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# PREPARATION OF CATIONIC CHELATE YLIDE COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

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## Summary

Cationic palladium(II) and platinum(II) complexes with chelate ylides and neutral ligands of the type, $[MCl(Y)(L)]^+BPh_4^-$ (M = Pd or Pt; Y = bdep or bdmp*; L = 4-methylpyridine, 3,5-dimethylpyrazole, $PPh_3$, $PCy_3$, $PMePh_2$, $P(OMe)_3$, $AsPh_3$ or $SbPh_3$) and $[M(bdep)(4\text{-methylpyridine})_2](BPh_4)_2$ (M = Pd or Pt) were prepared and characterized by means of infrared and $^1H$ NMR spectra.

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* $Ph_2P-(CH_2)_n-P^+(Ph)_2-C^-H-C(O)-Ph$, n = 2 (bdep) and n = 1 (bdmp)

## Introduction

In previous papers [1,2], we have reported the synthesis of keto-stabilized ylides derived from 1,2-bisdiphenylphosphinoethane and bisdiphenylphosphinomethane, $Ph_2P-(CH_2)_n-P^+(Ph)_2-C^-H-C(O)-Ph$*, and their palladium(II) and platinum(II) halide complexes. The metal-ylide carbon bonding in these complexes is rather stable and the ylide is not displaced by a neutral ligand such as pyridine or phosphines under mild conditions [2]. It was thus possible to prepare cationic chelate ylide complexes of the type $[MCl(Y)(L)]^+BPh_4^-$ (M = Pd or Pt; Y = bdep or bdmp; L = a neutral ligand) by treatment of the ylide complexes with sodium tetraphenylborate in the presence of a neutral ligand [3]. The present study has been undertaken to extend the scope of the chelate ylide complexes by preparing a series of cationic ylide complexes and to get more information on the chelate ylides as ligands. As these complexes are similar in some respects to the internal metallated complexes, MCl(P — C)(L) (M = Pd or Pt; P-C = $CH(CH_3)C_6H_4PBu^t_2$ or $C(CH_3)_2C_6H_4PBu^t_2$) reported by Shaw and his co-workers [4], the comparison of metal-alkyl and metal-ylide bondings seems interesting.

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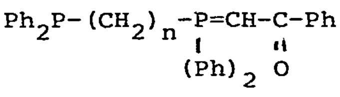
* n = 2, bdep(benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane); n = 1, bdmp(benzoylmethylenediphenyldiphenylphosphinomethylphosphorane)

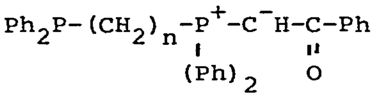
## Results and discussion

The results are summarized in Table 1. Conductivities of the solutions in nitromethane of some of the mono-cationic complexes (see Table) suggest that they are probably 1 : 1 electrolytes. The complexes decompose very slowly in air and the melting points (dec) are lower than those of the corresponding neutral ylide complexes [2]. Carbonyl stretching frequencies of the complexes are between those of bdep or bdmp (1526 $cm^{-1}$) and the phosphonium salts (bdepHBr 1664 $cm^{-1}$ and bdmpHBr 1670 $cm^{-1}$) suggesting that the ylide carbon is coordinated to the metal [2]. Bdep and bdmp are keto-stabilized ylides and are illustrated by the three canonical structures I $\sim$ III, and the contribution of II becomes larger upon the coordination of the ylide methine to the metal.



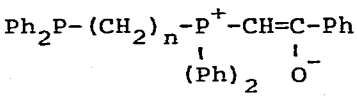
$\mathrm{Ph_2P{-}(CH_2)_n{-}\underset{(Ph)_2}{\underset{|}{P}}{=}CH{-}\underset{O}{\underset{\|}{C}}{-}Ph}$

I



$\mathrm{Ph_2P{-}(CH_2)_n{-}\underset{(Ph)_2}{\underset{|}{P^+}}{-}C^-H{-}\underset{O}{\underset{\|}{C}}{-}Ph}$

II



$\mathrm{Ph_2P{-}(CH_2)_n{-}\underset{(Ph)_2}{\underset{|}{P^+}}{-}CH{=}\underset{O^-}{\underset{|}{C}}{-}Ph}$

III

The coordination results in high-frequency shift of $\nu$(CO) and it is considered that the higher frequency shift of $\nu$(CO) reveals the larger coordinating strength of the methine

TABLE 1. YIELDS, PHYSICAL AND ANALYTICAL DATA OF CATIONIC YLIDE COMPLEXES

| Compound | Yield % | M.P. (dec) °C | IR[a] ν(CO) | $^1H$ NMR[b] δ(CH) | $^1H$ NMR[b] δ($CH_3$) | Conductivity[d] Λ | Analytical data, Found (calcd) % C | H | N | Cl |
|---|---|---|---|---|---|---|---|---|---|---|
| [PdCl(bdep)(4-methylpyridine)]$BPh_4$ | 34 | 147 | 1633 | | 2.12 | | 71.8(71.9) | 5.4(5.4) | 1.1(1.3) | 3.4(3.3) |
| [PdCl(bdep)(3,5-dimethylpyrazole)]$BPh_4$ | 24 | 136-7 | 1632 | | 1.90, 1.83 | | 70.0(70.5) | 5.6(5.5) | 2.5(2.6) | 3.5(3.3) |
| [PdCl(bdep)($PPh_3$)]$BPh_4$ | 39 | 130-2 | 1630 | 4.54 | | 49 | 73.4(73.6) | 5.3(5.3) | | 3.0(2.9) |
| [PdCl(bdep)($PCy_3$)]$BPh_4$ | 32 | 157-9 | 1630 | 4.02 | | 50 | 72.2(72.6) | 5.5(6.7) | | 2.9(2.8) |
| [PdCl(bdep)($PMePh_2$)]$BPh_4$ | 54 | 134-5 | 1624 | | | | 71.5(72.4) | 5.5(5.4) | | 3.1(3.0) |
| [PdCl(bdep)($P(OMe)_3$)]$BPh_4$·1/4$CH_2Cl_2$ | 23 | 140 | 1625 | | 3.30 | | 66.0(65.5) | 5.5(5.4) | | 5.2(4.7) |
| [PdCl(bdep)($AsPh_3$)]$BPh_4$ | 41 | 137-9 | 1625 | | | | 71.0(71.1) | 5.3(5.1) | | 2.7(2.8) |
| [PdCl(bdep)($SbPh_3$)]$BPh_4$·1/4$CH_2Cl_2$ | 37 | 138-140 | 1624 | | | | 67.9(67.7) | 4.9(4.9) | | 3.3(3.9) |
| [PdCl(bdmp)($PPh_3$)]$BPh_4$ | 33 | 153-5 | 1620 | 4.90 | | 44 | 73.2(73.5) | 5.0(5.2) | | 2.9(2.9) |
| [PdCl(bdmp)($PCy_3$)]$BPh_4$ | 20 | 175 | 1626 | 4.47 | | 48 | 72.0(72.4) | 7.0(6.6) | | 2.9(2.9) |
| [Pd(bdep)(4-methylpyridine)$_2$]($BPh_4$)$_2$·1/4$CH_2Cl_2$ | 14 | 120 | 1621 | 4.22 | 2.12, 1.90 | | 77.2(77.1) | 6.1(5.8) | 2.0(1.9) | 1.7(1.2) |
| [PtCl(bdep)(4-methylpyridine)]$BPh_4$ | 49 | 195 | 1638 | | | | 66.9(66.4) | 5.0(5.0) | 1.2(1.2) | 3.0(3.0) |
| [PtCl(bdep)(3,5-dimethylpyrazole)]$BPh_4$ | 29 | 191-3 | 1640 | | | | 66.1(66.1) | 5.3(5.2) | 2.2(2.3) | 2.8(2.9) |
| [PtCl(bdep)($PPh_3$)]$BPh_4$ | 38 | 224-6 | 1634 | 4.96 | | | 68.9(68.7) | 4.7(4.9) | | 3.3(2.7) |
| [PtCl(bdep)($PCy_3$)]$BPh_4$ | 35 | 213-4 | 1636 | 4.50 | | | 67.9(67.8) | 6.0(6.2) | | 3.1(2.6) |
| [PtCl(bdep)($P(OMe)_3$)]$BPh_4$ | 32 | 197-200 | 1633 | | 3.28 | | 60.8(61.5) | 5.1(5.0) | | 3.4(3.0) |
| [PtCl(bdep)($AsPh_3$)]$BPh_4$ | 41 | 215-7 | 1633 | | | | 65.9(66.5) | 4.8(4.8) | | 3.1(2.6) |
| [PtCl(bdep)($SbPh_3$)]$BPh_4$ | 36 | 230-2 | 1632 | | | | 64.0(64.3) | 4.6(4.6) | | 2.7(2.5) |
| [PtCl(bdmp)(4-methylpyridine)]$BPh_4$ | 28 | 153-6 | 1629 | 4.70 | 2.26 | | 65.7(66.1) | 5.2(4.9) | 1.2(1.2) | 3.1(3.1) |
| [PtCl(bdmp)($PPh_3$)]$BPh_4$ | 42 | 206-8 | 1630 | 4.50[c] | | | 68.7(68.5) | 5.1(4.8) | | 2.6(2.7) |
| [PtCl(bdmp)($PCy_3$)]$BPh_4$ | 30 | 234-6 | 1637 | 4.47 | | | 67.6(67.6) | 6.4(61.1) | | 2.9(2.7) |
| [Pt(bdep)(4-methylpyridine)$_2$]($BPh_4$)$_2$ | 14 | 153-6 | 1618 | | 2.19, 1.94 | | 73.7(73.5) | 5.6(5.5) | 1.6(1.8) | |

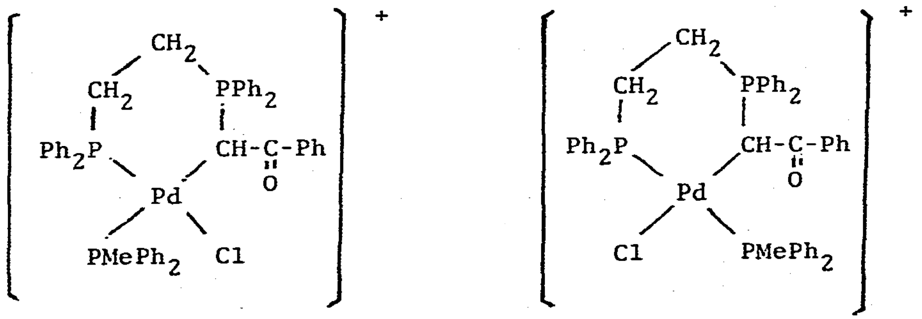
a) KBr disk. b) $CD_2Cl_2$ solution with TMS as an internal standard; c) $CDCl_3$ solution; d) at 25° for ca. $10^{-3}$M nitromethane solution.

carbon to the metal [5]. The $\nu$(CO) of the cationic bdep complexes in the present study for the N, P, As and Sb ligands do not vary significantly and this seems to indicate that the coordination of the ylide carbon to the metal is not affected very much by the change of the ligands which are used in the present study. Unfortunately we have so far been able to prepare only the cationic ylide complexes with Vb group ligands. The attempts to prepare CO complex from $PtCl_2$(bdep), CO and $NaBPh_4$ gave an impure complex with (CO) at 2118 $cm^{-1}$ which was presumably [PtCl(bdep)(CO)]$BPh_4$.

The chemical shifts of the ylide methine proton of the present cationic complexes are at higher fields than those of the neutral complexes, which are at about $\delta$6.0 [2]. This may be associated with the increase of the electron density on the central metal due to the coordination of a neutral ligand. However, it was generally difficult to detect and assign unequivocally the ylide methine proton and some of the complexes did not show any methine proton in the spectra. This is possibly due to the low solubility of the complexes, the small ratio of the methine proton (e.g. 1/65 for [PdCl(bdep)$AsPh_3$]$BPh_4$) and to the still uncharacterized temperature dependence of the signals of the methine proton [6]. Nevertheless, we believe that all the complexes in the present study are ylide complexes judging from the infrared spectra and from the stability of the ylide-metal bonding of the starting ylide complexes towards the neutral ligands under the experimental conditions for the preparation of the cationic complexes.

We were unable to compare the influence of N, P, As and Sb ligands on the chemical shifts of the ylide methine proton, because we could not detect the methine proton in the spectra of these complexes.

The $^1$H NMR spectrum of [PdCl(bdep)(PMePh$_2$)]BPh$_4$ shows two sets of methyl proton signals at $\delta$1.48 (1 : 1 doublet, $^2J$(P–H) 10.3 Hz) and at $\delta$1.90 (1 : 2 : 1 triplet, $|^2J(\text{P–H}) + {}^4J(\text{P–H})|$ 3.4 Hz (virtual coupling)) with the intensity ratio of ca. 7 : 1. These signals suggest that the ratio of the isomers (Fig. 1, a : b) is 7 : 1 and that methyldiphenylphosphine enters mainly into the position trans to the ylide carbon [7]. This is in contrast with the internal metallated complexes PtCl(P — C)(PMe$_2$Ph) and PdCl(P — C)(PMe$_2$Ph) which have PMe$_2$Ph trans to the phosphine phosphorus of the bidentate ligand [4] and may reflect the difference of the ylide and alkyl ligands. Both of them have sp$^3$ hybridized carbon bonded to the metal but differ in formal charge.



a

b

Figure 1

The methyl signal ($\delta$ 2.12) of the 4-methylpyridine complex [PdCl(bdep)(4-methylpyridine)]$BPh_4$ shows an upfield shift of 0.2 ppm as compared with that of the free ligand. The dicationic complex [Pd(bdep)(4-methylpyridine)$_2$]$(BPh_4)_2$ shows two methyl signals at $\delta$ 2.12 and $\delta$ 1.90 with the intensity ratio of 1 : 1. The two signals suggest magnetically different environments for the two 4-methylpyridine ligands, one of which is trans and the other is cis to the ylide carbon.

## Experimental

The chelate ylide ligands, bdep and bdmp, and their complexes $MCl_2(Y)$ (M = Pd or Pt; Y = bdep or bdmp) were prepared as previously described [2]. All operations for preparing the complexes were carried out in air except for $PMePh_2$ complex.

### Preparations of the cationic ylide complexes

(1) [PdCl(bdep)(4-methylpyridine)]$BPh_4$. In a mixed solvent of dichloromethane (20 ml) and acetone (10 ml), $PdCl_2$(bdep) (0.21 g, 0.3 mmol), 4-methylpyridine (0.034 g, 0.36 mmol), and sodium tetraphenylborate (0.21 g, 0.34 mmol) were reacted with reflux for 5 h. The solvents were removed in vacuo and the product was dissolved in dichloromethane (10 ml) and washed with water (10 ml). The dichloromethane layer was separated and diethyl ether (20 ml) was added to precipitate yellow brown solid.

(2) $[\mathrm{PtCl(bdep)(4\text{-}methylpyridine)}]\mathrm{BPh_4}$. The complex was prepared like (1) but chloroform was used for the extraction of the product. White crystals.

(3) $[\mathrm{PdCl(bdmp)(PPh_3)}]\mathrm{BPh_4}$. A solution of triphenylphosphine (0.13 g, 0.5 mmol) in dichloromethane (5 ml) and a solution of sodium tetraphenylborate (0.17 g, 0.5 mmol) ~~are~~ added to a suspension of $\mathrm{PdCl_2(bdmp)}$ (0.35 g, 0.5 mmol) in dichloromethane (20 ml) and the mixture was stirred for 30 min. The solvents were removed in vacuo, the product was dissolved in dichloromethane (10 ml), washed with water (10 ml) and the dichloromethane layer was separated. Toluene was added dropwise to the solution until precipitation occurred and it was kept at 5° for 24 h. The pale yellow crystals were filtered and dried in vacuo at 60 - 70°.

(4) $[\mathrm{PdCl(bdmp)(PCy_3)}]\mathrm{BPh_4}$. The complex was prepared like (3) to form pale yellow crystals.

(5) $[\mathrm{PtCl(bdmp)(PPh_3)}]\mathrm{BPh_4}$. The complex was prepared like (3) to form white crystals.

(6) $[\mathrm{PtCl(bdmp)(PCy_3)}]\mathrm{BPh_4}$. The complex was prepared like (3) to form white crystals.

(7) $[\mathrm{PdCl(bdep)(PPh_3)}]\mathrm{BPh_4}$. The complex was prepared like (3) except that n-hexane was added for the precipitation of the pale yellow crystalline product.

(8) $[\mathrm{PtCl(bdmp)(4\text{-}methylpyridine)}]\mathrm{BPh_4}$ The complex was prepared like (7) to form white powder.

(9) $[\mathrm{PdCl(bdep)(PCy_3)}]\mathrm{BPh_4}$. The complex was prepared like (7) to form pale yellow crystals.

(10) $[\mathrm{PtCl(bdep)(PPh_3)}]\mathrm{BPh_4}$. The complex was prepared like (7) to form white crystals.

(11) [PtCl(bdep)(PCy$_3$)]BPh$_4$. The complex was prepared like (7) to form white crystals.

(12) [PdCl(bdep)(PMePh$_2$)]BPh$_4$. The complex was prepared like (3) but in a nitrogen atmosphere and was crystallized from dichloromethane-diethyl ether to form pale yellow crystals.

(13) [PdCl(3,5-dimethylpyrazole)]BPh$_4$. The complex was prepared like (3) except that the dichloromethane solution after the addition of toluene (25 ml) was kept at 5° for 1 month to form orange yellow powder.

(14) [PtCl(bdep)(3,5-dimethylpyrazole)]BPh$_4$. The complex was prepared like (13) to form white powder.

(15) [PdCl(bdep)(P(OMe)$_3$)]BPh$_4$. In a mixed solvent of dichloromethane (20 ml) and acetone (10 ml), PdCl$_2$(bdep) (0.30 g, 0.43 mmol) , trimethylphosphite (0.071 g, 0.55 mmol) and sodium tetraphenylborate (0.16 g, 0.47 mmol) were reacted at 40° for 30 min with stirring. The solvents were removed in vacuo, the product was dissolved in dichloromethane (30 ml) and washed with water (10 ml). The dichloromethane layer was separated, diethyl ether (30 ml) was added, and the mixture was kept at 5° for 24 h. Very pale yellow crystals were filtered and dried in vacuo.

(16) [PdCl(bdep)(AsPh$_3$)]BPh$_4$. The complex was prepared like (15) to form yellow crystals.

(17) [PdCl(bdep)(SbPh$_3$)]BPh$_4$. The complex was prepared like (15) to form orange yellow crystals.

(18) [PtCl(bdep)(P(OMe)$_3$)]BPh$_4$. In a mixed solvent of chloroform (15 ml) and acetone (10 ml), PtCl$_2$(bdep) (0.32 g, 0.41 mmol), trimethylphosphite (0.063 g, 0.49

mmol) and sodium tetraphenylborate (0.17 g, 0.49 mmol) were reacted by refluxing for 1 h, and the rest of the procedure was like (15).

(19) $[PtCl(bdep)(AsPh_3)]BPh_4$. The complex was prepared like (15) to form white crystals.

(20) $[PtCl(bdep)(SbPh_3)]BPh_4$. The complex was prepared like (15) to form white crystals.

(21) $[Pd(bdep)(4\text{-methylpyridine})_2](BPh_4)_2$. A solution of 4-methylpyridine (0.14 g, 1.5 mmol) in dichloromethane (5 ml) and a solution of sodium tetraphenylborate (0.38 g, 1.1 mmol) in acetone (10 ml) were added to a solution of $PdCl_2(bdep)$ (0.25 g, 0.36 mmol) in dichloromethane (15 ml) and the mixture was stirred for 30 min at 20°. The solvents were removed in vacuo and the product was extracted with dichloromethane (15 ml). The solution was washed with water (10 ml) and toluene (10 ml) was added to form white crystals.

(22) $[Pt(bdep)(4\text{-methylpyridine})_2](BPh_4)_2$. The complex was prepared like (21) to form white crystals.

## Physical measurements

Elemental analyses were performed at the Organic Analysis Laboratory of our Department. Infrared spectra were recorded on a Hitachi EPI G2 spectrometer with KBr disks. $^1H$ NMR spectra were recorded on a JEOL PS 100 (100 MHz) spectrometer with TMS as an internal standard. Electronic conductivities were measured with a CDM 2d conductivity meter (Radiometer Inc.).

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