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**Preliminary communication**

# A NOVEL CONVERSION OF ALLYLAMINES TO π-ALLYLPLATINUM(II) COMPLEXES WITH CATIONIC PLATINUM(II) HYDRIDES

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## Summary

Allylamine and 2-methylallylamine are readily converted to the corresponding π-allylplatinum(II) complexes on treatment with cationic platinum(II) hydrides.

Various unsaturated compounds can be used to obtain π-allylmetal complexes depending on the type of metallic reagents used [1]. Allyl halides and alcohols are most frequently utilized. It was of interest to develop routes to π-allylmetal complexes in view of their role in many organic syntheses [2]. We report here the facile conversion of allylamines to π-allylplatinum(II) complexes on treatment with cationic platinum(II) hydrides. Some reactivities of π-allylplatinum(II) complexes toward $H_2$, HCl, $SO_2$, CO and olefins have previously been investigated [3].

The reaction of $CH_2{=}CRCH_2NH_2$ (I) (R = H, Me) with an equimolar amount of $[PtH(PPh_3)_2L]ClO_4$ (II) (L = CO, $PPh_3$, $AsPh_3$) in methylene chloride at room temperature afforded $[Pt(\pi\text{-}C_3H_4R)(PPh_3)_2]ClO_4$ (III) (R = H, Me) and ammonia in 60-90% yield** (see Scheme 1). A similar reaction of II (L = pyridine) with I required a much longer reaction period, while no π-allyl complexes could be obtained from *trans*-$PtHCl(PPh_3)_2$ and I.

The reaction of I with potentially cationic $PtH(ClO_4)(PPh_3)_2$ (IV) in benzene at room temperature gave almost quantitative yields of white, crystalline *trans*-$[PtH(PPh_3)_2(NH_2CH_2CR{=}CH_2)]ClO_4$ (V) (R = H, Me). The structure of V as shown in Scheme 1 was deduced from elemental analyses, IR and proton NMR data. Particularly, $\nu$(Pt—H) (2200 $cm^{-1}$, in Nujol), $\tau$(Pt—H) (26.45 triplet with $J$(PH) 14 Hz) and $J$(PtH) (1040 Hz, in $CDCl_3$) for V are comparable to those associated with the Pt—H bond *trans* to a nitrogen donor [4] rather than to a C=C ligand [5] in cationic platinum(II) hydrides.

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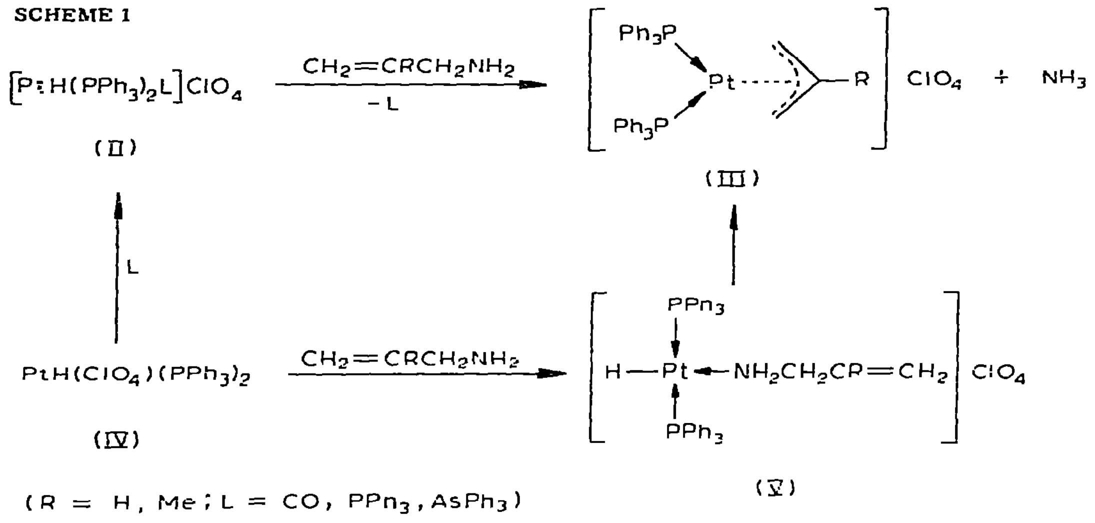
[**] Based on the amounts of III recrystallized and those of $NH_4BPh_4$ obtained by adding aqueous HCl to the volatile products followed by treatment with aqueous $NaBPh_4$.

SCHEME 1



(R = H, Me; L = CO, $PPh_3$, $AsPh_3$)

Compound V only slowly afforded III in methylene chloride at room temperature. However, when treated with a catalytic amount of L (L = CO, $PPh_3$, $AsPh_3$) in the same solvent, these compounds were converted to III much more rapidly. Pyridine is again less effective in this respect. We believe that an important role of L (L = CO, $PPh_3$, $AsPh_3$) in facilitating such C—N bond cleavage in the allylamines is possibly attributed to the ability of L, through coordination, to render the hydrogen atom attached to platinum more susceptible to nucleophilic attack by the nitrogen atom of the amines. It is worthy of note that complexes II (L = CO, $PPh_3$) are known to give readily $Pt_3(CO)_3(PPh_3)_4$ [6] or $Pt(PPh_3)_3$ [7] on treatment with strong bases such as $Et_3N$ and NaOH.

The reaction of I (R = H) with IV in acetone gave a mixture of comparable amounts of III (R = H) and a platinum(II) hydride which presumably involves the *N*-bound Schiff base ligand and is formulated as *trans*-$[PtH(PPh_3)_2(CH_2{=}CHCH_2N{=}CMe_2)]ClO_4$ *. We are currently investigating the reactions of other compounds bearing *N*-allyl bonds with platinum(II) hydrides.

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[*] $\nu(Pt—H)$ 2205 $cm^{-1}$ (Nujol). $\tau(Pt—H)$ 26.75 (t, $J(PH)$ 13 Hz, $J(PtH)$ 998 Hz), $\tau(CMe_2)$ 8.52s and 8.12s, $\tau(NCH_2)$ 6.88 (d, $J(HH)$ 7 Hz), $\tau(=CH_2)$ ca 5.2m and $\tau(CH=)$ ca 4.3m ($CDCl_3$).