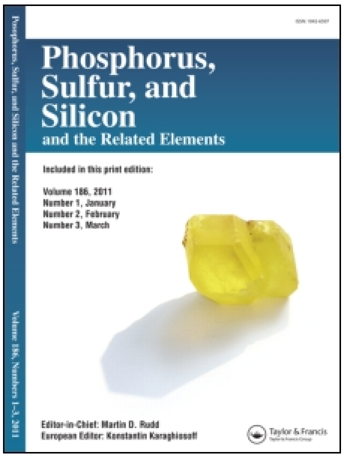

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Synthesis and Multinuclear NMR Study of Benzoyl Methylene Triparatolylphosphorane Ylide and the Reaction of this Ylide with Mercury(II) Halides

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The reaction of the title ylide $\{PhCOCHP(p\text{-}tolyl)_3\}$ *with Pd(II), Pt(II). Hg(II), and Ag(I) in equimolar ratios using* CH_3CN, CH_3OH, *and* CH_2Cl_2 *as solvents have yielded* $[\{(p\text{-}tolyl)_3PCHCOC_6H_5\}\ PdCl_2]_2$ *(I),* $[\{(p\text{-}tolyl)_3\ PCHCOC_6H_5\}\ PtCl_2]_2$*(2),* $[Hg(NO_3)_2\ \{(p\text{-}tolyl)_3\ PCHCOC_6H_5\}]$*(3), and* $[Ag\{(p\text{-}tolyl)_3\ PCHCOC_6H_5\}_2]^+$ *(4). The IR,* ^1H ^{13}C*, and* ^{31}P *NMR together with micro analysis data of the products were obtained.*

Keywords Benzoylmethylentriparatolylphosphorane; mercury(II); palladium(II); platinum(II); silver(I)

INTRODUCTION

The coordination chemistry of phosphoranes $R_3P\text{-}CH_2$ is well known.[1–4] Resonance-stabilized phosphorous ylides, particularly the keto ylides, are also successfully used as ligands in organometallic and coordination chemistry owing to their accessibility and stability towards air and moisture.[5,6] Although many bonding modes are possible for the keto ylides,[7] coordination through carbon is more predominant and observed with Pd(II), Pt(II), and Ag(I).[8–10] We are currently interested in the synthesis and reactivity of metal derivatives of such ylides.[11] As a general feature, the coordination chemistry of $R_3ECHCOR$ (E=P, As) ligands appears to be dominated by a C-(ylide) metal coordination, although a few examples of O-(ylide)-bound complexes are known.[12] P-and As-ylides are remarkable ligands, which have attracted much attention in

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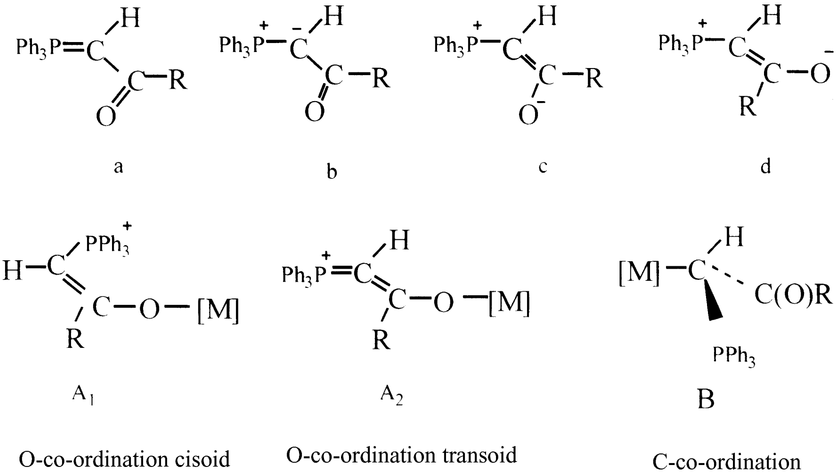
synthetic, catalytic, and theoretical fields of transition metal chemistry. The large number of reports on the organometallic ylide chemistry covering most of the d-block and some of the f-block elements may be explained with the structural variety of the ylide coordination modes. Carbonyl stabilized ylides $R_3E{=}C(R)COR(E{=}P$, As, S; R=H, alkyl or aryl groups) exhibit interesting properties such as a high stability (they can be handled in air) and an ambidentate character as ligands that can be rationalized in terms of resonance forms; form b and c account for metal C-coordination A and O-coordination B (either in cisoid or transoid), respectively (Scheme 1):



SCHEME 1

EXPERIMENTAL DETAIL

Methanol (MeOH) and diethyl ether (Et_2O) were distilled over Mg or Na, and CH_2Cl_2 was distilled over CaH_2 just before use. All other solvents were reagent grade and used without further purifications. Melting points were measured with a SMPI apparatus. Solid-state FTIR spectra in the region of 400–4000 cm^{-1} using KBr pellets were obtained on a (Perkin Elmer) spectrophotometer. ^1H and ^{31}P spectra were obtained using a 90 MHz instrument at regional sophisticated instrumentation Bu-Ali-Sina University in Iran, and ^{13}C NMR spectra were measured with a BRUKER DRX-500 spectrometer at Sharif University in Tehran, Iran. Elemental analyses were carried out at the Research Institute of Petroleum Industry.

Preparation of Ylide Ligand

Benzoylmethylenetriparatolylphosphorane was prepared and characterized by the published procedure.[13]

Synthesis of [{(p-Toly)$_3$PCHCOC$_6$H$_5$}.PdCl$_2$]$_2$

K_2PdCl_4 (0.163 g, 0.5 mmol) was refluxed with CH_3CN (15 mL), and when dissolution was complete, benzoylmethylenetriparatolylphosphorane (0.211 g, 0.5 mmol) was added. The solid was washed with water and diethylether until an orange precipitate appeared.
Yield 0.255 g (85%), m.p. 202–204°C. Anal. found: C, 57.1; H, 4.8. $C_{29}H_{27}OPPdCl_2$.0.5 H_2O (MW = 608.32). Calc.: C, 57.2; H, 4.6.

Synthesis of [{(p-Tolyl)$_3$PCHCOC$_6$H$_5$}. PtCl$_2$]$_2$

K_2PtCl_4 (0.207 g, 0.5 mmol) was refluxed with CH_3CN (15 mL), and when dissolution was complete, benzoylmethylenetriparatolylphosphorane (0.211 g. 0.5 mmol) was added. The soild was washed with water then with diethyether, a yellow precipitate was obtained. Yield 0.316 g (92%), m.p. 140–42°C. Anal. found: C, 48.5; H, 5.2. $C_{29}H_{27}OPPTPtCl_2 \cdot 2H_2O$ (MW = 726) Calc.: C, 48.06; H, 4.3.

Synthesis of [{(p-Tolyl)$_3$PCHCOC$_6$H$_5$}. Hg(NO$_3$)$_2$]

A solution of 0.382 g (0.5 mmol) of $HgNO_3 \cdot H_2O$ in methanol (15 mL) was added to a solution of 0.211 g (0.5 mmol) of benzoylmethylenetriparatolylphosphorane in dry methanol. The white product formed by slow evaporation of the solvent was dried in vacuo. Yield 0.325 g (86%). m.p. 190–192°C. Anal. found: C, 45.12; H, 4.51; N, 3.09. $C_{29}H_{27}O_7PHgN_2 \cdot 2H_2O$ (MW = 782.59) Calc.: C, 44.5; H, 3.96; N, 3.58.

Synthesis of [Ag{(p-Tolyl)$_3$PCHCOC$_6$H$_5$}$_2$]$^+$

To a solution of 0.089 g (0.5 mmol) $AgNO_3$ in dichloromethane (20 mL) were added 0.422 g (1 mmol) of the benzoylmethylenetriparatolylphosphorane. After 1–2 h the white product formed by slow evaporation of the solvent in darkness and was dried in vacuo. Yield 0.325 g (86%). m.p. 190–192°C. Anal. found: C, 64.4; H, 5.6; N, 0.6. $C_{58}H_{54}O_5P_2N_2Ag$.2.5 H_2O (MW = 1059) Calc.: C, 65.18; H, 5.62; N, 1.31.

RESULTS AND DISCUSSION

The ν(CO), which is sensitive to complexation, occurs at 1528 cm^{-1} in the parent ylide, as in the case of other resonance stabilized ylides.[11] The coordination of a ylide through carbon causes an increase in ν(CO), while for O-coordination, a lowering of ν(CO) is expected. The IR absorption bands observed for the four complexes around 1600 cm^{-1} indicate the coordination of the ylide thorough carbon (Table I). The ν(P$^+$-C), which is also diagnostic for the coordination, occurs at 879 cm^{-1} in (p-tolyl)$_3$P$^+$-CH. These assignments were confirmed by comparing the IR spectra of the corresponding ^{13}C substituted ylides. In the present study, the ν(P$^+$-C$^-$) values for all four complexes were shifted to lower

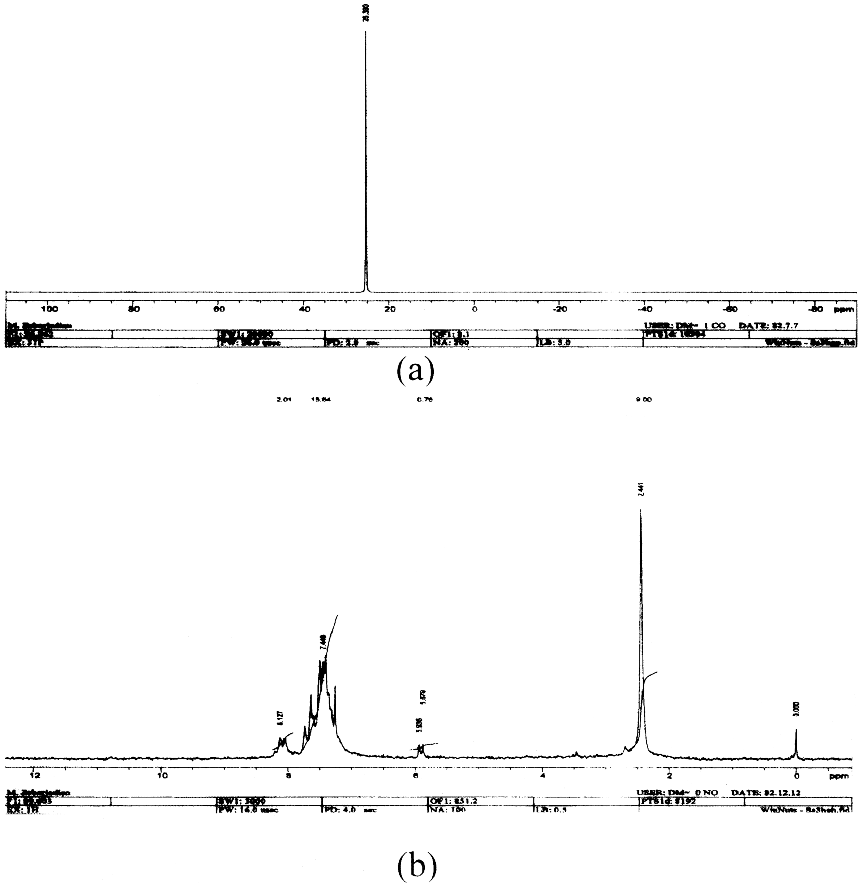


FIGURE 1 (a) ^{31}P and (b) ^{1}H NMR of [Hg(NO$_3$)$_2$. {(p-tolyl)$_3$PCHCOC$_6$H$_5$}] in CDCl$_3$ at 25°C.

TABLE I ν **(CO) of Selected and Benzoylmethyleneparatolylephosphoran and Their Complexes With the Transition of Metals**

Compound	n(CO)cm^{-1}	Ref.
{PhCOCHP(p-tolyl)$_3$}	1528	11
O-coordination		
[Sn(CH$_3$.BPPY)]Cl	1480	12
[Sn(Ph$_3$.BPPY)]Cl	1470	12
C-coordination		
[{(p-tolyl)$_3$PCHCOC$_6$H$_5$}.PdCl$_2$]	1598	This work
[{(p-tolyl)$_3$PCHCOC$_6$H$_5$}.PtCl$_2$]$_2$	1599	This work
[{(p-tolyl)$_3$PCHCOC$_6$H$_5$}. Hg(NO$_3$)$_2$]	1599	This work
[Ag{(p-tolyl)$_3$PCHCOC$_6$H$_5$}$_2$]$^+$	1678	This work

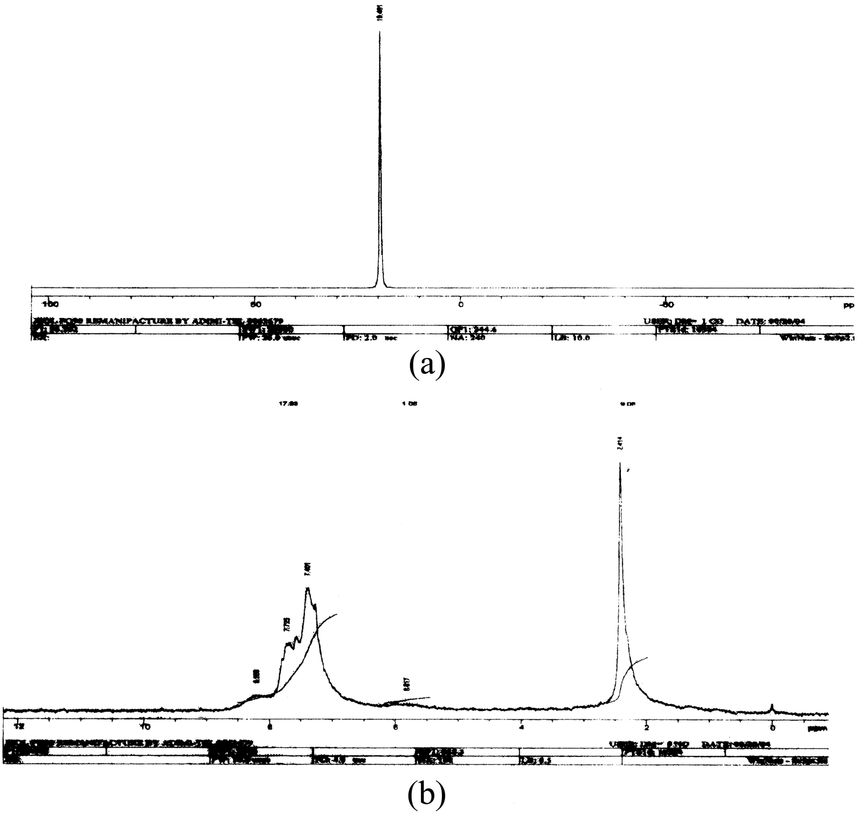


FIGURE 2 (a) ^{31}P and (b) ^{1}H NMR of [{(p-tolyl)$_3$PCHCOC$_6$H$_5$} in CDCl$_3$ at 25°C.

TABLE II ^{1}H and ^{31}PNMR Data of Benzoylmethyleneparatolylephsphoran and Their Complexes

Compound	^{1}HNMR			
	δ(CH)	$2_{J(P-H)}$	δPh	^{1}PNMR
$[\{(p\text{-tolyl})_3PCHCOC_6H_5\}.PtCl_2]$	5.59(br)	—	7.26–8.31(m)	18.31(s)
$[\{(p\text{-tolyl})_3PCHCOC_6H_5\}.PtCl_2]_2$	5.54(br)	—	7.4–8.21(m)	19.49(s)
$[\cdot\{(p\text{-olyl})_3PCHCOC_6H_5.Hg(NO_3)_2\}$	5.9 (d)	5.13	7.45–8.13(m)	25.33(s)
$[Ag\{(p\text{-tolyl})_3PCHCOC_6H_5\}_2]+$	4.86(br)	—	7.3–7.96(m)	18.75(s)

In $CDCl_3$. 90 MHz, values (ppm) were relative to internal TMS and to external 85% phosphoric acid.
S, singlet; d, doublet; m, multiplet; br, broad.

frequencies and observed around 805 cm^{-1} for four complexes, suggesting some removal of electron density in the P—C bond.

In the ^{1}H NMR spectra for three complexes, the CH ylide proton shifted downfield compared to that of a free ylide, as a consequence of the inductive effect of the metal center. The expected down field shifts of ^{31}P and ^{1}H signals for the PCH group upon complexation were observed in their corresponding spectra (Figure 1). The appearance of single signals for the PCH group in the ^{31}P and ^{1}HNMR spectra indicates the presence of only one type of molecule for all three complexes, as expected for C-coordination (Table II).

TABLE III ^{13}C NMR Data of Benzoylmethyleneparatolylphosphoran and Their Complexes

Compound	$[\{(p\text{-tolyl})_3PCHCOC_6H_5\}$ $PdCl_2]$	$[\{(p\text{-tolyl})_3$ $PCHCOC_6H_5\}PtCl_2]_2$	$[\cdot\{(p\text{-olyl})_3PCHCOC_6H_5.$ $Hg(NO_3)_2\}$
$3CH_3$	22.31(s)	22.24(s)	22.2(s)
CH	—	—	44.6(d)
$^2J_{PC}$			56
CO-Ph(o)	115.84(s)	115.91(s)	118.02(s)
CO-Ph(m)	116.57(s)	116.64(s)	118.76(s)
CO-Ph(p)	135.06(s)	135.07(s)	134.73(s)
CO-Ph(i)	146.22(s)	146.34(s)	146.21(s)
P-(p-tolyl)$_3$(o)	134.44(d)	134.39(d)	133.86(d)
$^2J_{PC}$	10.63	10.48	10.63
P-(p-tolyl)$_3$(m)	131.41(s)	131.27(d)	131.34(d)
$^3J_{PC}$	13.25	13.37	13.25
P-(p-tolyl)$_3$(p)	130.56(s)	130.58(s)	129.5(s)
P-(p-tolyl)$_3$(i)	129.49(s)	129.48(s)	128.96(s)
$^1J_{PC}$			
CO	192.9(s)	192.2(s)	193.76(s)

S, singlet; d, double; o, ortho; m, meta; p, para; i, ipso carbon.
Recorded in $CDCl_3$ at 25°C.

^{13}C NMR data of the complexes and the title ylide are listed in Table III along with possible assignments. ^{13}C NMR shifts of the CO group in complexes are around 190 ppm and are lower than 184 ppm noted for the same carbon in the parent ylide, indicating much lower shielding of carbon of the CO group in the complexes.

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