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PALLADIUM AND PLATINUM COMPLEXES OF A NEW CHELATE YLIDE

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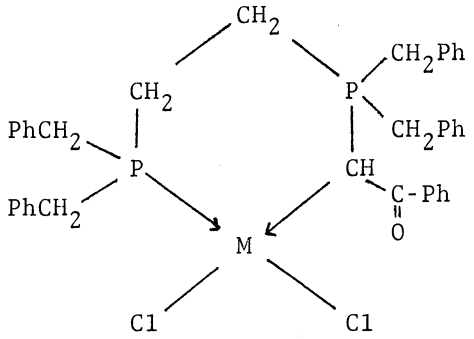
A new phosphorus chelate ylide, benzoylmethylenedibenzyl-2-dibenzylphosphinoethylphosphorane and its complexes of Pd(II) and Pt(II) have been prepared and characterized.

Recently, many types of ylides have raised a new surge of interest as ligands in organometallic chemistry.[1)-3)] We have already prepared some bidentate phosphorus chelate ylides and obtained Pd(II) and Pt(II) complexes of them.[4),5)]

We have now synthesized a new chelate ylide, benzoylmethylenedibenzyl-2-dibenzylphosphinoethylphosphorane (abbreviated as bdbep), an analog of benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane(bdep), and obtained its Pd(II) and Pt(II) complexes (Fig-1).



M=Pd(II), Pt(II)

Fig-1

The ylide was prepared in a good yield according to the same manner used in the synthesis of bdep.[4)]

$$(PhCH_2)_2PCH_2CH_2P(CH_2Ph)_2 + Ph\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2Br \longrightarrow [(PhCH_2)_2PCH_2CH_2P(CH_2Ph)_2CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ph]^+Br^-$$

$$\xrightarrow{(C_2H_5)_3N} (PhCH_2)_2PCH_2CH_2P(CH_2Ph)_2CH\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ph$$

The reaction of the ylide with Kharasch's salt yielded yellow crystalline complex $PdCl_2$(bdbep); by the similar reaction with dichloro(dimethylsulfide)platinum(II), white crystalline complex $PtCl_2$(bdbep) was obtained. We also isolated cationic complexes MClL(bdbep) BPh_4 (M=Pd,Pt L=PPh_3, PPh_2Me, $AsPh_3$) from above neutral complexes in the presence of the donor molecule and $NaBPh_4$. All the isolated complexes are stable towards air, but the cationic complexes rapidly change in color when exposed to light. The complexes were identified by elemental analyses. The characteristics of the obtained complexes are listed in Table.

In this way, the new chelate ylide, bdbep, shows excellent ability to form

ylide-metal(Pd, Pt) bond.

Table

Compounds	Color	M.P.(°C)	C=O$^{(cm^{-1})}$***
bdbep 0.6 benzene*	Yellow	41 - 43**	1500
$PdCl_2$(bdbep)	Yellow	226(dec)	1615
$PtCl_2$(bdbep)	White	233 - 234	1626
$PdCl(PPh_3)$(bdbep) BPh_4	Yellow	126(dec)	1624
$PtCl(PPh_3)$(bebep) BPh_4	White	129 - 131	1634
$PdCl(AsPh_3)$(bdbep) BPh_4	Yellow	118 - 120	1626
$PtCl(AsPh_3)$(bdbep) BPh_4	Pale yellow	130(dec)	1637
$PdCl(PPh_2Me)$(bdbep) BPh_4	Pale yellow	121 - 122	1622

* The quantity of benzene was determined by ^{1}H-NMR and elemental analysis.

** Measured in the vacuum-sealed capillary tube.
*** In KBr disk

Proton NMR of $PdCl(PPh_2Me)$(bdbep) BPh_4 suggests the existence of two isomers in CH_2Cl_2 solution. Two patterns of methyl proton signals have been observed. One of them is doublet (δ=2.18 from TMS, $^2J(CH_3\text{-}P)$=11 Hz) and the other is triplet (δ=1.94, $J(CH_3\text{-}P$, virtual coupling[6])=3.6 Hz). We tentatively assigned the doublet as the species of Fig-2a and the triplet as that of Fig-2b. The doublet triplet ratio (33/7) indicates that the amount of the complex of Fig-2a is larger than that of Fig-2b.

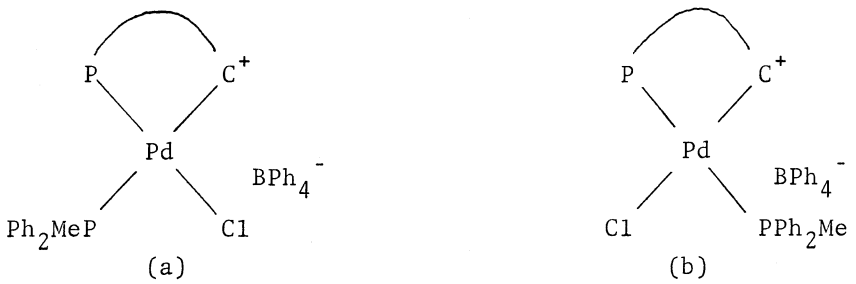


Fig-2

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