The High Activation of $(Ph_2P)_2C{=}CH_2$ by Palladium Acetate or Palladium Chloride towards Additions

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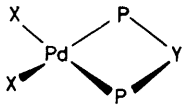
Palladium acetate very highly activates co-ordinated $(Ph_2P)_2C{=}CH_2$ towards additions of amines, hydrazines, amino acid esters, alcohols, phenols, thiols, acetylacetone, and acetoacetic ester; palladium chloride also activates but less strongly: additionally, $Pd(OAc)_2$ catalyses additions to the free ligand $(Ph_2P)_2C{=}CH_2$.

We have reported previously that $(Ph_2P)_2C{=}CH_2$ (vdpp), when complexed to Pt^{II} or Pt^{IV} is activated towards Michael additions.[1] Since Pd^{II} is much more substitution labile than Pt^{II} we anticipated that on treating complexes of the type $[X_2Pd(vdpp\text{-}PP')]$ with nucleophiles, attack would occur at Pd rather than at the vinylidene double bond. However, we have found this not to be the case and now report that $PdCl_2$ and particularly $Pd(OAc)_2$ induce very high activity of vdpp towards Michael additions. Pd–tertiary phosphine complexes are increasingly used as catalysts in organic synthesis and the present work constitutes a simple and versatile method of synthesising a wide range of Pd^{II} complexes containing functionalised diphosphines.

Addition of one equivalent of H_2NNMe_2 to a CH_2Cl_2 solution of $Cl_2Pd(vdpp\text{-}PP')$ (**1**) (0.0125 M) at −80 °C caused immediate conversion into a single product ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence) which was readily isolated and identified as (**2**), X = Cl, R = NMe_2.† Under similar conditions H_2NCH_2Ph also added immediately to give (**2**), X = Cl, R = CH_2Ph. These Michael additions could also be carried out at *ca.* 20 °C and in this way the following amines were added to give products of type (**2**) in 72—90% isolated yields: $H_2NCH_2CH{=}CH_2$, $H_2NCH_2C_6H_4OMe\text{-}4$, $H_2NC_6H_4Me\text{-}4$, H_2NPh, $NHMe\text{-}CH_2{\equiv}CH$. The chiral amines L- and D-$H_2NCH(Me)Ph$ were also added to (**1**), X = Cl and the products of type (**2**) showed 'AB' $^{31}P\text{-}\{^1H\}$ n.m.r. patterns. Similarly the amino acid esters L-$H_2NCH(CH_2Ph)CO_2Et$ and $H_2NCH_2CO_2Et$ were readily added. Alcohols added much more slowly than amines and often took several hours at *ca.* 20 °C for complete addition. These reactions could be conveniently carried out by treating a CH_2Cl_2 solution of $Cl_2Pd(NCPh)_2$ with vdpp followed by an excess of the alcohol. The product slowly crystallised from solution and in this way EtOH and Bu^nOH were added to give adducts of type (**3**), X = Cl in 83 and 89% yields respectively. Alkoxy exchange was found to be base-catalysed; thus on treating the ethoxy compound (**3**), X = Cl, R = Et with MeOH + 6 mol% Bu^tOK at 20 °C the corresponding methoxy compound (**3**), X = Cl, R = Me was formed ($^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. evidence). Phenol did not add to (**1**), X = Cl and even in the presence of Bu^tOK (*i.e.* PhOK) addition was only partial. In the presence of catalytic amounts of Bu^tOK, Bu^nSH

† The complexes referred to in this Communication were characterised by elemental analysis (C, H, N, halogen), i.r. spectroscopy, and $^{31}P\text{-}\{^1H\}$, ^1H, and $^1H\text{-}\{^{31}P\}$ n.m.r. spectroscopy.



(**1**) Y = $C{=}CH_2$
(**2**) Y = $CHCH_2NHR$
(**3**) Y = $CHCH_2OR$
(**4**) X = Cl, Y = $CHCH_2SBu^n$
(**5**) Y = $CHCH_2CH(COR)COR'$

was added to (**1**), X = Cl to give the adduct (**4**) in 78% isolated yield. In addition, treatment of (**1**), X = Cl with $MeCOCH_2CO_2Et$ in CH_2Cl_2 in the presence of anhydrous Na_2CO_3 gave the adduct (**5**), X = Cl, R = Me, R′ = OEt in 79% isolated yield.

We have found that $Pd(OAc)_2$ has a remarkably activating effect for additions across the double bond of vdpp. [$(AcO)_2Pd$(vdpp-*PP′*)] was prepared in 80—85% yield by treating $Pd(OAc)_2$ with vdpp in CH_2Cl_2 and was characterised by elemental analysis, molecular weight measurement, i.r., and n.m.r. spectroscopy. ^{31}P-{^1H} Studies established that EtOH and $CH_2{=}CHCH_2OH$ added immediately to give compounds of type (**3**), X = OAc. The adducts were difficult to purify as acetates but by treating the reaction product with NaI they were readily converted into the corresponding di-iodides of type (**3**), X = I which were fully characterised. Propan-2-ol caused *ca.* 90% conversion to an adduct of type (**3**), X = OAc in equilibrium with (**1**), X = OAc. Similarly addition occurred with menthol, the adduct showing a well-defined 'AB' ^{31}P-{^1H} n.m.r. pattern because of the chirality. Even geraniol or cholesterol added to (**1**), X = OAc at *ca.* 20 °C although the adducts have not yet been fully characterised. PhOH added partially to give an adduct (**3**), X = OAc, R = Ph in equilibrium with (**1**), X = OAc. Complexation to $Pd(OAc)_2$ also markedly increases the tendency for C–C bond formation, thus $CH_2(COMe)_2$ or $MeCOCH_2CO_2Et$ both added completely to (**1**), X = OAc without the need for Na_2CO_3 [contrast with (**1**), X = Cl]; the adducts were isolated in 70% yields as the di-iodides (**5**), X = I; R = R′ = Me or R = Me, R′ = OEt.

The highly activating effect of $Pd(OAc)_2$ prompted us to attempt catalytic additions to $(Ph_2P)_2C{=}CH_2$, and we can report encouraging results on this. The free diphosphine will not add amines, hydrazines *etc.*, but we find that when treated with an excess of H_2NNMe_2 in CH_2Cl_2 in the presence of 5 mol% $Pd(OAc)_2$ conversion of vdpp into a single product is observed (90 min, 20 °C, ^{31}P-{^1H} n.m.r. evidence). We presume this to be $(Ph_2P)_2CHCH_2NHNMe_2$ but have obtained it as a slightly impure oil. However, this oil reacts with $Cl_2Pd(NCPh)_2$ to give (**2**), X = Cl, R = NMe_2 in 76% isolated yield. We also find that $MeCOCH_2CO_2Et$, $CH_2(COMe)_2$, or L-$H_2NCH(Me)Ph$ can be added to vdpp in the presence of a catalytic amount of $Pd(OAc)_2$ but that conversion is not complete (*ca.* 50%).

We have also done some preliminary work on the activation of vdpp complexed to a cyclopalladated moiety. 8-Methylquinoline is readily cyclopalladated to give $[CH_2C_{10}H_{16}NPdCl]_2$[2] which with vdpp gives $[CH_2C_{10}H_{16}NPd\{(PPh_2)_2C{=}CH_2\}]^+Cl^-$. When we treated this with NH_4PF_6 in MeOH ^{31}P-{^1H} and ^1H n.m.r. studies indicated that the product was mainly $[CH_2C_{10}H_{16}NPd\{(PPh_2)CHCH_2OMe\}PF_6$ but we were unable to purify this and have so far failed to isolate products formed by treating $[CH_2C_{10}H_{16}NPd\{(PPh_2)_2C{=}CH_2\}]^+$ with nucleophiles.

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