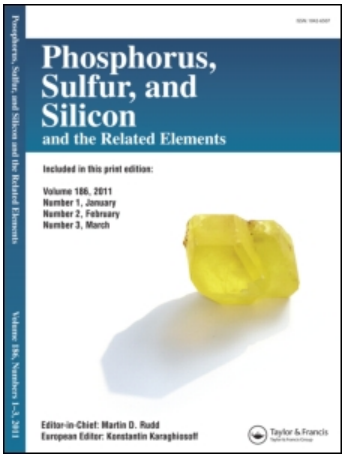

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PREPARATION AND MULTINUCLEAR NMR STUDY OF BENZOYL METHYLENE TRIPHENYLPHOSPHORNE AND BENZOYL METHYLENE TRI-n-BUTYLPHOSPHORANE Pt (0) AND Pd (0) COMPLEXES

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*The reactions of Pd (dba)$_2$ (dibenzylidene acetone palladium (0)) and Pt (dba)$_2$ (dibenzylidene acetone platinum (0)) with BPPY (Benzoyl Methylene Triphenylphosphorane) and BBuPY (Benzoyl MethyleneTri-n-butylphosphorane) in (1:2) ratios using tetrahydrofuran as solvent have yielded Pd (dba)(BPPY)$_2$ (**1**), {[Pd (dba)(C(H)COPh(PPh$_2$-o-C$_6$H$_4$)]}[PPh$_3$CH$_2$COPh](**2**), Pd (dba)(BBuPY)$_2$ (**3**), and Pt (dba)(BPPY)$_2$ (**4**) complexes. Upon heating complex (**1**) in THF, a cyclization reaction occurred to give complex (**2**). The products (**1**), (**2**), (**3**), and (**4**) are studied by IR, ^{1}H, ^{31}P, and ^{13}C NMR technique.*

Keywords: Dibenzylidene acetone; phosphorus ylide; platinum (0); palladium (0)

INTRODUCTION

Palladium complexes are widely used in catalysis.[1] Examples include the Heck reaction,[2] the Wacker process,[3] and the alkoxy-carbonylation of alkenes.[4] In several of these catalytic processes, palladium-hydrides have been claimed to be involved as key intermediates in the catalytic cycle.[5] Oxidative addition of zero-valent palladium with the organic derivatives is supposed to be the first step of the catalytic cycles and is therefore crucial. Among the various precursors of palladium (0)

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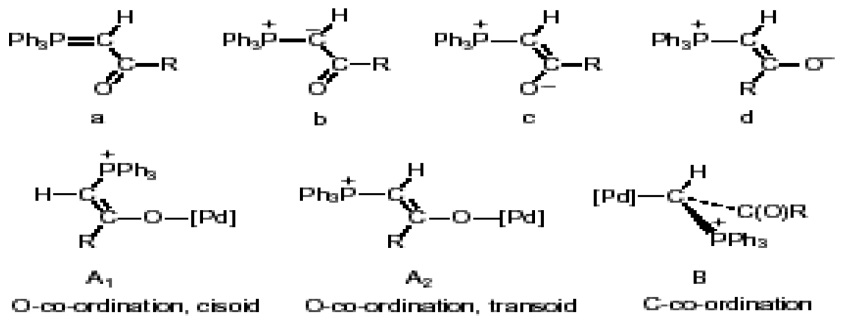
complex, mixtures of Pd $(dba)_2$ and phosphine ligands afforded efficient palladium (0) catalysts.[6] Moreover, Pd $(dba)_2$ is air stable and thus allows easy investigation of the role of different phosphine ligands in catalytic reactions. The reactivity of zero-valent metal complexes toward phosphorus ylides has attracted the interest of chemists due to the versatility of their reaction pathways, the varity of the resulting products, and their different applications.[7,8a] Among the phosphorus ylides of general stoichiometry R_3PCR'(R, R′=alkyl, alkoxy, etc.) the α-keto-stabilized ylides $Ph_3PCHCOR$ have shown useful application in organometallic chemistry (due to their ambidentate character as ligands[7]) and as reactants or valuable key intermediates in metal-mediated organic synthesis.[7,9] This ambidentate character facilitates the preparation of stable metal complexes in which the ylide could be O- (A_1, A_2, Scheme 1)[10] or C-coordinated (B).[11] With both modes rationalized in terms of the resonance forms a–c together with the isomeric form. However, while a large number of compounds containing C-coordinated ylides are known,[9–11] very few examples of O-bonded ones have been reported (Scheme 1).[10]



SCHEME 1

The phosphorus ylide complexes have been well investigated. They are versatile ligands for catalysts in a very small number of catalytic reactions, such as the hydrogenation of olefins and the cyclotrimerization and polymerization of acetylenes. However, the most important application is in the industrially used SHOP process.[12] Data on Pd (II) analogous to Pd (0) complexes studied in present work can be founded in Navarro's and Albanese's works.[8] Thus, complexes (**1**), (**2**), (**3**), and (**4**), obtained from the reaction of the α-carbonyl-stabilized ylides (BPPY and BBuPY) with Pd $(dba)_2$ and Pt $(dba)_2$, may be assumed to be catalytically active in a process that converts ethane to methyl propanoate (MEP).[13]

EXPERIMENTAL

Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium and CH_2Cl_2 over CaH_2 just before use. All other solvents were reagent grade and used without further purifications. All reactions were performed under N_2 atmosphere using standard schlenk tube techniques. ^1H, ^{31}P, and ^{13}C NMR spectra were obtained using a 90 MHz instrument at regional sophisticated instrumentation Bu-Ali Sina University, factually of science. Solid-state IR spectra in the region of 400–4000 cm^{-1} using KBr pellets were obtained on a Shimadzu-435 spectrophotometer. Elemental analyses were carried out at Tarbiate Modarres University.

Synthesis

Pd (dba) (BPPY)$_2$

To a solution of Pd $(dba)_2$ (0.0287 g, 0.05 mmol) in tetrahydrofuran (5 ml) a solution of BPPY (0.038 g, 0.1 mmol) in the same solvent (5 ml) was added, and the red solution was stirred for ca. 1 h. The solution was concentrated under reduced pressure to ca. 1.0 cm^3, and diethyl ether was (10.0 cm^3) added. The yellow product was collected by suction filtration (Anal. found: C, 71.85; H, 4.95. Calcd.: C, 71.62; H, 4.89).

Pd (dba)(BBuPY)$_2$

To a solution of Pd $(dba)_2$ (0.0287 g, 0.05 mmol) in tetrahydrofuran (5 ml) a solution of BBuPY (0.032 g, 0.1 mmol) in the same solvent (5 ml) was added, and the red solution was stirred for ca. 4 h. The solution was concentrated under reduced pressure to ca. 1.0 cm^3, and diethyl ether was (10.0 cm^3) added. The yellow solid was filtered off, washed with Et_2O (3×5 ml), and dried under vacuum.

Pt (dba)(BPPY)$_2$

To a solution of Pt $(dba)_2$ (0.0332 g, 0.05 mmol) in tetrahydrofuran (5 ml) a solution of BPPY (0.038 g, 0.05 mmol) in the same solvent (5 ml) was added, and the violet solution was stirred for ca. 8 h. The solution was concentrated under reduced pressure to ca. 1 cm^3, and diethyl ether was (5 cm^3) added. The yellow-formed solid was filtered off, washed with Et_2O (2×5 ml), and dried under vacuum (Anal. found: C, 63.92; H, 4.43. Calcd.: C, 63.78; H, 4.36).

Synthesis of [Pd (dba) C(H) $COPh(PPh_2\text{-}o\text{-}C_6H_4)](PPh_3CH_2COPh)$ (2)

A suspension of complex (**1**) in THF (15 ml) was refluxed for 12 h under N_2 atmosphere. The color of the solid changed from pale yellow to white. The final reaction mixture was filtered off, and the residue was washed several times with Et_2O (5 × 2 ml) and dried under vacuum.

RESULTS AND DISCUSSION

The υ (CO), which is sensitive to complexation, occurs at 1525 cm^{-1} in the parent ylide, as in the case of other resonance stabilized ylides.[14] Coordination of ylide through carbon causes an increase in υ (CO), while for O-coordination a lowering of υ (CO) is expected (Table I). Thus infrared spectra in the solid state show υ (CO) in the range of 1620–1680 cm^{-1}, at higher wave numbers with respect to the free ylide[14] (BPPY, υ (CO) 1525 cm^{-1}).

An increase of υ (CO) observed for these two complexes at 1675 and 1649 cm^{-1} indicated coordination of the ylide through the carbon atom. The υ (CO) observed for these two complexes at 1618 cm^{-1} indicated that dba coordinated to Pd and Pt. The υ (P—C), which is also diagnostic of the coordination, occurs at 998 cm^{-1} in $(C_6H_5)_3P{-}CH_2$ and at 887 cm^{-1} in $(C_6H_5)_3PCHCOC_6H_5$.[15] These assignments were confirmed by comparing the IR spectra of the corresponding ^{13}C

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

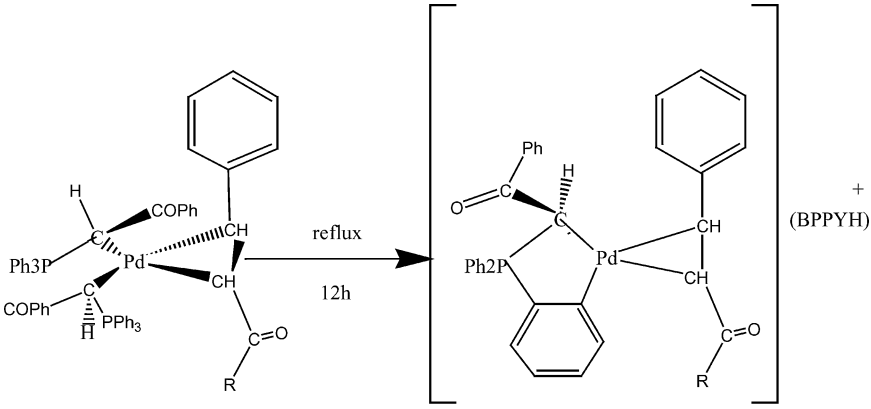
Compound	υ (CO) cm^{-1}	Ref.
$Ph_3PCHCOCH_3$ (APPY)	1530	18
$Ph_3PCHCOPh$ (BPPY)	1525	19
C-coordination		
Pd (dba)$(BPPY)_2$ (**1**)	1618,[a] 1675	This work
Pd (dba) C H COP $(PPh_2\text{-}o\text{-}C_6H_4)(PPh_3CH_2COPh)$ (**2**)	1711, 1585, 1618[a]	This work
Pt (dba)$(BPPY)_2$ (**4**)	1618,[a] 1649	This work
$BPPY{\cdot}HgCl_2$	1635	14
Au $[CH(PPh_3)CON(CH_3)_2]$	1605	21
O-coordination		
$[Sn(CH_3)_3{\cdot}BPPY]$ Cl	1480	20
$[(SnPh_3){\cdot}BPPY]$ Cl	1470	20
$[Pd(C_6F_5)(PPh_3)_2$ (APPY)$]ClO_4$	1513	20

[a] υ(CO) dba.

substituted ylides. In the present study the υ (P^+—C^-) values for two complexes were shifted to lower frequencies for Pd and Pt complexes, respectively, suggesting some removal of electron density in the P—C bond. The IR spectra show a weak band at 1510 cm^{-1}, which is characteristic for Pt-coordinated olefin complexes, due to coupled υ (CC) + (CH) modes of the olefinic systems. Transition metal complexes having coordinated olefins can react with ylides in two different ways: (1) by nucleophilic attack of the ylidic carbon atom to the coordinated unsaturated double bond with the formation of a metal-alkyl derivatives,[16] or (2) by attack of the ylide to the metal center with substitution of the olefin ligand and formation of a metal-C (ylide) σ-bonded.[17] The complex Pd (0)$(dba)_2$ associated with phosphine ligands is commonly used as a source of palladium (0) complexes.[6b] One can vary the phosphine ligand at will and thus test the reactivity of the resulting complexes in catalytic reactions. When alone Pd $(dba)_2$ is in solution, the complex Pd $(dba)_2$ is mainly present as Pd (dba) since 1 equiv. of the free dba ligand is always detected in ^{1}H NMR.[6b] Since this species is unsaturated (14 electrons), it probably aggregates. The external part of these aggregates should only be accessible for the reaction with BPPY, which is therefore always in high concentration relative to the reactive Pd(dba) at the interface. The following mechanism was established on the basis of ^{31}PNMR spectroscopy:

1. Pd $(dba)_2 \rightarrow$ Pd (dba) + dba
2. Pd (dba) + 2 BPPY $\rightarrow$ Pd $(dba)(BPPY)_2$
3. Pd $(dba)(BPPY)_2 \rightarrow$ $[Pd\ (dba)(BPPY—H)]^-(BPPYH)^+$ (cyclometalation)

The coordination geometry is nearly square planar. As a result of steric interactions, the coordination plane forms an angle with the remaining ligand fragment such that there is no molecular symmetry. The first dba ligand is easily exchanged by two BPPY ligands, while the second one is hard to remove. We ascribe these results, surprising at first glance, to a conflict between electronic and steric requirments. Thus in our view, one dba and two ylide ligands appear to be the best comprise between electronic factors (which lead to the exchange of the second dba by the third ylide) and steric constrains (which oppose this exchange). When a suspension of complex **1** was refluxed overnight, a color change from yellow to white of the insoluble material was observed. After filtration, the ^{31}PNMR spectrum exhibited a singlet at 26.52 ppm, a second resonance at 19.47 ppm very close to that of the phosphonium salt,[16c] and a third resonance at about 18 ppm related



R = PhCH=CH (**1**) R = PhCH=CH (**2**)

SCHEME 2

to free ylide. The IR spectrum of the complex (**2**) disappearance of υ (CO) at 1675 cm^{-1}, is characteristic of complex (**1**), as is the formation two new carbonyl bands at 1711 and 1585 cm^{-1}. In the ^1H NMR spectrum the ylide proton resonance complex **2** was observed a broad singlet at 4.7 ppm. On the basis of this data (IR, NMR), we suggested the cyclometalation reaction take place with a phenyl ring attached to the P atom. In the ^1H NMR spectrum the ylide proton resonance complex **1** was observed as a doublet at 6.2 ppm with $^2J_{HP}$ of 12.1 Hz, thus suggesting a direct bond of methine carbon with the palladium atom. Furthermore, the values of the $^2J_{HP}$ coupling constants between the methine proton and the phosphorus atom of the ylide ligands are lower than those of the free ylide (BPPY, 24.6 Hz) in agreement with a $SP^2 \rightarrow SP^3$ rehybridization of the ylide carbon upon coordination to the metal atom. On the other hand, the ylide bonds to the soft metal Palladium in the C-coordination form. In the ^1H NMR of complex (**4**) the ylide signal of BPPY appears to be a broad signal due to the value of $^2J_{HP} = 0$ Hz, as previously noted in similar derivatives.[15] This broad resonance probably arises from very close chemical shifts of the methinic proton of the two diastereoisomers. The same consideration can be applied to the broad signal of the BBuPY ligand in the complex (**3**).

The ^{31}P NMR spectrum of a mixture of Pd $(dba)_2$ (1 mmol) with 2 equiv. of BPPY exhibited after 4 h two signals (Figure 1a): one single signal at $\delta_1 = 27.96$ ppm, which is characteristic of Pd (dba)$(BPPY)_2$,

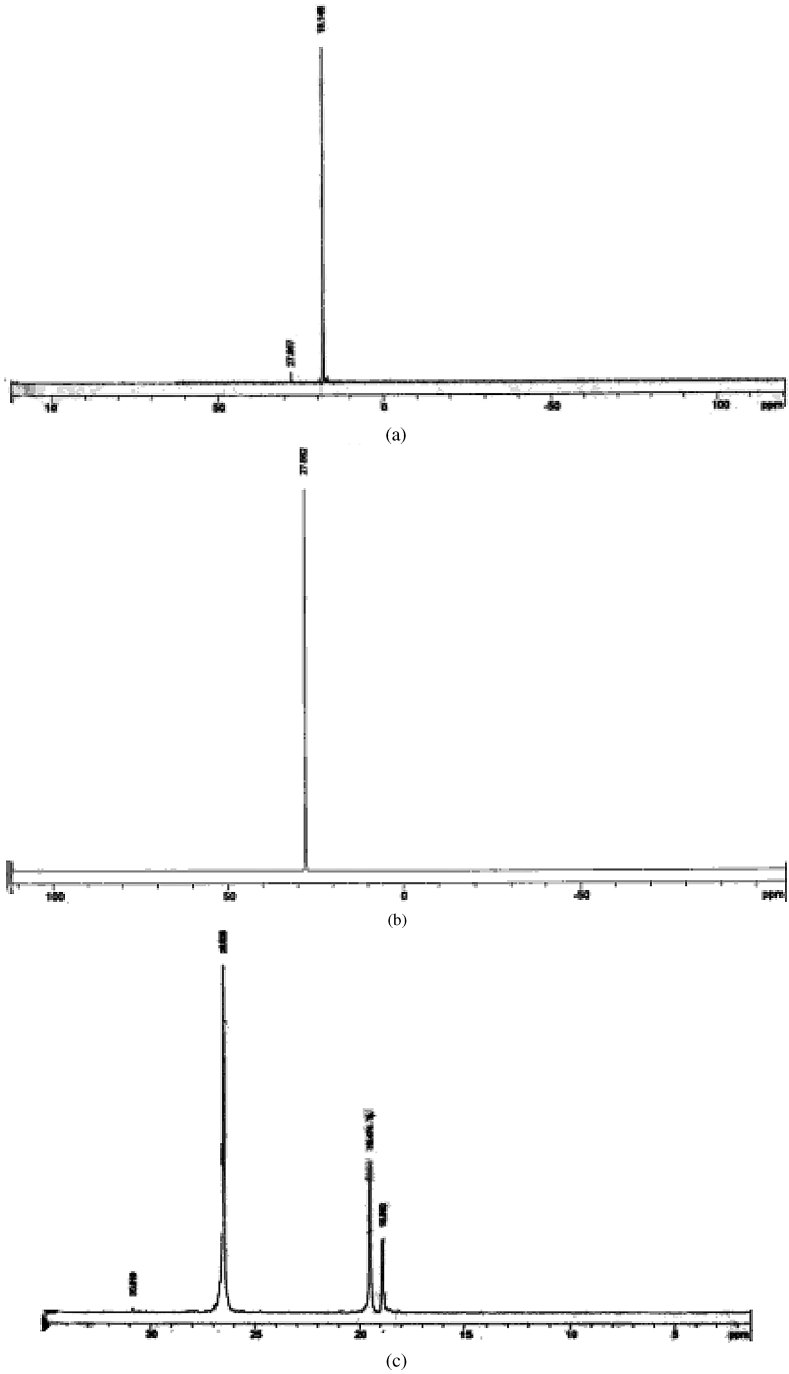


FIGURE 1 (a) ^{31}PNMR Pd $(dba)_2$ and BPPY (1:2) after 4 h. (b) ^{31}PNMR Pd $(dba)_2$ and BPPY (1:2) after 12 h. (c) ^{31}PNMR Pd $(dba)_2$ and BPPY in 40°C after 12 h.

$$\text{Pd (0)(dba)}_2 \rightarrow \text{Pd (0)(dba)} + \text{dba}$$
$$\text{Pd (0)(dba)} + 2\text{BPPY} \rightarrow \text{Pd (0)(dba)(BPPY)}_2$$

while free ylide (BPPY) at $\delta = 18.14$ ppm was detected (Figure 1a). After 12 h the signal of BPPY had disappeared (Figure 1b).

The system changed as a function of time and temperature because the solution of Pd (dba)$(BPPY)_2$ in THF was refluxed overnight. Complex (**2**) at $\delta = 26.52$ was detected (Figure 1c), while ^{31}P NMR spectrum exhibited a second resonance at $\delta = 19.47$ ppm very close to that of phosphonium salt.[16c]

$$\underset{}{\text{Pd(0)(dba)(BPPY)}_2} \rightarrow \underset{\delta = 27.96}{\text{Pd(0)(dba)(PhCOCHPPh2-o-Ph)}} + \underset{\delta = 26.5}{\text{BPPYH}^+} \qquad \delta = 19.47$$

The resonances of ^{31}P NMR complexes (**3**) and (**4**) were observed to occur at a lower field with respect to the free ylide (Table II), thus suggesting a direct bond of methine carbon with Pd and Pt atoms.

No coupling to Pt was observed at room temperature in ^{1}H and ^{31}P NMR spectra of complex (**4**). Failure to observe satellites in the above spectra was previously noted in the ylide complex of Hg (II)[22] and Ag (I)[23], which were assigned to fast exchange of the ylide.

The ^{13}C NMR data of the complexes (**1**), (**3**), (**4**) and the title ylide are listed in (Table III) along with possible assignments. The most interesting aspect of the ^{13}C of the complexes (**1**) and (**3**) is the up field shift of the CH's signals of the ylidic carbon, while the adjacent carbonyl carbon (BPPY and BBuPY, 184 ppm) is shifted downfield (189 ppm, complex (**1**); 188.5 ppm, complex (**3**); and 190 ppm, complex (**4**)). On the other hand, the ^{13}C shifts of CO group in complexes, (**1**) and (**3**) are around 189 ppm, lower than the 184 noted for the same carbon in the parent

TABLE II ^{1}H and ^{31}P NMR Data of BPPY and BBuPY and Their Complexes with Palladium and Platinum (0)

Compound	δ (CH)	$^2J_{HP}$	δ (PPh_3)	δ (CH_2)	δ (CH_3)	δ (^{31}P)
BPPY	4.2 (d)	24.6	7.33–7.99	—	—	18.1
BBuPY	3.7 (br)	—	7.2–7.9 (m)	1.37 (m)	0.8 (br)	20.02
Complex (1)	6.2 (d)	12.1	7.09–8.3 (m)	—	—	27.96
Complex (3)	3.73 (br)	—	7.15–7.95 (m)	1.25, 1.84	0.81	24.69, 31.86[a]
Complex (4)	4.4 (br)	—	7.15–7.95 (m)	—	—	28.93

BPPY, benzoylmethylene triphenyl phosphorane; BBuPY, benzoyl MethyleneTri-n-buthylphosphorane in DMSO-d_6 90 MHz, values (ppm) relative to internal TMS, in $CDCl_3$, 90 MHz, values (ppm) relative to external 85% phosphoric acid; d, doublet; br, broad; m, multiplet.

[a] δ (^{31}P) O═P(n-Bu)$_3$CHCOPh.

TABLE III Selected ^{13}CNMR Data of BPPY, BBuPY, and Their Complexes with Pd (0) and Pt (0)

	CH	Ph	C═O
BPPY	54.37	128–133	184
BBuPY	47 (d)	133.3–137.2 (m)	184 (s)
Complex (1)	29.45	125.48–130 131.96–134.85	189.18
Complex (3)	30.02	125, 128.62, 132.59	188.52
Complex (4)	48	125, 128.62, 133.7	190

In $CDCl_3$, 90 MHz, values (ppm); s, singlet; d, doublet; m, multiplet.

ylide, indicating much lower shielding of carbon of the CO group in the complexes, as expected for C-coordination.

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