

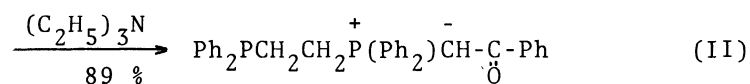
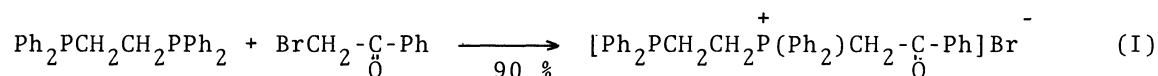
PALLADIUM AND PLATINUM COMPLEXES OF A CHELATE YLID

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A new type bidentate phosphorus ylid, benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane (L) and its complexes $MCl_2(L)$ (M = Pd and Pt) have been synthesized and characterized.

Several types of ylid complexes have been reported recently.^{1 - 6)} We have now synthesized a new type phosphorus ylid, benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane, from 1,2-bisdiphenylphosphinoethane and obtained palladium and platinum complexes coordinated by the ylid ligand.

The ylid was prepared in a good yield by the elimination of HBr from the corresponding phosphonium salt (I) which was formed by the reaction of 1,2-bisdiphenylphosphinoethane with α -bromoacetophenone.



The phosphonium salt (I) and the ylid (II) are stable white crystals and can be recrystallized from ethanol-hexane and tetrahydrofuran-hexane respectively.

The reaction of the ylid (II) with dichlorobis(benzonitrile)palladium forms a yellow crystalline complex $PdCl_2(L)$ and the reaction of the ylid (II) with dichlorobis(dimethylsulfide)platinum forms a white crystalline complex $PtCl_2(L)$. The complexes are soluble in chloroform, dichloromethane, tetrahydrofuran and dimethylformamide. The infrared spectra (KBr disc) show ν_{CO} at 1614 cm^{-1} ($PdCl_2(L)$) and at 1625 cm^{-1} ($PtCl_2(L)$) and the characteristic band (1526 cm^{-1}) for

the free ylid CO disappears. The ν_{CO} bands for the complexes are close to that of the phosphonium salt (I) (1664 cm^{-1}).³⁾ The ^1H n.m.r. chemical shift (CH_2Cl_2 solution, TMS) of the methine hydrogen (δ 6.28 ppm) of the palladium complex is close to that of the methylene hydrogens (δ 6.32 ppm) of the phosphonium salt (I). The ^{31}P n.m.r. chemical shift (CH_2Cl_2 solution, 85 % H_3PO_4) of the ylid P (δ -24 ppm) of the complex is close to that of the phosphonium salt (δ -26 ppm) and different from that of the free ylid (δ -17 ppm). The chemical shift of the phosphine P shifts from 13 to -30 ppm upon the complex formation. These spectral data can be interpreted in terms of the chelation of the ylid ligand to the metal. The above results together with satisfactory elemental analysis suggest that $\text{PdCl}_2(\text{L})$ and $\text{PtCl}_2(\text{L})$ are bidentate ylid complexes which are shown in the Figure. We have also obtained $\text{PdCl}_2(\text{L})_2$ which shows ν_{CO} at 1524 cm^{-1} in a solid state.

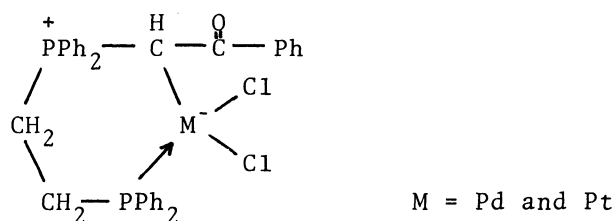


Figure Bidentate Ylid Complexes of Pd and Pt

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