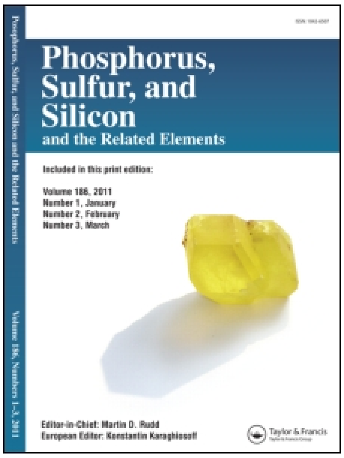

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# Synthesis of New Phosphorus Ligands and Their Reactions with Palladium (II) Halide: A Multi Nuclear NMR Study

S. J. Sabounchei[a]; A. R. Dadrass[a]; F. Eskandaripoure[a]
[a] Department of Chemistry, Bu-Ali-Sina University, Hamadan, Iran

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# Synthesis of New Phosphorus Ligands and Their Reactions with Palladium (II) Halide: A Multi Nuclear NMR Study

**S. J. Sabounchei**
**A. R. Dadrass**
**F. Eskandaripoure**
Department of Chemistry, Bu-Ali-Sina University, Hamadan, Iran

*Synthesis of new phosphorus ligands such as* $Ph_2PCH_3CO_2C{=}CHCO_2CH_3$ *(DMPPS) and* $Ph_2P(CH_3)_3CO_2CC{=}CHCO_2C(CH_3)_3$ *(DB*$^1$*PPS) in moderate to good yields by the reaction of CH-acid (nitromethane), dialkyl acetylenedicaboxylate, and chloro-diphenylphosphine, as well as their corresponding palladium (II) halide complexes* $[Pd(DMPPS)_2]Cl_2$ *(I) and* $[Pd(DB^tPPS)_2]Cl_2$ *(II), are reported. The structures of these compounds were confirmed by IR,* $^1H$, $^{31}P$, *and* $^{13}C$ *NMR spectroscopy and elemental analysis.*

**Keywords** Acetylacetone; chlorodiphenylphosphine; monophosphorus ligands; palladium(II)

Discovery of new phosphorus ligands plays a critical role in asymmetric catalysis.[1] These ligands of the type $Ph_2E\text{-}RC{=}C(H)R$ ($R = Me, Bu^t$, $E = P, As$), have been prepared during Wittig reactions.[2] Resonance-stabilized phosphorus ligands are successfully used in organometallic and coordination chemistry owing to their accessibility and stability towards air and moisture, such as ketoylides.[3,4] Many bonding modes are also possible for these ligands. The coordination through carbon is more likely and has been observed for ylides with Pd (II), Pt (II), and Ag (I).[5,6] Palladium complexes are used widely in catalysis examples, including the Heck reaction, the Wacker process,[7] and alkoxy-carbonylation of alkenes.[8] As a general feature, the coordination chemistry of phosphorus compunds of the type $Ph_2E\text{-}RC{=}C(H)R$, appears to be dominated

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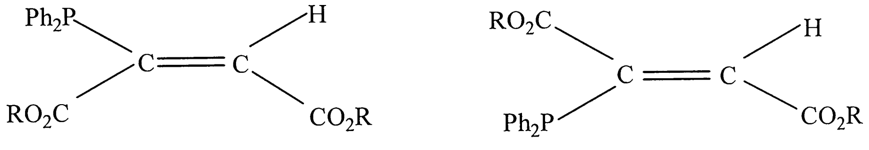
Address correspondence to Seyyed Javad Sabounchei, Department of Chemistry, Bu-Ali-Sina University, Hamadan, 65174 Iran. E-mail: jsabounchei@yahoo.co.uk



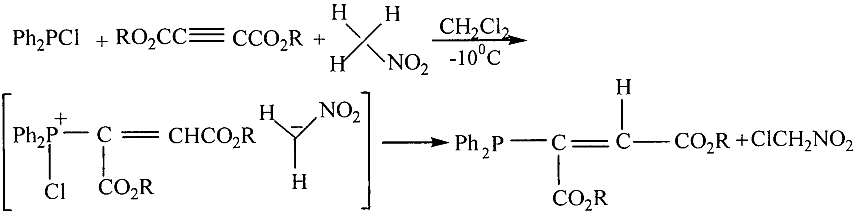
cis trans

**FIGURE 1** Cis and trans forms of DMPPS and DB$^t$MPPS (R = Me, Bu$^t$).

by a C-ligand metal coordination, and few examples of O-ligand bond complexes[9] and coordination through phosphorus[10] are known. These new ligands also are stable and may take any of two forms of cis and/or trans conformations. DMPPS ad DB$^t$PPS ligands, such as carbonyl-stabilized ylides, also exhibit interesting properties such as high stability; they can be handled in air and an ambidentate character as ligands can be rationalized in terms of cis and/or trans geometrical[10] (Figure 1). Symmetrical structures of two palladium complexes were formed by the reaction of DMPPS and DB$^t$PPS with palladium (II) halide. The aim of our present work is to determine correctly and to compare the molecular structures of the products formed by the title ligands with palladium(II) choride and to characterize all the products by IR, $^1$H, $^{13}$C, and $^{31}$P NMR techniques and microanalysis.

## RESULTS AND DISCUSSION

The ligands DMPPS and DB$^t$PPS may be synthesized from the direct addition of chlorodiphenylphosphine to the acetylenic ester and the concomitant protonation of the 1:1 adduct, followed by the attack of a CH-acid atom such as nitromethane on the vinylphosphonium cation to form the stabilized phosphorane.[2] The presence of $CH_2NO_2^-$ in the reaction medium causes the removal of chlorine from phosphonium leaving the uncharged product (Scheme 1).



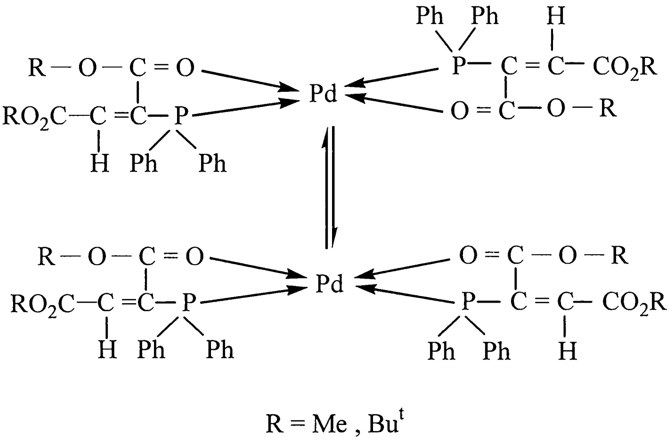
**SCHEME 1**

We believe that these ligands, such as $\alpha$-keto stabilized ylides,[11] have ambidentate character. This ambidentate character facilitates the

**TABLE I (CO) of Selected Phosphoranes and Their Metal Complexes**

| Compound | $\nu$(CO) cm$^{-1}$ | $\nu$(C=C) cm$^{-1}$ | Ref. |
|---|---|---|---|
| $Ph_2PCH_3CO_2C{=}CCO_2CH_3$ (DMPPS) | 1729 | 1590, 1483 | This article |
| $Ph_2P(CH_3)_3CO_2CC{=}CHCO_2C(CH_3)_3$ (DB$^t$PPS) | 1719 | 1589, 1483 | This article |
| $Ph_3PCHCOCH_3$(APPY) | 1530 | | [14] |
| $Ph_3PCHCOPh$(BPPY) | 1525 | | [15] |
| O-coordination | | | |
| [Pd(DMPPS)$_2$]Cl$_2$ (I) | 1736 | 1589, 1483 | This article |
| [Pd(DB$^t$PPS)$_2$]Cl$_2$ (II) | 1729 | 1589, 1483 | This article |
| O-coordination | | | |
| [Sn(CH$_3$)$_3$.BPPY]Cl | 1480 | | [4] |
| [(SnPh$_3$).BPPY]Cl | 1470 | | [4] |
| [Pd(C$_6$F$_5$)(PPh$_3$)$_2$(APPY)]ClO | 1513 | | [4] |

preparation of stable metal complexes in which the ligand could be O[12] or C-coordinated.[13] The same values of the $\nu$ (C=C) of the free ligands and the comparison with the related values in complexes (I) and (II) are in agreement that the C-coordination dose not take place in these complexes (Table I). The $\nu$0 CO in BMPPS and DB$^t$PPS occurs at 1729 and 1719 cm$^{-1}$; these are nearly in the same frequence range compared with their corresponding values in related complexes (I) and (II) at 1736 and 1729 cm$^{-1}$, respectively (Table I), which is not in good agreement with only the O-coordination of these ligands in their complexes. This is probably due to the P-coordinations, which also take place through the phosphorus atoms in these complexes (Scheme 2).



**SCHEME 2**

**TABLE II $^{1}$H and $^{31}$P NMR Data of DMPPS, DB$^{t}$PPS, and Their Complexes with Pd(II) Chloride (T = 298 K: J in Hz: TMS $\delta$ = 0.00 ppm). CDC13, 90 MHZ, values (ppm)**

| Compound | $\delta$ (CH) | $^{3}$JH-P | $\delta$ (OCH$_3$) | $\delta$ PPh$_2$ | $\delta$($^{31}$P) |
|---|---|---|---|---|---|
| DMPPS | 4.67 | 4.50 | 2.90 | 7.39–7.55 | 27.18 |
| DB$^{t}$PPS | 4.57 | 5.19 | 0.78 | 7.34–7.56 | 30.62 |
| (DMPPS)$_2$Pd | 3.72 | 5.65 | 2.91 | 7.39–7.50 | 23.60 |
| (DB$^{t}$PPS)$_2$Pd | 3.71 | 5.93 | 0.79 | 7.40–7.50 | 26.33 |

The difference in chemical shifts of highly pure phosphorus-free ligands ($\delta$ = 27.18 and 30.62 ppm) and their corresponding pure complexes ($\delta$ = 23.60 and 26.33 ppm) confirms the O-coordination of the ligand to palladium (Table II). It must be noted that the O-coordination of the ligand generally appears in a higher field and lower frequency and usually leads to the formation of cis and/or trans isomers[10] (Scheme 2).

The $^{1}$H NMR data of the palladium (II) complexes along with those of the parent ligands are listed in (Table II). In the $^{1}$H NMR spectra of (1) and (2), the electron density around the CH proton increases; this probably is due to the inductive effect of the $\pi$-back bonding from Pd to the phosphorus atom; therefore, we expect a higher field and lower chemical shift for the CH proton in complexes (I) 3.72 and complex (II) 3.71, compared to those of the free ligands DMPPS, 4.67, and DB$^{t}$PPS, 4.57 (Table II).

The $^{13}$C NMR data of the complexes [Pd (DMPPS)$_2$] and [Pd(DB$^{t}$PPS)$_2$] are listed in (Table III) along with possible assignments.

**TABLE III $^{13}$C NMR Data of DMPPS and DB$^{t}$PPS and Their Complexes with Pd (II) Chloride (T = 298°K; J in Hz; TMS $\delta$ = 0.00 ppm). In CDCl$_3$, 90 MHZ, Values (ppm); br, broad: d, doublet**

| Possible Assignments | (DMPPS) | [Pd(DMPPS)$_2$] | (DB$^{t}$PPS) | [Pd(DB$^{t}$PPS)$_2$] |
|---|---|---|---|---|
| (CH) | 133.73 (br) | 50.20 | 133.71 | 54.10 |
| P-C | 132.22 (d) | 62.60 | 132.30 | 49.20 |
| J(PC) | 49.40 | br | 52.82 | br |
| OCH3 | 52.17 | 51.70 | — | — |
| CH$_3$ | — | — | 27.22 | 27.85 |
| CO | 168.62 | 173.60 | 167.20 | 175.8 |
| C$_6$H$_5$ | 128–132 | 129–141 | 128—133 | 129–140 |
| OC(CH$_3$)$_3$ | – | — | 82.95 | 81.05 |

The most interesting aspect of the $^{13}C$ spectra of these complexes are the up-field shifts (50.20, 54,10) of the CH signals due to the coordination through oxygen and $\pi$-back bonding from the metal to the ligand, while in the ligands (DMPPS) and (DB$^{t}$PPS), the CH signals are shifted down field (133.73, 133.71 ppm; Table III).

## EXPERIMENTAL

### Preparation of Dimethyl 2-Diphenylphosphine Succinate General Procedure

To a magnetically stirred solution of chlorodiphenylphosphine, (0.367 mL, 2 mol) and nitromethane (0.1 mL, 2 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to a mixture of dimethylacetylenedica boxylate (0.24 mL) in $CH_2Cl_2$ (10 mL) at −10°C over 15 min. The mixture was allowed to warm-up to room temperature. The solvent was removed under reduced pressure and the residue was washed with petroleum ether and then filtered. The white crystals were obtained. (0.32 g), m.p. 170–172°C, yield 49.0%. (Anal. found: C, 65.00; H, 5.80; cal: C, 64.60; H, 4.85).

### Preparation of Ditertiarybuthyl 2-Dephenylphophine Succinate General Procedure

To a magnetically stirred solution of chlorodiphenylphosphine, (0.367 mL, 2 mmol and nitromethane (0.1 mL, 2 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to a mixture of ditertiarybuthylacetylenedicarboxylate (0.45 mL, 2 mmol) in $CH_2Cl_2$ (10 mL) at −10°C over 15 min. The mixture was allowed to warm up to room temperature. The solvent was removed under reduced pressure and the residue was washed with petroleum ether and then filtered. A white precipitate was obtained (0.35 g), m.p 180–182°C, yield 42%. (Anal. found: C, 67.30; H, 6.20; cal: C, 66.90; H, 7.2).

### Preparation of Ligands-Pd(II) Complexes

#### *[(DMPPS)$_2$Pd] (1)*

A solution of 0.328 g (1 mmol) of ligand (DMPPS) in $CHCl_3$ (10 mL) was added to a solution of potassium tetrachloro palladate (II) (0.328 g, (1 mmol) in CHCl3 (10 mL), and the mixture was stirred under the atmosphere of nitrogen for 72 h at 35°C. The solvent then was removed at room temperature. The green precipitate was obtained. (0.16 g), m.p.

232–234°C, yield C, yield 41% (Anal. found: C, 54; H, 4.5; cal: C, 54.1; H, 4.75).

### *[(DB$^t$PPS)$_2$Pd](2)*

A solution of 0.226 g (1 mmol) of ligand (DB$^t$PPS) in $CHCL_3$ (10 mL) was added to solution 0.163 g (0.5 mmol) of potassium tetrachloro palladate (II) in $CHCl_3$ (10 mL), and the mixture was stirred for 72 h at 35°C. The solvent was then removed at room temperature. The yellow precipitate was obtained. (0.17 g), m.p. 252–254°C, yield 37%. (Annal.found: C, 61.2; H, 5.2; H, 5.2; cal: C, 61.9; H, 6.2).

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