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PREPARATION OF CHELATE YLIDE LIGANDS AND THEIR PALLADIUM(II) AND PLATINUM(II) HALIDE COMPLEXES

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Summary

Keto-stabilized mono-ylides of 1,2-bisdiphenylphosphinoethane and bisdiphenylphosphinomethane, $Ph_2P—(CH_2)_n—P^+(Ph)_2—C^-H—C(O)—R$ ($Ph = C_6H_5$; $n = 1$ or 2; $R = C_6H_5$, CH_3 or OCH_3), and their palladium(II) and platinum(II) halide complexes were prepared and characterized by means of infrared, ^1H and ^{31}P NMR spectra. The chelate ylide ligands coordinate to the metal through the ylide carbon and phosphine phosphorus forming a six or five-membered chelate ring. The stability of the M—C(ylide) bonding is discussed on the basis of the results of the reaction of the complexes with pyridine.

Introduction

Transition metal complexes of keto-stabilized ylides have been well studied and are of interest because of the stability of the ylides as ligands and the ease of detection of the coordination of the ylide carbon to the metal by means of infrared spectroscopy [1—6].

We have tried to convert one of the two phosphine moieties in 1,2-bisdiphenylphosphinoethane or bisdiphenylphosphinomethane into keto-stabilized ylides to facilitate the coordination ability of the ylides. Thus we have synthesized a series of chelate ylide ligands, $Ph_2P—(CH_2)_n—P^+(Ph)_2—C^-H—C(O)—R$ ($Ph = C_6H_5$; $n = 1$ or 2; $R = C_6H_5$, CH_3 or OCH_3). They coordinate to palladium(II) or platinum(II) to form chelate ylide complexes of the type $MX_2(Y)$ (M = Pd or Pt; X = Cl, Br, I or SCN; Y = chelate ylide) with a six- or five-membered chelate ring [7—9]. A single crystal X-ray analysis of one of the complexes, $PdCl_2$(bdep) (bdep = benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane) confirmed that the ligand is coordinated to palladium via the ylide carbon and phosphine phosphorus in square planar geometry [10]. The chelate ylide complexes are notably more stable than complexes of keto-stabilized ylides of triphenylphosphine which are monodentate [5]. The chelate ylides provide a convenient series of complexes for comparison of the properties (e.g. *trans*-effect or influence) of a phosphine and an ylide occurring together in a complex. The present paper reports the details of the preparation and characterization of the ylides and their complexes.

Results and discussion

The yields, melting points and analytical data of the phosphonium salts, ylides and complexes are given in Table 1. The formation of the chelate ylide complexes is facile and the yields are generally good. The complexes are thermally stable and are not affected by air. Carbonyl stretching frequencies in the infrared spectra, recorded in KBr disks, and the chemical shifts and the coupling constants of the methine proton of the ylides adjacent to carbonyl group in ^{1}H NMR spectra, recorded in either chloroform-d_1, dichloromethane-d_2, *N,N*-dimethylformamide or dimethylsulfoxide, are given in Table 2. ^{31}P NMR data are also given in Table 2. The abbreviations of the names of the ylides are as follows.

1) $Ph_2P-CH_2-CH_2-P^+(Ph_2)-C^-H-C(O)-R$ type:
bdep ($R = C_6H_5$), benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane; adep ($R = CH_3$), acetylmethylenediphenyl-2-diphenylphosphinoethylphosphorane; cdep ($R = OCH_3$), carbomethoxymethylenediphenyl-2-diphenylphosphinoethylphosphorane; cedep ($R = OC_2H_5$), carboethoxymethylenediphenyl-2-diphenylphosphinoethylphosphorane;
2) $Ph_2P-CH_2-P^+(Ph_2)-C^-H-C(O)-R$ type:
bdmp ($R = C_6H_5$), benzoylmethylenediphenyldiphenylphosphinomethylphosphorane; admp ($R = CH_3$), acetylmethylenediphenyldiphenylphosphinomethylphosphorane; cdmp ($R = OCH_3$), carbomethoxymethylenediphenylphosphinomethylphosphorane;
3) $Ph_3P^+-C^-H-C(O)-R$ type:
btp ($R = C_6H_5$), benzoylmethylenetriphenylphosphorane; ctp ($R = OCH_3$), carbomethoxymethylenetriphenylphosphorane.

The carbonyl stretching frequency of keto-stabilized ylides and ylide complexes is a convenient probe to infer the coordination of the ylide to the metal. It has been suggested that the high-frequency shift of ν(CO) upon complex formation is an indication that the ylide coordinates to the metal through the ylide carbon to form an M—C(ylide) (sp^3) bond [2,7]. This is also the case for all the ylide complexes in the present study, except for $PdCl_2(bdep)_2$ (see Table 2), and the ylide carbon seems to coordinate to Pd or Pt. A single crystal X-ray analysis of $PdCl_2$(bdep) has shown that bdep coordinates through the ylide carbon and phosphine phosphorus to form a square planar coordination around Pd [10]. The ν(CO) (1526 cm^{-1}) for $PdCl_2(bdep)_2$ is identical with that of bdep indicating that the two ligands coordinate to palladium through phosphine phosphorus atoms only.

The carbonyl stretching frequencies of the keto-stabilized ylides are dependent on the basicity of the substituent [11]. The ν(CO) are in the order; cdep(1614) > adep(1532) > bdep(1526) and cdmp(1616) > admp(1532) > bdmp(1526), and this order reflects the electron releasing effect of the substituents which is in the order $OCH_3 > CH_3 > C_6H_5$. The frequencies become

(continued on p. 118)

TABLE 1

MELTING POINTS, YIELDS AND ANALYTICAL DATA OF PHOSPHONIUM SALTS, YLIDES AND COMPLEXES

Compound	M.p. (°C)	Yield (%)	Formula	Analytical data found (calcd.) (%)		
				C	H	Halogen
bdepHBr	201–203	90	$C_{34}H_{31}BrOP_2$	68.2(68.3)	5.5(5.2)	13.2(13.4)
adepHBr	205–206	84	$C_{29}H_{29}BrOP_2$	64.9(65.1)	5.3(5.5)	15.1(14.9)
cdepHBr	153–154	85	$C_{29}H_{29}BrO_2P_2$	63.4(63.2)	5.4(5.3)	14.6(14.5)
cedepHBr	135–137	85	$C_{30}H_{31}BrO_2P_2$	63.4(63.7)	5.7(5.5)	15.0(15.1)
bdmpHBr	195–197	89	$C_{33}H_{29}BrOP_2$	67.9(67.9)	5.2(5.0)	13.5(13.7)
admpHBr	173–176	82	$C_{28}H_{27}BrOP_2$	64.1(64.5)	5.2(5.2)	
cdmpHBr	152–154	89	$C_{28}H_{27}BrO_2P_2$	62.7(62.6)	5.1(5.1)	14.9(14.9)
bdep	139–141	81	$C_{34}H_{30}OP_2$	79.1(79.1)	6.0(5.9)	
adep	123–124	85	$C_{29}H_{28}OP_2$	75.5(75.6)	6.4(6.2)	
cdep	150–152	73	$C_{29}H_{28}O_2P_2$	74.0(74.0)	6.2(6.0)	
cedep	[a]	82	$C_{30}H_{30}O_2P_2$	73.5(74.4)	6.3(6.2)	
bdmp	108–110	85	$C_{33}H_{28}OP_2$	79.3(78.9)	5.3(5.6)	
admp	[a]	80	$C_{28}H_{26}OP_2$	[b]		
cdmp	[a]	[a]	$C_{28}H_{26}O_2P_2$	[b]		
$PdCl_2$(bdep)	258–261	82	$C_{34}H_{30}Cl_2OP_2Pd$ [c]	58.9(58.9)	4.1(4.4)	9.9(10.2)
$PdBr_2$(bdep)	255–257	59	$C_{34}H_{30}Br_2OP_2Pd$	52.4(52.2)	3.8(3.9)	20.5(20.4)
PdI_2(bdep)	247–249	24	$C_{34}H_{30}I_2OP_2Pd$	46.7(46.6)	3.3(3.5)	28.7(29.0)
$Pd(NCS)_2$(bdep)	215–217	26	$C_{36}H_{30}N_2OP_2PdS_2$	59.1(58.5)	3.9(4.1)	[d]
$PdCl_2$(adep)	258–260	56	$C_{29}H_{28}Cl_2OP_2Pd$	54.8(55.1)	4.6(4.5)	11.0(11.2)
$PdCl_2$(cdep)	229–231	85	$C_{29}H_{28}Cl_2O_2P_2Pd$	53.3(53.8)	4.3(4.4)	
$PdCl_2$(cedep)	250–252	85	$C_{30}H_{30}Cl_2O_2P_2Pd$	54.4(54.5)	4.6(4.6)	10.9(10.7)
$PdCl_2$(bdmp)	283–285	78	$C_{33}H_{28}Cl_2OP_2Pd$	58.1(58.3)	3.9(4.2)	10.1(10.4)
$PdCl_2$(admp)	296–298	85	$C_{28}H_{26}Cl_2OP_2Pd$	53.5(54.4)	4.2(4.2)	
$PdCl_2$(cdmp)	294–296	80	$C_{28}H_{26}Cl_2O_2P_2Pd$	52.1(53.1)	4.2(4.1)	
$PtCl_2$(bdep)	>300	79	$C_{34}H_{30}Cl_2OP_2Pt$	52.2(52.2)	3.9(3.9)	8.8(9.1)
$PtBr_2$(bdep)	[a]	[a]	$C_{34}H_{30}Br_2OP_2Pt$	47.5(46.9)	3.1(3.5)	21.5(18.3)
PtI_2(bdep)	310	7	$C_{34}H_{30}I_2OP_2Pt$	42.3(42.3)	3.2(3.1)	27.0(26.3)
$Pt(NCS)_2$(bdep)	[a]	[a]	$C_{36}H_{30}N_2OP_2PtS_2$	53.1(52.2)	3.0(3.7)	[e]
$PtCl_2$(adep)	243–245	80	$C_{29}H_{28}Cl_2OP_2Pt$	48.2(48.3)	4.2(3.9)	9.7(9.8)
$PtCl_2$(cdep)	262–264	72	$C_{29}H_{28}Cl_2O_2P_2Pt$	46.8(47.0)	4.0(4.0)	9.6(9.6)
$PtCl_2$(cedep)	>300	71	$C_{30}H_{30}Cl_2O_2P_2Pt$	47.3(48.0)	3.9(4.0)	
$PtCl_2$(bdmp)	>300	88	$C_{33}H_{28}Cl_2OP_2Pt$	51.5(51.6)	3.4(3.7)	9.2(9.2)
$PtCl_2$(admp)	300	85	$C_{28}H_{26}Cl_2OP_2Pt$	47.4(47.6)	3.7(3.7)	9.9(10.0)
$PtCl_2$(cdmp)	300	40	$C_{28}H_{26}Cl_2O_2P_2Pt$	45.2(46.6)	3.7(3.6)	
$PdCl_2(bdep)_2$	195–197	56	$C_{68}H_{60}Cl_2O_2P_4Pd$	67.2(67.5)	5.2(5.0)	5.7(5.9)

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[a] Not measured. [b] Analytically pure compounds were not obtained. [c] Molecular weight 740 by vapor pressure osmometry in dichloromethane (calculated for the monomer, 694). [d] N, 3.8(3.8). [e] N, 3.0(3.4).

TABLE 2

INFRARED, ^{1}H NMR AND ^{31}P NMR DATA OF PHOSPHONIUM SALTS, YLIDES AND COMPLEXES

	IR data[a] ν(CO) (cm^{-1})	^{1}H NMR data[b]					^{31}P NMR data[c]					
		Chem. shift (ppm)		Coupling const. (Hz)		Solvent	Chem. shift (ppm)		Coupling const. (Hz)			Solvent[d]
		δ(CH$_2$)	δ(CH)	^2J(PCH)	^2J(PtCH)		Phosphonium or ylide P	Phosphine P	J(PP)	^2J(PtCP)	J(PtP)	
bdepHBr	1664	6.01		13		$CDCl_3$	−26.4	12.2	42			$CHCl_3$
bdep	1526		4.30	22		$CDCl_3$	−17.1	12.4	38			$CHCl_3$
$PdCl_2$(bdep)	1614		6.06(s)[f]			CD_2Cl_2	−29.3	−22.5	24			DMF
$PdBr_2$(bdep)	1626		6.60			DMF[e]						
PdI_2(bdep)	1624		6.90			DMF[e]						
$Pd(NCS)_2$(bdep)	1628		6.18 & 6.46			DMF[e]						
$PtCl_2$(bdep)	1625		6.12(t)[g]		116 ± 8	CD_2Cl_2	−19.7	−5.5	19	145 ± 5	3949 ± 5	DMF
$PtBr_2$(bdep)	1638											
PtI_2(bdep)	1634											
$Pt(NCS)_2$(bdep)	1636											
adepHBr	1718	5.62		12		$CDCl_3$	−24.0	11.4	46			$CHCl_3$
adep	1532		3.56	24		$CDCl_3$[e]	−14.7	12.8	43			$CHCl_3$
$PdCl_2$(adep)	1649		5.36(s)			CD_2Cl_2	−24.7	−19.0	23			DMF
$PtCl_2$(adep)	1659		5.36(t)		112 ± 4	CD_2Cl_2	−16.0	−1.1	20			DMF
cdepHBr	1732	5.24		14		$CDCl_3$	−25.5	12.6	45			$CHCl_3$
cdep	1614		?			$CDCl_3$	−18.1	13.0	50			$CHCl_3$

$PdCl_2$(cdep)	1712 1692		4.90(d)[h]			CD_2Cl_2	−24.4	−20.6	27			DMF[j]
$PtCl_2$(cdep)	1716 1694		4.94(dt)[i]	2	108 ± 8	CD_2Cl_2	−17.5	−1.5	19	138 ± 5	3934 ± 5	DMF
cedepHBr	1715	5.15		13		$CDCl_3$	−25.5	12.6	45			$CHCl_3$
cedep	1608		?			$CDCl_3$	−18.2	12.9	46			$CHCl_3$
$PdCl_2$(cedep)	1674		4.87(d)	4		CD_2Cl_2	−24.3	−20.7	28			DMF
$PtCl_2$(cedep)	1709 1677		?			CD_2Cl_2	−17.2	−1.7	21			DMF
bdmpHBr	1670	5.91		12		$CDCl_3$	−23.3	26.8	68			$CHCl_3$
bdmp	1526		4.25	24		$CDCl_3$	−13.8	27.5	48			$CHCl_3$
$PdCl_2$(bdmp)	1626		6.01(s)			DMF	−36.9	−25.0	48			DMF[j]
$PtCl_2$(bdmp)	1630		6.00			DMF	−41.7	−3.1	40			DMF[j]
admpHBr	1712	5.47		12		$CDCl_3$	−21.2	27.2	68			$CHCl_3$
admp	1532		3.3(s)			$CDCl_3$	−11.4	27.6	63			$CHCl_3$
$PdCl_2$(admp)	1650		5.3			DMSO	−35.6	−24.4	46			DMF
$PtCl_2$(admp)	1659		5.2			DMSO	−40.3	−1.7	37			DMF
cdmpHBr	1734	5.15		13		$CDCl_3$	−22.7	27.7	63			$CHCl_3$
cdmp	1616		?			$CDCl_3$	−15.8	27.8	63			$CHCl_3$
$PdCl_2$(cdmp)	1723 1677		?			DMSO	−36.4	−22.3	51			DMF
$PtCl_2$(cdmp)	1728 1688		?			DMSO	−40.7	−2.3	34			DMF[j]
$PdCl_2(bdep)_2$	1526											

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[a] Measured in KBr. [b] Internal standard, TMS. [c] External standard, 85% H_3PO_4. [d] Measured at 30—32°C unless otherwise stated. [e] Measured at −28°C. [f] Singlet. [g] Triplet. [h] Doublet. [i] Double triplet. [j] Measured in situ, see text.

higher upon complex formation but the order is unaltered, (see Table 2).

The coordination of the ylide carbon to the metal is also suggested by the coupling of the ylide methine proton with the ^{195}Pt nucleus for the three platinum complexes (Table 2) [6]. The resonance of the ylide methine proton shifts to lower field upon coordination of the ylide ligand. The ^1H NMR spectrum of $Pd(SCN)_2(bdep)$ showed two ylide methine proton signals (δ 6.12 and δ 6.46 ppm with an intensity ratio of 1 : 2) indicating that the complexes with both *N*- and *S*-coordinated SCN group exist in solution. The signal at higher field has been tentatively assigned to the complex with *N*-coordination, because the chemical shifts of the proton in some complexes seem to be generally at higher field for *N*-coordination of the ambidentate SCN ligand [13,14]. However the ν(CN) for SCN in the infrared spectra of the complex in a solid state is only at 2082 cm^{-1}, suggesting *N*-coordination [12].

The ^{31}P NMR spectra of bdepHBr and bdep show two doublets with $^3J(PP)$ (42 Hz) and $^3J(PP)$ (38 Hz), respectively (Table 2). It seems reasonable to assign the signals at δ 12.2 and δ 12.4 ppm to $Ph_2P^*—CH_2—CH_2—$, δ —26.4 ppm to $—CH_2—P^*(Ph_2)—CH_2—C(O)—$, and δ —17.1 ppm to $—CH_2—P^*(Ph_2)—CH—C(O)—$ because the chemical shifts of the phosphine phosphorus are unlikely to change very much in the phosphonium salt and the ylide, whereas those of the phosphonium phosphorus and the ylide phosphorus are likely to shift considerably due to the significant change of the environment [15—17]. These assignments are compatible with the ^{31}P chemical shifts of $Ph_3P—CH—C(O)—Ph$ [11] and Ph_3P [19]. The signals in the spectra of the other phosphonium salts and the ylides have been assigned in similar fashion. The assignments of the signals in the spectra of $PtCl_2(bdep)$ and $PtCl_2(cdep)$ are possible by means of $^2J(PtCP)$ and $J(PtP)$. Thus in the case of $PtCl_2(bdep)$, the signal at δ —19.7 ppm ($^2J(PtCP)$ 145 ± 5 Hz) is assigned to $—CH_2—P^*(Ph_2)—CH—C(O)—$ and the one at δ —5.5 ppm ($J(PtP)$ 3949 ± 5 Hz) to $Ph_2P^*—CH_2—CH_2—$ by referring to the data for some tertiary phosphine complexes of platinum in the literature [18]. Similar assignments are possible for $PtCl_2(cdep)$ and for other platinum complexes by analogy. The assignments in the spectra of palladium complexes, however, are not so straightforward. The assignments given in Table 2 are tentative ones which were made on an assumption that a chemical shift of the ylide P is at lower field than that of the phosphine P. The shift values seem to be compatible with the data reported for some tertiary phosphine complexes of palladium [18].

The ylide ligands in the monodentate ylide complexes of palladium [5] were completely displaced on refluxing in pyridine within 30 min. This suggests that substitution of the ylide by pyridine occurs readily. The infrared spectra of the palladium chelate ylide complexes after refluxing in pyridine for 3 h showed the carbonyl stretching absorptions of both complexed and free ylide ligands. The absorption of the displaced free ylide was the strongest for $PdCl_2(cdep)$, medium for $PdCl_2(adep)$ and $PdCl_2(cdmp)$ and negligible for $PdCl_2(bdep)$, $PdCl_2(bdmp)$ and $PdCl_2(admp)$. The infrared spectra of the platinum complexes after refluxing in pyridine for 3 h indicated that the ligand had not been displaced at all from platinum. These results suggest that for the substituent of the ligand by pyridine, (1) the complexes of the chelate ligands are more stable than those of the monodentate ylides; (2) the platinum complexes are more stable than the palladium complexes; (3) the five-membered chelate rings of admp and cdmp are more stable than the six-membered chelate ring of adep and cdep; (4) the stability is also dependent on the substituents, i.e. $C_6H_5 >$ $CH_3 > OCH_3$ reflecting the electron inductive effect.

Experimental

1,2-Bisdiphenylphosphinoethane [20], bisdiphenylphosphinomethane [21], dichlorobis(benzonitrile)palladium(II) [22] and dichlorobis(dimethyl sulfide)-platinum(II) [23] were prepared according to the literature. All operations for preparing the ylide ligands were carried out under a nitrogen atmosphere and those for preparing the ylide complexes were carried out in air.

Preparation of ylide ligands

To a solution of a ditertiary phosphine (0.050 mol) in chloroform (70 ml), a solution of $BrCH_2C(O)R$ (0.050 mol) in chloroform (50 ml) was added dropwise at 20°C with stirring. After the addition was completed, the mixture was stirred for 1 h and was then added dropwise to diethyl ether (500 ml). The white precipitate of the phosphonium salt which formed immediately was washed with diethyl ether (150 ml) and dried in vacuo.

Triethylamine (0.50 mol) was added to a suspension of the phosphonium salt (0.050 mol) prepared as described above in benzene (350 ml) and the mixture was stirred for 2 h. It was filtered to remove $Et_3N \cdot HBr$ and benzene was distilled off under reduced pressure to give the ylide as a white powder. The yields are given in Table 1. The phosphonium salts are white crystalline solids which are soluble in polar solvents and insoluble in benzene, diethyl ether or n-hexane. The white crystalline ylides are soluble in polar solvents and benzene but insoluble in n-hexane.

Preparation of dichloro(benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane)palladium(II), $PdCl_2$(bdep), and related compounds

A solution of bdep (3.1 g, 0.6 mmol) in dichloromethane (30 ml) was added dropwise to a stirred solution of dichlorobis(benzonitrile)palladium(II) (2.3 g, 0.6 mmol) in dichloromethane (30 ml) at 20°C. n-Hexane (10 ml) was added to the mixture and it was concentrated to 30—40 ml. The yellow crystals which precipitated were filtered, washed with two 5 ml portions of diethyl ether and dried at 130—140°C in vacuo for 12 h, (3.4 g, yield 82%).

Other palladium(II) complexes, $PdCl_2(Y)$ (Y = adep, cdep, cedep, bdmp, admp or cdmp) were prepared similarly. The complexes are yellow and stable in air. They are soluble in dichloromethane, nitromethane and *N,N*-dimethylformamide and insoluble in benzene or n-hexane. The solubilities of the cedep, bdmp, admp and cdmp complexes are much lower than those of the bdep, adep and cdep complexes. PdX_2(bdep) (X = Br, I or SCN) were prepared by metathesis of a solution of $PdCl_2$(bdep) in dichloromethane with an alkali metal salt in methanol.

Preparation of dichloro(benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane)platinum(II), $PtCl_2$(bdep), and related compounds

A solution of bdep (3.1 g, 0.6 mmol) in chloroform (50 ml) was added dropwise to a stirred solution of dichlorobis(dimethyl sulfide)platinum(II) (2.3 g, 0.6 mmol) in dichloromethane (70 ml) at 60°C. After the addition was completed, the mixture was stirred for 20 min n-Hexane (20 ml) was added to the mixture and it was concentrated to 70 ml. The white crystals which precipitated were filtered, washed with two 5 ml portions of diethyl ether and dried at 130—140°C in vacuo for 12 h, (3.7 g, yield 79%).

Other platinum(II) complexes, $PtCl_2(Y)$ (Y = adep, cdep, cedep, bdmp, admp or cdmp) were prepared similarly. The bdep and bdmp complexes are pale yellow and the other complexes are white crystals. They are soluble in dichloromethane, nitromethane or *N,N*-dimethylformamide and insoluble in benzene or n-hexane. The solubilities of the cedep, bdmp, admp or cdmp complexes are much lower than those of the bdep, adep or cdep complexes. $PtX_2(bdep)$ (X = Br, I or SCN) were prepared by metathesis of a solution of $PtCl_2(bdep)$ in dichloromethane with a solution of an alkali metal salt in methanol.

Preparation of dichlorobis(benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane)palladium(II), $PdCl_2(bdep)_2$

A solution of dichlorobis(benzonitrile)palladium(II) (0.11 g, 0.03 mmol) in benzene (10 ml) was added dropwise to a solution of bdep (0.31 g, 0.06 mmol) in benzene (10 ml) at 60°C with stirring. n-Hexane (30 ml) was added and the mixture was kept at 5°C for 12 h. The yellow crystals which precipitated were filtered, washed with two 5 ml portions of diethyl ether and dried in vacuo, (0.20 g, yield 56%).

Preparation of dichlorobis(benzoylmethylenetriphenylphosphorane)palladium(II), $PdCl_2(btp)_2$, and dichlorobis(carbomethoxymethylenetriphenylphosphorane)palladium(II), $PdCl_2(ctp)_2$

A solution of btp (3.8 g, 1 mmol) in dichloromethane (50 ml) was added to a solution of dichlorobis(benzonitrile)palladium(II) (1.9 g, 0.5 mmol) in dichloromethane (50 ml) with stirring at 20°C. The mixture was kept at 20°C for 12 h. The pale brown solid which precipitated was filtered, washed with two 20 ml portions of diethyl ether and dried in vacuo, (3.3 g, yield 70%). $PdCl_2(ctp)_2$ was prepared similarly to give a pale yellow solid, (2.6 g, 6 g, yield 55%).

Physical measurements

Infrared spectra were recorded on a Hitachi EPI G2 spectrometer with KBr disks. ^1H NMR spectra were recorded on a JEOL PS-100 spectrometer (100 MHz) with tetramethylsilane as an internal standard. ^{31}P NMR spectra were recorded on a Hitachi R-20B spectrometer (24.3 MHz) with proton noise decoupling. ^{31}P chemical shifts (δ positive are measured up-field from 85% H_3PO_4 as an external standard. The spectra of the phosphonium salts and the ylides were recorded in chloroform with the concentrations of ca. 20 wt%. The solubilities at room temperature of the ylide complexes in the ordinary solvents were not enough for the ^{31}P NMR spectra measurements. Therefore, they are dissolved in *N,N*-dimethylformamide (DMF) by warming at about 80° C for 0.5—2 min to attain the concentrations of ca. 20 wt%. The spectra were recorded quickly at 35°C after the solutions were cooled at the temperature. No precipitation occurred during the measurements and the material recovered by addition of diethyl ether to the sample solutions showed that the complexes had not been decomposed by warming in DMF for a short time. Sufficient concentrations were not attained for $PdCl_2$(cdep), $PdCl_2$(bdmp), $PtCl_2$(bdmp) or $PtCl_2$(cdmp) even by this warming procedure. Consequently, the ylide complexes which had been prepared in DMF from an ylide ligand and $PdCl_2(PhCN)_2$ or $PtCl_2(Me_2S)_2$ were subjected to measurements in situ without the isolation of the complexes. The ^{31}P NMR spectra of $PdCl_2$(bdep) or $PtCl_2$(bdep) which were recorded by this in situ technique were identical with those of the isolated complexes, so that we may well regard the spectra recorded for $PdCl_2$(cdep), $PdCl_2$(bdmp). $PtCl_2$(bdmp) or $PtCl_2$(cdmp) in situ to be identical with those of the isolated samples. The solvent effects of ^{31}P chemical shifts generally were very small and we have found that the difference of the shifts for bdep in chloroform, dichloromethane and DMF within 1 ppm.

Reaction with pyridine

The ylide complex (0.3 g) was refluxed in pyridine (5 ml) for 3 h for the chelate ylide complexes or 30 min for the monodentate ylide complexes. Pyridine was removed in vacuo and the infrared spectrum of the residual solid was recorded in each case to check the displacement of the ylide ligand.

References

1 P.A. Arnup and M.C. Baird, Inorg. Nucl. Chem.,Lett., 5 (1969) 65.
2 H. Koezuka, G. Matsubayashi and T. Tanaka, Inorg. Chem., 13 (1974) 443.
3 G. Matsubayashi, M. Toriuchi and T. Tanaka, Bull. Chem. Soc. Japan, 47 (1974) 765.
4 H. Nishiyama, K. Itoh and Y. Ishii, J. Organometal. Chem., 87 (1975) 129.
5 E.T. Weleski, Jr., J.L. Silver, M.D. Jansson and J.L. Burmeister, J. Organometal. Chem., 102 (1975) 365.
6 H. Koezuka, G. Matsubayasji and T. Tanaka, Inorg. Chem., 15 (1976) 417.
7 Y. Oosawa, T. Miyamoto, T. Saito and Y. Sasaki, Chem. Lett., (1975) 33.
8 Y. Oosawa, T. Saito and Y. Sasaki, Chem. Lett., (1975) 1259.
9 M. Kato, H. Urabe, Y. Oosawa, T. Saito and Y. Sasaki, Chem. Lett., (1976) 51.
10 H. Takahashi, Y. Oosawa, A. Kobayashi, T. Saito and Y. Sasaki, Chem. Lett., (1976) 15.
11 J. Speziale and K.W. Ratts, J. Amer. Chem. Soc., 85 (1963) 2790.
12 D.W. Meek, P.E. Nicpon and V.I. Meek, J. Amer. Chem. Soc., 92 (1970) 5351.
13 J. Powell and B.L. Shaw, J. Chem. Soc., (1965) 3879.
14 A.H. Norbury, Adv. Inorg. Chem. Radiochem., 17 (1975) 231.
15 F. Heidenreich, A. Mollbach, G. Wilke, H. Dreeskamp, E.G. Hofmann, G. Schroth, K. Seevogel and W. Stempfle, Israel J. Chem., 10 (1972) 293.
16 H.H. Karsch and H. Schmidbaur, Chem. Ber., 107 (1974) 3784.
17 H.H. Karsch, H.F. Klein, C.G. Kreiter and H. Schmidbaur, Chem. Ber., 107 (1974) 3692.
18 S.O. Grim, R.L. Keiter and W. McFarlane, Inorg. Chem., 6 (1967) 1133.
19 S.O. Grim and R.L. Keiter, Inorg. Chim. Acta, 4 (1970) 56.
20 J. Chatt, F.A. Hart and H.R. Watson, J. Chem. Soc., (1962) 2537.
21 K. Sommer, Z. Anorg. Allg. Chem., 376 (1970) 37.
22 M.S. Kharasch, R.C. Seyler and F.R. Mayo, J. Amer. Chem. Soc., 60 (1934) 882.
23 G.B. Kauffman and D.O. Cowan, Inorg. Synth., 6 (1960) 211.