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NEW EQUILIBRIA IN ALLYL(CHLORO)PLATINUM(II) COMPLEXES

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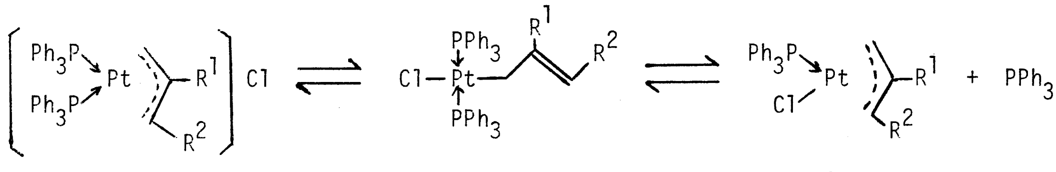
The complexes, Pt(allyl)ClL$_2$ (allyl= $CH_2CH{=}CH$, $CH_2CH{=}CHMe$, $CH_2CMe{=}CH_2$; L= PPh_3, $AsPh_3$),show varying degrees of equilibrium processes, depending on the nature of the allyl moieties, L, and solvents. A convenient method to synthesize complexes of the type, Pt(π-allyl)ClL,is also described.

In contrast to the studies of the "dynamic" character of allylpalladium(II) complexes,$^{1)}$ those of platinum(II) analogs are relatively few except for Pt(C_3H_5)Cl(PPh_3)$_2$ 1$^{2)}$ where a σ-allyl intermediate has been postulated to explain its ^{1}H NMR spectra in $CDCl_3$. We have studied more general structural aspects of Pt(allyl)ClL$_2$ with different allyl groups and L, and found evidence for the occurrence of σ-allyl structures for some of these complexes. During these studies, a convenient method to synthesize the complexes of the type, Pt(π-allyl)ClL,has also been developed.

The reaction of Pt(PPh_3)$_4$ with $CH_2{=}CR^1CHR^2Cl$ in benzene readily affords Pt($CH_2CR^1{=}CHR^2$)Cl(PPh_3)$_2$ (1 R^1= R^2= H; 2 R^1= H, R^2= Me; 3 R^1= Me, R^2= H). We propose that 1-3 exist in the forms of A, B, and C in eq. 1, the relative stabilities of these forms depending on R^1, R^2, and solvents. The form A has been reported to predominate for 1 in chloroform or nitromethane,$^{2)}$ and this may also be the case for 2 and 3 as deduced from their ^{1}H NMR spectra in $CDCl_3$ at -50° which are very similar to those$^{3)}$ of [Pt(π-allyl)(PPh_3)$_2$]ClO_4. Furthermore, the IR spectra of 1-3 in chloroform exhibited a very strong band at 545 cm^{-1} in agreement with two mutually cis PPh_3 ligands.$^{4)}$ On the other hand, the form B is assumed to be a preferred structure for 2 in the solid state$^{5)}$ and in benzene$^{6)}$ for the following reasons. As shown in the Table, the IR and Raman spectra of 2 in the solid state showed ν(C=C) and γ(=CH-) bands which are indicative of the presence of the free C=C bond. Furthermore, no strong IR bands appear in the region of 550 ± 5 cm^{-1}, suggesting a trans configuration. Quite similar spectral aspects were observed in benzene except that an additional very weak band appeared at 538 cm^{-1}. Probably then, the ^{1}H NMR spectrum of 2 in benzene (Table) is reasonably explained in terms of the predominant form B which lies in a rapid equilibrium with a very small concentration$^{7)}$ of Pt(π-C_4H_7)Cl(PPh_3) 2-C, since the IR spectrum of this complex showed a very strong band at 538 cm^{-1}. It is particularly noteworthy that the value of J(Pt-CH_2) in 2-B is very close to J(Pt-CH_3) (79.4 Hz) in trans-PtMeCl(PPh_3)$_2$.$^{8)}$ As expected from eq. 1, addition of a small amount of PPh_3 to the benzene solution of 2-C caused the signals at δ 2.07 and 2.61 to coalesce.



(1)

A B C

Table. IR[a)] and ^{1}H NMR[b)] Data for Crotylplatinum(II) Complexes.

	ν(C=C)	γ(=CH-)	ν(Pt-Cl)	Chemical Shifts (δ)				
				Me	CH_2		MeCH=	CH_2CH=
2	1640[c)]	965	264	1.53(d) J_H= 7	2.19(d) J_H= 7.5 J_{Pt}= 85		4.25(br)	5.2(br)
2-C	—	—	275	1.91(t) J_H= 6 J_P= 6	2.07(dd) J_H= 11 J_P= 3 J_{Pt}= 80	2.61(dd) J_H= 7 J_P= 3 J_{Pt}= 22	3.73(m) J_H= 6 $J_{H'}$= 12 J_P= 8	4.69(m)

a) In Nujol mulls (in cm^{-1}). b) In C_6D_6 for 2 and $CDCl_3$ for 2-C. δ in ppm, J in Hz.
d= doublet, t= triplet, dd= doublet of doublets, m= multiplet, br= broad, c) By Raman spectrum.

The occurrence of the equilibria in eq. 1 is also supported by some chemical properties of 1-3. Thus, treatment of these with $NaClO_4$ to give $[Pt(\pi\text{-allyl})(PPh_3)_2]ClO_4$ has already been known,[9)] and we have further found that the reaction of 1-3 with an equivalent amount of H_2O_2 in acetone readily affords $Pt(\pi\text{-allyl})Cl(PPh_3)$, 1-C—3-C, in good yields, the rest of PPh_3 being converted to $Ph_3P{=}O$. This method, although limited to the complexes with PPh_3, is more effective and convenient in obtaining $Pt(\pi\text{-allyl})Cl(PPh_3)$ than that reported,[10)] where 1-C and 3-C were synthesized through $[Pt(CH_2CR{=}CH_2)Cl]_n$ (R= H, Me) only in low yield. Moreover, $[Pt(CH_2CH{=}CHMe)Cl]_n$ has not yet been prepared.

The reaction of $Pt(AsPh_3)_4$ with allylic chlorides in benzene gave $Pt(\pi\text{-allyl})Cl(AsPh_3)$ (allyl= $CH_2CMe{=}CH_2$, $CH_2CH{=}CHMe$) in one step. This result suggests that the equilibrium between $Pt(allyl)Cl(AsPh_3)_2$ and $Pt(\pi\text{-allyl})Cl(AsPh_3)$ plus $AsPh_3$ lies far to the latter.

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5. One crystalline modification of 2 obtained by recrystallization from benzene/n-hexane. Repeated crystallizations from CH_2Cl_2/Et_2O increased the amounts of the other crystalline form due to 2-A whose IR spectrum showed no bands of ν(C=C), γ(=CH-), and ν(Pt-Cl) but a strong band at 545 cm^{-1}. Similarly, 1 gave two crystalline modifications corresponding to 1-A and 1-B.
6. 1 and 3 are almost insoluble in benzene.
7. Molecular weight of 2 in benzene at 45° was 700 at concentration, 0.76 wt % (Calcd. 810).
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