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CATIONIC PALLADIUM AND PLATINUM COMPLEXES OF BIDENTATE PHOSPHORUS YLIDE LIGANDS

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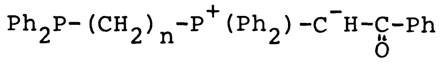
Cationic complexes of bidentate phosphorus ylide ligands, benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane(BDEP) and benzoylmethylenediphenyldiphenylphosphinomethylphosphorane (BDMP) $[MCl(L)PR_3]^+BPh_4^-$ and neutral complexes $MX_2(L)$ (M = Pd or Pt ; L = BDEP or BDMP ; R = Ph or Cy ; X = Br, I, or SCN) have been synthesized and characterized.

We have reported the synthesis of palladium and platinum complexes of benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane(BDEP*) and benzoylmethylenediphenyldiphenylphosphinomethylphosphorane(BDMP*).[1,2] In the present communication, the synthesis of cationic ylide complexes $[MCl(L)PR_3]^+BPh_4^-$ and some derivatives of the neutral complexes $MX_2(L)$ (M = Pd or Pt ; L = BDEP or BDMP ; R = Ph(=phenyl) or Cy(=cyclohexyl) ; X = Br, I, or SCN) is described and the trans effect of the ylide and the phosphine in the bidentate P —— C ligands is discussed.

The cationic complexes were prepared by the treatment of the corresponding chloride complexes $MCl_2(L)$ with sodium tetraphenylborate in the presence of triphenylphosphine or tricyclohexylphosphine and the neutral complexes were prepared by the treatment of the corresponding chloride complexes with alkali metal salts. The electronic conductivity of these complexes in nitromethane suggests that the cationic complexes are 1 : 1 electrolytes. The carbonyl stretching frequencies of all the complexes are between those of the corresponding free ylide ligands and phosphonium salts indicating that the ylide carbon coordinates to the metal.[1,2] The ^1H nmr of the hydrogen bonded to the ylide carbon of the cationic complexes are at higher fields than those of the corresponding neutral complexes. The up-field shifts can be interpreted in terms of the increase of the shielding due to the coordination of a tertiary phosphine to the metal.

The facile exchange of two chloride ligands at room temperature to form the neutral complexes suggests that the ylide as well as the phosphine of the bidentate P —— C ligands have rather high trans effect upon the ligand substitution in the square planar ylide complexes.[3] In the case of the cationic complexes, one of the two chloride ligands is substituted by a tertiary phosphine. The ligand of larger trans effect should cause the preferential substitution of the chloride ligand trans to it. As the data available at present do not indicate the position of the tertiary

* 
$Ph_2P\text{-}(CH_2)_n\text{-}P^+(Ph_2)\text{-}C^-H\text{-}\underset{\overset{\|}{O}}{C}\text{-}Ph$ ($Ph = C_6H_5$; n = 2, BDEP ; n = 1, BDMP)

phosphine, X-ray structure analysis of a cationic complex is being carried out for the study of the coordination position of an incoming tertiary phosphine and for the comparison of the trans effect of the ylide and phosphine in the bidentate ylide ligand.

Compound	IR data[c] ν_{CO} (cm^{-1})	^1H nmr data δ (ppm from TMS)	Temp(°C)
BDEP[a]	1526	4.30($CDCl_3$)	30
BDEP·HBr[a]	1664	6.06(CD_2Cl_2), 6.36(DMF)	32
$PdCl_2$(BDEP)[a]	1614	6.05(CD_2Cl_2), 6.29(DMF)	28
$PdBr_2$(BDEP)	1626	6.60(DMF)	-28
PdI_2(BDEP)	1624	6.90(DMF)	-28
$Pd(SCN)_2$(BDEP)	1628	6.18 & 6.46(DMF)	-28
$PtCl_2$(BDEP)[a]	1626	6.12(CD_2Cl_2), 6.30(DMF)	30
PtI_2(BDEP)	1634	overlapped by DMF	-28
[PdCl(BDEP)PPh_3]BPh_4	1630	4.54(CD_2Cl_2)	32
[PdCl(BDEP)PCy_3]BPh_4	1630	4.02(CD_2Cl_2)	32
[PtCl(BDEP)PPh_3]BPh_4	1634	4.96(CD_2Cl_2)	32
[PtCl(BDEP)PCy_3]BPh_4	1636	4.50(CD_2Cl_2)	32
BDMP[b]	1526	4.10($CDCl_3$), 4.42(DMF)	30
BDMP·HBr[b]	1670	5.91($CDCl_3$), 6.18(DMF)	30
$PdCl_2$(BDMP)[b]	1624	6.01(DMF)	23
$PtCl_2$(BDMP)[b]	1630	6.00(DMF)	23
[PdCl(BDMP)PPh_3]BPh_4	1620	overlapped by CH_2Cl_2 in CD_2Cl_2	32
[PdCl(BDMP)PCy_3]BPh_4	1626	4.28(CD_2Cl_2)	32
[PtCl(BDMP)PPh_3]BPh_4	1630	4.50($CDCl_3$)	32
[PtCl(BDMP)PCy_3]BPh_4	1637	4.47(CD_2Cl_2)	32

a ref.1) b ref.2) c KBr disc

Table Carbonyl stretching frequencies and chemical shifts of methine proton bonded to ylide carbon

References

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