

Hybrid ligands: synthesis, characterization and co-ordinative properties of a mixed phosphine- β -ketophosphorus ylide

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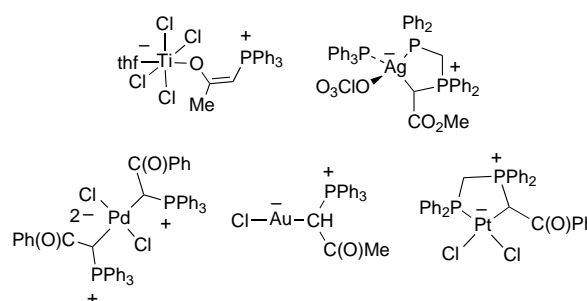
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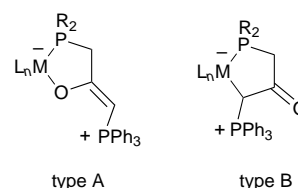
Direct *C*-phosphination at the methyl carbon of the keto-stabilized ylide MeC(O)CH=PPh₃ was achieved using 2 equivalents of LiBu and 1 equivalent of PPh₂Cl. The structure of the resultant phosphine-phosphorus ylide, Ph₂PCH₂C(O)CH=PPh₃, was shown by an X-ray diffraction study to comprise a 1 : 1 mixture of two rotamers built around the CH₂-C(O) axis, the C(=O)CH=PPh₃ moiety of both conformers adopting a cisoid form. A rotational barrier of 10 kJ mol⁻¹ between the two isomers was found using molecular-mechanics simulation. Oxidation of the ylide with sulfur resulted in quantitative formation of the corresponding phosphine sulfide Ph₂P(S)CH₂-C(O)CH=PPh₃. By treating 2 equivalents of Ph₃P=CHC(O)CH₂PPh₂ (L) with [{Pd(η^3 -C₃H₄Me-2)Cl}₂], the *P*-monodentate complex [PdCl(η^3 -C₃H₄Me-2)L] **1** was formed quantitatively. Reaction of 2 equivalents of L with [{PdCl(C₆H₄CH₂NMe₂-*o*)}]₂ in tetrahydrofuran afforded, in quantitative yield, the stable cationic complex [Pd(C₆H₄CH₂NMe₂-*o*)L]Cl **2** where the hybrid ligand is *P*,*O*-bonded to the palladium, thus illustrating the nucleophilic character of the oxygen atom of the ylide. The BF₄⁻ analogue of the latter complex, **3**, prepared in order to exclude counter-anion effects, was obtained by treating **1** with AgBF₄. The nickel complexes [Ni(η^5 -C₅Ph₅)L]X (X = I **4** or Br **5**), in which the ligand is bound as in **1** and **2**, were obtained by treating the corresponding [Ni(η^5 -C₅Ph₅)X(CO)] complexes with the ylide L.

Keto-stabilized phosphorus ylides of the type Ph₃PCH=C(O)R (R = alkyl, aryl or alkoxy) have been well studied in coordination chemistry,¹⁻¹¹ primarily because of their potential application for preparation of ethylene¹²⁻²⁰ and acetylene polymerization catalysts.²¹ With platinum and the coinage metals, such compounds usually co-ordinate *via* the ylidic carbon atom,²²⁻²⁴ whereas the early transition metals show a preference for binding at the oxygen atom.²⁵ This disparity in the binding mode is illustrated by the examples displayed in Scheme 1. It is interesting however that in certain platinum complexes co-ordination occurs through the oxygen atom,²⁷ although in solution such structures tend to be unstable with respect to isomerization to the corresponding *C*-co-ordinated species.² It is also known that low-valent metal atoms are capable of fragmenting carbonyl-stabilized ylides, leading in particular to acyl, alkylidene²⁸⁻³¹ or phosphinoenolato complexes.^{20,32} In contrast to phosphorus ylides where co-ordination does not take place at the phosphorus centre, the analogous phosphines bind to metals by way of the phosphorus(III) donor.

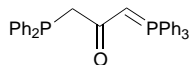
Hybrid ligands comprising mixed phosphine and phosphorus ylide subunits have long been known and exhibit interesting co-ordinative properties.⁵ Somewhat surprisingly, there are no known ylides having the generic formula Ph₃PCH=C(O)CH₂PR₂, a compound that combines a phosphine fragment with an ambidentate phosphorus ylide moiety. The interest in such multitopic ligands arises from their potential to form either five-membered *P*^{III},*O* (ketone) or *P*^{III},*C* (ylidic *C*) metallacycles. Furthermore, such structures are relevant to the preparation of bimetallic polymerization catalysts since they possess two discrete co-ordination domains suitable for connecting two metal centres in close proximity. A unique feature



Scheme 1 Examples of *C*- and *O*-bonded, keto-stabilized phosphorus ylides taken from the literature (Ti,²⁵ Ag,²² Pd,⁷ Au,⁴ Pt²⁶); thf = tetrahydrofuran



of hybrid ligands of this type is that both termini possess the necessary functionality to form phosphinoenolates³³⁻⁴³ around the central carbonyl. Using a previously developed methodology,⁴¹ the targeted hybrid Ph₂PCH₂C(O)CH=PPh₃ has now been synthesized in moderate yield and its ability to bind late transition metals is demonstrated. A remarkable feature of this ylide is that it forms *stable* palladium complexes by way of binding to the oxygen atom, these being the second known examples of such entities.



Experimental

General

All manipulations were carried out under an argon atmosphere using standard Schlenk-tube techniques. Solvents, including CDCl_3 , were dried over suitable reagents and freshly distilled under argon before use. Infrared spectra were recorded on an IFS 25 Bruker spectrometer. The ^1H NMR spectral data were referenced relative to residual protiated solvents (δ 7.27 for CDCl_3), ^{13}C relative to CDCl_3 (δ 77.0) and ^{31}P relative to external 85% H_3PO_4 . The mass spectrum of the compound $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$ was recorded on a TSQ70 Finnigan MAT instrument while spectra of other compounds were recorded on a ZAB HF VG analytical instrument using *m*-nitrobenzyl alcohol as matrix. The complexes $[\{\text{PdCl}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}o)\}_2]$,⁴⁴ $[\{\text{PdCl}(\text{C}_3\text{H}_4\text{Me})\}_2]$ ⁴⁵ and $[\text{Ni}(\eta^5\text{-C}_5\text{Ph}_5)(\text{X})(\text{CO})]$ ($\text{X} = \text{Br}$ or I)⁴⁶ were prepared according to published procedures. AgBF_4 was obtained from Aldrich Chemicals and silica gel 60 was obtained from Merck. Elemental analyses were performed by the Service de Microanalyse CNRS/Université Louis Pasteur and the Service Central du CNRS-Vernaison. The calculations were performed with HYPERCHEM⁴⁷ using PM3 parameters.

Syntheses

$\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$. A solution of LiBu^n (1.6 mol dm^{-3}) in hexane (8.30 cm^3 , 13.14 mmol) was added dropwise to a solution of $\text{Ph}_3\text{PCH}=\text{C}(\text{O})\text{Me}$ (2.000 g, 6.26 mmol) in thf (300 cm^3) maintained at -78°C . After 1 h a solution of PPh_2Cl (0.725 g, 3.29 mmol) in thf (60 cm^3) was added over a period of 1 h to the dark red mixture held at -78°C . The mixture was then stirred for 15 h at room temperature, before being concentrated to *ca.* 20 cm^3 . Addition of 12 mol dm^{-3} HCl (0.5 cm^3) caused the red colour to disappear. After removal of the solvent, the residue was dissolved in the minimum volume of CH_2Cl_2 and adsorbed onto a silica gel column (30 g, height *ca.* 70 cm, diameter 4 cm, 70–230 mesh). The column was first eluted with CH_2Cl_2 in order to eliminate an impurity, then with $\text{MeOH}-\text{CH}_2\text{Cl}_2$ (1:9 v/v) to yield $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ [$R_f(\text{thf}) = 0.71$]. Following chromatography, the phosphine may contain small amounts of an unidentified impurity [$R_f(\text{thf}) = 0.80$]. The latter remains attached to the Schlenk flask as a thin oily layer so that pure $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ can be isolated as white powder (1.750 g, 56%), m.p. 130–131 $^\circ\text{C}$. IR(KBr): 1545 cm^{-1} [$\nu(\text{C}=\text{O})$]. NMR: ^1H (C_6D_6), δ 3.47 [d, 2 H, PCH_2 , $^2J(\text{PH}) = 0.8$], 4.08 [d br, 1 H, $\text{P}=\text{CH}$, $^2J(\text{PH}) = 26.7$] and 6.79–7.80 (25 H, aromatic H); $^{31}\text{P}-\{^1\text{H}\}(\text{thf}-\text{C}_6\text{D}_6)$, δ 15.7 [d, PPh_3 , $^4J(\text{PP}) \approx 2$] and -14.6 [d, PPh_2 , $^4J(\text{PP}) \approx 2$]; $^{13}\text{C}-\{^1\text{H}\}(\text{C}_6\text{D}_6)$, δ 33.89 [pseudo t, PCH_2 , $J(\text{PC}) \approx 16$, $^3J(\text{P}'\text{C}) \approx 16$], 40.64 [dd, $\text{P}=\text{CH}$, $J(\text{PC}) \approx 109$, $^3J(\text{PC}) \approx 8$], 116.28–131.70 (aromatic C) and 178.94 [pseudo t, $\text{C}=\text{O}$, $^2J(\text{PC}) \approx 2J(\text{P}'\text{C}) \approx 6$ Hz] (Found: C, 78.75; H, 5.5. Calc. for $\text{C}_{33}\text{H}_{28}\text{OP}_2$: C, 78.85; H, 5.6%). Mass spectrum (FAB): m/z 519 ($M + \text{O} + \text{H}^+$, 100%).

$\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$. Octasulfur (0.010 g, 0.30 mmol) was treated with a solution of $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ (0.100 g, 0.20 mmol) in CH_2Cl_2 (10 cm^3). After 10 min the solution was concentrated to *ca.* 5 cm^3 and pentane was added to afford $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$ as a pale yellow powder (0.105 g, 98%), m.p. 146 $^\circ\text{C}$ (decomp.). IR(KBr): 1548s [$\nu(\text{C}=\text{O})$] and 632s cm^{-1} [$\nu(\text{P}=\text{S})$]. NMR: ^1H (CDCl_3), δ 3.69 [dd, 2 H, PCH_2 , $^2J(\text{PH}) = 14.6$, $^4J(\text{PH}) = 1.3$], 4.22 [d, 1 H, $\text{P}=\text{CH}$, $^2J(\text{PH}) = 24.8$] and 7.33–8.04 (25 H, aromatic H); $^{31}\text{P}-\{^1\text{H}\}(\text{CH}_2\text{Cl}_2-\text{C}_6\text{D}_6)$, δ 14.5 [d, PPh_3 , $^4J(\text{PP}) \approx 3$] and 40.3 [d, $\text{P}(\text{S})\text{Ph}_2$, $^4J(\text{PP}) \approx 3$]; $^{13}\text{C}-\{^1\text{H}\}(\text{CDCl}_3)$, δ 47.27 [dd, PCH_2 , $J(\text{PC}) \approx 45$, $^3J(\text{P}'\text{C}) \approx 14$],

55.07 [d, br, $\text{P}=\text{CH}$, $J(\text{P}'\text{C}) \approx 107$], 124.99–134.15 (aromatic C) and 180.79 [pseudo t, $\text{C}=\text{O}$, $^2J(\text{PC}) \approx 2J(\text{P}'\text{C}) \approx 3$ Hz] (Found: C, 73.9; H, 5.25. Calc. for $\text{C}_{33}\text{H}_{28}\text{OP}_2\text{S}$: C, 74.15; H, 5.3%). Mass spectrum (EI): m/z 534 (M , 18%).

$[\text{PdCl}(\text{C}_3\text{H}_4\text{Me-2})\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3\}]$ 1. Solid $[\{\text{PdCl}(\text{C}_3\text{H}_4\text{Me-2})\}_2]$ (0.098 g, 0.25 mmol) was added to a solution of $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3$ (0.250 g, 0.50 mmol) in CH_2Cl_2 (20 cm^3). After 2 h pentane was added, affording complex **1** as a pale yellow precipitate. The product was recrystallized from CH_2Cl_2 -pentane (0.280 g, 80%), m.p. 113–114 $^\circ\text{C}$. IR(KBr): 1543s cm^{-1} [$\nu(\text{C}=\text{O})$]. NMR: ^1H (CDCl_3), δ 1.66 (s, 3 H, Me), 2.56 (s br, 1 H, CH of allyl), 3.10 (s br, 1 H, CH of allyl), 3.15 [d, 1 H, CH of allyl, $^3J(\text{PH}) = 10$], 3.63 [dd, 2 H, PCH_2 , $^2J(\text{PH}) = 12$, $^4J(\text{PH}) = 1$], 4.19 [d, 1 H, CH of allyl, $^3J(\text{PH}) = 6$], 4.42 [d, 1 H, $\text{P}=\text{CH}$, $^2J(\text{PH}) = 23$] and 7.82–7.32 (25 H, aromatic H); $^{31}\text{P}-\{^1\text{H}\}(\text{CDCl}_3)$, δ 15.4 (s br) and 17.8 (s br); $^{13}\text{C}-\{^1\text{H}\}(\text{CDCl}_3)$, δ 22.96 (s, Me), 41.12 [pseudo t, PCH_2 , $^1J(\text{PC}) \approx 3J(\text{P}'\text{C}) = 16$], 53.20 [d, $\text{P}=\text{CH}$, $J(\text{PC}) = 100$ Hz], 59.68 (s, CH_2 of allyl), 67.87 (s, CH_2 of allyl), 125.31–133.73 (aromatic C + quaternary C of allyl) and 185.81 (s, CO) (Found: C, 59.65; H, 5.0. Calc. for $\text{C}_{37}\text{H}_{35}\text{ClOP}_2\text{Pd} \cdot 0.75 \text{CH}_2\text{Cl}_2$: C, 59.4; H, 4.8%). Mass spectrum (FAB): m/z 663.1 ($[M - \text{Cl}]^+$, 100%).

$[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}o)\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3\}]\text{Cl}$ 2. To a solution of $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ (0.134 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3) was added a solution of $[\{\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}o)\text{Cl}\}_2]$ (0.074 g, 0.12 mmol) in CH_2Cl_2 (10 cm^3). After stirring for 3 h the solution was concentrated to *ca.* 5 cm^3 and pentane was added affording complex **2** as a pale yellow precipitate (0.179 g, 92%), m.p. 127 $^\circ\text{C}$ (decomp.). IR: (KBr) 1512s [$\nu(\text{C}=\text{O})$], (CH_2Cl_2) 1520s cm^{-1} [$\nu(\text{C}=\text{O})$]. NMR: ^1H (CDCl_3), δ 2.18 [d, 6 H, NMe_2 , $^4J(\text{PH}) = 2.5$], 3.83 (d, 2 H, NCH_2 , $^4J(\text{PH}) = 2.1$], 3.91 [d, 2 H, PCH_2 , $^2J(\text{PH}) = 12.5$], 4.65 [d, 1 H, $\text{P}=\text{CH}$, $^2J(\text{PH}) = 22.9$] and 6.44–7.89 (29 H, aromatic); $^{31}\text{P}-\{^1\text{H}\}(\text{CDCl}_3)$, δ 14.9 [d, PPh_3 , $^4J(\text{PP}) = 3.5$] and 37.0 [d, PPd , $^4J(\text{PP}) = 3.5$]; $^{13}\text{C}-\{^1\text{H}\}(\text{CDCl}_3)$, δ 46.56 [dd, PCH_2 , $J(\text{PC}) = 30.6$, $^3J(\text{PC}) = 13.4$], 49.39 (d, NMe_2 , $^3J(\text{PC}) = 2.1$], 62.55 [dd, $\text{P}=\text{CH}$, $J(\text{PC}) \approx 104$, $^3J(\text{PC}) \approx 8$], 70.44 [d, NCH_2 , $^3J(\text{PC}) = 2.9$ Hz], 122.45–148.85 (aromatic C) and 185.93 (s br, $\text{C}=\text{O}$) (Found: C, 64.35; H, 5.1; N, 1.8. Calc. for $\text{C}_{42}\text{H}_{40}\text{ClNOP}_2\text{Pd}$: C, 64.8; H, 5.2; N, 1.8%). Mass spectrum (FAB): m/z 742 ($[M - \text{Cl}]^+$, 100%).

$[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}o)\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3\}]\text{BF}_4$ 3. Silver tetrafluoroborate (0.013 g, 0.06 mmol) was added to a solution of $[\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}o)\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3\}]\text{Cl}$ (0.050 g, 0.06 mmol) in CH_2Cl_2 (10 cm^3). After filtration over Celite, the solution was concentrated and hexane added to afford complex **3** as pale yellow crystals (0.049 g, 94%), m.p. 127 $^\circ\text{C}$ (decomp.). IR(KBr): 1512s [$\nu(\text{C}=\text{O})$] and 1056s cm^{-1} [$\nu(\text{B}-\text{F})$]. The ^1H and ^{31}P NMR data are substantially the same as for **2** (Found: C, 54.75; H, 4.55; N, 1.45. Calc. for $\text{C}_{42}\text{H}_{40}\text{BF}_4\text{NOP}_2\text{Pd} \cdot 1.5\text{CH}_2\text{Cl}_2$: C, 54.6; H, 4.55; N, 1.45%). The presence of CH_2Cl_2 was confirmed by NMR spectroscopy. Mass spectrum (FAB): m/z 742 ($[M - \text{BF}_4]^+$, 100%).

$[\text{Ni}(\eta^5\text{-C}_5\text{Ph}_5)\{\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3\}]$ 4. To a solution of $[\text{Ni}(\eta^5\text{-C}_5\text{Ph}_5)\text{I}(\text{CO})]$ ⁴⁶ (0.131 g, 0.20 mmol) in thf (5 cm^3) was added a solution of $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3$ (0.100 g, 0.20 mmol) in thf (5 cm^3). After stirring for 1 h, the solution was concentrated to *ca.* 5 cm^3 and pentane was added to yield a red precipitate. Recrystallization from CH_2Cl_2 -pentane at -20°C afforded complex **4** as red spindly crystals (0.160 g, 71%), m.p. 172 $^\circ\text{C}$ (decomp.). IR(KBr): 1521s cm^{-1} [$\nu(\text{C}=\text{O})$]. NMR: ^1H (CDCl_3), δ 3.61 [d, 2 H, PCH_2 , $^2J(\text{PH}) = 9.8$], 4.40 (d, 1 H, $\text{P}=\text{CH}$, $^2J(\text{PH}) = 33.6$] and 7.42–9.31 (50 H, aromatic H); $^{31}\text{P}-\{^1\text{H}\}(\text{CDCl}_3)$, δ 12.8 (s br, PPh_3) and 26.1 (s br, PNi); $^{13}\text{C}-\{^1\text{H}\}(\text{CDCl}_3)$, δ 48.28 [dd, PCH_2 , $J(\text{PC}) = 30$, $^3J(\text{PC}) = 14$],

65.49 [d, P=CH, $J(\text{PC}) \approx 102$ Hz], 109.37–133.11 (aromatic C) and 184.49 (s, C=O) (Found: C, 67.3; H, 4.65. Calc. for $\text{C}_{68}\text{H}_{53}\text{INiOP}_2 \cdot \text{CH}_2\text{Cl}_2$: C, 68.0; H, 4.55%). The presence of CH_2Cl_2 was confirmed by NMR spectroscopy. Mass spectrum (FAB): m/z 1005 ($[\text{M} - \text{I}]^+$, 100%).

[Ni($\eta^5\text{-C}_5\text{Ph}_5$)($\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3$)]Br **5.** To a solution of $[\text{Ni}(\eta^5\text{-C}_5\text{Ph}_5)\text{Br}(\text{CO})]$ (0.100 g, 0.16 mmol) in CH_2Cl_2 (20 cm^3) was added $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3$ (0.081 g, 0.16 mmol). After stirring overnight the red solution was concentrated and Et_2O was added to yield a brick-red precipitate. Compound **5** was recrystallized from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$ and dried *in vacuo* for 3 d at 60 °C (0.175 g, 85%), m.p. 192–194 °C. IR: (KBr) 1506s [$\nu(\text{C}=\text{O})$], (Nujol) 1505s cm^{-1} [$\nu(\text{C}=\text{O})$]. The ^1H , ^{31}P and ^{13}C NMR spectra are essentially identical with those of **3** (Found: C, 75.2; H, 4.85. Calc. for $\text{C}_{68}\text{H}_{53}\text{BrNiOP}_2$: C, 75.15; H, 4.9%). Mass spectrum (FAB): m/z 1005 ($[\text{M} - \text{Br}]^+$, 100%).

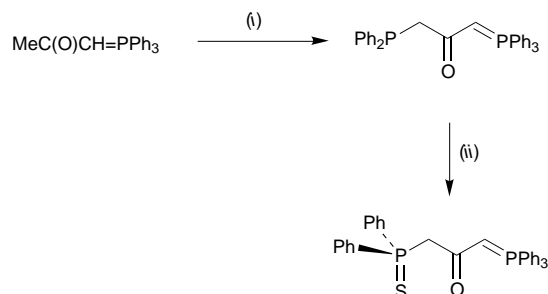
Crystallography

Suitable single crystals of $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ were obtained by slow diffusion of hexane into a solution in dichloromethane. A crystal of approximate size 0.30 × 0.30 × 0.45 mm was studied on a CAD4 Enraf-Nonius diffractometer. The cell parameters were obtained by fitting a set of 25 high- θ reflections. The data collection [$t_{\text{max}} = 60$ s, h 0–19, k 0–19, l –24 to 24, intensity controls without appreciable decay (0.2%)] gave 10 230 reflections from which 4691 were independent ($R_{\text{int}} = 0.019$) with $I > 2\sigma(I)$. After Lorentz-polarization corrections, the structure was solved with direct methods which revealed many non-hydrogen atoms of the two molecules of the asymmetric unit. The remaining ones were found after successive scale-factor calculations and Fourier-difference syntheses. After isotropic ($R = 0.10$), then anisotropic refinement ($R = 0.079$), many hydrogen atoms were found from a Fourier-difference map (between 0.37 and 0.17 $\text{e} \text{ \AA}^{-3}$). The entire structure was refined by the full-matrix least-squares technique {on F ; x, y, z, β_{ij} for P, C and O atoms and x, y, z fixed for H atoms; 650 variables; $w = 1/\sigma^2(F_o)^2 = [\sigma^2(I) + (0.04F_o)^2]^{-1}$ } with the resulting $R = 0.063$ and $S_w = 2.46$ (residual $\Delta\rho \leq 1.3 \text{ e} \text{ \AA}^{-3}$, residuals located around the phosphorus atoms). Atomic scattering factors were taken from ref. 48. All calculations were performed on a Digital Micro VAX 3100 computer with the MOLEN package.⁴⁹ No absorption corrections were applied. Main crystal data are summarized in Table 1.

Atomic co-ordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/522.

Results and Discussion

A rational synthetic procedure that should permit facile generation of the hybrid ligand from its natural precursors relies on the acidity of the methyl group in the simple ylide $\text{MeC}(\text{O})\text{CH}=\text{PPh}_3$. In fact phosphination of the methyl carbon of carbonyl compounds of the type $\text{MeC}(\text{O})\text{R}$ [$\text{R} = \text{aryl, alkoxy, dialkylamino or alkyl(aryl)amino}$] using a strong base and a chlorophosphine is now a well established method allowing the preparation of β -carbonyl phosphines of the type $\text{R}'_2\text{PCH}_2\text{C}(\text{O})\text{R}$.^{39,41,50–61} Molecular orbital calculations concluded that the acidity of the terminal methyl group in the ylidic precursor was comparable to that of acetophenone, the prototypic reagent for use in such phosphination reactions. Trying to apply this methodology for the synthesis of $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$, we found that treatment of $\text{Ph}_3\text{PCH}=\text{C}(\text{O})\text{Me}$ with 1 equivalent of LiBu in tetrahydrofuran at –78 °C followed by reaction with PPh_2Cl (1 equivalent) afforded the required compound in only



Scheme 2 (i) In thf at –78 °C, 2 equivalents LiBu, then PPh_2Cl (1 equivalent), room temperature (r.t.), 15 h, then HCl; (ii) in CH_2Cl_2 , r.t., S_8

ca. 15% yield after work-up. In contrast acetophenone gives almost quantitative yields under the same conditions.⁶² The presence of large amounts of unchanged $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{Me}$ in the product mixture suggests that much of the butyllithium is directly involved with the ylidic fragment and is unavailable for deprotonation of the methyl group. Consequently repeating the reaction with 2 equivalents of base caused a four-fold increase in yield after work-up (Scheme 2). It is noteworthy that by minor modification of the original synthetic approach⁴¹ the methodology has been extended to encompass the synthesis of highly polar β -ketophosphines.

The compound $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ was characterized by microanalysis, mass and multinuclear (^1H , ^{13}C and ^{31}P) NMR spectroscopy. The ^{31}P NMR spectrum displays a doublet at $\delta -14.6$ [$^1J(\text{PP}) = 2$ Hz], assigned as the phosphorus(III) atom, and another one at $\delta +15.7$ corresponding to the ylide moiety. The ylidic carbon resonance is found at $\delta 40.64$, while that of the PCH_2 carbon lies at $\delta 33.89$. In the ^1H NMR spectrum (200 MHz) the PCH_2 protons give rise to a sharp doublet [$^2J(\text{PH}) = 0.8$ Hz] at $\delta 3.47$, while the methine resonance appears as a relatively broad doublet centred at $\delta 4.08$. The $^2J(\text{PH}_{\text{ylide}})$ (26.7 Hz) and $J(\text{PC}_{\text{ylide}})$ (109 Hz) coupling constants are as expected for an sp^2 -hybridized carbon atom attached to the PPh_3 moiety. Calculations indicate that the methylene group is not acidic and there is no indication that a second diphenylphosphino residue is incorporated into the molecular framework.

X-Ray crystallography revealed that in the solid state $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ is evenly distributed between two rotamers (Fig. 1); important bond lengths and angles are given in Table 2. These rotamers differ according to the relative positioning of the carbonyl group which can be considered to be bisecting with respect to the adjacent methylene group. Taking the $\text{CH}_2\text{C}(\text{O})$ fragment as reference, rotamer **A** has the carbonyl group bisecting the HCH group at an angle of 25° whereas **B** has the carbonyl displaced to an angle of 165°. Molecular mechanics simulations suggest an energy barrier of only *ca.* 10 kJ mol^{-1} for interconversion between these rotamers. Owing to the multiple bond order within the PCCO fragment of the keto ylide part it is convenient to distinguish between these rotamers in terms of the geometry around the ylidic CC bond where both conformers adopt a cisoid arrangement. In fact this stereochemistry is normal for keto-stabilized ylides. It is noteworthy that the observed ^{31}P chemical shift for the ylidic phosphorus atom ($\delta 15$) confirms that the cisoid configuration persists in solution.⁶³

As expected, the $\text{Ph}_3\text{P}-\text{C}$ bond lengths, 1.708(5) Å in **A** and 1.723(6) Å in **B**, being typical for stabilized ylides,^{64,65} are significantly shorter than the $\text{P}-\text{C}$ bond of the corresponding phosphine fragments [1.830(6) for **A** and 1.840(6) Å in **B**]. Owing to conjugation, the carbonyl bonds [1.241(7) and 1.233(7) Å, respectively in **A** and **B**] are elongated while the intervening C–C bonds are significantly shortened [1.390(8) Å for C(19)–C(20) of **A**, 1.398(8) Å for C(59)–C(60) in **B**]. In each isomer the ylidic phosphorus atom adopts a slightly distorted tetrahedral

Table 1 Crystal data and details of data collection for $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3$

Formula	$\text{C}_{23}\text{H}_{28}\text{OP}_2$
<i>M</i>	502.54
Colour	White
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
<i>a</i> /Å	16.973(6)
<i>b</i> /Å	16.774(5)
<i>c</i> /Å	20.242(9)
β /°	108.89(3)
<i>U</i> /Å ³	5452(3)
<i>Z</i>	8
<i>F</i> (000)	2112
<i>D</i> _c /g cm ⁻³	1.224
μ /cm ⁻¹	1.775
Radiation	Mo-K α , graphite monochromated
λ /Å	0.710 73
Mode	2θ flying step-scan
<i>T</i> /K	294
θ Range/°	1–25
Number of data collected	10 230
Number of data with $I > 2\sigma(I)$	4691
<i>R</i> ^a	0.063
<i>R</i> ^b	0.061
Goodness of fit ^c	2.46

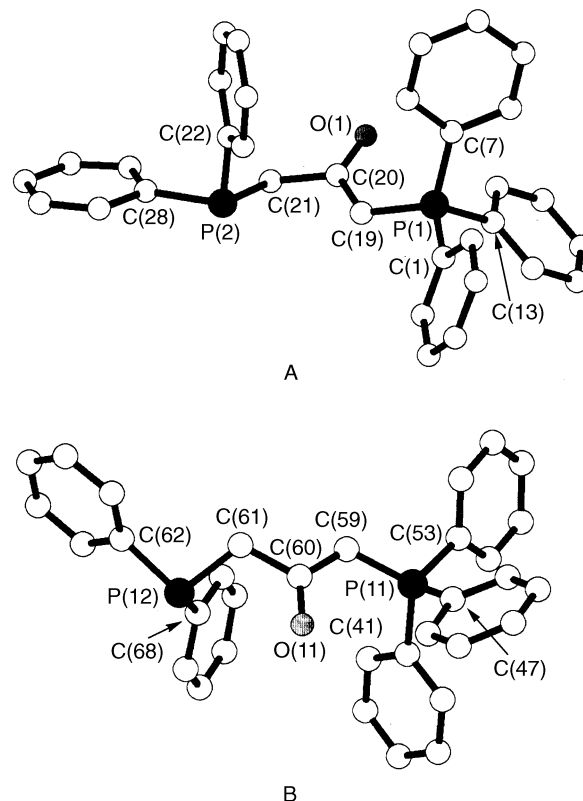
^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $R' = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^c $[\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$, where N_o , N_p are the number of observations and parameters.

Table 2 Selected bond distances (Å) and angles (°) for both isomers of $\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{CH}=\text{PPh}_3$

Molecule A			
P(1)–C(19)	1.708(5)	C(20)–O(1)	1.241(7)
P(1)–C(1)	1.811(6)	C(20)–C(21)	1.530(8)
P(1)–C(7)	1.824(5)	P(2)–C(21)	1.830(6)
P(1)–C(13)	1.799(6)	P(2)–C(28)	1.843(6)
C(19)–C(20)	1.390(8)	P(2)–C(22)	1.848(6)
C(7)–P(1)–C(19)	115.9(3)	C(22)–P(2)–C(28)	99.0(3)
C(1)–P(1)–C(19)	106.4(3)	C(21)–P(2)–C(22)	101.1(3)
C(13)–P(1)–C(19)	114.0(3)	C(21)–P(2)–C(28)	102.8(3)
C(1)–P(1)–C(13)	107.4(3)	P(1)–C(19)–C(20)	121.6(3)
C(13)–P(1)–C(7)	105.8(3)	P(2)–C(21)–C(20)	114.0(4)
C(7)–P(1)–C(1)	106.9(3)	C(19)–C(20)–C(21)	115.6(5)
Molecule B			
P(11)–C(59)	1.723(6)	C(60)–O(11)	1.233(7)
P(11)–C(53)	1.812(6)	C(60)–C(61)	1.533(8)
P(11)–C(47)	1.809(6)	P(12)–C(61)	1.840(6)
P(11)–C(41)	1.823(6)	P(12)–C(68)	1.837(6)
C(59)–C(60)	1.398(8)	P(12)–C(62)	1.848(6)
C(41)–P(11)–C(59)	113.6(3)	C(62)–P(12)–C(68)	100.2(3)
C(47)–P(11)–C(59)	116.9(3)	C(61)–P(12)–C(62)	99.9(3)
C(53)–P(11)–C(59)	106.2(3)	C(61)–P(12)–C(68)	102.2(3)
C(53)–P(11)–C(41)	107.7(3)	P(11)–C(59)–C(60)	120.0(5)
C(47)–P(11)–C(53)	107.3(3)	P(12)–C(61)–C(60)	112.1(4)
C(47)–P(11)–C(41)	104.6(3)	C(59)–C(60)–C(61)	117.1(6)

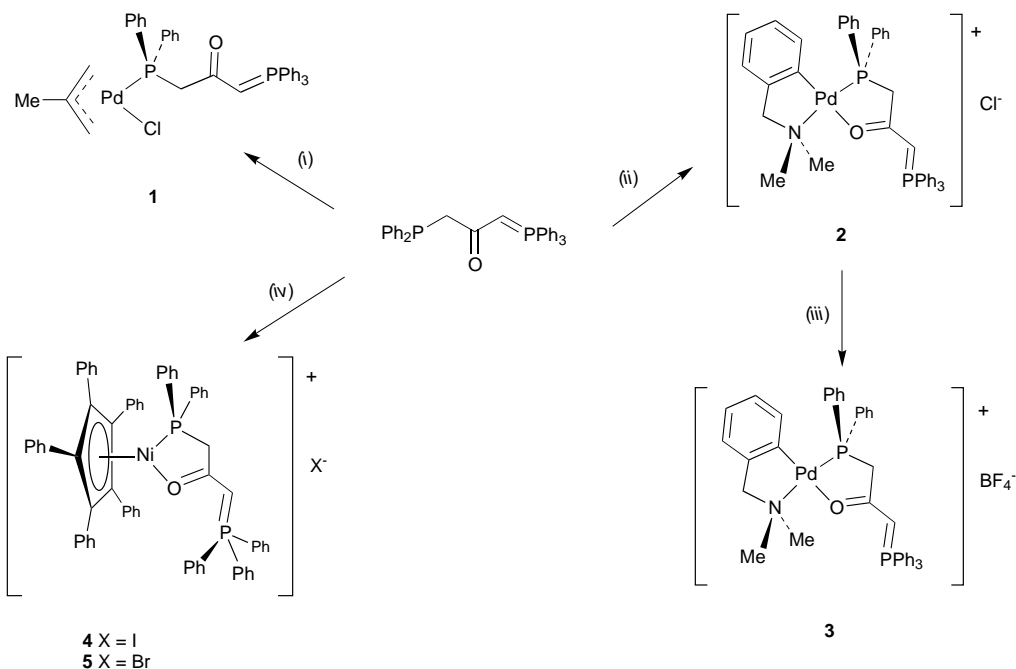
structure since the aryl groups are directed away from the P=C bond. This has the effect of extending the C (ylide)–P–C (aryl) angles (average 112° in **A** and **B**) while compressing the C (aryl)–P–C (aryl) bond angles (average 107° in **A** and **B**). The usual pyramidal compression⁶⁶ is observed for the phosphino P^{III} (C–P–C angles lying between 99.0 and 102.8° in **A**, between 99.9 and 102.2° in **B**).

Reaction of $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ with sulfur in CH_2Cl_2 gave the corresponding phosphine sulfide in quantitative yield (Scheme 2). Solid-state IR spectroscopy shows that the $\nu(\text{CO})$ bands of these two compounds appear at 1545 and 1548 cm^{-1} , respectively. These values, being approximately 100 cm^{-1} lower than for a normal ketone, appear to be in keeping with strong conjugation between C=O and P=C bonds.

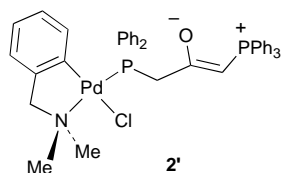
**Fig. 1** Molecular structure (MOLVIEW) of rotamers **A** and **B** of $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ showing the atom numbering scheme

The compound $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ has three binding sites, namely the phosphorus(III) centre, the oxygen atom, and the ylidic C atom, which could facilitate mono- and bi-dentate complexation with suitable metals. In particular, the diphenylphosphino moiety remains readily accessible and the ubiquitous co-ordinative ability of such donor sites provides the opportunity to generate an inordinately wide range of metal complexes. This concept was demonstrated by virtue of the preparation and characterization of the *P*-monodentate complex **1** as a prototype. This allylic palladium complex was obtained in essentially quantitative yield from $[\{\text{PdCl}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})\}_2]$ (Scheme 3). The ³¹P NMR spectrum clearly resolves the two types of phosphorus and indicates that the phosphine centre is co-ordinated. More significantly, the carbonyl function appears at 1543 cm^{-1} in the solid-state IR spectrum which remains very similar to that found for the free ylide. Such behaviour is a clear indication that the carbonyl group is not involved in the primary co-ordination sphere. Consequently it is interesting to compare this reaction with that described by Facchin *et al.*⁶⁷ where the incoming allylic palladium fragment forms a metal–carbon bond with the ylidic carbon atom. This suggests that the phosphino residue shows greater affinity for the metal centre than does the ylidic subunit despite that the latter bears a high negative charge.

In order to test the generality of the monodenticity of $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$, we made use of a related cyclometalated palladium(II) dimer. However, reaction of 2 equivalents of the ylide with $[\{\text{PdCl}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-}o)_2\}_2]$ in thf afforded complex **2** in quantitative yield (Scheme 3), but the expected **2'** was not observed. In fact compound **2'** can be considered to undergo an intramolecular substitution reaction in which the oxygen of the carbonyl group displaces the bound chloride ligand. We are aware of only one other example of a keto-stabilized phosphorus ylide *O*-bound to a palladium centre,²⁷ but here the cationic precursor might be expected to facilitate formation of the observed product. In our case oxygen binding is more surprising and involves competition for the metal centre between chloride, oxygen and the ylidic carbon. Preferential co-



Scheme 3 (i) In CH_2Cl_2 , $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_4\text{Me-2})\}_2]$ (0.5 equivalent); (ii) in CH_2Cl_2 , $[\{\text{PdCl}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe-}o)\}_2]$ (0.5 equivalent); (iii) in CH_2Cl_2 , AgBF_4 (1 equivalent); (iv) in thf or CH_2Cl_2 , $[\text{Ni}(\eta^5\text{-C}_5\text{Ph}_5)\text{X}(\text{CO})]$ (1 equivalent)



ordination at oxygen rather than carbon seems likely because of the higher negative charge on the oxygen atom and also because of stereochemical crowding. Displacement of the chloride ligand could be promoted by a high *trans* influence of the σ -bound aryl ring but even so a detailed understanding of the markedly disparate behaviour displayed by **2** and **2'** remains elusive.

Authentication of the assigned structure for complex **2** was obtained by elemental analysis, mass, NMR and IR spectroscopies. Critical information was obtained by solid-state IR in that the $\nu(\text{C}-\text{O})$ band appears at 1512 vs. 1545 for **1** and 1548 cm^{-1} for the ylides. This decrease in the $\nu(\text{C}-\text{O})$ frequency is characteristic of keto-stabilized ylide ligands bound through the oxygen atom.¹ Further support for an *O*-bound keto-ylide relates to the displacement of the ^{13}C signal of the ylidic carbon to lower field relative to the free ylide (δ 62.55 for **2** against 40.64 for the ylide).² Confirmation that the chloride anion of **2** is non-bonded was obtained by the facile formation of the corresponding BF_4^- salt **3** (Scheme 3). The latter complex had identical spectroscopic properties to those described for **2**. Finally it should be mentioned here that Keim and co-workers⁶⁸ have recently demonstrated that *P,O* chelation of β -carbonyl phosphines may occur under forcing conditions to a palladium allyl centre. This suggests that conditions might be found that would enable *P,O* chelation with $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{-CH}_2\text{PPh}_2$ and an allylic fragment.

A second illustration of the nucleophilicity of the oxygen atom in $\text{Ph}_3\text{P}=\text{CHC}(\text{O})\text{CH}_2\text{PPh}_2$ was found by reaction with $[\text{Ni}(\eta^5\text{-C}_5\text{Ph}_5)\text{I}(\text{CO})]$ (Scheme 3) where the chelated complex **4** was obtained in high yield. This product is a rare example of a keto-stabilized ylide nickel complex. That binding occurs through the oxygen atom was unequivocally demonstrated by the appearance of a single carbonyl band at 1521 cm^{-1} in the IR spectrum. The corresponding bromide salt, **5**, was obtained by treating the ylide with $[\text{Ni}(\eta^5\text{-C}_5\text{Ph}_5)\text{Br}(\text{CO})]$. It is noteworthy

that the $\nu(\text{C}=\text{O})$ band of **5** appears at a slightly lower frequency (1505 cm^{-1}) than that of **4**, possibly due to ion-pairing effects.

In summary, the ligand presented in this work combines a phosphine donor with a highly polarized subunit, a keto-stabilized ylide. Owing to the high negative charge localized on the ylidic function, this phosphine displays a marked tendency to form *P,O*-chelated complexes with palladium and nickel. Further investigations are in progress aimed at the use of such systems for the preparation of novel materials based on the presence of polar groups and/or the reactivity of the ylidic function.

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