# Novel Intermediates in Some Olefin Insertion Reactions of Platinum Hydrides

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*Summary* The complex *trans*-$PtHNO_3(PEt_3)_2$ undergoes insertion reactions with dienes to give cationic enylic or $\pi$-allylic platinum complexes, which provides a general method for the preparation of these classes of compounds.

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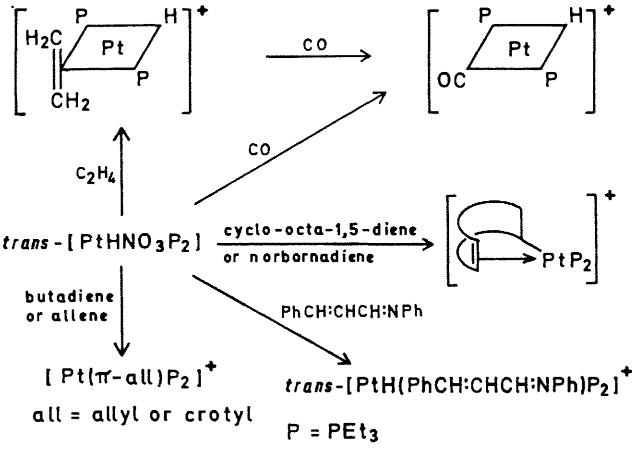
INSERTION of ethylene at 90° and 40 atm. into the platinum–hydrogen bond of *trans*-$PtHCl(PEt_3)_2$ has been shown to give a platinum–ethyl complex,[1,2] and recently reactions of (*o*-vinylphenyl)diphenylphosphine with *trans*-$PtHCl(PPh_3)_2$ have been shown to lead to $\sigma$-Pt–C bonds.[3] We now describe the insertion of dienes into the platinum–hydrogen bond of *trans*-$PtHNO_3(PEt_3)_2$[4] to give cationic enyl or $\pi$-allylic complexes. In contrast to the chemistry of palladium, allylic complexes of platinum appear to be much less readily formed. The reaction provides a good general method for the preparation of these derivatives. Thus, the reaction occurs rapidly at room temperature to give complexes of the type $[PtL(PEt_3)_2]^+$ where L = $\pi$-allyl (from allene), $\pi$-crotyl (from butadiene), cyclo-oct-4-enyl (from cyclo-octa-1,5-diene), or norbornenyl (from norbornadiene) (see Figure). The complexes were isolated as the $PF_6^-$ or $BPh_4^-$ salts. Analogous reactions also occur of the corresponding chloro-complex, but much less rapidly, and we believe that an important aspect of this work is the property of nitrate as an excellent leaving group. We suggest that the mechanism of these reactions is an initial substitution of the anionic ligand by diene, followed by an intramolecular nucleophilic attack of hydride on the co-ordinated olefin.

To test this idea, we attempted to isolate a cationic hydrido-olefin complex which would be an analogue of the suggested intermediates. On treatment of *trans*-$PtHNO_3(PEt_3)_2$ in methanol in the presence of $NaBPh_4$ with ethylene (1 atm.), one equiv. of ethylene was absorbed with the precipitation of *trans*-$[PtH(C_2H_4)(PEt_3)_2]BPh_4$ which is the first reported example of a stable hydrido-ethylene complex. The n.m.r. signal of the hydrido-ligand {$\tau$17·2, $J(^{195}Pt–H)$ 908 Hz, $J$(P–H) 12·0 Hz} demonstrates the mutually *trans*-disposition of the hydrido- and ethylene ligands and we believe that the stability of this complex may be associated with its configuration. The co-ordinated ethylene is readily substituted by carbon monoxide to give *trans*-$[PtH(CO)(PEt_3)_2]BPh_4$, the perchlorate analogue of which has been prepared previously.[5] In our attempts to bring about the reaction of the hydrido-ethylene complex with further ethylene, the only product isolated was the known complex $PtPh_2(PEt_3)_2$, a compound which is also obtained by the slow reaction of $PtHNO_3(PEt_3)_2$ with $NaBPh_4$ in methanol; the mechanism of this interesting phenylation reaction is under investigation.

We have also studied the reaction of $PtHNO_3(PEt_3)_2$ with the heterodienes, PhCH:CHCH:NPh, PhCH:CHCOPh, and $CH_2$:CHCOMe, to compare their reactivity with that of dienes. The Schiff base gave the complex *trans*-[PtH(PhCH:CHCH:NPh)$(PEt_3)_2]BPh_4$ in which the heterodiene is bonded as a monodentate ligand through the nitrogen lone-pair of electrons whereas cationic products (which contain no metal hydride) are obtained from the $\alpha\beta$-unsaturated ketones. We are at present investigating these products to determine whether the hydride has added to the $\alpha$- or $\beta$-positions of the $\alpha\beta$-unsaturated ketones.



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