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# OXIDATIVE ADDITION OF ALLYL-CHALCOGEN (O, S, Se) BONDS TO PALLADIUM(0). ISOLATION OF THE OXIDATIVE ADDITION PRODUCTS

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Allyl phenyl ether reacts with $Pd(PCy_3)_2$ to yield an oxidative addition product, $Pd(\eta\text{-}C_3H_5)(OPh)(PCy_3)$, with formation of a phosphonium salt. Allyl phenyl sulfide and selenide oxidatively add to $Pd(PCy_3)_2$ to give binuclear complexes, $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}ZPh)(PCy_3)_2$ (Z = S, Se). Allyl alcohol undergoes dehydration reaction on interaction with $Pd(PCy_3)_2$ to give $Pd(1\text{-}2\text{:}6\text{-}7\text{-}\eta\text{-diallyl ether})(PCy_3)$.

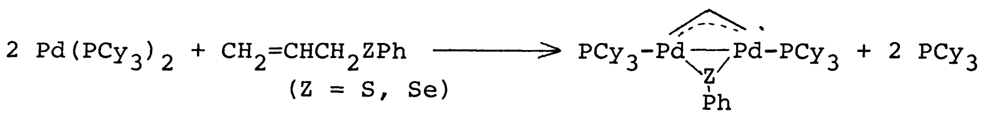
Oxidative addition of allylic compounds to Pd is widely applied to catalytic reactions,1) and several reports have been published on the isolation of the intermediate allylpalladium complexes formed by the oxidative addition of allylic halides to Pd.2) On the contrary, investigation of oxidative addition of allyl-chalcogen bond to Pd by isolating the allylpalladium complex has been much less developed although oxidative addition of the allyl-chalcogen bond to Pd is often postulated in the catalytic reactions.1,3) We have examined oxidative addition of allyl-chalcogen bonds in $CH_2{=}CHCH_2ZPh$ (Z = O, S, Se) and $CH_2{=}CHCH_2OH$ to Pd(0) complexes, and now report the results.

Stirring a toluene solution containing $Pd(PCy_3)_2$4) and allyl phenyl ether (6.5 mol/$Pd(PCy_3)_2$) at room temperature gave a white precipitate of $[Cy_3P{-}\!\diagup\!\!\diagdown][OPh]$, **1**,5) (58%/$Pd(PCy_3)_2$). From the filtrate obtained after removing **1**, we isolated crystals of $Pd(\eta\text{-}C_3H_5)(OPh)(PCy_3)$, **2**,5) (30%/$Pd(PCy_3)_2$) at -78 °C. Use of allyl *p*-cyanophenyl ether (2.7 mol/$Pd(PCy_3)_2$) gave $[Cy_3P{-}\!\diagup\!\!\diagdown][OC_6H_4\text{-}p\text{-}CN]$, **3**,5) and $Pd(\eta\text{-}C_3H_5)(OC_6H_4\text{-}p\text{-}CN)(PCy_3)$, **4**,5) in 79 and 47% yields, respectively. These results indicate that the coordinatively unsaturated $Pd(PCy_3)_2$ easily reacts with $CH_2{=}CHCH_2OC_6H_4\text{-}p\text{-}X$ to give the oxidative addition product and the phosphonium salt, the latter being considered to be produced by a Pd-catalyzed reaction as previously observed in the reaction of allyl acetate with $Pd(PCy_3)_2$.6)

$$\begin{array}{l} Pd(PCy_3)_2 + \underset{(X = H,\ CN)}{CH_2{=}CHCH_2OC_6H_4\text{-}p\text{-}X} \longrightarrow Pd(\eta\text{-}C_3H_5)(OC_6H_4\text{-}p\text{-}X)(PCy_3) + \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad [Cy_3P{-}\!\diagup\!\!\diagdown][OC_6H_4\text{-}p\text{-}X] \end{array} \qquad (1)$$

Treatment of **2** and **4** with morpholine and diethylamine gave N-allylated products.

Stirring a toluene solution containing $Pd(PCy_3)_2$ and allyl phenyl sulfide (1 mol/$Pd(PCy_3)_2$) at room temperature and work-up of the product gave binuclear $Pd_2(\mu\text{-}C_3H_5)(\mu\text{-}SPh)(PCy_3)_2$, **5**,5) in 85% yield. Werner reported preparation of an analogous 2-methylallyl and SPh-bridged binuclear complex by a different type of reaction.[7] An analogous 1:1 reaction of $Pd(PCy_3)_2$ with allyl phenyl selenide at room temperature gave $Pd_2(\mu-C_3H_5)(\mu-SePh)(PCy_3)_2$, **6**,[5] in 28% yield.



$$2\ Pd(PCy_3)_2 + CH_2{=}CHCH_2ZPh \xrightarrow[(Z\,=\,S,\ Se)]{} PCy_3{-}Pd(\mu-C_3H_5)(\mu-ZPh)Pd{-}PCy_3 + 2\ PCy_3 \qquad (2)$$

The $^{31}P\{^1H\}$-NMR spectrum taken just after mixing $Pd(PCy_3)_2$ and $CH_2{=}CHCH_2ZPh$ showed only two signals assigned to **5** or **6** and $PCy_3$, indicating high reactivity of intermediate $Pd(\eta-C_3H_5)(ZPh)(PCy_3)$ against $Pd(PCy_3)_2$. Similar binuclear complexes, $Pd_2(\mu-C_3H_5)(\mu-ZPh)\{P(\underline{t}-Bu)_3\}_2$,[5] were obtained also by reactions of $CH_2{=}CHCH_2ZPh$ with $Pd\{P(\underline{t}-Bu)_3\}_2$, but coordinatively saturated $Pd(PPh_3)_4$ showed very low reactivities against $CH_2{=}CHCH_2ZPh$ and allyl aryl ethers.

Interaction of allyl alcohol (neat, excess) with $Pd(PCy_3)_2$ at 30 °C led to an unprecedented reaction giving Pd(1-2:6-7-η-allyl ether)$(PCy_3)$, **7**,[5] in 61% yield.

$$Pd(PCy_3)_2 + 2\ CH_2{=}CHCH_2OH \longrightarrow Pd(1\text{-}2{:}6\text{-}7\text{-}\eta\text{-diallyl ether})(PCy_3) + H_2O + PCy_3$$

Glc analysis showed presence of diallyl ether (6 mol/$Pd(PCy_3)_2$) in the solution. Complex **7** was prepared also by a reaction of diallyl ether with $Pd(PCy_3)_2$. The formation of **7** in the reaction with allyl alcohol seems to proceed through oxidative addition of allyl alcohol giving intermediate $Pd(\eta-C_3H_5)(OH)(PCy_3)$ and ensuing nucleophilic attack of allyl alcohol to the allylpalladium intermediate.

## References

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