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Preliminary communication

STEREOCHEMISTRY OF INSERTION OF DISUBSTITUTED ACETYLENES INTO HYDRIDOPLATINUM(II) COMPLEXES

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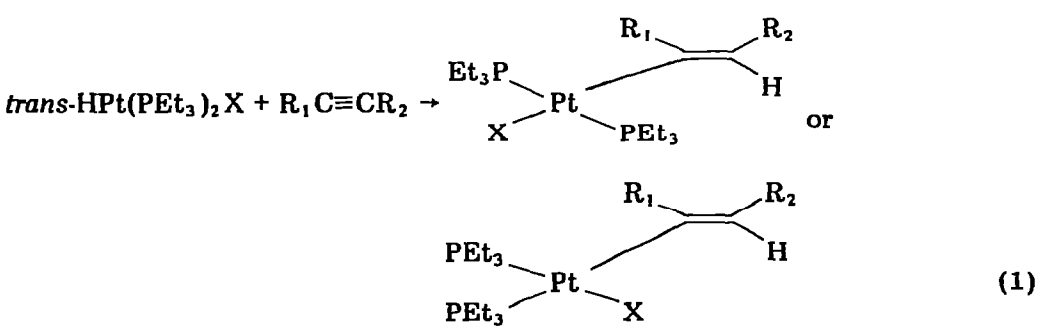
Summary

The stereochemistry of the insertion product of acetylenes with platinum hydrides depends on (1) the electron-withdrawing capabilities of the substituents on the acetylene, (2) the nucleophilicities of the solvent and/or anion present, and (3) the reaction temperature. These observations further substantiate our proposed mechanism involving the collapse of a 4-coordinate intermediate, *cis*-$HPt(PEt_3)_2(acetylene)^+$, to 3-coordinate $Pt(PEt_3)_2(vinyl)^+$.

Recently it has been demonstrated that insertions of olefins and acetylenes into Pt—H and Pt—alkyl bonds are facilitated by the ready displacement of an original ligand by the substrate [1-5]. Kinetic studies have provided evidence that such reactions proceed via a 4-coordinate cationic intermediate, *trans*-$HPt(PEt_3)_2(Un)^+$, (e.g. Un = ethylene [6], methyl acrylate [7]), subsequent rearrangement of which yields the insertion product. It has also been suggested [7] that this rearrangement probably involves a *trans* → *cis* isomerization followed by migratory insertion leading to a 3-coordinate, 14-electron intermediate, $Pt(PEt_3)_2(alkyl)^+$. We now wish to communicate the results of a stereochemical study on the insertion of acetylenes into the Pt—H bond (eqn.1).



(1)

(X = Cl, NO_3, solvents (as PF_6 salts))

Pt^{II} complexes are particularly suited to such stereochemical studies since the geometry of the resulting alkenyl complexes can readily be assigned from the various coupling constants in their ^1H NMR spectra. Thus, a *cis* or *trans* disposition of Pt and H in the alkenyl group is determinable from the magnitude of the ^3J(PtH) value [8-10]; the arrangement of the phosphine ligands is also apparent from ^4J(PH), typically ^4J(PH) being ca. 1.5-4 Hz for a *trans* complex [10, 11] and ca. 10 Hz for the *cis* [9]. Additional information can also be obtained from the relative intensities of the $PCH_2\underline{CH_3}$ quintet signals [12-14], and in favorable cases from the couplings of Pt and P with the R_1 group.

In all of the cases studied (Table 1), the alkenyl group has a *cis* disposition of Pt and H. The gross geometry about platinum, however, depends on several factors. Inspection of Table 1 shows that the formation of a *cis* isomer at platinum is favored by:

(1) Electron-withdrawing substituents in the acetylene substrate.

(2) The use of a coordinating solvent as reaction medium for cationic Pt complexes (X = solvent) and a non-polar solvent for neutral complexes (X = Cl, NO_3).

TABLE 1

STEREOCHEMISTRY OF THE REACTION $HPt(PEt_3)_2X + R_1C{\equiv}CR_2 \rightarrow Pt(PEt_3)_2(R_1C{=}CHR_2)X$ [a] AT ROOM TEMPERATURE

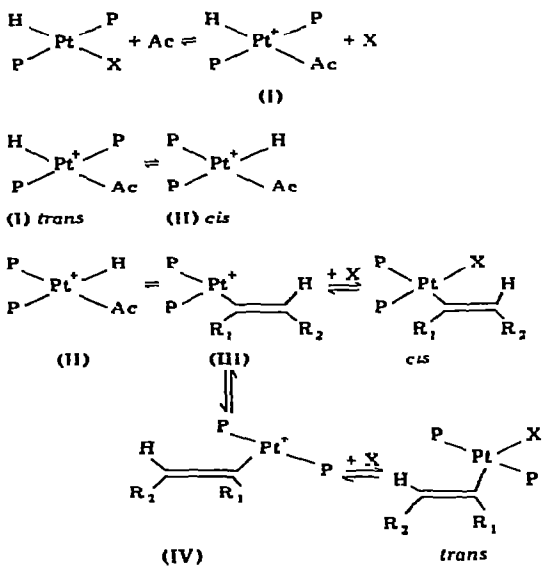
R_1	R_2	X	Solvent	Gross geometry	^1H NMR of vinyl proton [b]			
					δ	^3J(PtH)	^4J(PH)	Others
CH_3	Ph	NO_3^-	MeOH	*trans*	6.64tb	91.5		
CH_3	Ph	Cl^-	MeOH	*trans*	6.75tb	90.0		
Ph	Ph	Cl^-	MeOH	*trans*	6.92tb	98.2		
Ph	CF_3	NO_3^-	MeOH	*trans*	5.85tqt	102.0	1.2	^3J(HF) 9.6
Ph	CF_3	Cl^-	MeOH	*trans*	5.97tqt	98.5	1.2	^3J(HF) 9.8
Ph	CF_3	NO_3^-	benzene	*trans* and *cis* (1/5)	6.36tdq [c]	48.5	10.6	^3J(HF) 9.1
CH_3	$COOCH_3$	MeOD	MeOD	*trans*	5.90tb	95.0		
CH_3	$COOCH_3$	NO_3^-	MeOH	*trans*	6.18tq	88.0		^4J(HH) 1.2
CH_3	$COOCH_3$	Cl^-	MeOH	*cis*	6.22tdq	43.7	10.6	^4J(HH) 1.6
CH_3	$COOCH_3$	NO_3^-	benzene	*cis*	6.42tdq [c]	38.5	10.0	^4J(HH) 1.6
CF_3	CF_3	NO_3^-	MeOH	*cis*	6.24tqu	56.6	9.5	^3J(HF) 9.5
CF_3	CF_3	Cl^-	MeOH	*cis*	5.99tqu	61.8	9.8	^3J(HF) 9.8
$COOCH_3$	$COOCH_3$	NO_3	MeOH	*cis*	6.18td	55.6	10.0	
$COOCH_3$	$COOCH_3$	Cl^-	MeOH	*cis*	6.07td	60.5	10.0	
$COOCH_3$	$COOCH_3$	Cl^-	$CHCl_3$	*cis*				
$COOCH_3$	$COOCH_3$	Cl^-	benzene	*cis*				
$COOCH_3$	$COOCH_3$	acetone	benzene	*trans*	5.80tb [d]	110		
$COOCH_3$	$COOCH_3$	acetone	toluene	*trans*	5.88tb [d]	110		
$COOCH_3$	$COOCH_3$	acetone	$CDCl_3$	*trans*	5.73tb [d]	108		
$COOCH_3$	$COOCH_3$	acetone	acetone	*trans*	5.83tb [d]	110		
				and *cis* (1/4)	5.92td [d]	54	10	
$COOCH_3$	$COOCH_3$	MeOH	MeOH	*cis*	6.03td [d]	55	10	
$COOCH_3$	$COOCH_3$	MeOH	DMSO	*cis*	6.10td [d]	56	10	

[a] All the neutral compounds have been isolated and correctly analysed, unless otherwise stated. [b] Spectra were recorded on HA100 in $CDCl_3$ unless otherwise stated. Chemical shifts (δ) are in ppm downfield from TMS and coupling constants (*J*) are given in Hz. Multiplicity: d = doublet, t = triplet, q = quartet, qu = quintet, b = broad. [c] Not isolated, benzene solution. [d] As PF_6^- salts. Recorded on a T60 spectrometer in the solvent mentioned, isolable as the chloro complex (*trans* isomer: δ(vinyl H) = 5.96tt, ^3J(PtH) = 102.2 Hz, ^4J(PH) = 1.6 Hz).

(3) The presence of a more strongly coordinating anion e.g. for $R_1 = CH_3$, $R_2 = COOCH_3$, the *cis* product is obtained for X = Cl but the *trans* isomer when X = NO_3, MeOD (PF_6^- as anion).

The formation of a *cis* or *trans* isomer as the final product is also dependent on the reaction temperature. In reaction 1 ($R_1 = R_2 = COOCH_3$, X = solvent), carried out in MeOH or DMSO, the *cis* isomer is produced at room temperature. However, conversion to the *trans* form is complete at 50°C (1 h) in MeOH, but in DMSO requires 90°C (2 h). On the other hand, the same reaction in acetone/toluene (1/10) which yields the *trans* isomer at room temperature has the *cis* isomer as its major product at −40°C. Similarly, traces of a *cis* product ($R_1 = CH_3$, R_2 = Ph, X = acetone) are also detected in reaction 1 when carried out at −10°C in acetone; subsequent isomerization to the *trans* form proceeds rapidly on raising the temperature.

SCHEME 1



It is therefore apparent that the *trans* isomer is thermodynamically more stable. The formation of the less stable *cis* product, and the conditions under which it is formed provide strong support for the previously proposed mechanism (Scheme 1) which suggests that a *trans* to *cis* isomerization of I occurs prior to insertion. Subsequent rearrangement of II yields a 14 electron 3-coordinate intermediate III. Nucleophilic attack of III before or after its isomerization to IV leads to the formation of a *cis* or *trans* alkenyl complex respectively. The formation of a *cis* or *trans* product therefore depends on the relative rates of the isomerization of III and its recombination with X. The presence of electron withdrawing R_1 and R_2 groups in the alkenyl ligand renders III more susceptible to nucleophilic attack and hence favors the formation of a *cis* complex. Similarly,

the presence of stronger nucleophiles ($Cl^- > NO_3^-$, DMSO > MeOH > acetone > $CHCl_3$ ~ toluene ~ benzene) leads to more rapid reaction of III with X and reduces the probability of its isomerisation to IV. Lower reaction temperatures also inhibit this isomerization, accounting for the preferential formation of the *cis* isomer at lower temperatures. This inhibition of isomerization by coordinating ligands is similar to that observed in the *cis* → *trans* isomerization of $Pt(PEt_3)_2$-(*o*-tolyl)Cl [15], in which case the effect of Cl^- on the isomerization is also explained in terms of the involvement of '*cis*' and '*trans*' 3-coordinate intermediates.

Hence the above results provide evidence that in the reaction of acetylenes with platinum hydrides having labile leaving groups X, insertion proceeds via (1) the formation of *trans*-$HPt(PEt_3)_2$(acetylene)$^+$, (2) its *trans* to *cis* isomerization, (3) a collapse to 3-coordinate, 14 electron intermediate, $Pt(PEt_3)_2$(vinyl)$^+$, (4) a possible isomerization of this intermediate, and (5) a final recombination with X.

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