($^{ev}A_1$ and $^{ev}B_2$). The latter identification requires that transitions terminate on alternating $^{ev}B_1$, $^{ev}A_2$ vibronic levels which are (approximately) evenly spaced; i.e., they lie above the 1^1B_1 state double-minimum potential barrier for the b_2 vibration. Both explanations require that the intensity be uniformly c type (out of plane). We currently prefer the second interpretation since it is consonant with microwave[2-4] estimates of low-frequency 1^1A_1 state vibrational fundamentals. Isotope substitution and temperature studies now in progress will resolve this matter.

The integrated intensity of this band system—as indicated by the pressure-pathlength necessary for observation—is consistent only with an $\pi^* \leftarrow n$ transition in the molecule. The lack of a prominent origin band (ν_{oo}) is corroborative evidence for such an orbital designation. The energy of the measured transition is in agreement with our published[5] computational value of 3.2 eV and also that of Del Bene[6] for the $1^1B_1(n\pi^*) \leftarrow 1^1A_1$ transition in the planar molecule. Taken as a whole, the evidence for the measured band system being attributable to the intramolecularly hydrogen-bonded planar molecule is conclusive. Studies of the high-resolution infrared and electronic spectra of isotopes of malondialdehyde are in progress.

References and Notes

(1) This work supported in part by Research Corporation.
(2) W. F. Rowe, R. W. Duerst, and E. B. Wilson, *J. Am. Chem. Soc.*, **98**, 402 (1976).
(3) W. F. Rowe, R. W. Duerst, S. L. Baughcum, and E. B. Wilson, 31st Symposium on Molecular Spectroscopy, Columbus, Ohio, 1976.
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(6) J. E. Del Bene, *Chem. Phys. Lett.*, **44**, 512 (1976).
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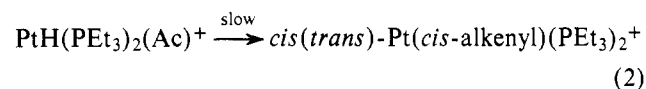**Carl J. Seliskar,* Richard E. Hoffmann**

Chemistry Department, University of Cincinnati
Cincinnati, Ohio 45221

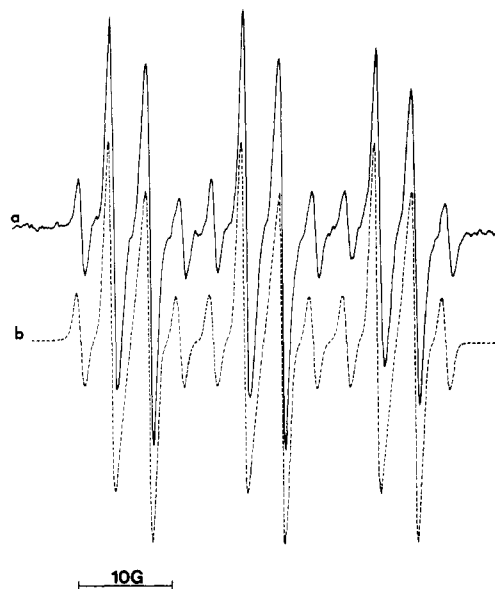## Free-Radical Participation in the Insertion Reaction of Acetylene with Platinum Hydride

Sir:

Previously we have demonstrated that the reaction of acetylenes with *trans*-PtHCl(PEt$_3$)$_2$ (I) in polar solvents such as methanol or acetone proceeds with the displacement of the chloride ligand by the acetylene, followed by a migratory insertion of acetylene into the Pt–H bond (eq 1-3).[1]
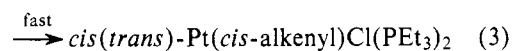
$$PtHCl(PEt_3)_2 + Ac \rightleftharpoons PtH(PEt_3)_2(Ac)^+ + Cl^- \quad (1)$$

$$PtH(PEt_3)_2(Ac)^+ \xrightarrow{slow} cis(trans)\text{-}Pt(cis\text{-alkenyl})(PEt_3)_2^+ \quad (2)$$

Figure 1. a (full line), the ESR spectrum of the spin adduct obtained by heating pheny-*tert*-butylnitrone with PtHCl(PEt$_3$)$_2$ and DMA in benzene at 70 °C; b (broken line), a computer-simulated spectrum using the hyperfine splittings $A_N = 14.32$, $A_H = 4.1$, and $A_{Pt} = 6.6$ G.

$$cis(trans)\text{-}Pt(cis\text{-alkenyl})(PEt_3)_2^+ + Cl^-$$

$$\xrightarrow{fast} cis(trans)\text{-}Pt(cis\text{-alkenyl})Cl(PEt_3)_2 \quad (3)$$

The vinylic complexes so formed have exclusively the cis arrangement of Pt and the vinylic proton about the alkenyl double bond. Thus I reacts completely with dimethylacetylenedicarboxylate (DMA) (eq 4)

$$trans\text{-}PtHCl(PEt_3)_2 + DMA \rightarrow Pt(DMAH)Cl(PEt_3)_2 \quad (4)$$
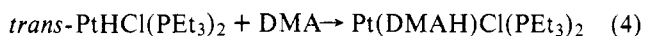
IIa, *cis,cis*[2,3]
b, *trans,cis*
c, *cis,trans*
d, *trans,trans*

in methanol within minutes of mixing at room temperature to give exclusively IIa. However, the same reaction in benzene takes more than a week for completion (Table I) with IIa as the major product plus a small amount of the trans,trans isomer IId. The percentage of IId increased significantly[4] when the reaction temperature was 70 °C, and interestingly an increase in acetylene concentration caused a decrease in the percentage of the *trans*-alkenyl product.

The dependence of the product geometry on the polarity of the solvent medium led us to suspect that different mechanisms might be operative. Reaction 4 was therefore performed in the presence of free-radical initiators such as benzoyl peroxide (BPO), acetyl peroxide (APO), and di-*tert*-butyl peroxyoxalate (DBPO). Not only were reaction times shortened, but the percentage of the *trans*-alkenyl product increased to 68, 78,

Table I. Reaction of PtHCl(PEt$_3$)$_2$ with DMA in Benzene

[I], M	[DMA], M	Initiator	Inhibitor	Temp, °C	Reaction time, hr	Total % yield	IIa	IIb	IIc	IId
0.42	0.42			Room	~10 days	74	85			15
0.22	0.25			70	29	73	38			62
1.4	1.6			70	21	78	92			8
0.22	0.25		Hydroquinone (11 mol %)	70	43	82	36	37		27
0.22	0.25		Hydroquinone (25 mol %)	70	45	86	42	41		17
1.1	1.35	BPO (50 mol %)		Room	10	69	32		46	22
0.85	0.98	DBPO (5 mol %)		Room	1	81			58	42
0.85	0.98	APO (50 mol %)		Room	20	77	2	20	53	25

and 100%, respectively (Table I). Addition of the initiators to preformed products did not cause isomerization of the alkenyl group, and, further, addition of hydroquinone in reaction 4 decreased the percentage of the *trans*-alkenyl product (Table I).
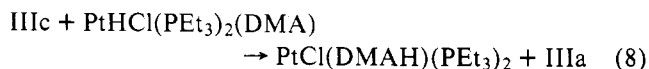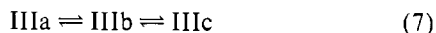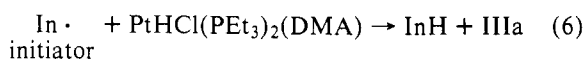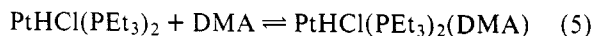
The involvement of free radicals was strongly suggested by the detection of spin adducts using phenyl-*N-tert*-butylnitrone (PBN) as spin trap.[5] Typically, the ESR experiment was conducted by adding deoxygenated benzene to a silica tube fitted with a serum cap and containing weighed amounts of PBN and I. DMA was then introduced through the serum cap to give final concentrations of PBN, I, and DMA of 0.1, 0.1 and 0.16 M, respectively. The very weak ESR signal observed at room temperature increased in intensity >10 times after the reaction mixture had been heated to 70 °C for 10 min. The same ESR signal (in addition to that of the butoxy adduct[6]) could be observed at room temperature if a small amount of DBPO was present (~5% mol ratio). The ESR signal (Figure 1a) shows no change in the relative intensities of the peaks over a period of >4 days and is apparently due to only one species. A computer-simulated spectrum with hyperfine constants A_N = 14.32, A_H = 4.1, and A_{Pt} = 6.6 G (g = 2.013) agrees well (Figure 1b) with the observed spectrum.

In the absence of either DMA or I, no spin adduct was observed,[7] nor was an ESR signal observed when I was replaced in the reaction by *trans*-PtCl$_2$(PEt$_3$)$_2$. However, the magnitudes of the various hyperfine splittings are affected by the anionic ligand (for NO$_3^-$ g = 2.013, A_N = 14.31 G, A_H = 4.3 G, A_{Pt} = 4.9 G) and also by the acetylene used (for CH$_3$C≡CCOOCH$_3$ g = 2.013, A_N = 14.58 G, A_H = 4.3 G, A_{Pt} = 5.2 G).[8] Thus the trapped platinum radical has the formula ·PtCl(PEt$_3$)$_2$(acetylene), a formally Pt(I) species and the spin adduct is

$$Ph—CH—N—t\text{-Bu}$$
$$\overset{\displaystyle O·}{\underset{\displaystyle PtCl(PEt_3)_2(acetylene)}{|}}$$
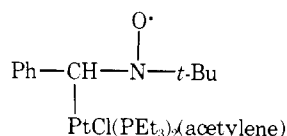
It must be emphasized that the platinum radical identified in the trapping experiments probably plays an important role in the actual insertion process since, in the presence of initiators and more importantly in the thermal reaction, increased yields of the trans vinylic product are always paralleled by observed increases (by ESR) in the concentration of the radical. Moreover, when I is allowed to react with DMA (0.5 molar equiv) in 2-butyne as solvent (ratio of DMA to 2-butyne 1: 100), at room temperature with 5% DBPO added, only the DMA insertion products are formed, leaving unreacted I. Apparently, it is essential to first form a five-coordinate acetylene–platinum complex, from which the platinum-containing radical is then generated.

Further, since in reaction 4 conducted with DBPO added the percentage of the *trans*-alkenyl product (100%) obviously exceeds the amount of radical initiator added (5%), the reaction must also proceed via a chain mechanism.[9] The absence of any detectable amount of *cis*-alkenyl isomer implies that (a) the free-radical mechanism dominates the reaction, and (b) the radical reaction is highly stereospecific. A mechanism consistent with these observations is depicted in eq 5–8.

$$PtHCl(PEt_3)_2 + DMA \rightleftharpoons PtHCl(PEt_3)_2(DMA) \quad (5)$$

$$\underset{\text{initiator}}{In·} + PtHCl(PEt_3)_2(DMA) \rightarrow InH + IIIa \quad (6)$$

$$IIIa \rightleftharpoons IIIb \rightleftharpoons IIIc \quad (7)$$

$$IIIc + PtHCl(PEt_3)_2(DMA)$$
$$\rightarrow PtCl(DMAH)(PEt_3)_2 + IIIa \quad (8)$$

The stereospecificity at the alkenyl bond is thought to be due to the fact that only IIIc has the ability to abstract H· from PtHCl(PEt$_3$)$_2$(DMA). Molecular models suggest that in this complex the H atom on Pt is so well shielded by the phosphine ethyl groups making abstraction by IIIb sterically unfavorable.

·PtCl(PEt$_3$)$_2$(DMA)

IIIa   *cis*- or *trans*-IIIb   *cis*- or *trans*- IIIc
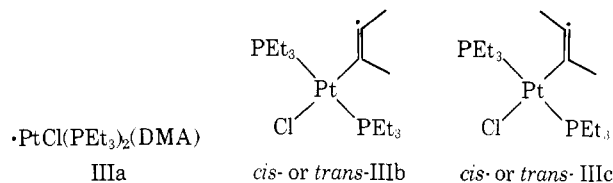
In the thermal reaction initiation may involve hydrogen abstraction by a second acetylene (eq 9).

$$PtHCl(PEt_3)_2(DMA) + DMA$$
$$\overset{\Delta}{\longrightarrow} DMAH· + · PtCl(PEt_3)_2(DMA) \quad (9)$$
$$\underset{\text{IIIa}}{}$$
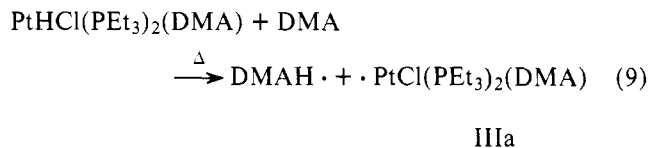
These results provide the first evidence of free-radical participation in acetylene insertions into transition metal hydrides, although related radical reactions have been described previously.[10,11] In view of current interest in the stereochemistry[12] of acetylene insertions into the metal–hydrogen bond, and in view of the high stereospecificity observed in this reaction, the possible involvement of free-radical addition in other stereospecific trans addition reactions should not be discounted.

References and Notes

(1) T. G. Attig, H. C. Clark, and C. S. Wong, *Can. J. Chem.*, **55**, 189 (1977), and references therein.
(2) The first prefix refers to the geometry at platinum, the second refers to geometry about the double bond.
(3) The various isomers were fully characterized by elemental analysis, melting point, and ^{1}H and ^{31}P spectra (see ref 1).
(4) Control experiments at 70 °C showed no isomerization of the alkenyl group, and only slow cis to trans isomerization at Pt.
(5) E. G. Janzen, *Acc. Chem. Res.*, **4**, 31 (1971).
(6) The butoxy adduct decomposes more rapidly so that, after 2 days, the ESR spectrum is identical with that obtained by thermal generation of the radicals.
(7) Although a mixture of PBN and DMA does not exhibit any ESR signal, PBN being a zwitterion does induce polymerization of DMA.
(8) Compound I reacted with CH$_3$C≡CCOOCH$_3$ in benzene, with DBPO added, to give the vinylic insertion product in >50% yield.
(9) Reaction 4 in the presence of DBPO is exothermic and is complete within an hour (cf. days of reaction time in the absence of initiator).
(10) T. G. Appleton, M. H. Chisholm, H. C. Clark, and K. Yasufuku, *J. Am. Chem. Soc.*, **96**, 6600, (1974).
(11) N. G. Hargreaves, R. J. Puddephatt, L. H. Sutcliffe, and P. J. Thompson, *J. Chem. Soc., Chem. Commun.*, 861 (1973).
(12) See, for example, S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, **14**, 245, (1976).

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Encapsulation of Hydrogen in Molecular Sieve Zeolites

Sir:

Recent interest in the use of hydrogen as a multipurpose fuel[1] has emphasized the necessity of a reliable storage system for this element. Among various methods previously suggested, storage as metal hydride seems the most promising.[2] Thus,