‘Phospha-Wittig’ reactions using isolable phosphoranylidenephosphines ArP=PR$_3$ (Ar = 2,6-Mes$_2$C$_6$H$_3$ or 2,4,6-But$_3$C$_6$H$_2$)

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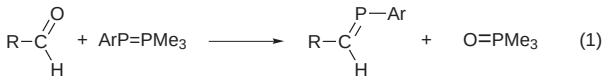
Phosphoranylidenephosphines DmpP=PMe$_3$ (1a, Dmp = 2,6-Mes$_2$C$_6$H$_3$) and Mes*P=PMe$_3$ (1b, Mes* = 2,4,6-But$_3$C$_6$H$_2$) act as ‘Phospha-Wittig’ reagents with aldehydes providing phosphaalkenes [ArP=C(H)R] in high yields.

The successful synthesis of a ‘true phosphobenzene’, Mes*P=PMes* (Mes* = 2,4,6-But$_3$C$_6$H$_2$),[1] signaled a new era in the study of phosphorus–phosphorus double bonds.[2] We have recently uncovered reactions of [Cp$_2$Zr=PDmp(PR$_3$)] (Dmp = 2,6-Mes$_2$C$_6$H$_3$) which produce phosphoranylidenephosphines DmpP=PR$_3$ (R = Me or Bu).[3] Phosphoranylidenephosphines are formally the products of phosphinidene transfer to phosphines.[4] These novel materials contain PP multiple bonding of a very differing nature, as exemplified by the following resonance forms:

$$\mathrm{ArP{=}PR_3 \leftrightarrow Ar\bar{P}{-}\overset{+}{P}R_3}$$

Similar resonance forms are commonly drawn for Wittig reagents R$_2$C=PR$_3$, and the nature of the bonding between the P and C atoms in these species has been reviewed.[5] Bearing such a close kinship to Wittig reagents, it was anticipated that phosphoranylidenephosphines could act as potential ‘phospha-Wittig’ reagents by reacting with aldehydes to generate phosphaalkenes RP=C(H)R [eqn. (1)]. Several transition metal containing systems have been reported that accomplish similar transformations.[6–8] Herein we present the reactivity of the phosphoranylidenephosphines DmpP=PMe$_3$ **1a** and Mes*P=PMe$_3$ **1b** with aldehydes to generate phosphaalkenes.



(1)

Compounds **1a** and **1b** are conveniently prepared by reduction of either DmpPCl$_2$ or Mes*PCl$_2$ with Zn dust in the presence of excess PMe$_3$ in 88–95% yields [**1a**: ^{31}P NMR (C$_6$D$_6$), δ −2.8, −114.7 (J_{PP} 582 Hz); **1b**: ^{31}P NMR (C$_6$D$_6$), δ 4.7, −134.0 (J_{PP} 581 Hz)].[3]‡ In the absence of air and water, compounds **1a**, **b** are stable yellow crystalline solids. Both **1a** and **1b** slowly decompose in solution to lose PMe$_3$ and form DmpP=PDmp and Mes*P=PMes*, respectively (days to weeks).[9]

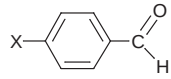
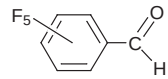
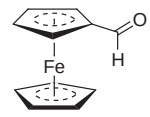
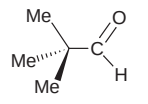
Reactions of **1a** and **1b** with C=O containing molecules were thus examined. A series of *para*-substituted benzaldehydes reacted with **1a**, **b** in THF to produce the desired phosphaalkenes in excellent isolated yields (Table 1). Work-up involves removal of THF and extraction of the phosphaalkene into hexanes to remove the relatively insoluble O=PMe$_3$. Reaction times, as well as product yields, varied with the nature of the substituent; the most electron releasing substituents required the longest reactions times (2–24 h) and provided the lowest yields. Each reaction produced a single isomer of the phosphaalkene, and the $^2J_{PH}$ coupling constants (24–25 Hz) are consistent with an assignment of *E*-isomers for the products.[10]§

Our new protocol can be contrasted to multistep procedures utilizing sterically hindered primary phosphines such as Mes*PH$_2$. For example, compound **2b** has been prepared in 80% yield after purification by chromatography [eqn. (2)].[10] The primary phosphine Mes*PH$_2$ is obtained by LiAlH$_4$ reduction of Mes*PCl$_2$ and isolated in 80% yield after recrystallization.[11] Our procedure thus represents not only a saving in time but also of material due to phosphaalkene access from the more readily available dichlorophosphine precursors. A more dramatic advance in the utility of the current reaction was realized by the discovery that compounds **1a** and **1b** can be generated and used *in situ*. For example, reaction of DmpPCl$_2$, benzaldehyde, zinc dust and excess PMe$_3$ gives an isolated yield of 95% of DmpP=C(H)Ph. Likewise, Mes*P=C(H)Ph is obtained in 87% yield from Mes*PCl$_2$ under the same conditions.

(2)

The scope of the phosphaalkene forming reactions using **1a** was also investigated. Pentafluorobenzaldehyde, ferrocenecarboxaldehyde and pivaldehyde provided phosphaalkenes **7a**–**9a** in good yields, demonstrating the remarkable tolerance of the phosphoranylidenephosphines to varying functional groups. Reactions of **1a** with ketones proved more problematic,

Table 1 Reactions of aldehydes to give phosphaalkenes

Aldehyde R(H)C=O		Phosphaalkene R(H)C=PAr	Yield (%)	^{31}P{^{1}H} (C$_6$D$_6$)§ δ
	X = H	**2a**	94	240.9
		2b	93	258.5[10]
	Cl	**3a**	90	243.8
		3b	90	261.4
	NO_2	**4a**	92	265.6
		4b	92	284.6
	OMe	**5a**	97	225.4
		5b	87	245.1[15]
	NMe_2	**6a**	78	210.4
		**7a**	96	286.8 (t, J_{PF} 98Hz)
		7b	97	304.3 (t, J_{PF} 93Hz)
		**8a**	61	222.1
		**9a**	91	221.2

however. Acetophenone, benzophenone and cyclohexanone showed no evidence of phosphaalkene formation and yielded extensive amounts of DmpP=PDmp over time.

Effords to extend the reactivity of phosphoranylidenephosphines to systems having less steric hindrance than Dmp or Mes* have been partially successful. Attempts to isolate TripP=PMe_3 (Trip = 2,4,6-$Pr^i_3C_6H_2$) by reduction of $TripPCl_2$ with Zn dust in the presence of PMe_3 resulted in rapid formation of $(TripP)_3$.[12] Addition of benzaldehyde, however, to such reactions results in mixtures of $(TripP)_3$ and TripP=C(H)Ph {$^{31}P\{^1H\}$ (C_6D_6), δ 254.7; ^1H NMR, δ 8.99 [TripP=C(*H*)Ph, d, J_{HP} 25.6 Hz]}, suggesting the presence of a transient TripP=PMe_3 capable of effecting phosphaalkene formation.

Reactions of phosphoranylidenephosphines with aldehydes would be of greater synthetic value if the more readily handled (and cheaper) PPh_3 could replace PMe_3 in these reactions. Unfortunately, efforts to prepare DmpP=PPh_3 by reduction of $DmpPCl_2$ with Zn in the presence of PPh_3 resulted in isolation of DmpP=PDmp. Attempts to generate DmpP=PPh_3 *in situ* for reaction with benzaldehyde also failed. Exchange of the PMe_3 unit in **1a** with added PPh_3 also proved futile. The PMe_3 groups in **1a** and **1b** do undergo exchange with certain non-hindered trialkylphosphines in solution. For example, **1a** and **1b** react quickly with PBu_3 to produce mixtures of **1a**, PMe_3 and DmpP=PBu_3 [**1c**, ^{31}P NMR(C_6D_6), δ 24.1, −151.3 (J_{PP} 589 Hz)] and mixtures of **1b**, PMe_3 and Mes*P=PBu_3 [**1d**, ^{31}P NMR(C_6D_6), δ 19.9, −153.7 (J_{PP} 612 Hz)], respectively.[13,14] Compound **1c** can also be generated *in situ* (as above) from PBu_3 and $DmpPCl_2$, which in the presence of benzaldehyde yields the phosphaalkene DmpP=C(H)Ph and O=PBu_3 in good yields. Work-up, however, requires more effort than the PMe_3 system due to the decreased volatility of PBu_3.

In conclusion, we have demonstrated that readily prepared and isolable phosphoranylidenephosphines are apt phosphinidene carriers in phospha-Wittig reactions. Our procedure represents a significant advance for the synthesis of phosphaalkenes as it utilizes dichlorophosphines directly, rather than derived primary phosphines. High yields and functional group tolerance are further highlights of this phospha-Wittig approach. Further studies of the phosphinidene and atom transfer reactions of these conveniently prepared phosphinidene-carriers are underway.

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Notes and References

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‡ Compound **1a**: ^1H NMR(C_6D_6), δ 7.08 (t, 1 H, J_{HH} 8 Hz), 6.96 (d, 2 H, J_{HH} 8 Hz), 6.90 (s, 4 H), 2.37 (s, 12 H), 2.22 (s, 6 H), 0.58 (dd, 9 H, $^2J_{HP}$ 12 Hz, $^3J_{HPP}$ 3 Hz). HRMS (EI) *m/z* calc. for $C_{27}H_{34}P_2$ 420.2138; found 420.2127. Compound **1a** has also been structurally characterized.[3] Compound **1b**: ^1H NMR(C_6D_6), δ 7.42 (s, 2 H), 1.90 (s, 18 H), 1.36 (s, 9 H), 0.69 (d, 9 H, $^2J_{HP}$ 11.5 Hz). HRMS (EI) *m/z* calc. for $C_{21}H_{38}P_2$ 352.2451; found 352.2446.

§ Other data for phosphaalkenes: **2a**: mp 162–164 °C; ^1H NMR(C_6D_6), δ 9.00 (d, $^2J_{HP}$ 25.0 Hz, 1 H), 7.21 (t, J_{HH} 8.0 Hz, 1 H), 7.16 (m, 2 H), 7.00 (d, J_{HH} 7.6 Hz, 2 H), 6.78 (s, 4 H), 6.73 (m, 1 H), 2.20 (s, 12 H), 2.07 (s, 6 H); HRMS (EI) *m/z* calc. for $C_{31}H_{31}P$ 434.2165; found 434.2141. **2b**: mp 149–152 °C (lit. 152–153 °C[10]); ^1H NMR (C_6D_6), δ 8.19 (d, $^2J_{HP}$ 25.4 Hz, 1 H), 7.64 (d, $^4J_{HP}$ 1.2 Hz, 2 H), 7.46 (m, 2 H), 7.00 (m, 3 H), 1.60 (s, 18 H), 1.35 (s, 9 H). **3a**: mp 113–115 °C; ^1H NMR(C_6D_6), δ 8.80 (d, $^2J_{HP}$ 24.9 Hz, 1 H), 7.20 (t, J_{HH} 7.6 Hz, 1 H), 6.98 (d, J_{HH} 7.4 Hz, 2 H), 6.83 (m, 2 H), 6.80 (s, 4 H), 6.66 (d, J_{HH} 8.5 Hz, 2 H), 2.18 (s, 12 H), 2.08 (s, 6 H); HRMS (EI) *m/z* calc. for $C_{31}H_{30}PCl$ 468.1776; found 468.1788. **3b**: mp 124–126 °C; ^1H NMR(C_6D_6), δ 7.97 (d, $^2J_{HP}$ 25.1 Hz, 1 H), 7.63 (s, 2 H), 7.13 (m, 2 H), 6.96 (d, J_{HH} 8.6 Hz, 2 H), 1.57 (s, 18 H), 1.35 (s, 9 H); HRMS (EI) *m/z* calc. for $C_{25}H_{34}PCl$ 400.2089; found 400.2086. **4a**: mp 131–132 °C; ^1H NMR(C_6D_6), δ 8.67 (d, $^2J_{HP}$ 24.9 Hz, 1 H), 7.40 (d, J_{HH} 8.6 Hz, 2 H), 7.20 (t, J_{HH} 7.7 Hz, 1 H), 6.96 (d, J_{HH} 7.7 Hz, 2 H), 6.80 (s, 4 H), 6.70 (m, 2 H), 2.14 (s, 12 H), 2.08 (s, 6 H); HRMS (EI) *m/z* calc. for $C_{31}H_{30}PNO_2$ 479.2016; found 479.2028. **4b**: mp 129–131 °C; ^1H NMR(C_6D_6), δ 7.83 (d, $^2J_{HP}$ 24.8 Hz, 1 H), 7.73 (d, J_{HH} 8.8 Hz, 2 H), 7.62 (s, 2 H), 7.01 (m, 2 H), 1.52 (s, 18 H), 1.35 (s, 9 H); HRMS (EI) *m/z* calc. for $C_{25}H_{34}PNO_2$ 411.2329; found 411.2329. **5a**: mp 121–122 °C; ^1H NMR(C_6D_6), δ 9.00 (d, $^2J_{HP}$ 24.9 Hz, 1 H), 7.22 (t, J_{HH} 7.6 Hz, 1 H), 7.11 (m, 2 H), 7.02 (d, J_{HH} 7.6 Hz, 2 H), 6.81 (s, 4 H), 6.34 (d, J_{HH} 8.6 Hz, 2 H), 3.04 (s, 3 H), 2.23 (s, 12 H), 2.09 (s, 6 H); HRMS (EI) *m/z* calc. for $C_{32}H_{33}PO$ 464.2271; found 464.2260. **5b**: mp 164–166 °C; ^1H (C_6D_6): δ 8.20 (d, $^2J_{HP}$ 25.1 Hz, 1 H), 7.66 (d, $^4J_{HP}$ 1 Hz, 2 H), 7.41 (m, 2 H), 6.44 (d, J_{HH} 8.4 Hz, 2 H), 3.20 (s, 3 H), 1.64 (s, 18 H), 1.37 (s, 9 H); HRMS (EI) *m/z* calc. for $C_{26}H_{37}PO$ 396.2584; found 396.2584. **6a**: mp 181–183 °C; ^1H NMR (C_6D_6): δ 9.06 (d, $^2J_{HP}$ 24.4 Hz, 1 H), 7.22 (m, 3 H), 7.04 (d, J_{HH} 7.6 Hz, 2 H), 6.82 (s, 4 H), 6.09 (d, J_{HH} 8.8 Hz, 2 H), 2.27 (s, 12 H), 2.22 (s, 6 H), 2.10 (s, 6 H); HRMS (EI) *m/z* calc. for $C_{33}H_{36}PN$ 477.2588; found 477.2596. **7a**: mp 159–161 °C; ^1H NMR (C_6D_6), δ 8.73 (d, $^2J_{HP}$ 24.9 Hz, 1 H), 7.21 (t, J_{HH} 7.7 Hz, 1 H), 6.97 (d, J_{HH} 7.4 Hz, 2 H), 6.82 (s, 4 H), 2.19 (s, 12 H), 2.06 (s, 6 H); HRMS (EI) *m/z* calc. for $C_{31}H_{26}PF_5$ 524.1694; found 524.1704. **7b**: mp 130–133 °C; ^1H NMR (C_6D_6), δ 7.94 (d, $^2J_{HP}$ 24.8 Hz, 1 H), 7.63 (d, J_{HP} 1.0 Hz, 2 H), 1.58 (s, 18 H), 1.32 (s, 9 H); HRMS (EI) *m/z* calc. for $C_{25}H_{30}PF_5$ 456.2007; found 456.2010. **8a**: mp 104–106 °C; ^1H (C_6D_6), δ 8.77 (d, $^2J_{HP}$ 24.2 Hz, 1 H), 7.20 (t, J_{HH} 7.7 Hz, 1 H), 6.96 (d, J_{HH} 8.1 Hz, 2 H), 6.84 (s, 4 H), 4.15 (m, 2 H), 3.89 (m, 2 H), 3.73 (d, *J* 0.5 Hz, 5 H), 2.21 (s, 12 H), 2.14 (s, 6 H); HRMS (EI) *m/z* calc. for $C_{35}H_{35}PFe$ 542.1817; found 542.1837. **9a**: mp 127–129 °C; ^1H NMR (C_6D_6), δ 8.37 (d, $^2J_{HP}$ 25.1 Hz, 1 H), 7.18 (t, J_{HH} 7.6 Hz, 1 H), 6.97 (d, J_{HH} 8.1 Hz, 2 H), 6.83 (s, 4 H), 2.16 (s, 12 H), 2.15 (s, 6 H), 0.79 (d, $^4J_{HH}$ 1.9 Hz, 9 H); HRMS (EI) *m/z* calc. for $C_{29}H_{35}P$ 414.2479; found 414.2474.

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