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π-Allylmetal Chemistry. IV*. Structures and Equilibria in Crotylplatinum(II) Complexes

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Summary

Simple methods to prepare crotylplatinum(II) complexes of the type, $Pt(CH_2CH{=}CHMe)Cl(PPh_3)_2$ and $Pt(CH_2CH{=}CHMe)ClL$ (L= PPh_3, $AsPh_3$), are described. ^1H NMR and vibrational spectral evidence suggests that the σ-allylic form is the dominant species in a benzene solution of $Pt(CH_2CH{=}CHMe)Cl(PPh_3)_2$, while in chloroform this compound has the ionic π-allyl structure with both the anti and syn-methyl isomers present. Various rate processes exhibited by $Pt(CH_2CH{=}CHMe)ClL_2$ (L= PPh_3, $AsPh_3$) in different solvents have been discussed in terms of the structures of intermediate σ-allylic complexes and the different coordinating abilities of L.

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*For Part III, see Ref. 5.

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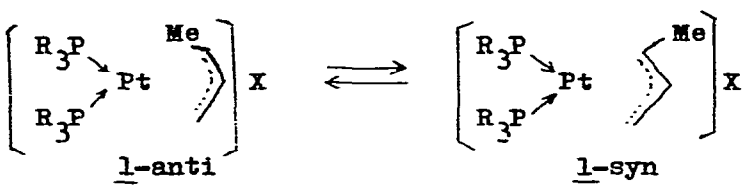
Introduction

Alkyl-substituted allyl complexes of transition metals have received much interest mainly because they play an important role in metal-catalyzed organic syntheses using dienes.[1] Particularly, the structures of these intermediate complexes are expected to have a crucial effect on the stereochemical course of such reactions. In contrast to numerous studies on crotyl as well as on related substituted allyl complexes of nickel and palladium,[2] those of the corresponding platinum analogs are rare except for those of the complexes of the type, $[Pt(\pi\text{-}C_4H_7)(PR_3)_2]X$ I (PR_3= PPh_3, PPh_2Me, PMe_2Ph, PEt_3; X= ClO_4, NO_3, PF_6) obtained by the reaction of $PtHX(PR_3)_2$ with 1,3-butadiene,[3,4] or through some novel routes to π-allyl complexes employing crotylamine[5,6] and crotyl alcohol.[7,8] The suggestion was made that in the former reaction the anti-methyl form of 1 (eq. 1) results as the kinetically controlled product due to a preferred cisoid configuration of the coordinated butadiene prior to its insertion into the Pt-H bond.[7] This anti form readily isomerized to the



(1)

more stable syn form under various conditions including treatment with the halide anions.[7] Relevant to the role of the halide anions in such anti→syn conversion is the observation of "dynamic σ-allyl ^1H NMR spectra" in the complexes $Pt(C_3H_5)Cl(PPh_3)_2$ 2[9] and $Pt(C_3H_5)Br(PPh_2Me)_2$,[7] but not in $[Pt(C_3H_5)(PR_3)_2]X$ (PR_3= PPh_3, PPh_2Me; X= ClO_4, PF_6[7]). However, no detailed

information concerning the structure of the intermediate complexes involved in such a dynamic system has been provided. In order to gain more insight into the nature of these intermediate species and to compare the dynamic equilibria in allylplatinum(II) complexes with those in their palladium analogs, we have studied structural aspects of Pt(allyl)ClL$_2$ (L= PPh$_3$, AsPh$_3$) spectroscopically, with emphasis on the crotyl analogs. We report here evidence for the presence of σ-allyl structures in some of these Pt(allyl)ClL$_2$ complexes, and discuss various rate processes exhibited by these complexes in different solvents in terms of the structures of the σ-allyl complexes.

Results and Discussion

Pt(CH$_2$CH=CHMe)Cl(PPh$_3$)$_2$ in benzene

The infrared and Raman spectra in the solid state of one isomeric form* of Pt(CH$_2$CH=CHMe)Cl(PPh$_3$)$_2$ 3, prepared from Pt(PPh$_3$)$_4$ and CH$_2$=CHCHMeCl or MeCH=CHCH$_2$Cl in benzene, showed bands due to ν(C=C) (1640 cm^{-1}), γ(=CH-) (965 cm^{-1}) and ν(Pt-Cl) (264 cm^{-1}), the former two of which are indicative of the presence of the free C=C bond. Further, no strong infrared absorption bands appeared in the region 550 ± 5 cm^{-1}, suggesting the

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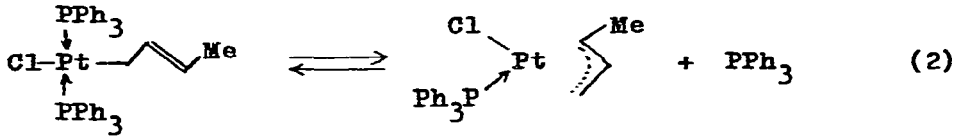
* This benzene-soluble isomer of 3 with trans phosphine configuration seems to be obtained preferably if crystallization of 3 is performed from benzene/n-hexane or methylene chloride/n-hexane solutions containing Ph$_3$P in only slightly excess. 3 has the other isomeric form in the solid state, probably with the structure [Pt(π-C$_4$H$_7$)(PPh$_3$)$_2$]Cl (see Experimental).

disposition of two mutually trans triphenylphosphine ligands.[10] Thus, we tentatively assign the solid state structure of this isomer of 3 as A shown in eq. 2. Quite similar vibrational

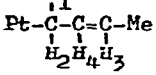
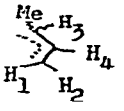


3-A 4 (2)

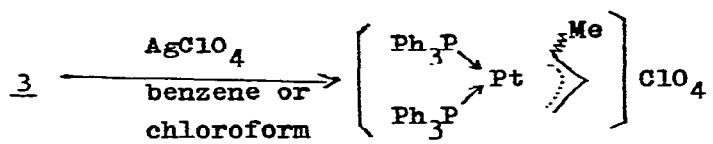
spectral aspects were observed for this complex in benzene except that an additional very weak band appeared at 538 cm^{-1} in the infrared spectrum. Since the infrared spectrum of the complex $Pt(\pi\text{-}C_4H_7)Cl(PPh_3)$ 4, prepared from 3 and H_2O_2 in acetone (see later), showed a very strong band at exactly this frequency and the observed molecular weight of 3 in benzene is less than that calculated (see Experimental), we interpret the ^1H NMR spectrum of 3 in benzene (Table 1) as arising from the predominant form 3-A which lies in equilibrium, rapid enough on the NMR time scale, with a small concentration of 4 (eq. 2). Strong support for this predominant existence of the σ-crotyl form also comes from the value of $J(Pt\text{-}CH_2)$ of 3 in benzene (85 Hz) which is by far larger than both the mean value of $J(Pt\text{-}H_1)$ and $J(Pt\text{-}H_2)$ of 4 (51 Hz) and $J(Pt\text{-}CH_2)$ of 3 measured in $CDCl_3$ (21 Hz) in which 3 exists as the π-allylic species (see later). The stereochemistry with respect to the C=C bond in 3-A was assumed to be trans on the basis of the almost 100 % syn-methyl configuration in 4 as deduced from the ^1H NMR data (Table 1). Furthermore, addition of a small amount of

Table 1. ^1H NMR[a] and Infrared[b] Data for Crotylplatinum(II) Complexes[c]

Compound	Chemical Shifts(δ)					ν(Pt-Cl)(cm^{-1})
	Me	H_1	H_2	H_3	H_4	
$Pt(C_4H_7)Cl(PPh_3)_2$						
3-A[d]	1.53(d)		2.19(d)	4.25(br)	5.2(br)	264
	J_{H_3}= 7		J_{H_4}= 7.5			
			J_{Pt}= 85			
3-B-anti[e]	1.08(br m)	2.5(v br)	4.02(br)	4.34(v br)	[f]	
3-B-anti	1.05(br m)	[f]	[f]	4.40(v br)	5.58(m)	
3-B-syn[e]	1.26(br m)	2.80(v br)	3.14(br)	3.68(v br)	5.26(v br)	
3-B-syn	1.27(br m)		3.10(d)	3.95(v br)	5.35(dt)	
			J_{H_4}= 10		J_{H_1}=J_{H_2}= 10	
			J_{Pt}= 21		J_{H_3}= 12	
$Pt(C_4H_7)Cl(PPh_3)$						
4	1.91(t)	2.07(dd)	2.61(dd)	3.73(m)	4.69(br m)	275
	J_{H_3}= 6	J_{H_4}= 11	J_{H_4}= 7	J_{Me}= 6		
	J_P= 6	J_{H_2}= 3	J_{H_1}= 3	J_{H_4}= 12		
		J_{Pt}= 80	J_{Pt}= 22	J_P= 8		
$Pt(C_4H_7)Cl(AsPh_3)$						
5	1.80(d)	1.96(dd)	2.97(dd)	3.49(m)	4.48(m)	290
	J_{H_3}= 6	J_{H_4}= 11	J_{H_4}= 7	J_{Me}= 6	J_{H_1}= 11	280
		J_{H_2}= 3	J_{H_1}= 3	J_{H_4}= 12	J_{H_2}= 7	
		J_{Pt}= 72	J_{Pt}= 18		J_{H_3}= 12	
5[g]	1.71(d)		2.62(d)	3.57(m)	4.58(dt)	
	J_{H_3}= 6		J_{H_4}= 9	J_{Me}= 6	J_{H_1}=J_{H_2}= 9	
			J_{Pt}= 44	J_{H_4}= 12	J_{H_3}= 12	

[a] In $CDCl_3$ at 23°C except as noted. δ in ppm, J in Hz. d= doublet; t= triplet; dd= doublet of doublets; dt= doublet of triplets; m= multiplet; br= broad; v br= very broad. [b] In Nujol mulls. [c] Proton numbering is  for 3-A and  for others. [d] In C_6D_6. [e] At -50°C. [f] Not observed. [g] In the presence of 1 mole of $AsPh_3$.

triphenylphosphine (ca. 0.1 mole per Pt) to the benzene solution of 4 caused the signals due to H_1 and H_2 of 4 to coalesce, as expected from eq. 2, but no resonances attributable to the anti form of 4 could be seen. Although ^1H NMR spectra of 3 at lower temperatures could not be obtained due to its limited solubility in benzene as well as in any other solvents in which the form 3-A is expected to predominate, more definitive evidence to show the similar trans phosphine arrangement and trans crotyl skeleton was presented in $Pt(C_6HCl_4)(\sigma\text{-}CH_2CH{=}CHMe)(PPh_3)_2$ by ^1H NMR spectroscopy.[11] Further evidence for the predominance of the trans crotyl skeleton in 3-A is the fact that treatment of 3 with $AgClO_4$ in benzene affords $[Pt(\pi\text{-}C_4H_7)(PPh_3)_2]ClO_4$ 1a, the ^1H NMR spectrum of which shows the presence of only the syn-methyl isomer (eq. 3), in contrast to the result of a similar treatment in chloroform (see later).*



1a (3)

Thus, the reaction of 3 with $AgClO_4$ in benzene provides another way of obtaining the syn isomer of 1a in a stereoselective fashion.[5-8]

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*It should be noted that interconversion between the anti and the syn isomers of 1a does not occur under the conditions employed in these experiments.

Of related interest with regard to the presence of the σ-crotyl form of 3 in the solid state as shown above is the fact that the infrared spectrum of one isomeric solid sample * of $Pt(C_3H_5)Cl(PPh_3)_2$ 2, prepared from $Pt(PPh_3)_4$ and allyl chloride in benzene, showed ν(C=C) (1615 cm^{-1}), $\rho_w(=CH_2)$ and γ(=CH-) (985 and 900 cm^{-1}), together with ν(Pt-Cl) (265 cm^{-1}) which has already been noted in previous work.[12] In addition, no strong bands in the region 550 ± 5 cm^{-1} appeared. Although ^1H NMR spectra of 2 in benzene could not be measured owing to poor solubility, such infrared data could suggest a σ-allyl structure similar to 3-A in eq. 2, rather than a five-coordinate structure[12] with both the π-allyl-platinum and the chloride-platinum bonds present. A similar trans σ-allylic structure has been established in $Pt(C_6HCl_4)(\sigma\text{-}CH_2CH{=}CH_2)(PPh_3)_2$.[11]

Pt(CH$_2$CH=CHMe)Cl(PPh$_3$)$_2$ in chloroform

The ^1H NMR spectrum of 3 in $CDCl_3$** at -50° can be explained in a different way as due to the ionic π-crotyl structure (3-B shown in eq. 4) with both the anti and syn-methyl isomers present,

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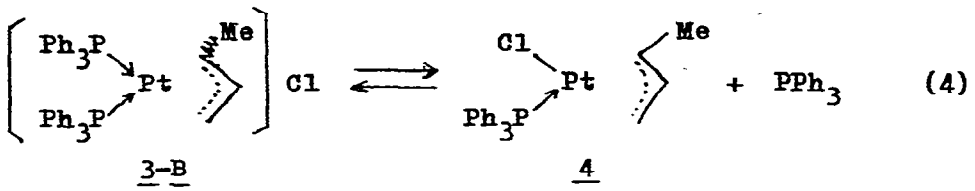
*This was obtained by the addition of n-hexane to the reaction mixture in benzene (see Ref. 9). Careful, repeated crystallizations in a manner similar to that for obtaining the cis form of 3 (see Experimental) also increased the amounts of the cis form of 2 contained in the solid mixture.

**Two isomeric forms of the solid sample of 3 gave the identical spectroscopic results in chloroform.



3-B 4 (4)

since these spectral patterns (Table 1) are very similar to those[7] of the corresponding isomers of 1a, and since the vibrational spectra of 3 in chloroform showed no bands associated with the free C=C bond and the Pt-Cl bond, but a very strong infrared band at 545 cm^{-1} which is indicative of the cis arrangement of the phosphines.[10] Similarly, 2 also was reported[9] to show the ^1H NMR spectra in $CDCl_3$ at below -10° assignable to $[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]Cl$. At room temperature, H_1 and H_2 of both isomers of the form 3-B exchange rapidly (Table 1), but the methyl and the methine proton resonances remained unchanged, indicating that interconversion between the anti and syn isomers of 3-B is slow on the NMR time scale. Treatment of 3 with $AgClO_4$ in chloroform gave a mixture of 20 % anti and 80 % syn forms of 1a (eq. 3). This isomer ratio is probably of thermodynamic origin, for a mixture of 1a with an almost similar anti/syn ratio arose quickly when a catalytic amount of triphenylphosphine or 3 had been added to a $CDCl_3$ solution of either 100 % anti or 100 % syn form of 1a.

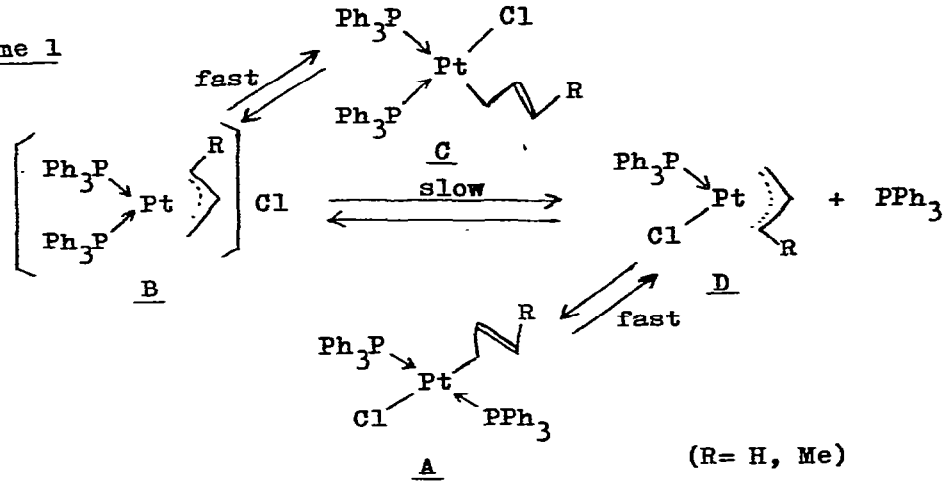
Addition of triphenylphosphine (0.1-1 mole per Pt) to 4 in $CDCl_3$ at room temperature caused no coalescence of H_1 and H_2, but three separate sets of resonances due to 4, the anti and the syn forms of 3-B appeared. The signals of 4 in this case were broader than those observed in the absence of 3-B, but there were no chemical shift differences between these two

cases. The amount of 3 thus produced was almost the same as that of the phosphine added, so that the equilibrium shown in eq. 4 would lie far to the left. Almost similar trends were observed for the mixture of $Pt(\pi\text{-allyl})Cl(PPh_3)$ and $[Pt(\pi\text{-allyl})(PPh_3)_2]Cl$ (allyl= $CH_2CH{=}CH_2$, $CH_2CMe{=}CH_2$) in $CDCl_3$. On the other hand, it has been reported[13] that in analogous palladium complexes, the extent to which the cationic species $[Pd(\pi\text{-allyl})(PPh_3)_2]Cl$ are formed from $Pd(\pi\text{-allyl})Cl(PPh_3)$ and Ph_3P is not so large as that in the platinum complexes. Addition of $[PtCl_2(PPh_3)]_2$ to the mixture of the two forms of 3-B in $CDCl_3$ resulted in recovery of 4 together with $PtCl_2(PPh_3)_2$. However, rather surprisingly, the ^1H NMR spectrum of 4 thus recovered still showed the presence of the syn isomer only. This apparently suggests the much smaller equilibrium ratio of anti/syn in 4 than in 3-B, which seems to be inconsistent with an isomer ratio predicted from consideration of steric effects in these complexes. At present we have no reasonable explanations for such different stereoselectivities as observed in 4 and 3-B.

Several rate processes involved in the equilibrium represented by eq. 4 deserve comments. The observation at room temperature of separate sets of resonances due to $[Pt(\pi\text{-allyl})(PPh_3)_2]Cl$ (B in Scheme 1) and $Pt(\pi\text{-allyl})Cl(PPh_3)$ (D) as described before indicates that there exists a considerably high barrier at least to the step of the formation of D from B. On the other hand, the rapid syn-anti proton exchange in the complex B where R= H[9] and Me (3-B) presumably proceeds through an intermediate σ-allylic species lying at a relatively low energy level. We propose that this intermediate has not the structure trans-$Pt(\sigma\text{-allyl})Cl(PPh_3)_2$ (A in Scheme 1), but rather

cis-Pt(σ-allyl)Cl(PPh_3)$_2$ (C) for the following reasons. The rate of the dissociation of the phosphine from A to form D has

Scheme 1



been shown to be rapid on the NMR time scale in the case of R= Me (3-A→4). Apparently then, the formation of A, if any, from B may b process requiring rather a high activation energy, otherwise the spectra of the system consisting of the complexes B and D would not have given the distinct resonances due to D. On similar grounds, the conversion of C to D, if it were to occur, would be very slow. The high barrier to the formation of the trans σ-allyl complex from the cationic π-allyl complex may, in part, be associated with the change of cis to trans phosphine arrangement. The slower rate of interconversion between the anti and syn isomers of 3-B than that between H_1 and H_2 in both isomers of 3-B is understandable in terms of a greater steric constraint in the intermediate cis-Pt(σ-CHMeCH=CH_2)Cl(PPh_3)$_2$ than in cis-Pt(σ-CH_2CH=CHMe)Cl(PPh_3)$_2$.

Triphenylarsine complex

The reaction of $Pt(AsPh_3)_4$ with CH_2=CHCHMeCl in benzene gave $Pt(\pi\text{-}C_4H_7)Cl(AsPh_3)$ 5 in one step. This result indicates that the equilibrium between $Pt(C_4H_7)Cl(AsPh_3)_2$ and 5 plus the free arsine lies far in favor of the latter species because of the much weaker coordinating ability of the arsine ligand. In accord with this equilibrium trend, addition of triphenylarsine (0.1-1 mole per Pt) to 5 in benzene or $CDCl_3$ caused only a slight change in the chemical shifts of H_3, H_4 and Me (see Table 1), while the resonances due to H_1 and H_2 coalesced to one doublet with $J(Pt\text{-}CH_2)$= 44 Hz, which is very close to the mean value of $J(Pt\text{-}H_1)$ and $J(Pt\text{-}H_2)$ of 5. Thus, the process occurring in this case is mainly the exchange of the syn and anti protons probably through trans-$Pt(\sigma\text{-}CH_2CH{=}CHMe)Cl(AsPh_3)_2$, but the contribution of this species as well as of $[Pt(\pi\text{-}C_4H_7)(AsPh_3)_2]Cl$ to the observed spectra would not be very significant in view of the value of $J(Pt\text{-}CH_2)$ above.

Synthetic route to $Pt(\pi\text{-allyl})ClL$ (L= PPh_3, $AsPh_3$)

The reaction of $Pt(allyl)Cl(PPh_3)_2$ with H_2O_2 in acetone and the reaction of $Pt(AsPh_3)_4$ with allylic chloride provide very convenient, alternative ways of synthesizing $Pt(\pi\text{-allyl})ClL$ (allyl= $CH_2CH{=}CH_2$, $CH_2CH{=}CHMe$, $CH_2CMe{=}CH_2$; L= PPh_3, $AsPh_3$) in moderate to good yields. Previously, $Pt(\pi\text{-allyl})ClL$ were prepared from $[Pt(allyl)Cl]_n$ and L.[14] Though limited to triphenylphosphine and triphenylarsine analogs, the present methods are particularly effective for the β-methallyl and crotyl complexes, since it was rather difficult to obtain $[Pt(CH_2CMe{=}CH_2)Cl]_2$ in high yield and since $[Pt(CH_2CH{=}CHMe)Cl]_n$ has been yet unavailable.[14,15]

Experimental

Reactions employing platinum(0) complexes were carried out under nitrogen. $Pt(PPh_3)_4$ and $Pt(AsPh_3)_4$ were prepared by reported methods.[16] Allylic chlorides were purchased from Nakarai Chemicals Ltd.

$Pt(CH_2CH{=}CHMe)Cl(PPh_3)_2$ This was prepared from $Pt(PPh_3)_4$ and $CH_2{=}CHCHMeCl$ or trans-$MeCH{=}CHCH_2Cl$ by a method similar to that[9] for obtaining $Pt(CH_2CH{=}CH_2)Cl(PPh_3)_2$. Recrystallization from benzene/n-hexane in the refrigerator gave a white crystalline solid, m.p. 173-175° (decomp.). [Found: C, 59.46; H, 4.67. Calcd. for $C_{40}H_{37}P_2ClPt$: C, 59.30; H, 4.60 %.] Molecular weights found by vapor pressure osmometry in benzene at 45° were 700 and 684 at concentrations of 0.76 and 0.48 wt %. Calcd. for the monomer, 810. Recrystallization of this benzene-soluble product possibly with trans phosphine configuration from benzene/n-hexane or methylene chloride /n-hexane solutions containing a small amount (ca. 5 mole %) of triphenylphosphine gave solids showing identical infrared and Raman spectra. Repeated crystallizations of this isomer from methylene chloride/n-hexane (1:1 ratio by volume) in the absence of triphenylphosphine gave products which contained increasing amounts of the isomer poorly soluble in benzene probably with the cis phosphine arrangement. This was readily followed by observing the increase in the intensity of the infrared band at 545 cm^{-1}. Furthermore, no bands attributable to $\nu(C{=}C)$, $\gamma(=CH-)$ and $\nu(Pt-Cl)$ could be seen in the infrared and Raman spectra of this isomer in the solid state, suggesting the structure $[Pt(\pi\text{-}C_4H_7)(PPh_3)_2]Cl$. This isomer was converted again to the other on crystallization from methylene chloride/

n-hexane containing a small amount of triphenylphosphine. Two isomeric forms of $Pt(CH_2CH=CH_2)Cl(PPh_3)_2$ were prepared in similar manners. $Pt(CH_2CMe=CH_2)Cl(PPh_3)_2$ was prepared from $Pt(PPh_3)_4$ and $CH_2=CMeCH_2Cl$ in benzene; the infrared spectrum of solid products showed the presence of the seemingly cis isomer only.

Pt(π-CH_2CH=CHMe)Cl(PPh_3) An acetone solution (20 ml) containing $Pt(CH_2CH=CHMe)Cl(PPh_3)_2$ (810 mg; 1.0 mmole) and 0.11 ml of 30 % aqueous H_2O_2 (1.0 mmole) was heated at reflux for 1 hr. The solvent was evaporated, and the residual solid mixture was washed by n-hexane. Recrystallization from benzene/n-hexane gave 220 mg (40 %) of $Pt(C_4H_7)Cl(PPh_3)$, m.p. 184° (decomp.). [Found: C, 47.95; H, 3.98. Calcd. for $C_{22}H_{22}PClPt$: C, 48.23; H, 4.05 %.] Molecular weight by vapor pressure osmometry in chloroform at 37° was 540 at a concentration of 0.71 wt %. Calcd. for the monomer, 548. From the n-hexane washings was obtained triphenylphosphine oxide which was identified by melting point and infrared spectrum. Pt(π-CH_2CH=CH_2)Cl(PPh_3) (76 % yield) and Pt(π-CH_2CMe=CH_2)Cl(PPh_3) (94 % yield) were obtained similarly.

Pt(π-CH_2CH=CHMe)Cl($AsPh_3$) The reaction between $Pt(AsPh_3)_4$ and $CH_2=CHCHMeCl$ to give $Pt(C_4H_7)Cl(AsPh_3)$ was carried out in a manner similar to that used with $Pt(PPh_3)_4$ as described above. Recrystallization from methylene chloride/n-hexane in the refrigerator afforded white crystals (40 % yield), m.p. 176° (decomp.). [Found: C, 44.57; H, 3.84. Calcd. for $C_{22}H_{22}AsClPt$: C, 44.65; H, 3.75 %.] Molecular weight by vapor pressure osmometry in chloroform at 37° was 581 at a concentration of 0.86 wt %. Calcd. for the monomer, 592.

Infrared spectra were measured on Hitachi 225 (4000-600 cm^{-1}) and Hitachi EPI-2G (700-200 cm^{-1}) spectrophotometers, both equipped with gratings. Raman spectra were obtained on a JASCO R-800 spectrophotometer. ^{1}H NMR spectra were obtained on a Japan Electron Optics JNM-PS-100 spectrometer operating at 100 MHz. Tetramethylsilane was used as internal standard.

Acknowledgment

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