The Very High Activity of $(Ph_2P)_2C{=}CH_2$ to Michael Additions when complexed to Platinum(II) or Platinum(IV)

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Complexes of the types $[PtMe_2(vdpp)]$, $[PtMe_3I(vdpp)]$, or $[PtX_2(vdpp)]$ $\{X = Cl$ or I, $vdpp = (Ph_2P)_2C{=}CH_2\}$ undergo Michael additions with various amines, hydrazines, or carbon nucleophiles (ethyl acetoacetate or acetone) to the vinylidene double bond; $[PtMe_3I(Ph_2P)_2CHCH_2NHCH_2Ph]$ isomerizes to $[PtMe_3I\{Ph_2PCH(PPh_2)CHNHCH_2Ph\}]$.

We have reported previously that the complex $[(OC)_4W\{(Ph_2P)_2C{=}CH_2\}]$ undergoes Michael type addition with a variety of amines, hydrazines, and carbon nucleophiles to give functionalized phosphine complexes whereas the free ligand, $(Ph_2P)_2C{=}CH_2$ (vdpp), is inactive towards these additions.[1,2] We now report that vdpp, when complexed to Pt^{II} or Pt^{IV} is very highly activated towards Michael type additions and a variety of novel complexes† can be prepared.

Treatment of $[Me_2Pt(cyclo\text{-}octa\text{-}1,5\text{-}diene)]$ with vdpp gave $[Me_2Pt(vdpp)]$ (**1**), which in toluene solution reacted smoothly with $H_2NNH_2{\cdot}H_2O$ or H_2NNHMe to give (**2**), R = H or Me, in high (80—90%) yield. Treatment of (**1**) with an excess of allylamine at 20 °C gave, after a few minutes, a 60% yield of the adduct (**3**), $R^1 = H$, $R^2 = CH_2CH{=}CH_2$. Other adducts of type (**3**) were prepared similarly using $NHMeCH_2CH{=}CH_2$, $H_2NCH_2C{\equiv}CH$, $NHMeCH_2C{\equiv}CH$, H_2NCH_2Ph, $H_2NCH_2C_6H_4OMe\text{-}4$, and the chiral amines (*R*)- and (*S*)-α-methylbenzylamine. The products of type (**3**) were isolated in 55—90% yields and fully characterized. We expected that Pt^{IV} would activate vdpp towards nucleophilic attack more than Pt^{II}. Treatment of $[Me_2Pt(vdpp)]$ with an excess of MeI at *ca.* 20 °C gave the oxidative addition product $[Me_3IPt(vdpp)]$ (**4**). This Pt^{IV} complex (**4**) reacted with an excess of benzylamine at *ca.* 20 °C in $CDCl_3$ to give a single, readily isolable, product $[Me_3IPt\{(Ph_2P)_2CHCH_2\text{-}NHCH_2Ph\}]$ which we formulate, because of the subsequent reactions described below, with the stereochemistry (**5**), $R = CH_2Ph$, with the CH hydrogen and the iodine on opposite sides of the P_2Pt plane. Treatment of (**4**) with an excess of benzylamine in $CDCl_3$ immediately led to complete conversion into (**5**) but then (**5**) gradually changed into two other similar products (A and B) each showing an AX $^{31}P\text{-}\{^1H\}$ n.m.r. pattern with satellites due to ^{195}Pt. Gradually (over a period of 72 h at *ca.* 20 °C) (A) was converted completely into (B) and (B) was isolated, characterized, and its crystal structure (details to be published elsewhere) determined as (**6**). We suggest (A) has the structure (**7**) and the initial adduct has the structure (**5**). The isomerization (**5**) → (**6**) is presumably promoted by the sterically hindered Pt^{IV} forming the less sterically demanding 5-membered ring with the 'harder' (N) donor atom.

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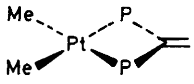
† The complexes described in this Communication have been characterized by elemental analyses (C, H, N, halogen) and by ^1H, $^1H\text{-}\{^{31}P\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r. and i.r. spectroscopy; selected data were available to the referees.



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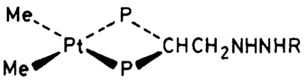

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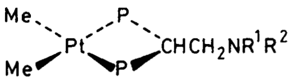

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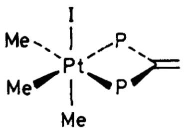

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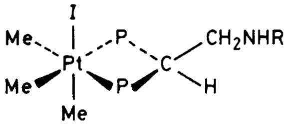

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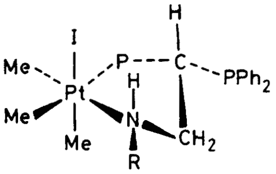

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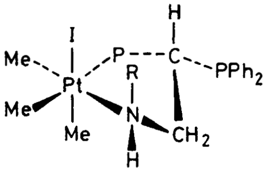

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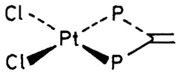

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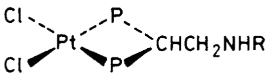

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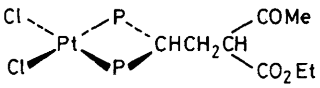

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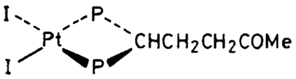

(11)

We thought initially that $PtCl_2$ would activate vdpp but that a nucleophile might, preferentially, displace the Cl rather than attack the vinylidene double bond. However, we have found this not to be the case. Thus, such is the remarkably activating effect of $PtCl_2$ that a 0.02 M solution of $[Cl_2Pt(vdpp)]$ (**8**) in CD_2Cl_2 at −80 °C reacts immediately and quantitatively with the equivalent amount of $H_2NCH_2C_6H_4OMe$-4 to give the adduct (**9**), R = $CH_2C_6H_4OMe$-4 [^{31}P-{^1H} n.m.r. evidence]. The adduct (**9**) has been fully characterized. H_2NNMe_2 immediately adds to (**8**) at −40 °C to give (**9**), R = NMe_2. Other amines have been added to (**8**) and their adducts of type (**9**) fully characterized, *viz.* $H_2NCH_2CH{=}CH_2$, the chiral amine (*R*)-α-methylbenzylamine, and $H_2NCH_2CO_2Et$. Also, and remarkably, ethyl acetoacetate and (**8**), both 0.012 M, in CH_2Cl_2, in the presence of anhydrous Na_2CO_3, gave the compound (**10**) in good (86%) yield. We find that although the dichloride (**8**) does not react with acetone, the corresponding di-iodide $[I_2Pt(vdpp)]$ reacts with acetone to give the *C*-alkylated product (**11**). This reaction is promoted by sodium iodide. Recently Schmidbauer[3] and co-workers have shown that methanol is added reversibly to vdpp in the 8-membered ring $[(vdpp)AuCl]_2$ but vdpp complexes of Ag or Cu did not add methanol. We suggest that vdpp, when chelated to a single metal with a 4-membered ring, is more likely to undergo Michael type additions than in larger rings or in open-chain structures because the strain in the 4-membered chelate ring will be relieved somewhat as the central carbon goes from $sp^2 \rightarrow sp^3$ hybridisation on Michael addition.

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