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CHELATE PHOSPHORUS YLIDE COMPLEXES OF PALLADIUM AND PLATINUM

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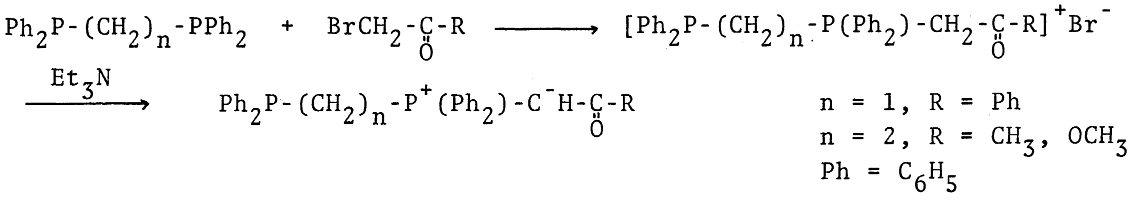
Several bidentate phosphorus ylide ligands of the type $Ph_2P\text{-}(CH_2)_n\text{-}P^+(Ph_2)\text{-}C^-H\text{-}C(O)\text{-}R$ (n = 1, R = Ph; n = 2, R = CH_3, OCH_3) and their complexes of palladium(II) and platinum(II) chlorides have been synthesized and characterized.

We have reported the synthesis and properties of a chelate ylide ligand, benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane (BDEP) and its complexes MCl_2(BDEP) (M = Pd or Pt).1) X-ray structure analysis of the palladium complex confirmed that the ligand coordinates to palladium through the ylide carbon and phosphine phosphorus thus forming, together with two chlorine atoms in mutually cis positions, a square planar configuration around palladium.2)

In the present communication, we wish to report the synthesis and properties of analogous chelate ylide ligands, acetylmethylenediphenyl-2-diphenylphosphinoethylphosphorane (ADEP), carbomethoxymethylenediphenyl-2-diphenylphosphinoethylphosphorane (CDEP), and benzoylmethylenediphenyldiphenylphosphinomethylphosphorane (BDMP), and their complexes of palladium(II) and platinum(II) chlorides. ADEP and CDEP were prepared from the corresponding phosphonium salts of 1,2-bisdiphenylphosphinoethane with bromoacetone or methyl bromoacetate, respectively, and BDMP was prepared from the phosphonium salt of bisdiphenylphosphinomethane with α-bromoacetophenone. The phosphonium salts and the ylides are stable white crystals.



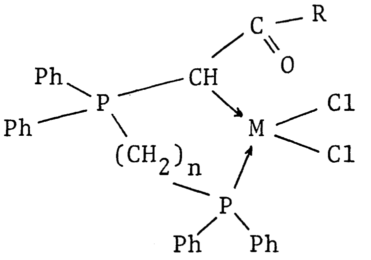
$$Ph_2P\text{-}(CH_2)_n\text{-}PPh_2 \;+\; BrCH_2\text{-}\underset{\overset{\|}{O}}{C}\text{-}R \longrightarrow [Ph_2P\text{-}(CH_2)_n\text{-}P(Ph_2)\text{-}CH_2\text{-}\underset{\overset{\|}{O}}{C}\text{-}R]^+Br^-$$

$$\xrightarrow{Et_3N} Ph_2P\text{-}(CH_2)_n\text{-}P^+(Ph_2)\text{-}C^-H\text{-}\underset{\overset{\|}{O}}{C}\text{-}R \qquad \begin{array}{l} n = 1,\ R = Ph \\ n = 2,\ R = CH_3,\ OCH_3 \\ Ph = C_6H_5 \end{array}$$

The reaction of the ylides (L) with dichlorobis(benzonitrile)palladium or dichlorobis(dimethylsulfide)platinum forms yellow crystalline complexes, $PdCl_2(L)$ or white crystalline complexes, $PtCl_2(L)$, respectively. The stretching frequencies of the carbonyl group in the ir spectra of the phosphonium salts, ylides and complexes are given in the Table. The frequencies of the ylide complexes are between those of the corresponding ylide ligands and phosphonium salts. The shifts of ν_{CO} to higher frequencies upon complex formation of this type of the ylide ligands are considered to indicate the coordination of the ylide carbon to the metals.[1,3] Judging by this criterion, all the ylide complexes obtained in the present study seem to have the ylide carbon-metal bonding. Consequently, by analogy with the BDEP palladium complex,[1,2] the ylide ligands of the present study probably form six- or five-membered chelate rings by the coordination of an ylide carbon and a phosphine phosphorus to the metals as shown in the Figure.

Table ν_{CO} measured in KBr discs (cm^{-1})

L	LH^+Br^-	L	$PdCl_2(L)$	$PtCl_2(L)$
ADEP	1718	1532	1649	1659
CDEP	1732	1614	1712 1692	1716 1694
BDMP	1670	1526	1624	1630



n = 1,2

References

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