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π-ALLYLMETAL CHEMISTRY

III *. A FACILE CLEAVAGE OF ALLYL GROUPS FROM QUATERNARY NITROGEN BY PLATINUM(0) COMPLEXES

HIDEO KUROSAWA

Department of Petroleum Chemistry, Osaka University, Suita, Osaka (Japan)

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Summary

Reactions of $Pt(PPh_3)_2L$ (I, L = PPh_3; II, L = C_2H_4) with $[(CH_2{=}CRCH_2)NH_{n}Et_{3-n}]X$ (R = H, n = 0, 1; R = Me, n = 0; X = ClO_4, BPh_4) in acetone or methylene chloride readily afford the corresponding π-allylplatinum(II) complexes, $[Pt(\pi\text{-}C_3H_4R)(PPh_3)_2]X$ and NH_nEt_{3-n} in good yields. The reactivity patterns in the rapid formation of the π-allyl complexes from II and $[(allyl)NH_3]ClO_4$ (allyl = $CH_2{=}CHCH_2$, $CH_2{=}CHCHMe$, $CH_2{=}CMeCH_2$, *trans*-$MeCH{=}CHCH_2$) are compared with those in the synthetically equivalent conversion of allylamines to the π-allyl complexes induced by platinum(II) hydrido complexes.

Introduction

We have reported previously on a novel conversion of allylamines to π-allylplatinum(II) complexes induced by cationic platinum(II) hydrido complexes in which nucleophilic attack of the nitrogen atom in the amines on the hydridic hydrogen was suggested to play a key role [1,2]. One important consequence of such attack of the nitrogen on the hydrogen would be to produce a better leaving group from the amino function, thereby making the allyl group more susceptible to nucleophilic substitution by the platinum atom. Since deprotonation of platinum(II) hydrides leads to platinum(0) species, it seemed of interest to investigate the substitution of the platinum(0) nucleophile for the amine group in *N*-allylammonium compounds. We now describe some results of such substitution reactions which appear to be potentially applicable in removing the allyl groups used for protecting amino functions under mild conditions. These reactions are some of the few examples of nucleophilic substitution by metallic reagents at carbon bonded to quaternary nitrogen.

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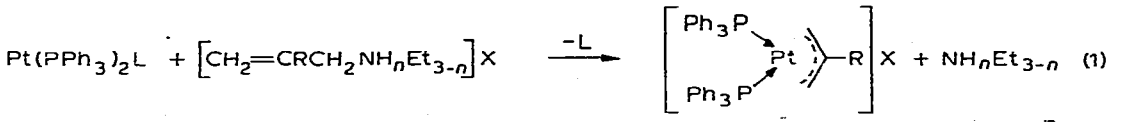
* For Part II see ref. 1.

Results and discussion

Allyl halides are known to add rapidly to $Pt(PPh_3)_3$ (I) to give the π-allylplatinum(II) complexes [3]. Reactions of I or $Pt(PPh_3)_2(C_2H_4)$ (II) with $[CH_2{=}CR\text{-}CH_2NH_nEt_{3-n}]X$ (R = H, n = 0, 1; R = Me, n = 0; X = ClO_4, BPh_4) in acetone or methylene chloride have also been found to afford moderate to good yields of the corresponding π-allyl complexes and NH_nEt_{3-n} with liberation of the phosphine or ethylene (eq. 1).



(L = PPh_3, C_2H_4 ; R = H, Me ; n = 0, 1; X = ClO_4, BPh_4)

The reactions with $[CH_2{=}CHCH_2NH_n\,Et_{3-n}]X$ (n = 0, 1) were shown by ^1H NMR spectroscopy to proceed almost instantaneously even at −30°C, indicating that the platinum(0) complexes are very strong nucleophiles toward the allyl group bonded to the quaternary nitrogen. On the other hand, the benzyl group, which often shows comparable reactivity in common nucleophilic substitutions, was found to be much more inert to these platinum(0) species, as no reaction between I and *N,N,N,N*-benzyltriethylammonium tetraphenylborate was observed to occur under similar conditions. These results may be contrasted with the ease of hydrogenolysis of both allyl— and benzyl—nitrogen bonds in ammonium compounds catalyzed by metallic palladium or sodium amalgam [4,5].

The reactions of I with $[CH_2{=}CHCH_2NH_nEt_{3-n}]ClO_4$ (n = 2, 3) in methylene chloride/methanol mixture at room temperature gave only low yields of the π-allyl complex, possibly due to a competing proton transfer process to produce $[PtH(PPh_3)_3]ClO_4$ *. On the other hand, very fast, exclusive formation of the π-allyl complex was observed to occur in the reaction of II with $[CH_2{=}CHCH_2NH_2Et]ClO_4$ and $[(allyl)NH_3]ClO_4$ (allyl = $CH_2{=}CHCH_2$, $CH_2{=}CHCHMe$, $CH_2{=}CMeCH_2$, *trans*-$MeCH{=}CHCH_2$) under similar conditions. The π-crotyl complex obtained this way from *trans*-but-2-enylammonium perchlorate was shown by its ^1H NMR spectrum [6] to contain almost exclusively the *syn*-methyl isomer, while the same complex from the 1-methylprop-2-enylammonium salt was a mixture of the two isomers with the ratio of *anti*-Me/*syn*-Me being approximately 1/3. Thus, the preservation of the stereochemistry in the former case is most probably a kinetic consequence **.

As for the reaction path involved in the π-allyl formation from II and $[(allyl)NH_3]ClO_4$ above, two possibilities arise in principle, i.e., one encompassing the initial proton transfer from the nitrogen to the platinum as in the reaction of I, and the other through the attack of a platinum(0) nucleophile at carbon at either position 1 or 3. The former is often encountered in the reactions of I and II with

* The formation of the π-allyl complex from this hydride and allylamine was reported to be a much

various protonic acids [7,8]; the reaction of II with HX (X = $OOCCF_3$ [9], Cl [10]) readily gave $PtHX(PPh_3)_2$. However, we believe that the species *trans*-$\{PtH(PPh_3)_2[(allyl)NH_2]\}ClO_4$ (III) or $PtH(ClO_4)(PPh_3)_2$ (IV) cannot be formed during the course of the reactions of II with $[(allyl)NH_3]ClO_4$ for the following reasons. First, the rearrangement of III to the π-allyl complexes in methylene chloride was previously shown [1] to require much longer periods (>1 day) at room temperature *. Further, the yields of the π-allyl complexes in such reactions were lower, and depended on the type of the allylic moiety in the amines to much greater extent (from ca. 70% for allylamine to 30% for *trans*-but-2-enylamine) than those from II and the ammonium compounds. Second, that the π-allyl complex was produced in high yield from the reaction of II with $[CH_2{=}CHCH_2NH_3]ClO_4$ carried out even in acetone is in marked contrast to the formation of only a moderate yield of the π-allyl complex from either III (allyl = $CH_2{=}CHCH_2$) or an allylamine/IV mixture in the same solvent due to the formation of a considerable amount of the by-product, *trans*-$[PtH(PPh_3)_2(CH_2{=}CHCH_2N{=}CMe_2)]ClO_4$ [1]. In view of the readiness with which the reaction between II and $[CH_2{=}CRCH_2NEt_3]X$ occurs as described before, the π-allyl formation from II and $[(allyl)NH_3]ClO_4$ most likely involves the direct displacement of the NH_3 group by the platinum(0) nucleophile, probably $Pt(PPh_3)_2$ [11], which could interact effectively with the C=C bond prior to the C—N bond cleavage. However, the possibility that some other type of intermediate with a Pt—H bond such as *cis*-$\{PtH(PPh_3)_2[(allyl)NH_2]\}ClO_4$ exists cannot be ruled out completely.

In conclusion, the reactions of *N*-allylammonium compounds with platinum(0) complexes are shown to be synthetically equivalent to those between the cationic platinum(II) hydrido complexes and allylamines for forming π-allyl complexes and amines. The former method will presumably have wider application in organic synthesis owing to the greater reactivity of the platinum atom in the lower oxidation state.

Experimental

All reactions except for those run in an NMR tube (in vacuo) were performed under nitrogen. Tris(triphenylphosphine)platinum (I) [12] and bis(triphenylphosphine)(ethylene)platinum (II) [13] were prepared by reported methods. $[CH_2{=}CHCH_2NEt_3]ClO_4$ and $[CH_2{=}CHCH_2NH_3]ClO_4$ were prepared using literature methods [14]. Other *N*-allylammonium perchlorates were prepared from the corresponding allylamines and perchloric acid (0.1 *N*) in methanol and used for the reaction with platinum(0) complexes without isolation. $[CH_2{=}CHCH_2NHEt_2]BPh_4$, $[CH_2{=}CMeCH_2NEt_3]BPh_4$ and $[PhCH_2NEt_3]BPh_4$ were prepared from the corresponding ammonium chlorides and $NaBPh_4$ in water. These were recrystallized from aqueous acetone and found to be analytically pure.

Infrared spectra were recorded on Hitachi 225 (4000—600 cm^{-1}) and Hitachi EPI-2G (700—200 cm^{-1}) spectrometers in Nujol mulls. ^1H NMR spectra were run on a Japan Electron Optics JNM-PS-100 spectrometer. Tetramethylsilane was used as internal standard.

Reaction of I or II with $[CH_2{=}CRCH_2NH_nEt_{3-n}]BPh_4$

In a typical experiment, a methylene chloride solution (4 ml) of $[CH_2{=}CHCH_2NHEt_2]BPh_4$ (43 mg, 0.10 mmol) was added to 75 mg (0.10 mmol) of II in the same solvent (3 ml). The solution was let stand at room temperature for 5 min and then was evaporated to dryness under vacuum. Recrystallization of the residual solids from methylene chloride/diethyl ether followed by cooling in the refrigerator gave fine crystals of $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]BPh_4$ (81 mg; 75%), m.p. 180—185°C (decomp.). (Found: C, 69.94; H, 5.17. $C_{63}H_{55}BP_2Pt$ calcd.: C, 70.07; H, 5.13%.) ^{1}H NMR ($CDCl_3$): δ (ppm) 2.60 (dd, J(H) 13, J(P) 8, J(Pt) 40 Hz; *anti*-H), 3.55 (d, J(H) 7 Hz; *syn*-H), 4.8 (m; 2-H). The ^{1}H NMR spectrum of the same reaction mixture in a sealed NMR tube in vacuo measured at —30°C indicated that almost quantitative formation of the π-allyl complex and diethylamine had occurred during the periods required for scanning (ca. 3 min). Similarly, the reaction of II with $[CH_2{=}CMeCH_2NEt_3]BPh_4$ in acetone for 1 h afforded $[Pt(\pi\text{-}C_4H_7)(PPh_3)_2]BPh_4$ in 70% yield, m.p. 187—190°C (decomp.). (Found: C, 70.35; H, 5.25. $C_{64}H_{57}BP_2Pt$ calcd.: C, 70.27; H, 5.25%.) ^{1}H NMR ($CDCl_3$): δ (ppm) 1.82 (s, J(Pt) 63; Me), 2.67 (d, J(P) 8, J(Pt) 40; *anti*-H), 3.28 (s; *syn*-H). The reactions of I with the *N*-allylammonium tetraphenylborates also gave the π-allyl complexes in similar yields.

Reaction of I or II with $[(allyl)NH_nEt_{3-n}]ClO_4$

The products, $[Pt(\pi\text{-allyl})(PPh_3)_2]ClO_4$ (allyl = $CH_2{=}CHCH_2$, $CH_2{=}CHCHMe$, $CH_2{=}CMeCH_2$) were identified by comparing their infrared and ^{1}H NMR spectra with those of authentic samples [6]. The reactions of I and II with $[CH_2{=}CHCH_2NEt_3]ClO_4$ in methylene chloride were performed in a manner similar to that between II and $[CH_2{=}CHCH_2NHEt_2]BPh_4$ described above. Rapid, quantitative formation of the π-allyl complex and triethylamine was confirmed by the ^{1}H NMR spectra at —30°C, and the yields of the π-allyl complex isolated were around 70%. The reactions of II (75 mg; 0.10 mmol) in methylene chloride (3 ml) with $[CH_2{=}CHCH_2NH_2Et]ClO_4$ or $[(allyl)NH_3]ClO_4$ (allyl = $CH_2{=}CHCH_2$, $CH_2{=}CHCHMe$, $CH_2{=}CMeCH_2$, *trans*-$MeCH{=}CHCH_2$) (0.10 mmol) in methanol (1 ml) were carried out similarly. The solvents were evaporated after 3 min, and recrystallization of the residual solids from methylene chloride/diethyl ether gave the corresponding π-allyl complexes in 80, 87, 81, 63 and 65% yields, respectively. The reaction of II with $[CH_2{=}CHCH_2NH_3]ClO_4$ in acetone gave, after recrystallization, 82% of the π-allyl complex. The reactions of I with $[CH_2{=}CHCH_2NH_nEt_{3-n}]ClO_4$ (n = 2, 3) were carried out similarly in methylene chloride/methanol. The infrared spectrum of the solid mixture obtained by evaporation of the solvents exhibited a weak, sharp band at 2110 cm^{-1} which could have been due to $[PtH(PPh_3)_3]ClO_4$ [15]. The ^{1}H NMR spectrum of this mixture in CH_2Cl_2 showed the presence of only a small amount of the π-allyl complex. A weak, broad doublet at δ —5.75 ppm (J(P) 160) in the spectrum may be due to the hydride, since this is very similar to the signal observed in the spectrum of $[PtH(PPh_3)_3](CF_3CO_2)_2H$ [9].

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