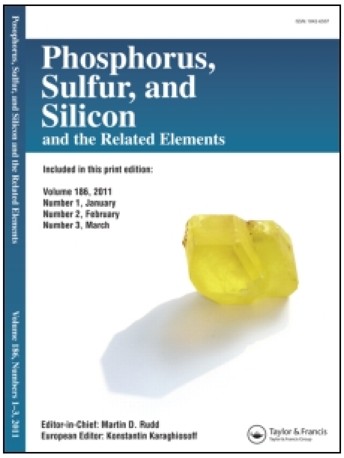

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CHARACTERIZATION REACTION OF BENZOYL METHYLENE TRIPHENYLPHOSPHORANE AND BENZOYL METHYLENE TRI-N-BUTHYLPHOSPHORANE WITH RHODIUM (III) AND RUTHENIUM (III) CHLORIDE. A MULTINUCLEAR NMR STUDY

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*The reactions of title ylide $(C_6H_5)_3PCHCOC_6H_5$, (BPPY) and $(n\text{-}C_4H_9)_3PCHCOC_6H_5$, (BBuPY) with rhodium (III) and ruthenium (III) chloride in equimolar ratios using methanol as solvent have yielded crystals of $[(BPPY\text{-}H)_3Rh]$, (**1**), $[(BPPY)_2Ru(MeOH)_2(H_2O)_2]Cl_3$, (**2**), and $[Ru(BBuPY)Cl_2S_2]Cl$ ($S = H_2O$ or CH_3OH), (**3**). The IR and ^1H, ^{13}C, ^{31}P NMR data of the products were obtained. Analytical and NMR data are consistent with the cyclometalated and octahedral structures for (**1**) and (**2**) respectively.*

Keywords: Phosphorus ylide; rhodium; ruthenium; ylide

The coordination chemistry of the phosphoranes of the type $R_3P\text{-}CH_2^+$ is well known.[1–4] Resonance stabilized phosphorus ylides, particularly the keto ylides are also successfully used as ligand 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] the 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. As a general feature, the coordination chemistry of $R_3ECHCOR$-type (E=P, As) ligands appears to be dominated by C-(ylide) metal coordination although a few examples of O-(ylide)-bond complexes are known. P and As-ylides are remarkable ligands which

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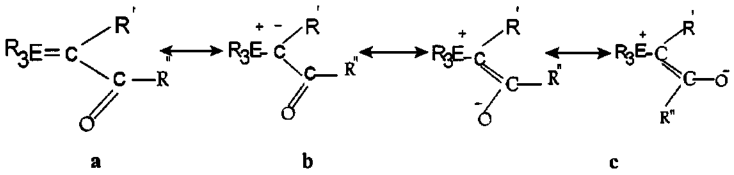
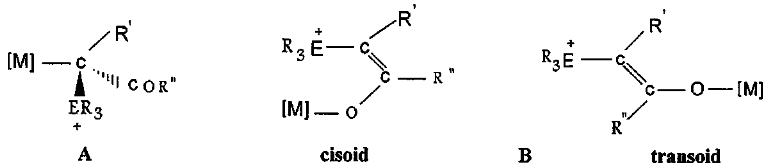
have attracted much attention in synthetic, catalytic and theoretical fields of transition metal chemistry.[11] The large number of reportes on the organometallic ylide chemistry covering most of the d-block and some of the f-block elements may be explained with the structural variety of the ylide coordination modes. Carbonyl stabilized ylides of the type $R_3E{=}C(R)COR$ (E=P, As, S; R = H, alky 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 the resonance forms (a-c) (where c is represented by the cis and trans geometrical isomers):



Forms b and c account for the metal C-coordination A and O-coordination B (either in the cisoid or transoid form) respectively:



The chemical behavior of carbonyl-stabilized ylides is largly dominated by the C (ylide)-coordination,[11,12] while very few example of O-coordinated ylides are known.[13] A symmetrical chloro-bridged dimeric structure for the analogous complex data formed by the reaction of BPPY and BBuPY with potassium hexachloro rhodate (III) and ruthenium (III) chloride to account for its molecular weight data the structure and their NMR data are not available. The aims of our present work are (i) to correctly determine and compare the molecular structures of the products formed by the title ylide with rhodium (III) chloride and ruthenium (III) chloride, and (ii) to characterize all the products by IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra.

EXPERIMENTAL DETAILS

Preparation of Ylide Ligand

Benzoyl methylen triphenyl phosphorane was prepared and characterized by the published procedure.[14]

Preparation of Ylide-Rh (III) and Ru (III) Complexes

[(BPPY-H)$_3$Rh] (1)

A solution of .0434 g (0.1 mmol) of potassium hexachloro rhodate (III) in a mixture of methanol and water was added to a methanolic solution of .038 g (0.01 mmol) of benzoylmethylenetriphenyl phosphorane in methanol and the mixture was stirred for 72 h at 35°C. The solvent was then removed at room temperature. The yellow-brrown product was washed with benzene and dried at room temperature. (Anal found: C, 75.9; H, 5.4 cal: C, 75.55; H, 4.84)

[(BPPY)$_2$Ru(MeOH)$_2$(H$_2$O)$_2$]Cl$_3$ (2)

A solution of .380 g (1 mmol) of the above ylide in methanol was added to 0.2075 g (1 mmol) of $RuCl_3$ in methanol and the mixture was stirred for 24 h. On concentration by removing the solvent in the vaccuum, a brown dark, precipite was obtained. The brown product was washed with benzene and dried at room temperature. (Anal found: C, 59.6; H, 4.9 cal: C, 60.4; H, 4.85)

[Ru(BBuPY)Cl$_2$S$_2$]Cl Complex (3)

A solution of 0.320 g (1 mmol) of the BBuPY in methanol was added to 0.2074 g (1 mmol) of $RuCl_3$ in methanol and the mixture was stirred for 12 h at room temperature. On concentration by removing the solvent in the vaccuum, a brown dark, precipite was obtained. The brown product was washed with diethylether and dried at room temperature.

RESULTS AND DISCUSSION

The v (CO) which is sensitive to complexation occurs at 1525 cm^{-1} in the parent ylide, as in the case of other resonance stabilized ylides.[15] Coordination of ylide through carbon cause an increase in v (CO) while for O-coordination a lowering of v (CO) is expected (Table I). Thus infrared spectra in the solid state show v (CO) in the range of 1620–1670 cm^{-1}, at higher wave numbers with respect to the free ylide (BPPY, v (CO) 1525 cm^{-1}).[15]

A lowering of v (CO) observed for these two complexes at 1625 and 1620 cm^{-1} indicated coordination of the ylide through the carbon atom. The v (P—C) which is also diagnostic of the coordination occurs at 998 cm^{-1} in $(C_6H_5)_3P\text{-}CH_2$ and at 887 cm^{-1} in $(C_6H_5)_3PCHCOC_6H_5$.[16] These assignments were confirmed by comparing the IR spectra of the

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

Compound	v (CO) cm^{-1}	Ref.
$Ph_3PCHCOCH_3$(APPY)	1530	16
$Ph_3PCHCOPh$(BPPY)	1525	13
C-coordination		
BPPY·$RhCl_3$	1625	this work
BPPY·$RuCl_3$	1620	this work
BPPY·$HgCl_2$	1635	15
AuCl{CH(PPh_3)CON(CH_3)$_2$	1605	1
O-coordination		
[(Sn(CH_3)$_3$·BPPY]Cl	1480	6
[($SnPh_3$)·BPPY]Cl	1470	6
[Pd{C_6F_5)(PPh_3}$_2$(APPY)]ClO_4	1513	6

corresponding ^{13}C substituted ylides. In the present study the v (P^+-C^-) values for two complexes were shifted to lower frequencies for Rh and Ru complexes, respectively, suggesting some removal of electron density in the P—C bond.

The ^1H NMR data of the rhodium (III) and ruthenium (III) ylide complexes along with those of the parent ylides are listed in Table II. The signals due to methine protons, when recorded in DMSO-d_6 were either broad or unobserved probably due to very low solubility of the two complexes in DMSO-d_6. The similar behavier was observed earlier in the case of ylide complexes of platinum (II) chloride[17] and mercury (II) halides.[18]

In the ^1H NMR spectra (**1**), (**2**), and (**3**), the CH ylide proton is shifted down field compared to that of the free ylide (BPPY, 4.41) and (BBuPY, 2.4) as a consequence of the inductive effect of the metal center. The

TABLE II ^1H and ^{31}P NMR Data of BPPY, BBuPY, and Their Complexes with Rh (III) and Ru (III) Chloride (T = 298 K: J in Hz: TMS $\delta = 0.00$ ppm)

Compound	δ (CH)	^1J (P-H)	δ (PPh_3)	δ (CH_2)	δ (CH_3)	δ (^{31}P)
BPPY	4.35–4.63 (d)	24.6	7.33–7.99 (m)	—	—	18.1
BBuPY	2.4 br	—	7.2–7.9 (m)	1.37 br	0.80 br	20.9
Complex (**1**)	6.2–6.33 (d)	12.1	7.3–8.1 (m)	—	—	21.8
Complex (**2**)	4.1 br	—	7.56 (m)	—	—	30.4
Complex (**3**)	4.15 br	—	7.6 (m)	1.41 br	0.87 br	31.4

BPPY benzoylmethylene triphenyl phosphorane, 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.

values of the $^{2}J_{(H\text{-}P)}$ coupling constant between the methine proton and the phosphorus atom of the ylide ligands are lower than those of the free ylide in agreement with a $SP^2 \rightarrow SP^3$ rehybridization of the coordination to the metal atom.

The expected down field shifts of ^{31}P and ^{1}H signals for the PCH group upon complexation were observed in their corresponding spectra (Figures 1 and 2). The appearance of single signals for the PCH group in the ^{31}P and ^{1}H NMR spectra indicates the presence of only one molecule for all three complexes, as expected for C-coordination. It must be noted that O-coordination of the ylide generally leads to the formation of *cis*

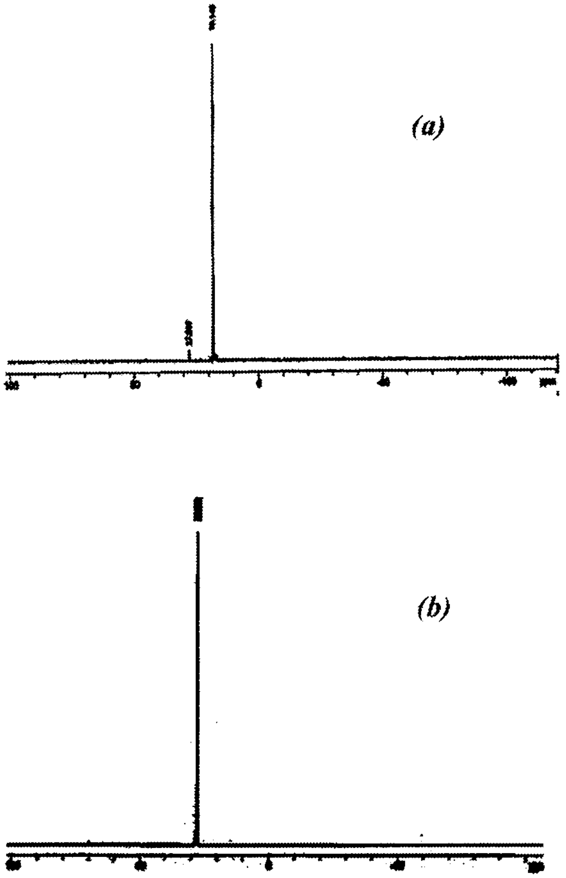


FIGURE 1 ^{31}P NMR spectrum of the free ylide BPPY (a) and the Rh (III), complex (b).

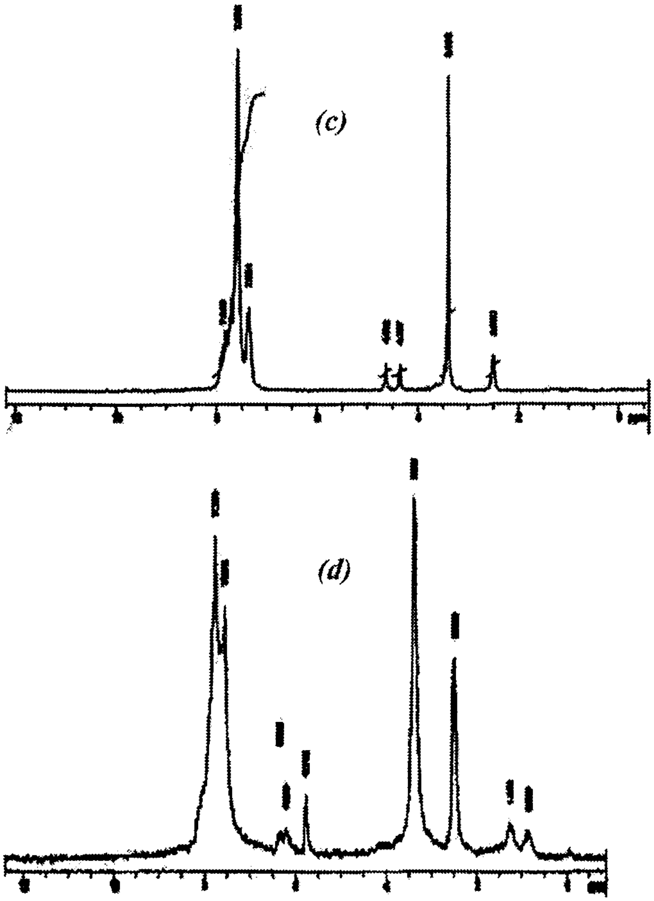


FIGURE 2 ^{1}H NMR spectrum of the free ylide BPPY (c) and the Rh (III) complex (d).

and *trans* isomers giving rise to two different signals in the ^{31}P and ^{1}H NMR spectra.[8] The Rh (III) chloride reacts with the carbonyl stabilized ylide (BPPY) in methanol to form (**1a**) (reaction 1).

$$K_3[RhCl_6] + 3BPPY \longrightarrow \underset{(\mathbf{1a})}{[Rh(BPPY)_3Cl_3]} + 3KCl \quad \text{(reaction 1)}$$

Reaction 1 represents an easy method for preparation in proper yield of tris (BPPY) rhodium (III) complex, containing three BPPY, that those C-coordinated to the rhodium. Upon refluxing the complex $[Rh(BPPY)_3Cl_3]$, the cyclo metalated derivative (**1**) was obtained

TABLE III ^{13}C NMR Data of BPPY and its Complexes with Rh (III) and Ru (III) Chloride (T = 298°K; J in Hz; TMS $\delta = 0.00$ ppm)

Possible assignments	(BPPY)	$[Rh(BPPY\text{-}H)_3]$	$[(BPPY)_2Ru(MeOH)_2(H_2O)_2]Cl$
(CH)	54.37 (t)	44.67	
J(PC)	111.9[c]		
(CO-Ph) (o)	128.03 (s)	125.99 (s)	
(PPh_3) (i)	129.03 (d)	127.13 (m)	123.29
^{1}J (PC)	79.0[c]		
(CO-Ph) (m)	129.17 (s)	132.35 (m)	
(PPh_3) (m)	129.72 (d)	130.64 (d)	123.18
^{3}J (PC)	12.4	6.53	
(CO-Ph) (p)	129.89 (s)	134.43 (m)	
(PPh_3) (p)	130.47 (s)	135.18 (d)	127.09
$PPh_3)$ (o)	132.34 (d)	138.05 (m)	128.457
^{3}J (PC)	10.1	12.88	
(CO-Ph) (i)	133.83 (d)	139.63 (m)	
^{3}J (PC)	14.7		
(CO)	160.88		

In $CDCl_3$, 90 MHz, values (ppm); s, singlet; d, doublet; m, multiplet; t, triplet; i, ipso; m, meta; o, ortho; p, para.

(reaction 2).

$$\underset{(\mathbf{1})}{[Rh(BPPY)_3Cl_3] \longrightarrow [Rh(BPPY\text{-}H)_3]} + 3HCL \quad \text{(reaction 2)}$$

The ^{13}C NMR spectra show the ylidic carbon atom shifted upfield (<40 ppm) with respect to the free ylide (BPPY, 54.3), while the adjacent carbonyl carbon (BPPY, 184.9 ppm BBuPY, 199 ppm) is strongly shifted downfied (>200 ppm) (Table III). The ^{13}C NMR data of the three complexes and title ylides are listed in Table III and Table IV along with possible assignments. The most interesting aspect of the ^{13}C spectra of the complexes is the upfield shift of the signals due to ylidic carbon. Such upfield shift observed in $PdCl(\eta^3\text{-}2\text{-}XC_3H_4)(C_6H_5)_3PCHCOR$ (X=H, CH_3; R=CH_3, C_6H_5) was attributed to the change in hybridization of the ylidic carbon.[19]

TABLE IV ^{13}C NMR Data of BBuPY and the Complex with Ru(III) Chloride (T = 298°K; J in Hz; TMS $\delta = 0.00$ ppm)

Compound	δ (Ph)	δ (CH)	δ (CO)	δ (CH_2)	δ (CH_3)
BBuPY	133.3, 137.2 (m)	34 (d)	199.6 (s)	23.25, 28.76 (d)	18.6 (s)
Complex (**3**)	125.13–132.58	57.68	184.5, 188.9	48.01, 53.13	30.019

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

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