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Chemistry of Metal Hydrides. XIII. Insertion and Isomerization Reactions of Allylic Compounds with Cationic Platinum(II)-Hydrido Complexes

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Received May 24, 1972

Migration and insertion of the C=C bond occur in reactions of allylic acetates and *N*-allylacetamide with several platinum(II) hydrides to give five-membered chelate complexes of platinum(II). Similar behavior explains the formation of π-allylplatinum(II) complexes and aldehydes from reactions of allylic alcohols or diallyl ethers with platinum(II) hydrides. Stereospecific formation of two isomers of π-crotylplatinum(II) complexes is reported.

Introduction

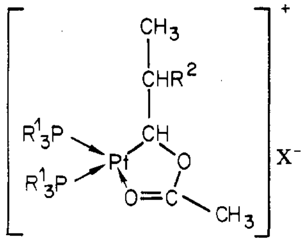
The insertion of an olefin into the metal-hydrogen bond is thought to be one of the key steps in the homogeneous hydrogenation, isomerization, and oligomerization of olefins in the presence of certain metal complexes as catalysts.[1] It has generally been accepted that in such insertion reactions, the formation of a hydridoolefin complex may well be the rate-determining step,[1,2] and indeed the importance of coordinative unsaturation of the central metal atom in both metal-hydrido complexes[3] and certain alkylplatinum(II) complexes[4,5] has been proposed to explain specific reactivities toward a variety of unsaturated organic molecules. Thus, we previously reported[6] facile insertion of olefins into the Pt-H bond involving four-coordinate intermediate complexes *trans*-[PtH(PR$_3$)$_2$(olefin)]$^+$ which can be formed readily by replacement by olefins of the ligand trans to hydrogen. Although the reactions of platinum(II)-hydrido complexes with simple monoolefins were found to give rise to *n*-alkylplatinum(II) complexes[6,7] and π-allyl- or π-enylplatinum(II) complexes with diolefins,[6,8] very few reactions have been studied with olefins which contain electronegative functional groups at or near the olefinic carbons. The reactions of such olefins with metallic complexes appear to be particularly interesting on both electronic and steric grounds since the functional groups should have a significant effect on the ability of the C=C bond to coordinate to the metal. Moreover, some functional groups are capable of coordination themselves and this is often found to affect the course of the reactions.[9] Thus, for example, Brookes and Nyholm reported[10] the reaction of platinum(II)-hydrido complexes with (*o*-vinylphenyl)diphenylphosphine to give an unusual *sec*-alkylplatinum(II) complex stabilized by the intramolecular coordination by phosphorus, while the reactions of platinum(II) hydrides with tetracyanoethylene[11] yielded the noninsertion products. In the present paper, we report a novel type of insertion reaction of some allylic derivatives into the Pt-H bond of cationic platinum(II)-hydrido complexes;[12] the initial migration of the double bond is followed by addition of the Pt-H bond. The double-bond migration process is of particular interest as far as the mechanism of the homogeneous isomerization of olefins by platinum(II) catalysts[13] is concerned.

Results and Discussion

Previously,[6] ethylene was found readily to replace an acetone or nitrate ligand in *trans*-[PtH(PR$_3$)$_2$(acetone)]$^+$X$^-$ (I) (PR$_3$ = PPh$_3$ or PPh$_2$Me; X = BF$_4$ or PF$_6$) or *trans*-PtH(NO$_3$)(PPh$_2$Me)$_2$ (II) to give *trans*-[PtH(PR$_3$)$_2$(C$_2$H$_4$)]$^+$X$^-$. Similarly, *trans*-PtH(ClO$_4$)(PPh$_3$)$_2$ (III) was recently found to react with ethylene to give the analogous perchlorate complex in benzene solution[14,15] and the insertion product in acetone solution.[16] These olefin substitution reactions are obviously a consequence of the very weak coordinating ability of oxygen-donor ligands and are consistent with the very large chemical shifts of the hydridic hydrogen, the *J*(Pt-H) values, and high frequencies of ν(Pt-H) in I-III.[14,17]

When I and III were allowed to react with allylic acetates or *N*-allylacetamide at room temperature, insertion products were obtained in which the formation of a platinum(II)-carbon bond occurred at an allylic position in the original olefins (eq 1 and 2). The structures of IV and V were

I, III + CH$_2$=CR^{2}CH$_2$OCOCH$_3$ →



X$^-$ (1)

IVa, PR$^1_3$ = PPh$_2$Me, R^2 = H, X = BF$_4$
b, PR$^1_3$ = PPh$_2$Me, R^2 = CH$_3$, X = BF$_4$
c, PR$^1_3$ = PPh$_3$, R^2 = H, X = ClO$_4$

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(1) R. S. Coffey, "Aspects of Homogeneous Catalysis," Vol. 1, R. Ugo, Ed., Manfredi, Milan, 1970, p 1.

(2) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 121 (1965).

(3) See, *e.g.*, M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1347 (1967); R. F. Heck, *Advan. Chem. Ser.*, No. 49, 185 (1966).

(4) M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, **94**, 1532 (1972), and references therein.

(5) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **10**, 2699 (1971).

(6) H. C. Clark and H. Kurosawa, *J. Chem. Soc. D*, 957 (1971); *Inorg. Chem.*, 11, 1275 (1972).

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(8) A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. D*, 598 (1970).

(9) R. Jones, *Chem. Rev.*, **68**, 785 (1968).

(10) P. R. Brookes and R. S. Nyholm, *J. Chem. Soc. D*, 169 (1970).

(11) P. Uguagliati and W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 5446 (1968).

(12) For a preliminary communication see H. C. Clark and H. Kurosawa, *J. Chem. Soc., Chem. Commun.*, 150 (1972).

(13) F. R. Hartley, *Chem. Rev.*, 69, 799 (1969); see p 838.

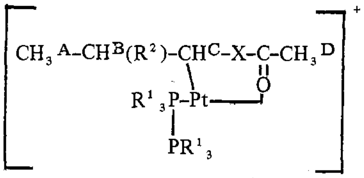
(14) I. V. Gavrilova, M. I. Gel'fman, N. V. Ivannikova, and V. V. Razumovskii, *Russ. J. Inorg. Chem.*, 16, 596 (1971).

(15) Reference 14 reported the observation of a strong band at 2089 cm^{-1} due to ν(Pt-H) in the infrared spectrum of *trans*-[PtH(PPh$_3$)$_2$(C$_2$H$_4$)]$^+$ClO$_4^-$. However, we failed to confirm the occurrence of such a band in the spectrum of the same complex which was prepared according to the reported method.

(16) H. C. Clark and H. Kurosawa, unpublished results.

(17) H. C. Clark and H. Kurosawa, *J. Organometal. Chem.*, 36, 399 (1972).

Table I. Relevant Infrared Absorption Bands[a] and Nmr Data[b] for Some Platinum(II) Complexes

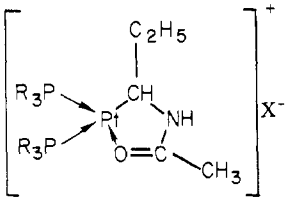


(X = O or NH)

Compd	ν(C=O)	Amide II	ν(N–H)	τ_A	J_{HH}	τ_B	τ_C	τ_D	τ(P–CH$_3$)	J(P–CH$_3$)	J(Pt–PCH$_3$)
IVa	1575 s			9.25 t	7	8.45 vb (20)	4.66 b (13)	7.73 s	8.20 d	9.0	15.5
									7.99 d	11.0	53.0
IVb	1575 s			9.46 d	7		4.77 b (10)	7.75 s	8.25 d	9.0	15.0
				8.96 d	7				8.00 d	11.5	52.0
IVc	1573 s			9.25 t	7	8.55 vb (22)	4.82 b (12)	7.75 s			
Va[c]	1615 s	1528 s	3315 m	9.21 x		8.74 b (11)	6.30 vb (17)	7.87 s	8.36 d	9.0	14.5
	(1615 s)	(1527 s)	(3315 m)						8.09 d	11.0	49.0
Vb[d]	1615 s	1532 s	3280 m	9.21 x		8.72 vb (18)	6.53 vb (21)	7.95 s			
	(1615 s)	(1528 s)	(3290 m)								

[a] Measured in Nujol mulls and in CH_2Cl_2 (parentheses, 0.04 *M*) (cm^{-1}). Key: s, strong; m, medium. [b] Measured in $CDCl_3$. τ in ppm; *J* in Hz. Key: s, singlet; d, doublet; t, triplet; x, collapsed triplet; b, broad; vb, very broad. Half-height width given in parentheses. [c] τ(NH) 1.72. [d] τ(NH) 1.82.

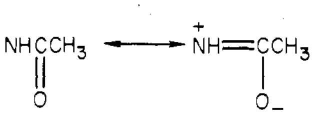
I, III + CH_2=CHCH$_2$NHCOCH$_3$ →



X$^-$ (2)

Va, PR$_3$ = PPh$_2$Me, X = BF$_4$
b, PR$_3$ = PPh$_3$, X = ClO$_4$

deduced from elemental analyses and infrared and proton nmr spectra (Table I and Figure 1). The infrared spectra of IV (Table I) showed strong absorption bands due to the C=O stretching mode at *ca.* 1575 cm^{-1}, which is far lower than those usually found in the alkyl esters of acetic acid (higher than 1700 cm^{-1}).[18] This strongly suggests that the carbonyl group is coordinated to platinum. The infrared spectra of V, both in the solid state and in solution, contained two strong bands in the region between 1500 and 1650 cm^{-1} (Table I). These are probably associated with C=O stretching and amide II vibrations, although due to coupling they may not be pure modes. The decrease in ν(C=O) frequencies from those of *N*-alkylacetamides measured in very dilute solution (*ca.* 1700 cm^{-1})[18] may indicate that coordination occurs through oxygen, since the contribution of the resonance form B will increase on complexation



A B

through oxygen. This is particularly interesting since platinum(II)-urea complexes have Pt–N bonds as demonstrated by the increase in ν(C=O) and the decrease in ν(C–N)[19] and since nitrogen is generally a stronger donor than oxygen in alkylplatinum(II)[20] or hydridoplatinum(II) complexes.[17] This unusual coordination through oxygen in V may be due to steric requirements and/or to the ease of isomerization of the initial olefins (see later).

Proton nmr spectra of IVa, IVc, Va, and Vb showed signals attributable to the CH_3-CH_2- moiety, although very broad bands were observed for the methylene protons, probably due to nonequivalence of these two protons caused by a neighboring asymmetric carbon (see below) and also to spin-spin couplings of these protons with ^{31}P, ^{195}Pt, and

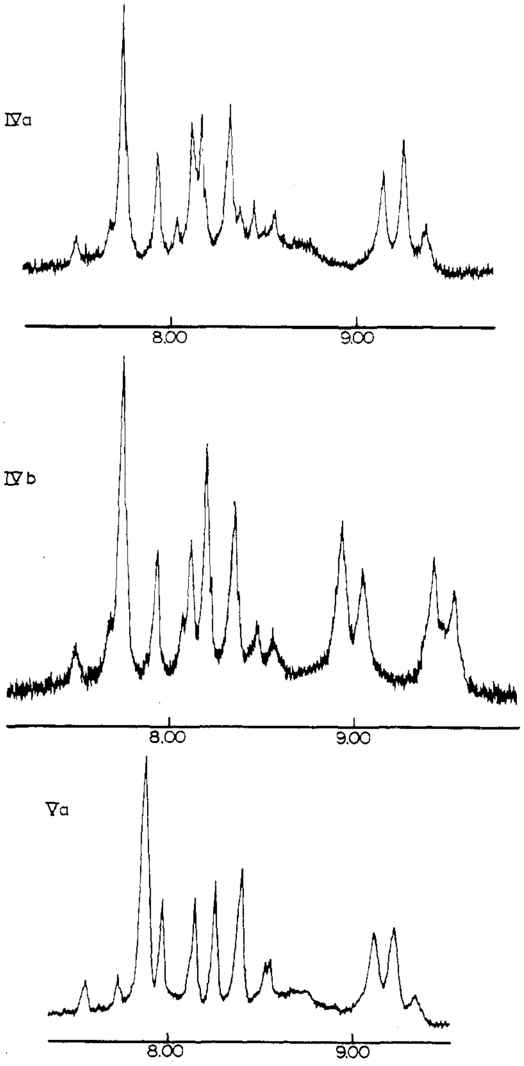


Figure 1. Proton nmr spectra of some platinum(II) complexes recorded on $CDCl_3$ solution at 60 MHz.

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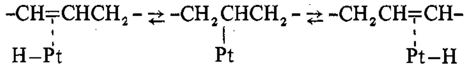
other hydrogen nuclei. Again because of such couplings, the signals due to methine protons also appeared as very broad peaks. Of particular significance is the appearance of two nonequivalent doublets due to the methyl protons of an isopropyl group in IVb; this is in good agreement with the proposed structure since two methyls in an isopropyl group attached to an asymmetric carbon atom should be magnetically nonequivalent. Absorptions due to the methine proton of the isopropyl group are overlapped by strong peaks of acetoxy methyl and phosphine methyl groups. Also notable is the fact that the proton spectra of IVa, IVb, and Va showed two doublets for the phosphorus methyl protons with different $J(\text{Pt-PCH}_3)$ and $J(\text{P-CH}_3)$ values (Table I). The lower field doublet has the larger values of both $J(\text{Pt-PCH}_3)$ and $J(\text{P-CH}_3)$, and we assign it to the methyls of the phosphine trans to oxygen, and hence the higher field doublet to the phosphine methyls trans to carbon; it was previously shown[17,21] that $J(\text{Pt-PCH}_3)$ values are dependent on the trans influence of the ligand, and hence the very large difference in the observed $J(\text{Pt-PCH}_3)$ is consistent with the proposed structure in view of the difference in the trans influences of oxygen and carbon. Furthermore, the absolute values of $J(\text{P-CH}_3)$ in the coordinating phosphines are reported[22] to increase as the metal-phosphine bond strength increases, and therefore the larger values of these coupling constants for the phosphine trans to oxygen are consistent with a stronger Pt-P bond as a result of the weaker trans influence of oxygen.

The double-bond migration in the presence of the platinum(II) hydride complexes, as in reactions 1 and 2, may well occur by an addition elimination mechanism which has been proposed for the homogeneous isomerization of olefins using a platinum(II) catalyst.[13] (See eq 3.) This double-bond migration may then be followed by addition of the Pt–H bond across the newly formed C=C bond. This in turn may be facilitated by the presence of an additional coordinating group such as carbonyl. Indeed there was no indication of the formation of free propenyl acetate even in the reaction of III with excess allyl acetate. In agreement with the expectations from such a mechanism, we also find that III is capable of isomerizing allyl phenyl ether or allyl methyl ether catalytically at room temperature to propenyl phenyl ether or propenyl methyl ether (see Experimental Section).

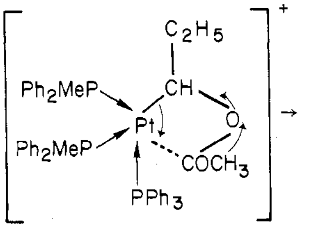


$$\underset{\text{H-Pt}}{\text{-CH=CHCH}_2\text{-}} \rightleftarrows \underset{\text{Pt}}{\text{-CH}_2\text{CHCH}_2\text{-}} \rightleftarrows \underset{\text{Pt-H}}{\text{-CH}_2\text{CH=CH-}} \qquad (3)$$

The relative stabilities of chelate ring systems in the reaction products may also affect the course of the reactions. Of the several possible chelate structures produced from the addition of the Pt–H bond across either terminal or internal C=C bond in allylic or propenyl derivatives, consideration of molecular models indicates that only the five-membered rings in IV or V can be both planar and free of ring strain. This causes π delocalization in the Pt-O-C-X systems (X = O or NH) to occur more effectively, thus making the structures IV and V of lower energy.

Interestingly, both IV and V have a *sec*-alkyl-platinum(II) bond which would not be very stable in the absence of intramolecular coordination by oxygen. Thus, the attempted preparation of isopropyl- and cyclohexylplatinum(II) complexes resulted only in the formation of platinum(II)-hydrido complexes,[7,23] although a few acetylacetonatoplatinum(II) complexes were reported to contain such a *sec*-alkyl-platinum(II) bond.[24] A similar chelate effect stabilizing a *sec*-alkyl-platinum(II) bond has been found in a number of products formed by the nucleophilic attack by X^- (X = OR, OAc, etc.) on olefin-platinum(II) complexes[24] and by insertion reactions of both a phosphine-substituted olefin[10] and cyclic diolefins[8,25] into the Pt-H bond. That the present *chelate* system in IV or V is stable may also be seen from the fact that the reaction of a 1 molar equiv of triphenylphosphine with IVa proceeded only very slowly at room temperature to the extent that most of the original complexes remained unchanged after 24 hr. This contrasts with the observation[20] that in the displacement of L in *trans*-$[\text{PtMe(PMe}_2\text{Ph)}_2\text{L}]^+$, L = acetone was found to be the weakest donor and L = phosphines were among the very strong donors. Moreover, the infrared spectrum of the reaction mixture after 1 week showed, in addition to the strong bands due to IVa, weak bands at 1630 and 1735 cm^{-1}, the latter of which was due to propionaldehyde, this being confirmed by the proton nmr spectrum. Propionaldehyde may be formed by the sequence of eq 4, so that the band at 1630 cm^{-1} could be assigned to an acylplatinum(II) complex although the proton nmr spectrum of the reaction mixture in CH_2Cl_2 at 30° failed to confirm this. A similar reaction sequence for the formation of propionaldehyde will be described below for reactions involving allylic alcohols or diallyl ethers.

$\text{IVa} + \text{PPh}_3 \rightleftarrows$

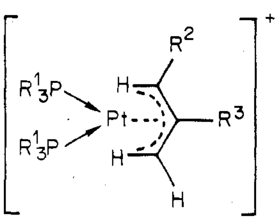


$\rightarrow$

$\text{C}_2\text{H}_5\text{CHO} + [\text{Pt(CH}_3\text{CO)(PPh}_2\text{Me)}_2\text{(PPh}_3)]^+ \quad (4)$

I-III reacted with several diallyl ethers at room temperature according to eq 5. The same products were obtained when 2 molar equiv of allylic alcohols were used instead of 1 equiv of diallyl ethers. Methyl ethyl ketone was not observed in the reaction of II with *trans*-$\text{CH}_3\text{CH=CHCH}_2\text{OH}$. These

$$\text{I, II, III} + \left\{\begin{matrix}(\text{CHR}^2\text{=CR}^3\text{CH}_2)_2\text{O} \\ 2\text{CHR}^2\text{=CR}^2\text{CH}_2\text{OH}\end{matrix}\right\} \rightarrow \text{CH}_2\text{R}^2\text{CHR}^3\text{CHO} +$$



X^- (5)

VIa, $\text{PR}^1_3 = \text{PPh}_2\text{Me}$, $R^2 = \text{H}$, $R^3 = \text{H}$, $X = \text{BF}_4$ or PF_6
b, $\text{PR}^1_3 = \text{PPh}_2\text{Me}$, $R^2 = \text{H}$, $R^3 = \text{H}$, $X = \text{NO}_3$
c, $\text{PR}^1_3 = \text{PPh}_2\text{Me}$, $R^2 = \text{CH}_3$, $R^3 = \text{H}$, $X = \text{NO}_3$
d, $\text{PR}^1_3 = \text{PPh}_3$, $R^2 = \text{H}$, $R^3 = \text{H}$, $X = \text{BF}_4$ or PF_4
e, $\text{PR}^1_3 = \text{PPh}_3$, $R^2 = \text{H}$, $R^3 = \text{H}$, $X = \text{ClO}_4$
f, $\text{PR}^1_3 = \text{PPh}_3$, $R^2 = \text{H}$, $R^3 = \text{CH}_3$, $X = \text{ClO}_4$
g, $\text{PR}^1_3 = \text{PPh}_3$, $R^2 = \text{CH}_3$, $R^3 = \text{H}$, $X = \text{ClO}_4$

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[21] T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, 11, 1786 (1972).

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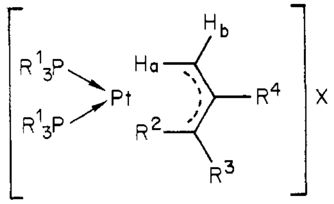
[25] M. A. Schwartz and T. J. Dunn, *J. Amer. Chem. Soc.*, 91, 4007 (1969).

Table II. Nmr Data[a] for Some π-Allylplatinum(II) Complexes

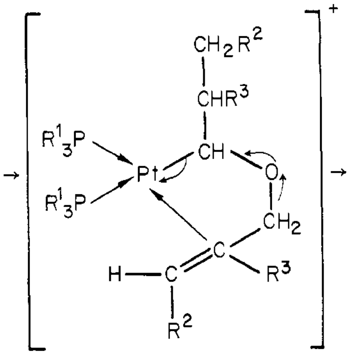


Compd												
PR^1_3	R^2	R^3	R^4	X	$\tau(H_a)$	$\tau(H_b)$	$\tau(R^2)$	$\tau(R^3)$	$\tau(R^4)$	τ(P-CH$_3$)	J(P-CH$_3$)	J(Pt-PCH$_3$)
PPh_2Me	H	H	H	PF_6[b]	7.10 dd ($J_{HH} = 13$) ($J_{PH} = 8$) ($J_{PtH} = 43$)	6.14 d ($J_{HH} = 7$)			4.75 m	8.07 d	9.5	37.5
PPh_2Me	H	H	H	Br[c]	6.67 vb (30)	6.37 b (15)			4.76 vb (30)	7.90 d	10.0	34.0
PPh_2Me	H	H	H	Br[d]	6.50 vb (20)	6.50 vb (20)			4.58 m	7.88 d	10.0	34.0
PPh_3	H	H	H	BF_4	7.05 dd ($J_{HH} = 13$) ($J_{PH} = 8$) ($J_{PtH} = 40$)	6.18 d ($J_{HH} = 7$)			4.58 m			
PPh_2Me	H	H	Me	NO_3	7.00 d ($J_{PH} = 8.5$) ($J_{PtH} = 39$)	6.46 s			8.09 s ($J_{PtH} = 62$)	8.04 d	10.0	37.5
PPh_3	H	H	Me	ClO_4	6.89 d ($J_{PH} = 9.0$) ($J_{PtH} = 40$)	6.52 s			7.96 s ($J_{PtH} = 64$)			
PPh_2Me	Me	H	H	PF_6[b]	7.23 m	6.22 b (15)	8.98 b (12)	5.47 vb (20)	~4.70 m	8.10 d 8.00 d	9.5 9.5	38.0 38.0
PPh_2Me	H	Me	H	PF_6[b]	7.32 m	6.54 b (14)	6.25 m	8.68 m	4.95 m	8.13 d 8.10 d	10.0 9.5	39.5 37.0
PPh_3	Me	H	H	ClO_4[e]	7.37 dd ($J_{HH} = 13$) ($J_{PH} = 9$)	6.06 b (16)	8.99 b (14)	5.56 vb (21)	~4.48 m			
PPh_3	H	Me	H	ClO_4	7.08 m	6.74 b (14)	6.14 m	8.78 b (15)	~4.65 m			

[a] Measured in CD_2Cl_2 at 30° unless otherwise noted. τ in ppm; J in Hz. Key: s, singlet; d, doublet; dd, doublet of doublets; m, unresolved multiplet; b, broad; vb, very broad. Half-height width given in parentheses. [b] Reference 6. [c] In $CDCl_3$ at $-50°$. [d] In $CDCl_3$ at 30°. [e] Prepared from III and 1,3-butadiene in benzene.

products were identified by analyses and/or proton nmr and infrared spectra. Some of the π-allylplatinum(II) complexes (VI) have been prepared previously from I and allene or butadiene.[6] The order of ease of reaction between II and diallyl ethers is allyl > 1-methylallyl ≫ 2-methylallyl, and in each case small amounts of unidentified products were also observed. Nmr data for the π-allylplatinum(II) complexes are shown in Table II, including those of $[Pt(2\text{-methallyl})(PPh_2Me)_2]^+NO_3^-$ which could not be isolated as a pure solid. Assignment of the two isomers, anti and syn, in π-crotylplatinum(II) complexes was based on the appearance of the anti group at higher field than the syn group[26,27] in the nmr spectrum.

$$\mathrm{I, II, III} + (CHR^2{=}CR^3CH_2)_2O \rightarrow$$



VII

$$\mathrm{VI} + CH_2R^2CHR^3CHO \qquad (6)$$

The sequence of the reactions with diallyl ethers probably involves the isomerization of, and insertion into, the C=C double bond, chelation by another C=C bond, and cleavage of the Pt–C and C–O bonds, processes which are similar to those described in eq 1, 2, and 4. Although such isomerization of allylic alcohols to aldehydes was reported to occur in the reactions of the alcohols with Rh(III) or Ru(III) catalysts,[28] with $Fe(CO)_5$,[29] or with $HCo(CO)_4$[30] and although π-allylpalladium(II) chloride dimer was produced from $PdCl_2$ and allyl alcohol,[31] the present reactions with allylic alcohols are apparently different in that equivalent amounts of VI and the aldehydes are formed simultaneously. Since a diallyl ether-platinum(II) complex has been obtained from K_2PtCl_4 and allyl alcohol,[32] the reaction sequence for allylic alcohols may be very similar to that described in (6), although the presently available evidence does not provide any information about the mechanism of formation of allylic ethers from allyl alcohols.

Of particular interest is the fact that the proton nmr spectrum of VIg showed the resonances attributable to only the syn isomer of the π-crotylplatinum(II) complex, while the reaction of butadiene with I ($PR_3 = PPh_3$) or III gave

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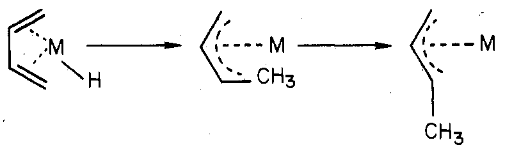
$[Pt(C_4H_7)(PPh_3)_2]^+X^-$ (VIII) (X = BF_4 or ClO_4) whose proton spectrum can be explained in terms of the anti configuration. Furthermore, there was no tendency for this anti form to isomerize to the syn form under conditions similar to those used in reaction 5. The reactions of butadiene with certain metal-hydrido complexes have been found[26,27] to give initially the anti π-crotylmetallic complexes due to the preference for the cisoid configuration of butadiene prior to addition to the M-H bond.



anti syn

On the other hand, the preferred trans configuration of $CH_3CH{=}CHCH_2OH$,[33] as well as probably of $(CH_3CH{=}CHCH_2)_2O$,[33] would be retained throughout the reaction of eq 6, especially in complex VII, which should yield only the syn form as indeed we have found in VIg. An analogous complex, $[Pt(\pi\text{-crotyl})(PPh_2Me)_2]^+PF_6^-$ (IX), which was prepared previously[6] from I ($PR_3 = PPh_2Me$; X = PF_6) and butadiene, has now been shown to exist predominantly in the anti form immediately after preparation, but isomerization takes place gradually in solution at room temperature to give an equilibrium mixture of the two forms after 24 hr, with the syn isomer being more abundant. A similar syn:anti ratio was found for VIc. The ready isomerization of anti to syn configuration in 1-substituted π-allylmetallic complexes has previously been reported for nickel,[26] cobalt,[27] and palladium[35] analogs, probably because of the greater steric repulsion between substituent and the metal atom as well as other ligands in the anti form. Thus, the conversion of VIII into the corresponding syn isomer was readily performed by adding a catalytic amount of $Pt(C_3H_5)(PPh_2Me)_2Br$ (X) to a methylene chloride solution of VIII. It was suggested previously[36] that syn-anti conversion in π-allylmetallic complexes probably proceeds *via* a $\pi \rightarrow \sigma \rightarrow \pi$ mechanism. Thus, it is not surprising that X, which can be prepared from the slow reaction of *trans*-$PtHBr(PPh_2Me)_2$ with allene, behaved similarly to $Pt(C_3H_5)(PPh_3)_2Cl$;[36] both complexes show a syn-anti proton exchange reaction which is rapid on the nmr time scale at room temperature, while all of VI have frozen π-allylplatinum(II) structures at room temperature possibly because chloride or bromide can stabilize a σ-allylplatinum(II) complex in the transition state much more effectively than BF_4^-, PF_6^-, NO_3^-, or ClO_4^- ions. This could also account for the ready isomerization of the otherwise stable anti form of VIII in the presence of a catalytic amount of X.

Experimental Section

The preparations of *trans*-$[PtH(PR_3)_2(acetone)]^+X^-$ (I) (PR_3 = PPh_3 or PPh_2Me; X = BF_4 or PF_6),[6] *trans*-$PtH(NO_3)(PPh_2Me)_2$[17] (II), and *trans*-$PtH(ClO_4)(PPh_3)_3$[14] (III) have been reported previously. Allylic alcohols were obtained from Eastman Kodak Co. Other allylic derivatives were prepared by standard methods. Microanalyses were performed by Dr. A. B. Gygli, Toronto, and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were obtained using a Beckman IR-10 spectrophotometer, with samples prepared as Nujol mulls or in solution. Spectra were calibrated against the spectrum of polystyrene film. Proton nmr spectra were obtained on Varian T-60 and HA-100 spectrometers using TMS as internal standard (τ 10.00).

Reactions of I or III with Allylic Acetates or *N*-Allylacetamide. In a typical reaction, allyl acetate (0.021 g) was added to a methylene chloride (4 ml)-acetone (2 ml) solution of *trans*-$[PtH(PPh_2Me)_2(acetone)]^+BF_4$ which was prepared from *trans*-$PtHBr(PPh_2Me)_2$ (0.144 g) and $AgBF_4$ (0.041 g). After the solution had been stirred for 6 hr at room temperature, the solvents were evaporated under vacuum. The crude solids thus obtained were dissolved in methylene chloride (5 ml), and the solution was passed through a Florisil column. The pale yellow solution was concentrated to *ca.* 1 ml, and *n*-pentane (10 ml) was added to give a pale yellow oily product. The solvents were decanted off and this product was dried under vacuum to give a fluffy solid (IVa) (0.155 g, 93%) which decomposed at about 100° without melting. *Anal.* Calcd for $C_{31}H_{35}O_2BF_4P_2Pt$: C, 47.53; H, 4.50. Found: C, 47.70; H, 4.74. Similarly, IVb (yield, 92%; dec pt > 100°) and Va (yield, 68%; mp 116-119°) were obtained. *Anal.* Calcd for IVb, $C_{32}H_{37}O_2BF_4P_2Pt$: C, 48.19; H, 4.68. Found: C, 48.28; H, 4.96. Calcd for Va, $C_{31}H_{36}NOBF_4 \cdot P_2Pt$: C, 47.58; H, 4.64; N, 1.79. Found: C, 47.66; H, 4.73; N, 1.75. The reaction of III (0.140 g) with *N*-allylacetamide (0.05 g) was carried out in benzene (25 ml) at room temperature for 20 hr. The fine crystals were filtered and dried under vacuum to give Vb (0.130 g, 83%); mp 157-159° dec. *Anal.* Calcd for $C_{41}H_{40}NO_5ClP_2Pt$: C, 53.57; H, 4.39; Cl, 3.86. Found: C, 53.54; H, 4.40; Cl, 3.67. Similarly IVc was obtained for which analyses showed the presence of 1 mol of benzene per platinum atom; yield, 75%; mp 182-185° dec. *Anal.* Calcd for $C_{47}H_{45}O_6ClP_2Pt$: C, 56.54; H, 4.54; Cl, 3.55. Found: C, 56.42; H, 4.39; Cl, 3.10.

Reactions of I, II, or III with Allylic Alcohols or Diallyl Ethers. A very similar procedure was used in all the reactions except that the reaction time varied from less than 1 hr for allyl alcohol or diallyl ether to 30 hr for 1-methylallyl derivatives to more than 4 days for 2-methylallyl derivatives. The solvents used were benzene in the case of III and methylene chloride in the case of I or II. The reaction products were identified by analyses and/or infrared and proton nmr spectra. The aldehydes were also identified by distilling off volatile products under vacuum and then forming the 2,4-dinitrophenylhydrazone adducts. The π-allylplatinum(II) products obtained from the reactions using II were converted in good yields into the previously characterized BF_4^- or PF_6^- salts.[6] The preparation of VIf, for example, was done as follows. To a benzene solution (25 ml) of III (0.200 g) was added 0.05 g of bis(2-methylallyl) ether or 0.06 g of 2-methylallyl alcohol at room temperature. The mixture was stirred for 5 days, and the crystalline complex gradually appeared. This was filtered, washed with benzene, and dried under vacuum to give VIf (0.157 g, 75%); mp 235-240° dec. *Anal.* Calcd for $C_{40}H_{37}O_4ClP_2Pt$: C, 54.96; H, 4.27; Cl, 4.06. Found: C, 55.22; H, 4.27; Cl, 4.25. Similarly, VIe (80% yield; mp 255-260° dec.) and VIg (90% yield; mp 227-230° dec) were obtained. *Anal.* Calcd for VIe, $C_{39}H_{35}O_4ClP_2Pt$: C, 54.45; H, 4.10; Cl, 4.12. Found: C, 54.72; H, 4.14; Cl, 4.32. Calcd for VIg, $C_{40}H_{37}O_4ClP_2Pt$: C, 54.96; H, 4.27. Found: C, 54.92; H, 4.38. The complex VId (X = BF_4) was obtained similarly in methylene chloride-acetone solution, with recrystallization from methylene chloride-*n*-pentane; yield, 85%; mp >250°. *Anal.* Calcd for $C_{39}H_{35}BF_4P_2Pt$: C, 55.27; H, 4.16. Found: C, 55.50; H, 4.13.

Preparation of Other π-Allylplatinum(II) Complexes. The complex VIII (X = BF_4) was prepared by a method similar to that for IX;[6] yield, 65%; mp 238-240° dec. *Anal.* Calcd for $C_{40}H_{37}BF_4P_2Pt$: C, 55.76; H, 4.33. Found: C, 55.68; H, 4.43. Compound X was obtained from an acetone solution (6 ml) of *trans*-$PtHBr(PPh_2Me)_2$ (0.15 g) into which allene gas was bubbled at room temperature for 1 hr. The solvent was evaporated under vacuum, and the resulting oily products were recrystallized from methylene chloride-*n*-pentane to give fine crystals (0.135 g, 85%); mp 179-180°. *Anal.* Calcd for $C_{29}H_{31}BrP_2Pt$: C, 48.61; H, 4.36. Found: C, 48.26; H, 4.18.

Isomerization of Allyl Phenyl Ether or Allyl Methyl Ether. The isomerization reaction was performed in an nmr sample tube at room temperature. To a benzene-d_6 solution (0.3 ml) of allyl phenyl ether (0.15 mmol) was added III (0.003 mmol). The reaction was complete within about 10 min to give almost 100% of *cis*-propenyl phenyl ether as indicated by the nmr spectrum. A similar procedure was employed in the reaction between allyl methyl ether (0.22 mmol) and III (0.003 mmol) to give, after 60 mm, an almost quantitative

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(33) A commercial sample of $CH_3CH{=}CHCH_2OH$ was found to consist of only trans isomer by forming its 3,5-dinitrobenzoic acid ester.[34] Bis(1-methylallyl) ether, which was prepared from this alcohol, sodium, and *trans*-crotyl chloride, therefore, would have a trans,trans configuration.

(34) L. F. Hatch and S. S. Nesbitt, *J. Amer. Chem. Soc.*, **72**, 727 (1950).

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(36) H. C. Volger and K. Vrieze, *J. Organometal. Chem.*, 9, 527 (1967); K. Vrieze, A. P. Praat, and P. Cossee, *ibid.*, **12**, 533 (1968).

yield of *cis*-propenyl methyl ether and a trace amount of *trans*-propenyl methyl ether.

Registry No. IVa, 36608-66-9; IVb, 36608-67-0; IVc, 36608-68-1; Va, 37036-01-4; Vb, 37383-70-3; VId, 36484-04-5; VIe, 36484-05-6; VIf, 37036-84-3; VIg, 37036-86-5; VIII, 37036-85-4; X, 37036-81-0; [Pt(2-methylallyl)-$(PPh_2Me)_2]NO_3$, 37036-83-2; *trans*-$[PtH(PPh_2Me)_2(CH_3)_2CO]BF_4$, 37036-02-5; *trans*-$[PtH(ClO_4)(PPh_3)_2]$, 32109-29-8; *trans*-$[PtH(NO_3)(PPh_2Me)_2]$, 36464-75-2; *trans*-$[PtH(PPh_3)_2(CH_3)_2CO]BF_4$, 37036-05-8; allyl acetate, 591-87-7; 2-methylallyl acetate, 820-71-3; *N*-allylacetamide, 692-33-1; 2-methylallyl alcohol, 513-42-8; 2-methylallyl ether, 628-56-8; allyl alcohol, 107-18-6; allyl ether, 557-40-4; *trans*-crotyl alcohol, 504-61-0; *trans*-crotyl ether, 7023-45-2; allyl phenyl ether, 1746-13-0; allyl methyl ether, 627-40-7.

Acknowledgment. The financial assistance of the National Research Council of Canada is gratefully acknowledged.

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Cationic Organometallic Complexes with Unsaturated Systems. V. Trimethylplatinum(IV) Complexes and Reductive Elimination Reactions

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Received May 24, 1972

A series of platinum(IV) cations of the type *fac*-$[Pt(CH_3)_3Q_2L]^+$, where Q = $P(CH_3)_2C_6H_5$, NC_5H_5, $As(CH_3)_3$, or *p*-$CNC_6H_4CH_3$ and L is a variety of neutral ligands including a carbene, have been prepared, although in some cases the preparative reactions lead to elimination of ethane and formation of *trans*-$[Pt(CH_3)Q_2L]^+$. Factors governing the stability of the platinum(IV) cations are discussed. The oxidative addition of CD_3I to *cis*-$Pt(CH_3)_2Q_2$, where Q = $P(CH_3)_2C_6H_5$ and $As(CH_3)_3$, gives exclusively the trans adduct. Pyrolysis and reductive elimination reactions of the CD_3Pt^{IV} compounds show that the CD_3-Pt bond is more resistant to cleavage than the CH_3-Pt bond. Isomerization occurs during the preparation of $[Pt(CH_3)_2CD_3Q_2L]^+$ supporting a dissociative mechanism for octahedral substitution. The Raman spectra of the trimethylplatinum(IV) complexes have been examined and $\nu(Pt-CH_3)$ is shown to vary with the trans influence of L.

Introduction

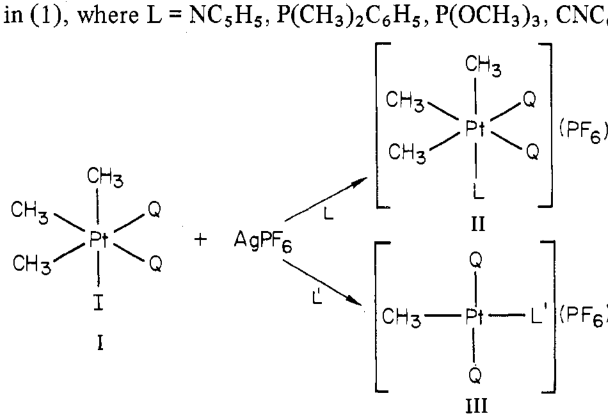
Many neutral, anionic, and cationic platinum(IV) complexes[1] have been prepared from the first organoplatinum(IV) compound, trimethylplatinum(IV) iodide.[2] In contrast to the methyl-platinum(II) bond, which is readily cleaved,[3] the methyl-platinum(IV) bond in the complexes $[Pt(CH_3)_3X]_4$ is quite stable and may be cleaved only under vigorous conditions.[4] However, complexes of the type $Pt(CH_3)_3L_2I$, where L = phosphine or arsine, have been found to pyrolyze[5] smoothly at temperatures >100° with loss of ethane.

In the previous paper of this series[6] we discussed the preparation and reactivity of a wide variety of cationic dimethylplatinum(IV) complexes of the type $[Pt(CH_3)_2Q_2L_2]^{2+}$ or $[Pt(CH_3)_2Q_2LI]^+$, where Q is dimethylphenylphosphine and L is a neutral or anionic ligand. These complexes were found to be quite stable; reduction occurred only when the L was a large and bulky ligand such as triphenylphosphine, -arsine, and -stibine or when the platinum-ligand bond required much Pt $d\pi \rightarrow L\ \pi^*$ back-bonding for its stability (*i.e.*, CO, olefins, and acetylenes).

In this paper we discuss the preparation and stability, with respect to reductive elimination, of the complexes *fac*-$[Pt(CH_3)_3Q_2L]^+$, where Q = $P(CH_3)_2(C_6H_5)$, $CNC_6H_4CH_3$, $As(CH_3)_3$, or NC_5H_5 and L is a variety of neutral ligands. The oxidative addition of CD_3I to *cis*-$Pt(CH_3)_2Q_2$ (Q = $P(CH_3)_2C_6H_5$ and $As(CH_3)_3$) and the stereochemistry of the CD_3Pt^{IV} compounds are discussed.

Results and Discussion

(i) Preparation. The iodide in *fac*-$Pt(CH_3)_3Q_2I$ (I), where Q is dimethylphenylphosphine, may be removed easily in solution, as silver iodide, by the addition of AgX where X is a noncoordinating anion, *e.g.*, $AgPF_6$. In the presence of a neutral ligand L, a variety of platinum(IV) cations, II, are obtained although, for L′, reductive elimination occurs to give the corresponding methylplatinum(II) cations, III, as shown in (1), where L = NC_5H_5, $P(CH_3)_2C_6H_5$, $P(OCH_3)_3$, $CNC_6H_4CH_3$, $CNC_6H_4OCH_3$, $CNCH_3$, CNC_2H_5, or $Sb(CH_3)_3$ and L′ = CH_3COCH_3, CH_3OH, $NCCH{=}CH_2$, $NCC_6H_4OCH_3$, $Sb(C_6H_5)_3$, $P(C_6H_5)_3$, $As(C_6H_5)_3$, CO, or $HC{\equiv}CCH_2CH_2OH$.



(1a)

(1b)

Thus, addition of silver hexafluorophosphate to a solution of I in acetone or methanol readily causes discoloration with

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