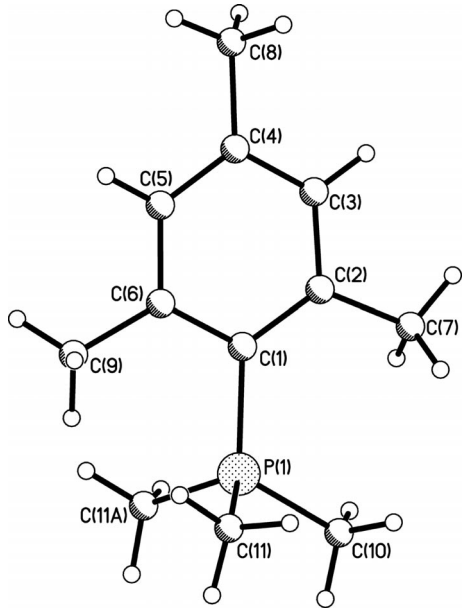


Figure 1. Structure of the $[2,4,6\text{-}Me_3C_6H_2PMe_3]^+$ cation of **1**. Selected bond lengths [Å] and angles [°]: P(1)–C(1) 1.806(3), P(1)–C(10,11) range 1.786(3)–1.796(3); C–P–C range 103.3(1)–118.6(2).

Surprisingly, in preliminary small-scale studies, the lithiation of **1** with *t*BuLi in THF (1:3 equiv., respectively) led to the isolation of crystals of benzylic phosphonium salt $[(3,5\text{-}Me_2C_6H_3)CH_2PMe_3]^+I^-$ (**6**). This was fully characterised by analytical and spectroscopic techniques. While (like **1**) the ^1H-coupled ^{31}P NMR spectrum of **6** reveals an apparent 10-line multiplet (in theory 12-line), this is found at significantly more positive chemical shift (δ = 26.1 ppm) than that in **1** (δ = 20.1 ppm). The presence of a benzylic CH_2 group is also obvious from the ^{13}C and ^1H NMR spectra, which show doublets for the C (δ = 30.7, $^1J_{C-P}$ = 50.3 Hz) and H atoms (δ = 4.10, $^2J_{H-P}$ = 16.00 Hz). The X-ray structure of **6** is entirely consistent with these data (Figure 2).[9]

The probable mechanism for this reaction is intramolecular on the basis of entropy and kinetics, and a direct indication of this is provided by the fact that a large reduction of the concentration of the starting phosphonium salts has no apparent effect on the reaction rate. However, we cannot exclude a contribution from an intermolecular pathway at this stage. The proposed intramolecular mechanism is outlined in Scheme 3. In Step 1, the deprotonation of the *ortho*-

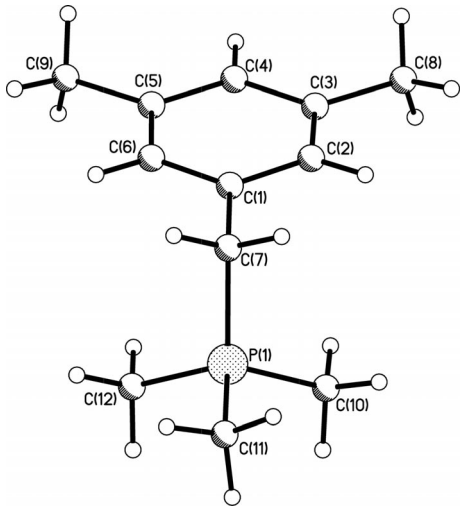
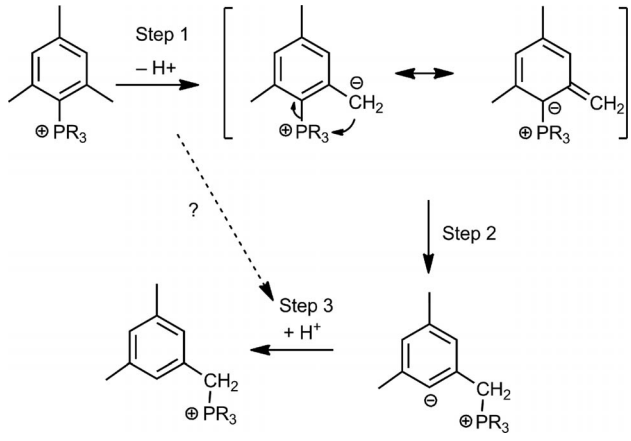


Figure 2. Structure of the $[(3,5\text{-}Me_2C_6H_3)CH_2PMe_3]^+$ cation of **6**. Selected bond lengths [Å] and angles [°]: P(1)–C(7) 1.817(6), P(1)–C(10,11,12) range 1.779(6)–1.793(6); C–P–C range 107.6(3)–110.9(3), P(1)–C(7)–C(1) 109.6(4).



Scheme 3. The proposed mechanism of the rearrangement reaction producing **6** (R = Me) and **7** (R = Et).

methyl group occurs, followed by intramolecular attack of the anionic C centre onto the phosphonium centre (Step 2). The overall reaction is potentially base-catalysed, because protonation of the final intermediate could be accomplished by deprotonation of the initial phosphonium salt. In an attempt to understand the mechanism further, a series of in situ ^{31}P NMR spectroscopic studies were undertaken in THF as the solvent. These studies reveal that: (1) conversion of **1** into **6** does not occur (even with prolonged reflux) without the addition of *t*BuLi; (2) complete conversion occurs within 18 h at reflux, in THF; and (3) quantitative conversion of **1** into **6** requires a 1:1 stoichiometric ratio of *t*BuLi/**1**, and substoichiometric amounts of *t*BuLi result in an incomplete reaction (i.e., addition of 0.5 equiv. of *t*BuLi results in the rearrangement of only half of the **1** into **6**). These features strongly indicate that the reaction is *not* catalytic and that Steps 1 and 3 (Scheme 3) are not coupled. In the absence of an added acid to complete the protonation in Step 3 of the reaction, the only possible proton source available is the solvent (THF). Previous precedents for the role of THF as a proton source in reactions with alkali metal organometallics are well established.[10] On the basis of the above NMR spectroscopic studies, a preparative-scale synthesis of **6** was developed (giving a 48% crystalline yield) by the 1:1 reaction of *t*BuLi/**1** at reflux in THF for 18 h (see Exp. Sect.). The crude solid residue from the reaction is crystallised from EtOH (acting jointly as a solvent and proton source).

We were also able to show that the same rearrangement occurs in the case of phosphonium salt **2**, which gives benzylic phosphonium salt $[(3,5\text{-}Me_2C_6H_3)CH_2PEt_3]^+I^-$ (**7**) (in 55% crystalline yield after workup, see Supporting Information). In situ ^{31}P NMR spectroscopic studies show exactly the same features as described previously for the rearrangement of **1** into **6**. In contrast, in situ ^{1}H and ^{31}P NMR spectroscopic studies of the crude products of the reactions of **3** and **4** with 3 equiv. of *t*BuLi in THF strongly suggest that the ligands are deprotonated solely at the P–Me groups, giving complexes of the type $[\{4\text{-}R''C_6H_4\text{-}P(CH_2)_3\}(Li{\cdot}THF)_n]_m$ {R″ = *t*Bu (**8**), R″ = Me (**9**)}. Particularly diagnostic are the upfield shifts of the doublet resonances of the $P(CH_3)_3$ protons of **3** and **4** on addition of *t*BuLi (moving from ca. δ = 2.60 to 1.52 ppm), which is associated with the build-up of negative charge on the CH_2 groups of the $[R'P(CH_2)_3]^{2-}$ anions (see Supporting Information).[3] The fact that no rearrangement of the 2-Me phosphonium salt **5** was also observed under these conditions suggests that the rearrangement is highly substrate-dependent.

Although this phosphonium rearrangement has, to the best of our knowledge, never been observed before, it clearly bears a close relationship to a few previously reported reactions involving *ortho*-C–H deprotonation of 2-methyl-substituted phenol, aniline and aryl Grignard reagents.[11] Perhaps the closest of these is the rearrangement of 2-methylphenylmagnesium bromide into benzylmagnesium bromide.[11b]

Hybrid DFT calculations were performed with the B3LYP[12] functional and the LanL2DZ basis set[13] in order to examine the thermodynamics of the rearrangement of the phosphonium cations of **1** and **2** into benzylic phosphonium cations **6** and **7**, respectively. The results for the gas-phase and solution-phase (THF) reactions are shown in Table 1.

These calculations show (as expected) that the gas-phase and solution-phase reactions are thermodynamically favourable, $\Delta G°$ becoming more favourable in THF. This dependence on solvent polarity is perhaps unsurprising, since the stability of the phosphonium cation reactants and products will be very sensitive to solvent–cation interactions. Clearly the rearrangement is strongly enthalpically driven, $\Delta H°$ accounts for most of the thermodynamic favourability and $\Delta S°$ is small and positive in both the gas-phase and in THF. Interestingly, DFT calculations of the rearrangement of the 2-Me phosphonium derivative **5** show a significant reduction in favourability, in line with the ex-

Table 1. DFT calculations on the reactions **1** → **6** and **2** → **7** in the gas phase and in THF.

Reaction[a]	$\Delta G°$ [kJ mol^{-1}]	$\Delta H°$ [kJ mol^{-1}]	$\Delta S°$ [J mol^{-1} K^{-1}]
Gas-phase			
1 → **6**	–48.6	–41.7	19.0
2 → **7**	–38.2	–31.3	17.4
THF			
1 → **6**	–62.1	–53.0	26.8
2 → **7**	–57.5	–49.2	25.3

[a] The data in the gas phase concern the isolated cations, whereas those in THF relate to the salts (including I^-), all data is at 298.15 K.

perimentally observed substrate dependence.[14] Further theoretical studies are currently underway to probe the mechanism of the reaction, particularly the transition state and the intermediate involved in the second step of the reaction (Scheme 3) and will be reported in a future full paper on this work.

Conclusions

The primary conclusion of the current study is that mesitylphosphonium salts rearrange intramolecularly in the presence of organometallic bases to give benzylic phosphonium salts. Although this new rearrangement may have some synthetic uses, its main influence on the design of new phosphonium precursors to the desired $[R'P(CHR)_3]^{2-}$ ligands is that the mesityl substituent should be avoided on aryl bridgeheads (R′). Instead, using substituents (like those present on the phosphonium salts **3**–**5**) is a better strategy for promoting greater solubility (without the danger of rearrangement).

Experimental Section

All syntheses were undertaken under dry, O_2-free N_2, on a vacuum line. A glove-box was used to handle and store the products. The phosphonium salts are not air-sensitive but are hygroscopic to varying degrees. The syntheses of **1** and **6** are given here, and the syntheses and characterisation of **2**, **3**, **4**, **5**, **7**, **8** and **9** are provided in the Supporting Information. It can be noted that the literature procedure for the synthesis of **1** (ref.[5]) only gives a brief outline of the method and no detailed characterisation.

1: To a solution of 2,4,6-$Me_3C_6H_2PCl_2$ (26.5 mmol, 5.87 g) in anhydrous Et_2O (60 mL) was added dropwise methyllithium (55.0 mmol, 35 mL, 1.6 M solution, diethyl ether) at –78 °C and the mixture was stirred (15 min). The reaction was warmed to room temperature and left to stir (18 h). The LiCl precipitate was filtered (P4, Celite) to give a colourless, cloudy solution (the cloudiness is LiCl, which is impossible to remove completely). The filtrate was treated with iodomethane (26.5 mmol, 3.76 g, 1.65 mL) dropwise at room temperature, with stirring, to give a precipitate, and the reaction mixture was stirred (18 h). The diethyl ether was removed under vacuum to give a white solid, replaced with anhydrous methanol (50 mL), and any remaining undissolved solid was heated into solution. The solution was stored at –30 °C (18 h) to give large colourless, needle-like crystals. The solution was removed by syringe and the crystals were dried and isolated. Yield (first batch) 5.07 g (59%). ^{1}H NMR (400.14 MHz, $CDCl_3$, +25 °C): δ = 2.29 [br. s, 3 H, *p*-CH_3(mes)], 2.61 [br. s, 6 H, 2× *o*-CH_3(mes)], 2.65 [d, $^2J_{P-H}$ = 12.00 Hz, 9 H, P(CH_3)$_3$], 6.98 (d, $^4J_{P-H}$ = 4.00 Hz, 2 H, Ar C*H*) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, +25 °C): δ = 15.9 [d, $^1J_{P-C}$ = 54 Hz, P(*C*H$_3$)$_3$], 21.1 [br. s, *p*-*C*H$_3$(mes)], 24.7 [s, *o*-*C*H$_3$(mes)], 115.5 [d, $^1J_{P-C}$ = 82 Hz, *ipso*-P*C*(mes)], 132.5 (d, $^3J_{P-C}$ = 11 Hz, Ar *C*H), 142.4 [d, $^2J_{P-C}$ = 11 Hz, *o*-*C*(CH$_3$)(mes)], 144.8 [s, *p*-*C*(CH$_3$)(mes)] ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$, +25 °C, rel. 85% H_3PO_4 in D_2O): δ = 20.1 (binomial decet, $^2J_{P-H}$ = 13.7 Hz) [^{31}P(^{1}H), δ = 20.1 (s)] ppm. Electrospray HR-MS (positive ion): calcd. for $[2,4,6\text{-}Me_3C_6H_2P(CH_3)_3]^+$ 195.1303; found 195.1299. $[2,4,6\text{-}Me_3C_6H_2P(CH_3)_3]^+I^-$ (**1**): calcd. C 44.7, H 6.3, found C 44.7, H 6.3.

6: To a solution of **1** (1.0 mmol, 0.32 g) in anhydrous THF (20 mL) was added dropwise *tert*-butyllithium (1.0 mmol, 0.59 mL, 1.7 M solution, pentanes) at –78 °C, and the mixture was stirred (30 min). The reaction mixture was warmed to room temperature to give a cloudy yellow solution. A reflux condenser was attached and the reaction was heated to reflux (18 h), which resulted in a pale yellow cloudy solution. The reaction was cooled to room temperature to give a crop of fine colourless crystals. The solution was removed by syringe, and the solid was dried under vacuum. Yield 78 mg (48%). ^{1}H NMR (400.14 MHz, $CDCl_3$, +25 °C): δ = 2.17 [d, $^2J_{P-H}$ = 16.00 Hz, 9 H, P(CH_3)$_3$], 2.31 [s, 6 H, *m*-CH_3(Ar); 4.10, d, $^2J_{P-H}$ = 16.00 Hz, 2 H, Ar-CH_2P(CH$_3$)$_3$], 6.96 (br. s, 2 H, Ar C*H*), 6.99 (br. s, 1 H, Ar C*H*) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, +25 °C): δ = 8.92 [d, $^1J_{P-C}$ = 54.3 Hz, P(*C*H$_3$)$_3$], 21.2 [s, *m*-*C*H$_3$(Ar)] 30.7 [d, $^1J_{P-C}$ = 50.3 Hz, *C*H$_2$P(CH$_3$)$_3$], 127.2 [d, $^2J_{P-C}$ = 9.0 Hz, *ipso*-P*C*(Ar)], 127.6 (d, $^3J_{P-C}$ = 5.0 Hz, Ar *C*H), 130.4 (d, $^5J_{P-C}$ = 4.0 Hz, Ar *C*H), 139.4 [d, $^4J_{P-C}$ = 4.0 Hz, *m*-*C*(CH$_3$)(Ar)] ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$, +25 °C, rel. 85% H_3PO_4 in D_2O): δ = 26.1 (apparent 10-line multiplet, $^2J_{P-H}$ = 14.5, 12.9 Hz) [^{31}P(^{1}H), δ = 26.1 (s)] ppm. Electrospray HR-MS (positive ion): calcd. for $[(3,5\text{-}Me_2C_6H_3)CH_2PMe_3]^+$ 195.1381; found 195.1373. $[(3,5\text{-}Me_2C_6H_3)CH_2PMe_3]^+I^-$ (**6**): calcd. C 44.7, H 6.3, found C 44.3, H 6.0.

CCDC-962443 (for **1**), -962444 (for **2**), -962446 (for **3**), -962445 (for **4**), -973078 (for **5**), -962447 (for **6**) and -962448 (for **7**) contain the supplementary crystallographic files for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H, ^{13}C, ^{31}P, ^{31}P{^{1}H} NMR spectra, electrospray HR-MS (positive ion) of **1**, **2**, **3**, **4**, **5**, **6** and **7**. Syntheses of **2**, **3**, **4**, **5**, **7**, **8** and **9**.

Acknowledgments

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[14] Data for **5**: gas-phase $\Delta G°$ = –14.6 kJ mol^{-1}, $\Delta H°$ = –11.7 kJ mol^{-1}, $\Delta S°$ = 10.1 J mol^{-1} K^{-1} and in solution $\Delta G°$ = –26.7 kJ mol^{-1}, $\Delta H°$ = –21.4 kJ mol^{-1}, $\Delta S°$ = 15.4 J mol^{-1} K^{-1}.

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