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Chemistry of Metal Hydrides. 27. Kinetic and ESR Studies of Acetylene Insertion Reactions with Platinum(II) Dihydrides and the Crystal Structure Determination of *trans*-PtH(P-*t*-Bu$_2$-*n*-Bu)$_2$(CH$_3$OOCC=CHCOOCH$_3$)

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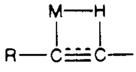
Abstract: Platinum(II) dihydrides react with both internal and terminal activated alkynes to give alkenyl products that are trans with respect to Pt and H about the C=C bond. The stereochemistry of both the alkenyl groups and the metal center can be deduced unambiguously through analysis of ^{1}H, ^{31}P, and ^{13}C NMR spectral parameters. These assignments have been confirmed by a crystallographic investigation of *trans*-PtH(P-*t*-Bu$_2$-*n*-Bu)$_2$(CH$_3$OOCC=CHCOOCH$_3$) which crystallizes in the monoclinic system, space group $P2_1/c(C_{2h}^5)$ with a = 9.218 (2) Å, b = 14.437 (2) Å, c = 27.892 (3) Å, β = 105.27 (1)°, U = 3580.8 Å^3, and Z = 4. The structure was refined to R = 0.039 and R_w = 0.043 and is in full accord with that deduced from NMR spectral parameters. The Pt atom has distorted square planar geometry with Pt-P 2.293 (4) Å, 2.311 (4) Å, and Pt-C 2.086 (12) Å and P-Pt-P (163.5 (1)°, C-Pt-P 95.5 (4)°, and 100.34 (4)°. Kinetic studies of these reactions provide evidence that formation of these monoalkenyl products occurs via an electron-transfer process. The ability of the Pt(II) dihydrides, in contrast to the monohydrides, to participate in charge-transfer mechanisms is discussed and is further illustrated by the reaction with 2,3-dichloro-5,6-dicyanoquinone. ESR studies of the reaction mixtures of Pt(II) dihydrides with acetylenes show the unexpected presence of persistent platinum-containing radicals. Evidence is presented to indicate that these are novel bis(phosphine)hydridoplatinum(II) (π-acetylene) species in which the unpaired electron is delocalized over an unsaturated three-membered metallacyclic ring.

The 1,2-addition of transition metal hydride or alkyl complexes to alkynes has generated considerable interest,[1-8] both in terms of the chemistry of the hydride or alkyl species and also in terms of the nature and stereochemistry of the products. Until recently, it has not been possible to predict the sterochemistry of the resulting alkenyl product, which may be regarded as formed by either a cis or trans addition of M-H (or M-R) across the C=C bond. A delicate balance of factors appears to affect the sterochemistry of the product. For example, the reactions of (η^5-C$_5$H$_5$)$_2$MoD$_2$ with CF$_3$C≡CH, C$_6$H$_5$C≡CC$_6$H$_5$, or CH$_3$OOC-C≡CCOOCH$_3$ (DMA) were all reported as giving the cis insertion products, whereas with CF$_3$≡CCF$_3$ the trans product was formed.[1] Subsequently,[9] however, a crystal structure determination of the DMA product showed it to have the trans alkenyl geometry. In some reactions, stereorandom products have been observed, but in other cases exclusively trans products have been formed, sometimes under kinetic conditions.[1-11] One of the more recent studies was that of Huggins and Bergman[4] who investigated the reactions of internal and terminal alkynes with methyl (2,4-pentanedionato)(triphenylphosphine)nickel(II). They conclude that the mechanism involves concerted cis addition of alkyne into the nickel-methyl bond; this gives a coordinatively unsaturated vinyl-nickel intermediate capable of isomerization at the C=C bond at a rate competitive with product formation. Such a mechanism can explain how different alkynes can give products with different stereochemistry, without having to postulate different addition pathways.[12] However, the mechanism proposed for the alkenyl isomerization requires a coordinatively unsaturated metal center, and this is certainly not available in all other cases of facile alkyne insertion into metal-hydrogen or metal-alkyl bonds.

In general, the formation of the cis addition alkenyl derivative as the kinetic product is thought to involve a concerted process involving a four-center cyclic transition state A.



A

Where the trans isomer is formed, various suggestions have been made as to the insertion mechanism; these include a concerted trans insertion[2] and a nonconcerted backside attack of the M-H (R) moiety on the coordinated acetylene.[5] Clearly, however, the possibility of occurrence of facile cis-trans alkenyl isomerization requires that the stereochemistry of the kinetically controlled product be determined unambiguosuly before any mechanistic conclusions can be drawn.

Previously,[13] we have demonstrated that the reaction of acetylenes with *trans*-PtHCl(PEt$_3$)$_2$ in polar solvents such as methanol

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[12] However, an ESR examination of this reaction indicates the presence of a complex mixture of radicals. Clark, H. C., Wond, C. S., unpublished results).

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or acetone proceeds with the displacement of chloride by acetylene, followed by a migratory insertion of acetylene into a Pt–H bond to give only the cis alkenyl product. No cis–trans alkenyl isomerization could be induced for these platinum(II) compounds under a variety of conditions,[7] so that all results indicate a mechanistic pathway involving a four-center transition state. Subsequently, we observed that the same reaction (eq 1), conducted in a nonpolar

$$\mathrm{PtHCl(PEt_3)_2 + DMA \rightarrow PtCl(DMA\text{-}H)(PEt_3)_2} \quad (1)$$
$$\mathrm{(DMA = CH_3OOCC{\equiv}CCOOCH_3)}$$

solvent such as benzene, gave a mixture of cis and trans alkenyl products, suggesting that another reaction pathway has become energetically feasible. When the reaction is carried out in the presence of a catalytic amount of an efficient free radical initiator, DBPO (di-*tert*-butyl peroxyoxalate) in benzene, reaction 1 becomes exothermic, and only the trans alkenyl product is observed.[6] Thus, under these conditions, our observations led to the conclusion that a radical chain mechanism is operative.

In order to further substantiate this conclusion, we have now investigated the comparable reactions of several platinum(II) dihydrides, *trans*-$\mathrm{PtH_2L_2}$ (L = bulky phosphine) with acetylenes. Such reactions cannot proceed by the first of the above two competing pathways seen for *trans*-$\mathrm{PtHCl(PEt_3)}$ (i.e., displacement of the ligand trans to H by acetylene followed by migratory insertion) since this would involve hydride ion formation and would be highly unfavorable energetically. Radical pathways would, however, potentially be possible. We report now on the course of these reactions, on the characterization of the alkenyl products including the single crystal structural investigation of *trans*-Pt(DMA-H)H(P-*t*-$\mathrm{Bu_2}$-*n*-Bu)$_2$, and on kinetic and ESR investigations of the reaction mechanism.

Experimental Section

The hydride complexes, *trans*-$\mathrm{PtH_2L_2}$ (L = tertiary phosphine) were prepared from the corresponding dichlorocomplexes as described previously.[14] Acetylenes were obtained and purified as follows: dimethylacetylene dicarboxylate, $\mathrm{HC{\equiv}CCOOCH_3}$ and $\mathrm{CH_3C{\equiv}CCOOCH_3}$ (Aldrich Chemical Co.), distilled; hexafluorobut-2-yne and 1,1,1-trifluoropropyne (PCR Research Chemicals Inc.), used without purification; $\mathrm{C_6H_5C{\equiv}CCOOCH_3}$ was prepared by esterification of $\mathrm{C_6H_5C{\equiv}CCOOH}$ (Aldrich Chemical Co.) and distilled; $\mathrm{C_6H_5C{\equiv}CCF_3}$ was prepared and purified by the literature method;[15] $\mathrm{HC{\equiv}CCN}$, $\mathrm{CH_3C{\equiv}CCN}$, and $\mathrm{C_6H_5C{\equiv}CCN}$ were prepared by converting the corresponding esters to the amides, followed by dehydration with $\mathrm{P_2O_5}$ in vacuo to give the crude nitriles; these were purified by distillation and characterized by their ^{1}H NMR and IR spectra. $\mathrm{HC{\equiv}CCOOCH_2CH{=}CH_2}$ and $\mathrm{HC{\equiv}CCOOCH_2C{\equiv}CH}$ were prepared by condensing methyl propiolate with $\mathrm{HOCH_2CH{=}CH_2}$ and $\mathrm{HOCH_2C{\equiv}CH}$, respectively.

Nuclear magnetic resonance spectra were recorded as follows: (a) ^{1}H NMR on a Bruker WP-60, Bruker AM-250, or Bruker WH-400 in 5-mm tubes. Spectra run on the high-field instruments were generally processed by using resolution enhancement techniques. (b) ^{19}F NMR on a Bruker WP-60 and Bruker CXP-200 with resolution enhancement for the CXP-200 spectra. (c) ^{13}C NMR on a Bruker WH-400 without proton decoupling. (d) ^{31}P NMR on a Bruker WP-60, Bruker AM-250, or Bruker WH-400. Usually, two spectra for each sample were recorded, the first with normal broad band decoupling and the second with selective decoupling of the aliphatic region of the ^{1}H NMR region to show the multiplicity due to hydride ligands.

Elemental analyses were obtained from Midwest Microlab Ltd., Indianapolis, IN and from Guelph Chemical Laboratories Ltd., Guelph, Ontario.

(a) Preparation of Insertion Products. The method of preparation was essentially the same for all solid or liquid acetylenes, except for minor variations in the reaction time and the solvents of recrystallization as indicated below. Typically, *trans*-$\mathrm{PtH_2(PCy_3)_2}$ (100 mg) was dissolved in ~1 mL of toluene, and DMA (13μL) was introduced. After 30 min, the reaction mixture was concentrated by partial evaporation of the solvent by using a rotary evaporator. Addition of methanol afforded colorless crystals of *trans*-$\mathrm{PtH(DMA\text{-}H)(PCy_3)_2}$, (88 mg, 75% yield). ^{1}H and ^{31}P NMR spectra of this product always showed the presence of ca. 5% of the Pt(0) complex, $\mathrm{(PCy_3)_2Pt(DMA)}$. Others were as follows: L = *i*-$\mathrm{Pr_3P}$, $^1/_2$ h, from aqueous ethanol; L = *n*-Bu-*t*-$\mathrm{Bu_2P}$, 5 h, aqueous ethanol; L = Me-*t*-$\mathrm{Bu_2P}$, 5 h, $\mathrm{CH_2Cl_2}$/ethanol/water. The reactions of *trans*-$\mathrm{PtH_2(PCy_3)_2}$ with $\mathrm{HC{\equiv}CCOOCH_3}$, $\mathrm{C_6H_5C{\equiv}CCOOCH_3}$, $\mathrm{C_6H_5C{\equiv}CCF_3}$, $\mathrm{C_6H_5C{\equiv}CCN}$, and $\mathrm{CH_3C{\equiv}CCN}$ were, similarly, conducted overnight in benzene, by using a slight excess of the acetylene; the addition of methanol to the reaction mixture gave colorless crystals of the product. For the product from $\mathrm{HC{\equiv}CCN}$, a treatment over charcoal and subsequent filtration through a short florisil column was necessary to remove a brown-red polymer of the acetylene. The reaction of *trans*-$\mathrm{PtH_2(PCy_3)_2}$ (50 mg) with $\mathrm{CH_3C{\equiv}CCOOCH_3}$ (0.5 mL) in benzene (3 mL) required 10 days for completion, with recrystallization of the product from methanol/dichloromethane.

(b) Preparation of *trans*-$\mathbf{PtH(C_4F_6H)L_2}$. *trans*-$\mathrm{PtH_2L_2}$ (100 mg) was dissolved in 20 mL of toluene. A slow stream of hexafluorobut-2-yne was then passed into the solution for 5 min, and the reaction mixture was stirred magnetically for a certain period of time indicated below. Evaporation of the solvent under vacuum, followed by recrystallization afforded white crystals of *trans*-$\mathrm{PtH(C_4F_6\text{-}H)L_2}$: for L = $\mathrm{PCy_3}$, 1 h, from benzene/hexane; for L = P-*i*-$\mathrm{Pr_3}$, 1 h, from ethanol/water; for L = *n*-Bu-*t*-$\mathrm{Bu_2P}$, 5 h, from $\mathrm{CH_2Cl_2}$/aqueous ethanol; for L = Me-*t*-$\mathrm{Bu_2P}$, 5 h, from hot hexane.

The reaction of *trans*-$\mathrm{PtH_2(PCy_3)_2}$ with 1,1,1-trifluoropropyne was performed in a similar manner by passing trifluoropropyne gas through a benzene solution of the dhydride for 10 min. The product was crystallized by adding methanol.

(c) Preparation of *trans*-Dideuteriobis(tricyclohexylphosphine)platinum(II). *trans*-$\mathrm{Pt(PCy_3)_2Cl_2}$ (4.0 g), naphthalene (1.24 g), and sodium metal (0.25 g) were stirred in anhydrous THF (ca. 120 mL) under nitrogen until a greenish-blue color was obtained. The mixture was then evaporated to dryness, and the residue was extracted with deaerated *n*-hexane (ca. 75 mL). The solution was filtered under a nitrogen atmosphere, and the filtrate was again evaporated to dryness. The residue was redissolved in deaerated toluene (ca. 10 mL), and the solution was purged with $\mathrm{D_2}$ for about 24 h. The solution was then stirred, with free access to air, to transform all of the unreacted bis(phosphine)platinum(0) complex to the dioxygen complex. After evaporation to dryness, the residue was extracted with hexane, and the extract was chilled to −78 °C to afford white crystals. These were filtered off, washed with methanol, and recrystallized from benzene/methanol. The reactions of *trans*-$\mathrm{PtD_2(PCy_3)_2}$ with acetylenes were performed as described above for the dihydride. ν(PtD) 1226 cm^{-1}. Anal. Calcd for $\mathrm{C_{36}H_{66}D_2P_2Pt}$: C, 57.0; H, 8.7. Found: C, 56.8; H, 8.5.

Analytical data for the products are given in Table I. Tables II–V provide ^{1}H, ^{31}P, and ^{13}C NMR data.

Crystal Structure Determination. Crystals of Pt(DMA-H)H(P-*t*-$\mathrm{Bu_2}$-*n*-Bu)$_2$ formed as small needles. Preliminary cell data were obtained from Weissenberg and precession photographs; accurate cell dimensions were determined from a least-squares fit of the setting angles of 12 general reflections measured on a Hilger and Watts four-circle diffractometer.

Crystal data (at 21 °C): formula $\mathrm{C_{30}H_{62}O_4P_2Pt}$, M_r = 743.9; monoclinic a = 9.218 (2) Å, b = 14.437 (2) Å, c = 27.892 (3) Å, β = 105.27 (1)°, U = 3580.8 Å^3, Z = 4, D_{calcd} = 1.42, $F(000)$ = 1528; Mo Kα radiation, λ = 0.71069 Å, μ(MO Kα) = 38.6 cm^{-1}; space group $P2_1/c(C^5_{2h})$, from systematic absences $h0l$ absent if $l = 2n + 1$, $0k0$ absent if $k = 2n + 1$.

The intensities of reflections with h −8 to 8, k 0 to 13, and l 0 to 26 with $2° < \theta < 20°$ were measured by the ω-2θ method by using graphite monochromatized Mo Kα radiation. The intensities of three reflections chosen as standards were monitored every 2 h and showed no evidence of crystal decay. The intensities of 3785 reflections were measured. Of these, 2237 had $I > 3\sigma(I)$ and were used in the structure solution and refinement. Data were corrected[16] for Lorentz and polarization effects and for absorption. The crystal used for the data collection measured 0.27 × 0.11 × 0.110 mm; the maximum and minimum values of the transmission coefficients are 0.736 and 0.590, respectively.

The Pt coordinates were determined from a three-dimensional Patterson function and the remaining non-hydrogens via the heavy atom method. Initial refinement was by full-matrix least-squares calculations with isotropic thermal parameters. A difference synthesis then revealed maxima in positions expected for the hydrogen atoms, but no clear position could be found for hydrogen bonded to platinum. In the remaining cycles, the hydrogen atoms were placed from geometrical considerations (C–H 1.08 Å), an overall U_{iso} for hydrogens was refined, and the non-hydrogen atoms were allowed anisotropic motion.

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Table I. Analytical Data for the Reaction Products *trans*-PtH(σ-alkenyl)L_2

phosphine	acetylene	C found (calcd)	H found (calcd)	F found (calcd)	N found (calcd)
PCy_3	$CH_3OOCC{\equiv}CCOOCH_3$	55.87 (56.04)	8.29 (8.29)		
	$CF_3C{\equiv}CCF_3$	51.82 (52.22)	7.10 (7.45)	12.36 (12.39)	
	$CH_3C{\equiv}CCOOCH_3$	57.19 (57.52)	8.73 (8.71)		
	$C_6H_5C{\equiv}CCOOCH_3$	60.83 (60.18)	8.52 (8.34)		
	$CH_3C{\equiv}CCN$	60.99, 56.66 (58.37)	8.93, 9.01 (8.69)		1.62, 1.54 (1.70)
	$C_6H_5C{\equiv}CCN$	60.57 (61.06)	8.66 (8.31)		1.56 (1.58)
	$C_6H_5C{\equiv}CCF_3$	(58.24)	(7.83)	(6.14)	
	$HC{\equiv}CCOOCH_3$	57.54 (57.06)	8.79 (8.62)		
	$HC{\equiv}CCN$	59.30, 56.77 (57.90)	8.56, 8.86 (8.60)		1.88, 1.94 (1.73)
	$HC{\equiv}CCF_3$	55.37 (54.98)	8.53 (8.16)	6.83 (6.69)	
P-*i*-Pr_3	$CH_3OOCC{\equiv}CCOOCH_3$	43.71 (43.69)	7.57 (7.64)		
P-*i*-Pr_3	$CF_3C{\equiv}CCF_3$	38.32 (38.88)	6.40 (6.53)	16.50 (16.77)	
P-*t*-Bu_2-*n*-Bu	$CH_3OOCC{\equiv}CCOOCH_3$	48.35 (48.44)	8.77 (8.40)		
P-*t*-Bu_2-*n*-Bu	$CF_3C{\equiv}CCF_3$	44.05 (44.03)	6.68 (7.39)	13.91 (14.93)	
P-*t*-Bu_2Me	$CH_3OOCC{\equiv}CCOOH_3$	43.66 (43.69)	7.74 (7.64)		
P-*t*-Bu_2Me	$CF_3C{\equiv}CCF_3$	38.91 (38.88)	6.20 (6.53)	17.26 (16.77)	

Table II. ^{31}P NMR Data for *trans*-PtH(σ-alkenyl)L_2

phosphine	acetylene	$\sigma\ ^{31}P$	$^1J(^{195}Pt)$
PCy_3	$CH_3OOCC{\equiv}CCOOCH_3$	35.0	2823
PCy_3	$CF_3C{\equiv}CCF_3$	34.9	2794
PCy_3	$CH_3C{\equiv}CCOOCH_3$	36.7, 34.9	2829, 2816
PCy_3	$C_6H_5C{\equiv}CCOOCH_3$	35.8	2792
PCy_3	$CH_3C{\equiv}CCN$	37.4	2770
PCy_3	$C_6H_5C{\equiv}fCCN$	36.2	2750
PCy_3	$C_6H_5C{\equiv}CCF_3$	36.2	2790
PCy_3	$HC{\equiv}CCOOCH_3$	34.8	2830
PCy_3	$HC{\equiv}CCN$	35.7	2763
PCy_3	$HC{\equiv}CCF_3$	34.6	2813
PCy_3	$HC{\equiv}CCOOCH_2CH{=}CH_2$	35.0	2835
PCy_3	$HC{\equiv}COOCH_2{\equiv}CH$	35.0	2826
PCy_3	$C_6H_5C{\equiv}CC_6H_4NO_2$	34.9	2847
P-*i*-Pr_3	$CH_3OOCC{\equiv}CCOOCH_3$	43.6	2844
P-*i*-Pr_3	$CF_3C{\equiv}CCF_3$	42.9	2820
P-*t*-Bu_2-*n*-Bu	$CH_3OOCC{\equiv}CCOOCH_3$	53.7	2891
P-*t*-Bu_2-*n*-Bu	$CF_3C{\equiv}CCF_3$	53.8	2856
P-*t*-Bu_2Me	$CH_3OOCC{\equiv}CCOOH_3$	45.1	2866
P-*t*-Bu_2Me	$CF_3C{\equiv}CCF_3$	43.6	2849

At convergence $R = 0.039$ and $R_w = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2} = 0.043$ for the 2237 observed reflections. A final difference synthesis showed two maxima (1.1 eÅ^{-3}) at the Pt atom (above and below the coordination plane) but no clear indication of the hydrogen bonded to Pt. In the last refinement cycle the largest coordinate error shift/error ratio was 0.15 for the x-coordinate of C(2). In the refinement calculations, scattering factors and anomalous dispersion corrections were taken from ref 17; the weighting scheme was of the form $w = 1/[\sigma^2F_o + 0.005F_o^2]$.

Figure 1 is a view of the molecule which shows the crystallographic numbering scheme. The final fractional coordinates for the non-hydrogen atoms are in Table VI, and Table VII contains interatomic distances. The calculated hydrogen coordinates, details of molecular geometry, thermal parameters, and a listing of structure factors are available as supplementary material.

Measurement of the Transient Charge-Transfer Spectrum. A solution of *trans*-$PtH_2(PCy_3)_2$ in toluene (~4 × 10^{-2} M) in a 1-cm path length quartz cell was cooled in a frozen chlorobenzene bath (-46 °C); 20 μL of dimethylacetylenedicarboxylate (DMA) was then introduced, causing the immediate development of an orange-red coloration. The visible spectrum of this reaction mixture, measured with a Cary 118C UV-vis spectrophotometer, gave λ_{max} at 515 nm. Similar colorations were observed at low temperatures with all acetylenes.

Spectral Titration. (a) With DMA. To a solution of *trans*-$PtH_2(PCy_3)_2$ in toluene (3.2 mL; 1 × 10^{-3} M) contained in a quartz cell were introduced 5-μL portions of a DMA solution in toluene (6.35 × 10^{-2} M), and the UV absorption spectrum was measured after each addition. The spectral change exhibited well-defined isosbestic points at 336 and 321.5 nm, and a constant absorption spectrum was obtained after addition of 1 equiv of DMA.

(b) With $HC{\equiv}CCOOCH_3$. Since the reaction of *trans*-$PtH_2(PCy_3)_2$ with $HC{\equiv}CCOOCH_3$ was considerably slower than that with DMA, the above titration method could not be applied. Instead, a series of seven samples containing the dihydride and the acetylene, ranging from 40 × 10^{-4} to 2.8 × 10^{-3} M, was made up in deaerated toluene in flasks sealed with serum caps. The reaction was allowed to proceed for ca. 12 h, and the UV absorption spectra were recorded. Again, a constant spectrum was obtained after the addition of 1 equiv of acetylene.

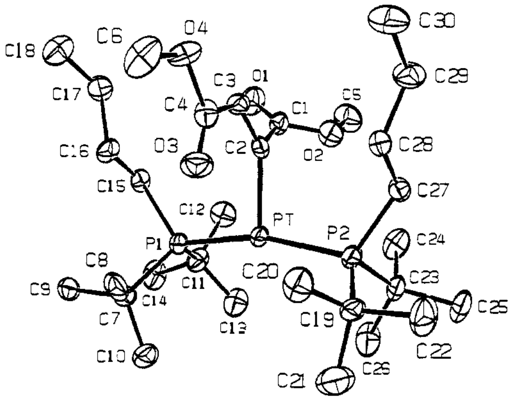

Figure 1. A view of the $C_{30}H_{62}O_4P_2Pt$ molecule with the crystallographic numbering scheme; ellipsoids are at the 50% level.

Kinetic Studies. The reactions of *trans*-$PtH_2(PCy_3)_2$ with $HC{\equiv}CCOOCH_3$ were slow enough to be followed by conventional methods. Typically, to a solution of *trans*-$PtH_2(PCy_3)_2$ (0.5 × 10^{-3}–1 × 10^{-3} M) in toluene, contained in a quartz cell sealed with a serum cap, was introduced an aliquot of $HC{\equiv}CCOOCH_3$ via a microsyringe. The decrease in absorbance at 325 nm with time was monitored by a Cary 118C UV-vis spectrophotometer. The temperature of the reaction cell compartment was controlled by thermostatted water by using a Forma temperature control bath equipped with a refrigeration unit. Temperatures were controlled to within ±0.1° of the reaction temperature.

The reactions with DMA were sufficiently fast that stopped-flow techniques had to be employed, by using a Durrum stopped-flow spectrophotometer Model D-110 equipped with an Aminas DASAR and Teletype Systems. The reactions were monitored at 330 nm. All kinetic runs were carried out under pseudo-first-order conditions by using excess of the appropriate acetylene (i.e., [acetylene]:[dihydride: $\not<9$), and the pseudo-first-order plots were linear for at least 3 half-lives. The observed kinetic data (Table VIII) show that the reactions of *trans*-$[PtH_2(PCy_3)_2]$ with DMA or $HC{\equiv}CCOOCH_3$ are second order, being first order in either reagent. For the reaction with $HC{\equiv}CCOOCH_3$ with *trans*-$PtH_2(PCy_3)_2$, the slope and intercept of the plot of ln $k(T)$ vs. $1/T$ gives values for ΔH^* and ΔS^* of 8.6 kcal.mol^{-1} and -29 eu, respectively.

Effect of Free-Radical Chain Inhibitors on Reaction Kinetics. When the insertion reaction of DMA with *trans*-$PtH_2(PCy_3)_2$ in C_6D_6 is followed by ^1H NMR spectroscopy, in addition to the resonances of the main product, PtH(DMA-H)$(PCy_3)_2$, two other high field signals were observed (δ -22.44, triplet, J(HP) = 13.6 Hz; δ -8.21, triplet, J(HP) = 15.6 Hz, relative intensities about 5% to each of the main product). The ^{195}Pt satellites for both resonances were too small to be observed. When this reaction was repeated by using a dilute solution of *trans*-$PtH_2(PCy_3)_2$ (0.1 mM) saturated with oxygen ($[O_2]$ > 1 mM), the ^1H NMR spectrum showed an increase in intensity of the resonance at δ -22.44 to ca. 16%, while the intensity of the other resonance remained relatively unchanged.

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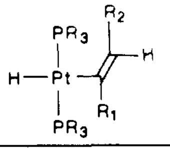
(17) *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table III. ^{1}H NMR Data for



				hydride					vinyl			
R_1	R_2	PR_3	solvent	δ ^{1}H	$^1J(^{195}Pt,^1H)$	$^2J(^{31}P,^1H)$	$^4J(H,H)$	$4J(H,F)$	δ H	$J(Pt,H)$	$4J(^{31}P,H)$	$J(H,F)$
$COOH_3$	$COOCH_3$	PCy_3	*a*	−9.33	645	16.9	3.9		7.71	84.4	3.2	
			b	−9.68	646	16.9	4.4		6.92	86	2.2	
		P-*i*-Pr_3	*b*	−9.53	620	16.0	3.8		7.42	83	1.9	
		P-*t*-Bu_2-*n*-Bu	*b*	−9.31	594	16.0	4.5		7.23	86	2.0	
		P-*t*-Bu_2Me	*b*	−8.45	620	16.5	4.2		7.31	86	2.1	
CF_3	CF_3	PCy_3	*a*	−10.04	611	17.0	3.9	2.2	6.80	89.9		8.0/2.2
		P-*i*-Pr_3	*b*	−10.02	599	16.8			6.87	84	NR^i	
		P-*t*-Bu_2-*n*-Bu	*b*	−9.84	562	16.1			6.83	86	NR^i	
		P-*t*-Bu_2Me	*b*	−9.16	602	16.5			7.03	85	NR^i	
$COOCH_3$	H	PCy_3	*a*	−9.39	637	16.9			7.35^c	97.6		
$COOCH_3$	CH_3		*a*	−8.71	635	17.2	3.8		6.99^d	75.3	2.2	
$COOCH_3$	Ph		*a*	−8.63	643	16.6	4.4		8.45	84.0		
CN	H		*a*	−9.36	687	15.9	3.3		7.30^e	99.1		
CN	CH_3		*a*	−8.55	676	16.0	3.6		7.73	78.2		
CN	Ph		*a*	−8.99	673	16.3	4.2		8.70	87.1		
CF_3	H		*a*	−9.55	650	17.4	3.7	3.6	6.47^f	96.8		2.2
CF_3	Ph		*a*	−9.43	601	16.8	4.3	2.9	7.86	82.1		2.2
$COOCH_2CH{=}CH_2$	H		*a*	−8.79	640	16.8	3.0		7.37^g	88.6		
$COOOH_2C{\equiv}CH$	H		*a*	−8.88	645	16.6	3.3		7.33^h	98.0		

[a] In benzene. [b] In $CDCl_3$. [c] H vinyl cis to Pt: δ H = 5.84, $^2J(HH)$ = 4.8 Hz, $J(PtH)$ = 59.6 Hz. [d] $J(H,CH_3)$ = 6.5 Hz. [e] H vinyl cis to Pt: δ H = 6.03, $J(PtH)$ = 59.8 Hz. [f] H vinyl cis to Pt: δ H = 5.24, $^2J(HH)$ = 3.6 Hz, $J(H,F)$ = 1.4 Hz, $J(PtH)$ = 57.4 Hz. [g] H vinyl cis to Pt: δ H = 5.82, $J(PtH)$ = 57.8 Hz. [h] H vinyl cis to Pt: δ H = 5.82, $J(PtH)$ = 58.0 Hz. [i] NR = not resolved.

Table IV. ^{1}H NMR Data for *trans*(*cis*)-$Pt(PEt_3)_2Cl$(*trans*(*cis*)-$CH_3OOCC{=}CHCOOCH_3$)

	vinylic H		
isomer	δ	$^3J(PtH)$, Hz	$^4J(PH)$, Hz
trans, cis	5.86	102.0	1.5
trans, trans	6.75	138.0	1.6
cis, cis	6.07	60.5	10.0
cis, trans	7.03	80.5	16.6, 1.1

This result, together with the high field position of the hydride resonance (δ −22.44), suggested[18] that the hydride ligand may be trans to some oxygen bonded ligands such as –OH, –OOH, or $-OOPtH(PCy_3)_2$. It was, therefore, necessary to determine whether the observed kinetic data were influenced by the presence of oxygen or of other free-radical chain inhibitors, such as phenyl-*tert*-butylnitrone (PBN). The results, summarized in Table IX, show that oxygen and PBN have no effect on the rate of insertion.

Kinetic Isotope Effect. The kinetic isotope effect was studied by measuring the absolute second-order rate constants for the insertion of *trans*-$PtH_2(PCy_3)_2$ and *trans*-$PtD_2(PCy_3)_2$ with either $HC{\equiv}CCOOCH_3$ or DMA. The kinetic data are presented in Table X.

Exchange Reaction. *trans*-$PtD_2(PCy_3[_2$ (0.1 mM) and *trans*-$PtH_2(PCy_3)_2$ (0.025 mM) were allowed to react with DMA (0.125 mM) in $C_6H_5CD_3$ (0.5 mL). Since the kinetic isotope effect is ~1, and if a radical chain mechanism is involved, H-D exchange products such as *trans*-$PtD(DMA-H)(PCy_3)_2$ and *trans*-$PtH(DMA-D)(PCy_3)_2$ should be formed in addition to *trans*-$PtD(DMA-D)(PCy_3)_2$ and *trans*-$PtH(DMA-H)(PCy_3)_2$; their statistical distribution should be 4:4:16:1, respectively. If such exchange had occurred, the hydride resonances in the ^{1}H NMR spectrum should show a simple triplet with ^{195}Pt satellites for the hydride of *trans*-$PtH(DMA-D)(PCy_3)_2$ and a triplet of doublets with ^{195}Pt satellites for the hydride of *trans*-$PtH(DMA-H)(PCy_3)_2$. The observed spectra show the hydride resonance as a triplet of doublets with no detectable simple triplet, indicating that exchange has not occurred.

Procedure for ESR Studies. With the exception of those experiments in which air or oxygen was purposely introduced, all experiments were conducted under deaerated conditions. Thus, neat deaerated acetylene was introduced via a hypodermic syringe into a solution of platinum(II) dihydride, contained in a quartz tube sealed with a serum cap and which had previously been flushed with nitrogen. The ESR spectrum was then observed by using a Varian E-4 spectrometer. In certain cases, considerable care was necessary to ensure that "secondary" radicals were not produced by the reaction of molecular oxygen with the "primary" radicals. Such experiments were conducted in an all-glass quartz apparatus with the quartz ESR tube connected via a ground glass joint directly to an H-shaped glass vessel.[19] Solutions of the platinum dihydride and acetylene were introduced into separate compartments of the H-shaped vessel and degassed by four successive freeze–thaw–pump cycles. The solutions were then mixed thoroughly and subsequently transferrred to the quartz ESR tube.

For those experiments in which phenyl-*N*-*tert*-butylnitrone (PBN) was used as a spin-trapping agent, the solutions of PBN were introduced via a hypodermic syringe into the reaction mixture after the formation of the radical.

Reaction with 2,3-Dichloro-5,6-Dicyanoquinone. *trans*-$PtH_2(PCy_3)_2$ (40 mg) was dissolved in benzene (0.5 mL) in an NMR tube; addition of the quinone (4 mg, 0.4 mol equiv) produced an immediate dark green coloration which faded to yellow within 4–5 min. The ^{1}H NMR spectrum of the resulting solution showed, in addition to the resonances of the dihydride, a new hydride resonance at δ −17.7 ppm with $J(PtH)$ = 1159 Hz. Addition of a further sample of the quinone (4 mg, 0.4 mol equv) regenerated the dark green color and gave an approximate doubling in intensity of the hydride resonance at δ −17.7 ppm in the ^{1}H NMR spectrum. Addition of a further sample of the quinone (3 mg, total additions = 1 mol equiv) repeated these effects but also caused complete loss of the original dihydride ^{1}H NMR resonance at δ −3.0 ppm.

When the quinone (1 equiv) was added to a fresh benzene solution of *trans*-$PtH_2(PCy_3)_2$, we observed a single, broad (3G) line ESR spectrum for the resulting dark green solution. Both the green color and the ESR signal decayed in parallel fashion over 3–4 min. Interestingly, a further addition of the quinone regenerated both the color and the ESR signal.

Results and Discussion

Insertion Reactions. *trans*-PtH_2L_2 (L = PCy_3, P-*i*-Pr_3, P-*t*-Bu_2-*n*-Bu, P-*t*-Bu_2Me) was found to react with activated acetylenes, both internal and terminal, with the reaction rate being influenced by both the acetylene and the nature of the phosphine ligand. Thus, for $RC{\equiv}CR$ with R=$COOCH_3$ or CF_3, reaction was essentially instantaneous for L = PCy_3 or P-*i*-Pr_3 but took up to a few hours for L = P-*t*-Bu_2Me or P-*t*-Bu_2-*n*-Bu. For an acetylene such as $CH_3C{\equiv}CCOOCH_3$, the reaction as followed by ^{1}H NMR spectroscopy is even slower and takes days to reach completion. Reaction yields were generally high (70–75%), and only one product was isolated. Mixtures showed the presence of minor products ($\not>$ 10%), but these were not observed when

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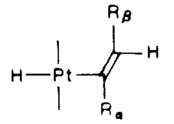
[18] See, for example, McLendon, C.; Mortell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1.

[19] Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807.

Table V. ^{13}C NMR Data for the Alkenyl Moiety of Insertion Products[c]



R_α	R_β	C_α	C_β	CO	OCH_3
$COOCH_3$	$COOCH_3$	195.9 {691}[a]	124.8	179.3, 171.1 {31}	50.3, 50.2
		196.0[b]	124.5 d (156)	179.8, 171.3	50.5 a (146)
$COOCH_3$	H	168.5[a]	125.2	178.6 {23}	50.1
		168.1 {744}[b]	125.7 t (154)		50.7 a (144)
$COOCH_3$	C_6H_5	168.4 {694}[a]	125.5 d (160)	180.3	50.2 a (144)
CF_3	H	not obsd[b]	123.7 t × q (160)[12]		

[a] = Benzene-d^6. [b] = CD_2Cl_2. [c] { } ≙ $J(^{195}Pt, ^{13}C)$; ( ) ≙ $J(^{13}C, ^1H)$; [ ] ≙ $J(^{19}F,^{13}C)$; d = doublet, q = quartet; t = triplet.

Table VI. Table of Positional Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*
P1	0.32275 (6)	0.20323 (3)	0.11024 (2)
P1	0.3673 (4)	0.3072 (2)	0.0536 (1)
P2	0.2775 (5)	0.0689 (2)	0.1490 (1)
O1	0.6341 (13)	0.3650 (9)	0.1956 (4)
O2	0.6148 (12)	0.2185 (8)	0.2163 (4)
O3	0.0638 (13)	0.3260 (8)	0.1411 (4)
O4	0.1101 (13)	0.4321 (7)	0.2020 (4)
C1	0.5593 (19)	0.2992 (13)	0.1949 (5)
C2	0.3933 (15)	0.2904 (9)	0.1716 (4)
C3	0.3120 (18)	0.3510 (9)	0.1921 (5)
C4	0.1465 (19)	0.3644 (11)	0.1745 (6)
C5	0.7785 (19)	0.2150 (14)	0.2370 (7)
C6	−0.0472 (19)	0.4519 (12)	0.1853 (7)
C7	0.2029 (20)	0.3186 (9)	−0.0041 (5)
C8	0.0604 (17)	0.3251 (11)	0.0152 (6)
C9	0.2121 (19)	0.4052 (10)	−0.0359 (5)
C10	0.1893 (23)	0.2332 (11)	−0.0367 (6)
C11	0.5486 (21)	0.2750 (11)	0.0363 (6)
C12	0.6827 (20)	0.2933 (13)	0.0828 (7)
C13	0.5503 (22)	0.1720 (12)	0.0255 (7)
C14	0.5713 (22)	0.3271 (13)	−0.0092 (7)
C15	0.4118 (15)	0.4280 (9)	0.0758 (5)
C16	0.2890 (16)	0.4842 (9)	0.0885 (5)
C17	0.3646 (18)	0.5629 (11)	0.1256 (6)
C18	0.2477 (22)	0.6283 (12)	0.1356 (7)
C19	0.0797 (19)	0.0286 (10)	0.1252 (5)
C20	−0.0255 (17)	0.1129 (13)	0.1211 (6)
C21	0.0503 (26)	−0.0149 (15)	0.0723 (7)
C22	0.0353 (20)	−0.0465 (12)	0.1576 (7)
C23	0.4181 (19)	−0.0237 (9)	0.1452 (5)
C24	0.5776 (19)	0.0121 (12)	0.1719 (7)
C25	0.3944 (21)	−0.1181 (10)	0.1683 (6)
C26	0.4212 (28)	−0.0443 (13)	0.0905 (6)
C27	0.3113 (15)	0.0756 (9)	0.2169 (4)
C28	0.2093 (16)	0.1410 (9)	0.2372 (4)
C29	0.2806 (19)	0.1675 (12)	0.2913 (5)
C30	0.1818 (23)	0.2324 (14)	0.3107 (7)

carefully deaerated solvents were used. As discussed later, in a few cases, more than one alkenyl isomer was observed, and in the reaction of *trans*-$PtH_2(PCy_3)_2$ with DMA, the ^1H and ^{31}P NMR spectra of the reaction mixture prior to workup showed that the Pt° complex $(PCy_3)_2Pt(DMA)$ was also formed in about 5% yield. This will be discussed in a later paper.

All products were white, crystalline solids for which the elemental analyses (Table I) showed that the overall stoichiometry of the reaction in every case was 1:1. In other words, even in the presence of excess acetylene and over long periods of time, insertion occurred with only one Pt–H bond; we comment on this later. There is also no evidence of further insertion of acetylene into the platinum–alkenyl bond, as has been observed for some Ir,[20] Ru,[21] Pt,[21] and Pd[22] complexes.

Complete structural characterization of the products was achieved by the use of NMR spectroscopic and X-ray crystal structure determination methods. The $\{^1H\}^{31}P$ NMR spectra all showed (Table II) a 1:4:1 triplet with δ ^{31}P being characteristic of the tertiary phosphine and $^1J(^{195}Pt-^{31}P)$ in the range 2750–2891 Hz. These data establish the geometry of the platinum fragment as trans and with the alkenyl groups trans to hydride, and this is fully supported by the ^1H NMR parameters. In particular, the spectra all show (Table III) the hydride resonances as a complex multiplet with ^{195}Pt satellites in the characteristic region of δ −8.45 to −10.04 with coupling constants to ^{195}Pt of 562–637 Hz and to ^{31}P of 15.9–17.4 Hz.

Of particular interest is the question of the stereochemistry of the alkenyl group. The assignment of geometry can be based on the ^1H NMR parameters, with verification provided by the single crystal structure determination reported later. These assignments can be established by using data from a series of related compounds which we have previously characterized from reaction 1.[7] Table IV summarizes the NMR data for *trans*(*cis*)-Pt-$(PEt_3)_2Cl$[*trans*(*cis*)-$CH_3OOCC{=}CH(COOCH_3)$]; inspection of Table IV shows two pertinent trends.

(a) Chemical Shift. The chemical shift of the alkenyl proton (derived from Pt–H) depends on the geometry of the group and is relatively independent of the ligand trans to the alkenyl moiety. Thus, when Pt and H have a cis disposition across the double bond, the alkenyl proton resonates at ca. δ 6 ppm; when they are trans, the resonance is at δ 7 ppm. This high field shift for the cis arrangement is presumably due to greater Pt and H interaction.

(b) Coupling Constants. The magnitude of $^3J(PtH)$ is dependent on both the trans ligand and the geometry of the vinylic group. For the same trans ligand, the trans vinylic group has the bigger $^3J(PtH)$ value. For example, when the trans ligand is PEt_3, the trans alkenyl H has a coupling constant of 80.5 Hz with ^{195}Pt, and the cis alkenyl H has a value of only 60.5 Hz. In general, the data of Table IV show a unique combination of chemical shift and coupling constants for each isomer, so that the geometry of the alkenyl group can be readily determined by NMR parameters alone.

To determine the geometry of the alkenyl group in the products derived from Pt(II) dihydrides, the ^1H NMR data of these products can be compared with those of Table IV. Data from complexes with similar trans groups must be employed to provide a meaningful comparison of $^3J(PtH)$ values. Since the hydride ligand and the tertiary phosphine ligand have approximately the same trans influence,[23] it is reasonable first to compare the cis–cis and cis–trans complexes (Table IV) with the dihydride products (Table III) derived from symmetrically substituted acetylenes. The latter gave $^3J(PtH)$ values in the range of 83–88 Hz which are similar to those of the cis–trans complex. Further, where R = CF_3, $^5J(FF)$ is less than 3 Hz, which is in agreement with a trans disposition of two CF_3 groups about the C=C bond.[24] Moreover, the chemical shift for the alkenyl proton is in the range

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Table VII. Table of Bond Distances in Å

atom 1	atom 2	distance[a]	atom 1	atom 2	distance[a]	atom 1	atom 2	distance[a]
Pt	P1	2.293 (4)	O3	C4	1.18 (2)	C15	C16	1.51 (2)
Pt	P2	2.311 (4)	O4	C4	1.34 (2)	C16	C17	1.57 (2)
Pt	C2	2.086 (12)	O4	C6	1.43 (2)	C17	C18	1.51 (2)
P1	C7	1.905 (14)	C1	C2	1.50 (2)	C19	C20	1.54 (2)
P1	C11	1.915 (20)	C2	C3	1.37 (2)	C19	C21	1.56 (2)
P1	C15	1.861 (13)	C3	C4	1.49 (2)	C19	C22	1.53 (2)
P2	C19	1.862 (17)	C7	C8	1.55 (2)	C23	C24	1.55 (2)
P2	C23	1.885 (16)	C7	C9	1.55 (2)	C23	C25	1.55 (2)
P2	C27	1.842 (13)	C7	C10	1.52 (2)	C23	C26	1.52 (2)
O1	C1	1.17 (2)	C11	C12	1.56 (2)	C27	C28	1.54 (2)
O2	C1	1.35 (2)	C11	C13	1.52 (2)	C28	C29	1.53 (2)
O2	C5	1.47 (2)	C11	C14	1.54 (2)	C29	C30	1.50 (2)

[a] Numbers of parentheses are estimated standard deviations in the least significant digits.

Table VIII. Kinetic Data for the Reaction of *trans*-$PtH_2(PCy_3)_2$ with DMA or $HC{\equiv}CCOOCH_3$ in Deaerated Toluene

$[HC{\equiv}CCOOCH_3]$M ($\times 10^{-2}$)	$[PtH_2(PCy_3)_2$M ($\times 10^3$)	T °C (± 0.1)	k_{obsd} s^{-1} ($\times 10^2$)
1.89×10^{-2}	1.0	5.0	1.1
3.78	1.0	5.0	2.3
5.67	1.0	5.0	3.5
7.56	1.0	5.0	4.4
1.89	0.5	8.0	1.3
3.78	0.5	8.0	2.7
5.67	0.5	8.0	3.8
7.56	0.5	8.0	5.4
1.89	1.0	15.0	1.7
3.78	1.0	15.0	3.6
5.67	1.0	15.0	5.6
6.80	1.0	15.0	7.0
7.56	1.0	15.0	8.3
0.378	0.25	22.5	0.65
0.945	0.50	22.5	1.5
0.945	1.0	22.5	1.5
1.89	1.0	22.5	3.0
2.83	1.0	22.5	4.5
3.78	1.0	22.5	6.0

[DMA]M ($\times 10^{-2}$)	$[PtH_2(PCy_3)_2]$M ($\times 10^3$)	T °C (± 0.1)	k_{obsd} s^{-1}
0.488	0.5	25.0	0.53
0.50	0.5	25.0	0.76
1.22	0.5	25.0	1.7
2.0	0.5	25.0	2.6
2.44	0.5	25.0	3.6
4.0	0.5	25.0	5.6

Table IX. Kinetic Data for the Effect of Oxygen or PBN on the Rate of Insertion

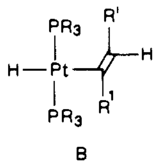
$[HC{\equiv}CCOOCH_3]$ ($M \times 10^2$)	[PBN] ($M \times 10^3$)	$[PtH_2(PCy_3)_2]$ ($M \times 10^3$)	T °C (± 0.1)	k_{obsd} s^{-1} ($\times 10^2$)
1.89	0	2.0	22.5	3.6
1.89	1.0	2.0	22.5	3.6
1.89	2.0	2.0	22.5	3.6
		O_2		
2.83	0	1.0	22.5	4.5
2.83	O_2-saturtd	1.0	22.5	4.5

[DMA]M	$[O_2]$	$[PtH_2(PCy_3)_2]$ ($M \times 10^{-4}$)	T °C (± 0.1)	k_{obsd} s^{-1}
4.88×10^{-3}	0	5.0	22.5	0.53
4.88×10^{-3}	+	5.0	22.5	0.50
1.22×10^{-2}	0	5.0	22.5	1.7
1.22×10^{-2}	+	5.0	22.5	1.5
		[PBN]		
4.88×10^{-3}	1.0×10^{-3}	5.0	22.5	0.51
4.88×10^{-3}	2.0×10^{-3}	5.0	22.5	0.51

Table X. Deuterium Kinetic Isotope Effect for the Insertion of $[PtH_2(PCy_3)_2$ and $[PtD_2(PCy_3)_2]$ with $HC{\equiv}CCOOCH_3$ or DMA

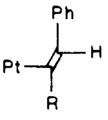
M	k_H (M^{-1} s^{-1})	k_D (M^{-1} s^{-1})	k_H/k_D
	$[HC{\equiv}CCOOCH_3]$		
1.51×10^{-2}	1.7	1.6	1.0
2.27×10^{-2}	1.6	1.7	1.0
	[DMA]		
4.88×10^{-3}	110	88	1.2
1.22×10^{-2}	140	120	1.2
2.44×10^{-2}	150	130	1.2

δ 6.83–7.42 ppm which is the expected region for a trans addition product. The geometry of the dihydride products is thus unambiguously established as trans, trans, i.e., structure B.

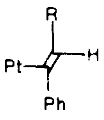


B

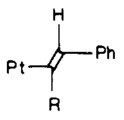
Considering now the unsymmetrically substituted acetylenes, PhC≡CR, the values of ^3J(PtH) lie in the range 82.1–87.1, clearly suggesting again a trans geometry for the alkenyl group, i.e., either C or D of the four possible configurations C–F.



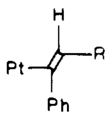
C



D



E

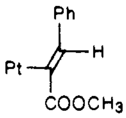


F

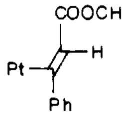
For R = CF_3, the ^{19}F NMR spectrum showed that 95% of the insertion product has a CF_3 in the α-position (see δ F and J(PtF) values in Table III) while the minor product (~5%) shows a resonance in the usual range for a β-CF_3 group and has the typical gem J(F,H) of ca 7.7 Hz. The major product thus has structure C. For R = $COOCH_3$ or CN, the ^{31}P NMR spectra showed only one product in each case; the alkenyl geometry of each can be determined by the incremental method of Matter et al.[25] for the estimation of chemical shifts in substituted ethylenes. From the spectra of platinum–alkenyl products of known stereochemistry, a shielding increment for the platinum-containing group can be calculated to be

$$Z_{trans}(Pt) = 0.70 \pm 0.44 \text{ ppm}$$

By using Matter's incremental method,[25] the chemical shift for the alkenyl proton for G and H can then be calculated as



G
8.11 ppm



H
7.11 ppm

The observed value is 8.45 ppm in agreement with G; however,

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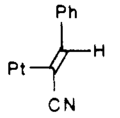
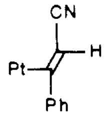
(25) Matter, U. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; Sternkell, S. *Tetrahedron* **1969**, *25*, 691.

for R = CN, the observed shift value of 8.70 ppm is much greater than those calculated similarly for I and J. If, however, the Z(Pt) increment is calculated by using the Z_{gem}(phenyl) increment value, the estimated shift value for I is 8.68 ppm in very good agreement with the observed value of 8.70 ppm.

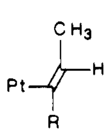

I

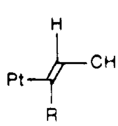
8.08 ppm


J

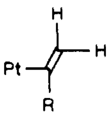
6.58 ppm

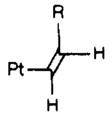
For the methylacetylenes, $CH_3C{\equiv}CR$, R = CN or $COOCH_3$, the ^1H NMR data, and in particular the J(H,H) values, show that the CH_3 group is in the β-position so that only structures K and L are possible. For R = CN, only trans addition (K) is observed (^3J(Pt,H) value of 78.2 Hz) but for R = $COOCH_3$, 90% trans (i.e., K) and 10% cis (L) is observed. However, with this acetylene, which is not highly activated, reaction is very slow taking days to completion.

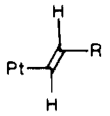

K


L

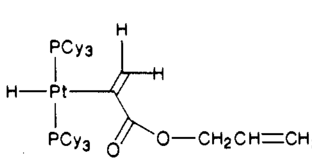
With terminal acetylenes, $HC{\equiv}CR$, R = $COOCH_3$, CN, or CF_3, the Pt(II) dihydrides could give three alkenyl insertion products, M–O. The ^{31}P NMR spectra show only one product is formed, for which the ^1H NMR spectrum in each case shows J(HH) to be 4–5 Hz consistent with M or N. However, the proton-coupled ^{13}C NMR spectra for these products (see Table V) each show a triplet for C_β (i.e., $C{=}C^\beta H_2$) consistent only with M. Since this did not distinguish between cis and trans additions, the reactions of these three acetylenes with trans $PtD_2(PCy_3)_2$ were performed. All three products were found to have D trans to Pt, since only the high field resonance attributable to the alkenyl proton cis to Pt was observed in each ^1H NMR spectrum, confirming that *only* trans addition has occurred.

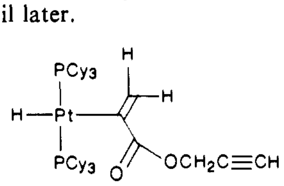

M


N


O

The ^1H NMR data (Table III) for the products with the acetylenes $HC{\equiv}CCOOCH_2CH{=}CH_2$ and $HC{\equiv}CCOOCH_2C{\equiv}CH$ show them to have structures P and Q. These two reactions are discussed in more detail later.


P


Q

Crystal Structure Determination. The above deductions of alkenyl stereochemistry are based on NMR parameters and are thus indirect. Since an observed trans addition with Pt(II) dihydrides might indicate a substantially different reaction pathway than for comparable Pt(II) monohydrides or other transition-metal hydrides, an unambiguous characterization of the alkenyl geometry is desirable. This is provided by the single crystal structure determination of *trans*-PtH(P-*t*-Bu_2-*n*-Bu)$_2$[C($COOCH_3$)=CH($COOCH_3$)]. The crystal structure contains discrete molecules separated by normal van der Waals distances. The molecule has trans phosphine ligands and the Pt atom distorted square-planar geometry. The DMA–H ligand (Figure 1) is coordinated to Pt via a normal Pt–C σ bond (2.086 (12) Å). The analysis establishes that the DMA–H ligand has the CO_2Me moieties trans not cis to the C(2)–C(3) double bond; this is entirely in accord with our expectations based on assignments of NMR parameters.

The DMA–H ligand is sandwiched between the maximally extended *n*-butyl chains of the phosphine ligands; this conformation leads to a Pt···O(3) intramolecular contact of 3.266 Å; the Pt–C(2)–C(3) angle (129.9 (1.0)° is significantly larger than Pt–C(2)–C(1) (118.0 (1.0)°) to accommodate this overcrowding. Bond lengths of the DMA–H ligand (Table VI) are in accord with expected values.

Intramolecular repulsions cause several angles associated with the phosphine ligands to be significantly different from values found in uncrowded systems. Thus the P–Pt–P angle is nonlinear (163.5 (1)°), and the C–Pt–P angles are greater than 90° (95.5 and 100.3 (4)°). The Pt–P–C and C–P–C angles vary irregularly from tetrahedral; e.g., the Pt–P(1)–C(15) (116.9°) and Pt–P(2)–C(27) (115.8°) angles are enlarged to accommodate intramolecular interactions between the DMA–H ligand and the *n*-butyl chains (see Figure 1). The Pt–P bond lengths (2.293 and 2.311 Å) and the P–Pt–P angle are in accord with dimensions found[26] in related systems, e.g., Pt–P 2.332 and 2.329 Å, P–Pt–P 163.8° in [*trans*-PtH(1,1-dimethylallene)$(PCy_3)_2]^+$.

Mechanism of the Insertion Reaction. In deducing the mechanism for the reactions of Pt(II) dihydrides with acetylenes, four items of evidence need to be considered. Firstly, a 1:1 stoichiometry is clearly established. Both product analyses and the spectral titrations of *trans*-$PtH_2(PCy_3)_2$ with DMA and with $HC{\equiv}CCOOCH_3$, described in the Experimental Section, establish it. It is also established above that the resulting alkenyl products are trans with respect to the disposition of the Pt and H about the C=C bond.

Secondly, there is evidence that Pt(II) dihydrides can react via charge-transfer processes. The most substantial evidence for this is the reaction of *trans*-$PtH_2(PCy_3)_2$ with dichlorodicyanoquinone which is discussed in detail later.

Thirdly, the kinetic study of the reactions of *trans*-$PtH_2(PCy_3)_2$ with DMA and with $HC{\equiv}CCOOCH_3$ show that the rate-determining step is bimolecular involving one molecule of acetylene and one molecule of the dihydride. The absence of any significant kinetic isotope effect as demonstrated by the data of Table X and the low enthalpy of activation ($\Delta H^{\ddagger}$ = 8.6 kcal mol^{-1} for the reaction with $HC{\equiv}CCOOCH_3$) are all in agreement with an electron transfer mechanism. Further, the 100-fold increase in reaction rate upon replacement of H (from $HC{\equiv}CCOOCH_3$) by the more electron-withdrawing group $COOCH_3$ is consistent with the acetylene acting as an electron acceptor and the platinum dihydride as an electron donor.

Fourthly, the bimolecular radical chain mechanism which, under appropriate conditions (nonpolar solvent, e.g., benzene, ambient temperature) describes[6] the reaction pathway for the insertion of activated acetylenes with Pt(II)monohydrides is clearly not applicable to the similar reactions of Pt(II) dihydrides, for the following reasons: (a) When in the insertion reaction with DMA, a mixture of *trans*-$PtH_2(PCy_3)_2$ and *trans*-$PtD_2(PCy_3)_2$ is used, no scrambling of hydrogen and deuterium in the insertion product was observed. A radical chain mechanism would require such scrambling. (b) The presence of free-radical chain inhibitors or spin traps such as oxygen or PBN had no effect on the rate of reaction. The presence of oxygen, however, did cause a modest increase in yield (from 5 to 16%) of a minor reaction product; this is discussed later.

On the basis of the above evidence, we, therefore, conclude that the rate-determining step in this insertion reaction involves an electron-transfer process via charge-transfer interaction, as described in eq 2. The product of the rate-determining step is thus

$$\textit{trans}\text{-}PtH_2(PCy_3)_2 + DMA \rightarrow \underline{\{PtH_2(^{\delta+}PCy_3)_2\cdots DMA^{\delta-}\}} \rightarrow Pt^{III}H_2(PCy_3)_2{}^{+}\cdots DMA^{\bullet-} \quad (2)$$

a geminate radical pair (i.e., contained within the solvent cage), consisting of a Pt^{III} cation (or alternatively a Pt(II) radical cation)

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[26] Clark, H. C.; Dymarski, M. J.; Payne, N. C. *J. Organomet. Chem.* **1979**, *165*, 117.

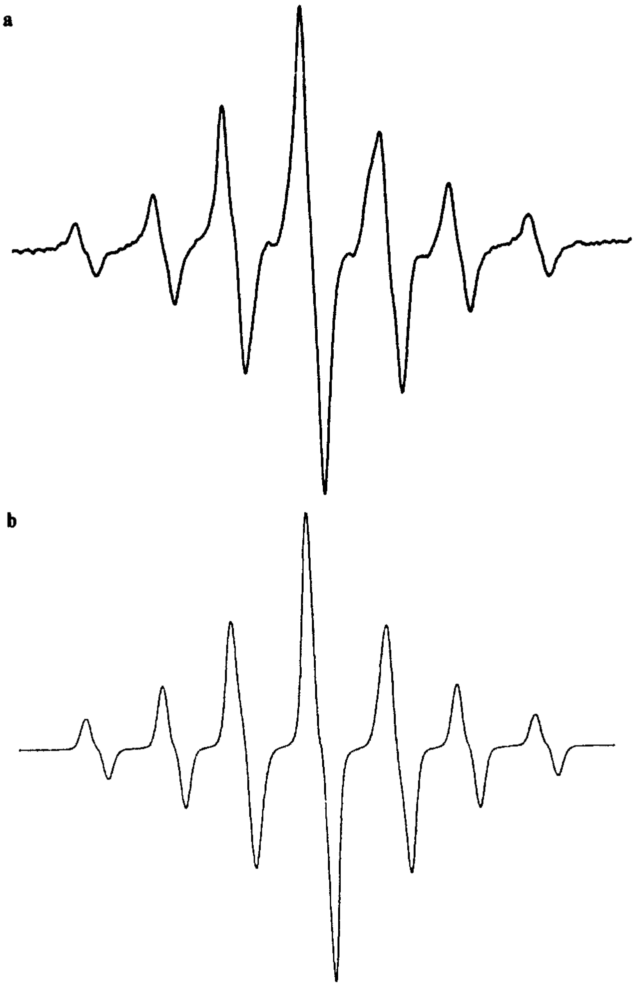


Figure 2. The ESR spectrum (a) observed and (b) computer-simulated for *trans*-PtH$_2$(PCy$_3$)$_2$ with DMA (1 equiv) in benzene at room temperature.

and the acetylene radical anion; rearrangement within the solvent cage then leads rapidly to the alkenyl product, according to eq 3. Such a proposed mechanism follows exactly that developed by Kochi et al.[27,28] for reactions involving hydrogen transfer from metal hydrides such as trialkyl hydrides of silicon, germanium, and tin to tetracyanoethylene; there appears to be no prior evidence supporting its application to similar reactions of transition-metal hydrides, although Kochi et al.[29] have shown that tungstenocene hydrides can be electrochemically oxidized to form transient, paramagnetic radical cations.

$$\mathrm{Pt^{III}H_2(PCy_3)_2{}^{+}\cdots DMA^{\bullet-}} \rightarrow trans\text{-}\mathrm{PtH(PCy_3)_2(DMA{-}H)} \tag{3}$$

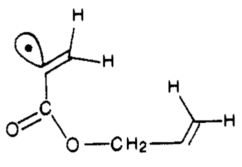
While there is thus considerable evidence in support of eq 2, at least two aspects of eq 3 need amplification. These are (a) the mechanism of hydrogen transfer to the acetylene and (b) the identification of the factors causing the stereospecificity of that transfer (i.e., why is a trans alkenyl product always formed?). With regard to (a), Kochi has previously discussed[30] the instability of paramagnetic organometallic cation radicals, of which our species PtH$_2$(PCy$_3$)$_2$$^{\bullet+}$ is an example. Such a species should, therefore, undergo either facile homolytic or heterolytic cleavage, eq 4 or 5, respectively. Our observations show an increase in the amount of oxygen-containing byproduct in the presence of a large excess of oxygen. This suggests a heterolytic cleavage of the cation radical (i.e., H$^+$ transfer), since homolytic cleavage would form a stable Pt(II) cation unreactive toward oxygen. The Pt(I) radical produced by heterolytic cleavage would be easily trapped by oxygen, although, of course, any solvent cage escape of the radical pair would similarly cause an increased yield of the oxygen-containing byproduct.

$$\mathrm{MH^{\bullet+} \rightarrow M^{+} + H^{\bullet}} \tag{4}$$

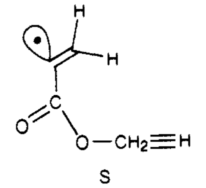
$$\mathrm{MH^{\bullet+} \rightarrow M^{\bullet} + H^{+}} \tag{5}$$

The exclusively trans stereochemistry of the alkenyl products is a natural consequence of the mechanism proposed above. An acetylene radical anion generated in eq 1 above represents an excited state of the acetylene and will, therefore, have C_{2h} (i.e., trans) geometry.[31] Transfer to it of H$^+$ followed by the Pt-containing moiety would then always generate trans alkenyl products. This is consistent with the observation[32] that the diphenylacetylene radical anion quite rapidly generates *trans*-stilbene exclusively through hydrogen abstraction from solvent. Indirect evidence that acetylene radical anions are transient species in these insertion reactions comes from the following observation. Diphenylacetylene, for which the reduction potential[33] required to generate such a radical anion is −2.11 V, is inert toward insertion with *trans*-PtH$_2$(PCy$_3$)$_2$; in contrast, the acetylene $C_6H_5C{\equiv}C$-(p-$C_6H_4NO_2$) for which the comparable potential[33] is only −0.89 V undergoes complete insertion with the dihydride in about 1 h.

Although we have proposed above that the electron transfer is the rate-determining step, so far no information has been presented which might indicate the relative rate of the final rearrangement leading to the alkenyl product, i.e., the relative rate of reaction 3. For this reason, we examined the reactions of *trans*-PtH$_2$(PCy$_3$)$_2$ with $HC{\equiv}CCOOCH_2CH{=}CH_2$ and $HC{\equiv}CCOOCH_2C{\equiv}CH$. Assuming that electron transfer produces the respective acetylene radical anions, subsequent H$^+$ transfer would then yield the vinyl radicals R and S. Such radicals are known to undergo cyclization very rapidly;[34,35] we observed, however, in both these reactions only the formation of the single direct insertion of the acetylenic bond and no evidence of cyclization.[36] This implies that while electron transfer is the rate-determining step, subsequent steps are very fast, far more rapid than a competing cyclization process; the latter are often comparable in rate to spin-trapping processes.[37]



R



S

ESR Spectroscopic Studies. In the course of this mechanistic study, we have examined these reactions by using ESR spectroscopy. For example, upon mixing equivalent amounts of *trans*-PtH$_2$(PCy$_3$)$_2$ and DMA in deaerated toluene or benzene, a seven-line ESR spectrum (Figure 2a) was observed. This spectrum persists over a period of approximately 90 min ($t_{1/2} \sim$ 30 min) but is much shorter lived in dichloromethane being observed for only about 10 min. The radical readily reacts with

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(27) Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.

(28) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961.

(29) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am Chem. Soc.* **1980**, *102*, 208.

(30) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; p 479.

(31) Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; D. Van Nostrand: Princeton, NJ, 1967; p 517.

(32) Furderer, P.; Garson, F.; Krebs, A. *Helv. Chim. Acta* **1977**, *60*, 1226.

(33) Sinoda, R. E.; Cowan, D. O.; Koski, W. S. *J. Am. Chem. Soc.* **1967**, *89*, 230.

(34) Kochi, J. K. *Free Radicals*; Wiley: New York, 1973; Vol. I, p 418–446.

(35) Heiba, E. I.; Dessau, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 2238.

(36) In the reaction with $HC{\equiv}CCOOCH_2C{\equiv}CH$, the alkenyl insertion compound constitutes ca. 70% of the product; a structural assignment of the remaining product(s) based on the ^{1}H NMR spectrum could not be deduced.

(37) Schmid, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 6434.

Table XI. ESR Data of Observed Radicals in the Reaction: *trans*-PtH_2L_2 + Acetylene

L	acetylene	*g*	a_{Pt}	a_P	a_H	a_H	a_F
PCy_3	$CH_3OOCC{\equiv}CCOOCH_3$	2.0056	24.5	6.5	0.9		
PCy_3	$HC{\equiv}CCOOCH_3$	2.0058	22.5	6.0	0.9	3.9	
PCy_3	$DC{\equiv}CCOOCH_3$	2.0057	23.0	6.0	0.9		
PCy_3	$C_6H_5C{\equiv}CCOOCH_3$		20.3	5.7	0.9		
PCy_3	$C_6H_5C{\equiv}CCF_3$		20.3	4.8			1.3
P-*t*-Bu_2Me	$CH_3OOCC{\equiv}CCOOH_3$		12.7	3.9	0.5		

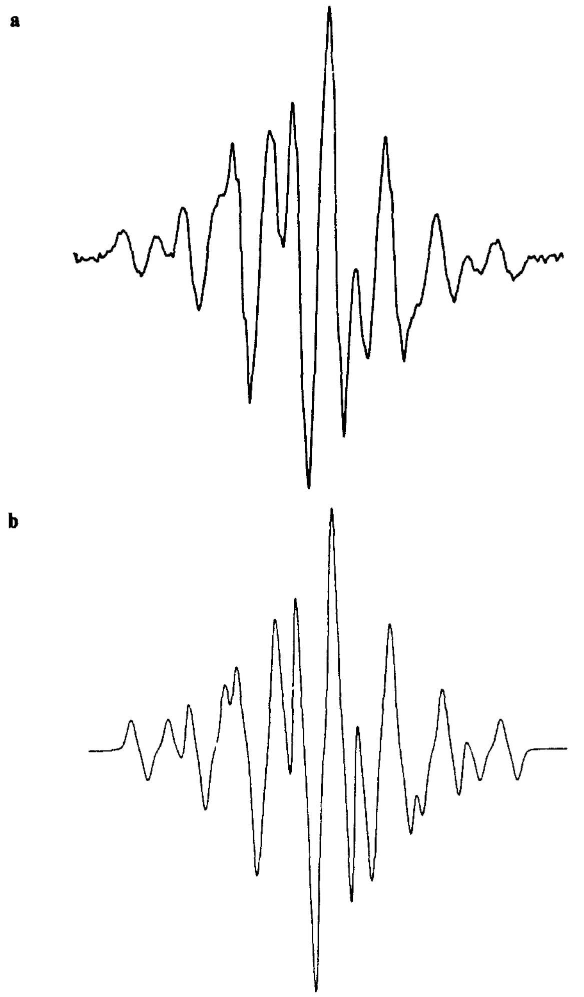

Figure 3. The ESR spectrum (a) observed and (b) simulated for *trans*-$PtH_2(PCy_3)_2$ with $HC{\equiv}CCOOCH_3$ in benzene at room temperature.

oxygen: by using oxygen-saturated benzene, the same seven-line spectrum is observed but with much weaker intensity and with shorter half-life (~2 min). Furthermore, the formation of the radical is unaffected by the presence of either a hydrogen donor (e.g., 2-propanol) or a proton acceptor (e.g., *N,N,N′,N′*-tetramethyl-1,8-naphthalenediamine—"proton sponge"). The relative intensities of the seven lines are in the ratio 1:2:5:8:5:2:1, in agreement with a hyperfine splitting caused by two equivalent nuclei of spin $^1/_2$ (^{31}P, see later) with partially overlapping ^{195}Pt ($I = {}^1/_2$, abundance 33.7%) satellites. Careful inspection of the ESR spectrum in Figure 2a reveals a shoulder on each line indicating a further splitting into a doublet with a very small hyperfine coupling constant.[38] Replacement of the Pt(II) dihydride with the dideuteride removes this splitting without otherwise affecting the ESR spectrum. A computer-simulated spectrum using the values of a_{Pt}, a_P, and a_H given in Table XI is depicted in Figure 2b; the shapes and relative intensities of the lines are

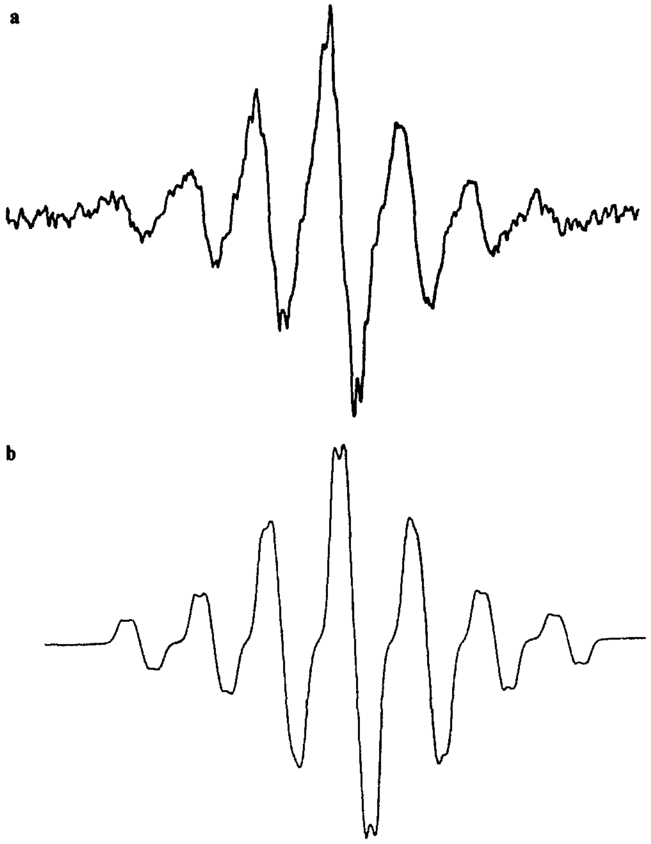

Figure 4. The ESR spectrum (a) observed and (b) simulated for *trans*-$PtH_2(PCy_3)_2$ with $DC{\equiv}CCOOCH_3$ in benzene at room temperature.

in excellent agreement with those of the observed spectrum.[39]

When in the platinum(II) dihydride, PCy_3 is replaced by P-*t*-Bu_2Me, a similar ESR spectrum but with different hyperfine splitting constants is observed. Thus, in the reaction with DMA, the spectrum now observed with *trans*-PtH_2(P-*t*-$Bu_2Me)_2$ shows less overlap between the ^{195}Pt satellite peaks and the main signal, so that all nine peaks are observable. The fact that changing the phosphine ligand affects the ESR signal implies that the observed radical is phosphine-containing and this, together with the analysis of each spectrum, requires each radical to contain two *equivalent* phosphine ligands. That the observed radical also contains the acetylene moiety is confirmed by the fact that the hyperfine splittings are dependent on the nature of the acetylene. Table XI gives values for a_{Pt}, a_P, and a_H for both different phosphine ligands and different acetylenes; in particular, note that the observed spectra with $HC{\equiv}CCOOCH_3$ and $C_6H_5{\equiv}CCF_3$ show additional hyperfine structure attributable to couplings with the terminal acetylenic hydrogen and with ^{19}F, respectively. Indeed, with methyl propiolate ($HC{\equiv}CCOOCH_3$), a 14-line spectrum was observed with $a_H = 3.9$ G; with $DC{\equiv}CCOOCH_3$, this becomes a seven-line spectrum with a small extra hyperfine splitting due to the deuterium,[40] $a_D = 0.16a_H$. Computer simulations of

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[38] In the ESR spectrum, a doublet will appear as a singlet with a shoulder, when the hyperfine splitting constant is similar to the line width. The shoulder observed here is correctly reproduced by using a line width of 1.0 G and the hyperfine splitting constant shown in Table IV.

[39] The calculated isotopic ratios ^{195}Pt ($I = {}^1/_2$):$^{194,196,198}Pt$ ($I = 0$) in the simulated spectra are in excellent agreement with the theoretical value of 33.8:66.2. Typically, a value of 33.85:66.15 was found for the radical $[HPt(PCy_3)_2DMA]^\bullet$.

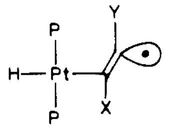
both spectra closely resemble the observed spectra (Figure 3 and 4).

In order to establish that the observed radicals are indeed produced from the reactions of the dihydrides with the various acetylenes, the following control experiments were performed: (a) No ESR signal was observed for any solution containing either a Pt(II) dihydride or an acetylene alone. (b) Although the ^{31}P NMR spectrum of, say, *trans*-$PtH_2(PCy_3)_2$ exhibits only one ^{31}P resonance, traces of an impurity which is not detectable in the NMR spectrum might be sufficient to produce a detectable ESR signal. Possible impurities which might be present in the synthesis of *trans*-$PtH_2(PCy_3)_2$ are $PtCl_2(PCy_3)_2$, $Pt(PCy_3)_2O_2$, and $Pt(PCy_3)_2CO_4$. Purified authentic samples of these three complexes were allowed to react with DMA under identical conditions, but no ESR signals were observed. Furthermore, $Pt(PCy_3)_2HCl$, $Pt(PPh_3)_4$, and *trans*-$Pt(PCy_3)_2H(DMA-H)$ were also tested with negative results. (c) No ESR signals were observed in similar experiments by using nonactivated acetylenes which do not react with *trans*-$PtH_2(PCy_3)_2$ (i.e., with diphenylacetylene or 2-butyne). (d) The use of different batches of the dihydride obtained in different preparations, including some using different methods,[41] and the use of different bottles of DMA, with samples either taken directly from the bottle or purified by passage through alumina followed by vacuum distillation, did not change the observed spectra.

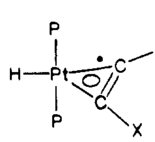
Since the radicals were observed under deaerated conditions, with the lifetime of the radical significantly decreased by the introduction of oxygen, it is most unlikely that they are peroxy radicals. The above results do, however, establish that the observed radicals are a genuine product of the reactions of Pt(II) dihydrides with activated acetylenes and that each radical contains one platinum, two equivalent phosphines, one hydride ligand, and an acetylene moiety. Importantly, the considerable stability of this radical ($t_{1/2} \sim 30$ min at room temperature) shows clearly that it cannot be the active intermediate of the insertion reaction itself for which $t_{1/2}$ (e.g., the reaction with DMA) is of the order of ms.

Since the ESR spectra indicate that the two phosphine ligands are equivalent, the unpaired electron of the radical cannot possibly be located on either of the phosphines. The only possible locations are then at platinum or in the acetylene moiety. Because of the very large spin-orbit coupling for the 5d metals, the spin-lattice relaxation times are usually very short.[40] Thus, it is unlikely that a platinum- centered radical could be observed at room temperature. Moreover, if the observed radical which we will formulate as $[PtH(PCy_3)_2DMA]$ is platinum-centered, it should be readily trapped by phenyl-*tert*-butylnitrone (PBN) to form a spin adduct.[6] When PBN was added to a benzene solution containing *trans*-$PtH_2(PCy_3)_2$ and 1 equiv of DMA, a slow decay of the ESR signal described above occurred over ca. a 2-h period, with the simultaneous growth of a new ESR spectrum. After 2 h, a clean six-line spectrum ($g = 2.0091$, $a_N = 14.2$ G, and $a_H = 2.9$ G) (2.e., a triplet of doublets) was observed, resulting from the expected α-N and β-H splittings. Thus, the formation of a PBN spin adduct occurs only at a rate which corresponds roughly to the observed rate of decomposition of the original radical, suggesting that PBN is just trapping decomposition products; this further emphasizes the considerable stability of the original radical. Certainly this establishes that the latter cannot be a single, platinum-centered radical which would be very rapidly trapped by PBN[6] to give a spin adduct showing ^{195}Pt hyperfine coupling.

Only two possible structures can be considered for the $[PtH(PCy_3)_2DMA]$ radical, a vinyl radical T, or a π-acetylene radical, U, of a type not previously observed. The following arguments provide persuasive evidence that the radical has structure U. (a) The stability of the observed radicals, some with $t_{1/2} \not< 30$ min,

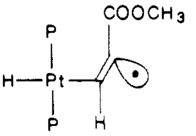


T



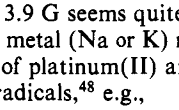
U

is far greater than would be expected for vinyl radicals. It can, of course, be argued that the steric bulk of the $[HPtP((Cy_3)_2]$ substituent group would impart "persistence"[42] to the resulting vinylic species; however, Ingold et al.[42] observed that vinyl radicals with two bulky Me_3Si substituents had half-lives of the order of 5–500 s and that three bulky substituents were necessary to give half-lives of hours. (b) PBN would trap any vinyl radical extremely rapidly, whereas we observe spin adduct formation occurring slowly as the original radical decomposes, i.e., trapping of the decomposition products. (c) A vinyl radical generated by addition to methyl propiolate would have[43] the structure V



V

and would have a value of a_H in excess of 50 G,[44] in contrast to our observed value of 3.9 G. (d) For a vinyl radical with the odd electron in a Csp^2 orbital, the g factor should have a value close to or smaller than the free spin value of 2.00232,[45] whereas our radicals give g values in excess of 2.005 (see Table IV). It is interesting to note that metal participation causes such increases in g factor values.[45] (e) In the reaction of *trans*-$PtH_2(PCy_3)_2$ with DMA in benzene, we always observe the Pt(0) complex, $(PCy_3)_2Pt(DMA)$, as a secondary product in about 5% yield. This might be readily formed from the π-acetylene radical U. (f) The ESR data, especially for the radical formed with methyl propiolate, are at least consistent with formation of the metallocycle ring required for D. Notably, the observed a_H value of 3.9 G can be compared to the a_H value[46] of 13.5 G for the cyclopropenyl radical, W. The latter also displays a g factor value of 2.0061 compared



W

with 2.0058 for our methyl propiolate derived radical. For the cyclopropenyl radical,[46] INDO calculations based on C_{2v} symmetry show a marked dependence of $a_{H2(\text{or } H3)}$ on the angle α, with a value of less than 4 G for $\alpha < 60°$. In our platinacycle radical, the C–Pt–C angles are markedly less than 60°,[47] so that our observed value of a_H of 3.9 G seems quite reasonable. (g) The electrochemical or alkali metal (Na or K) reduction of bipyridine cycloalkane derivatives of platinum(II) are thought to produce relatively stable anion radicals,[48] e.g.,

$$(bpy)PtCH_2CH_2CH_2 \xrightarrow{e^-} (bpy)PtCH_2CH_2CH_2$$

In such derivatives, because the ESR signal is very broad (11–14

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(40) Wertz, J. E.; Bolton, J. R. *Elementary Theory and Practical Applications of Electron Spin Resonance*; McGraw Hill: New York, 1972; p 63, 335.

(41) The dihydride can also be prepared by the reaction of $Pt(PCy_3)_2$ with H_2. Howard, J. A.; Spencer, J. L.; Store, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 3.

(42) Griller, D.; Cooper, J. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 4269.

(43) Reference 12, Vol. II, p 100–102.

(44) Iwasaki, M.; Eda, B. *J. Chem. Phys.* **1970**, *52*, 3837.

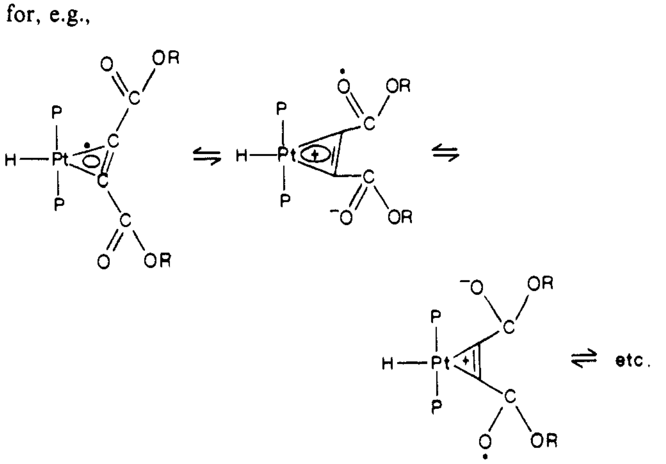
(45) Reference 12, Vol. II, p 453–4.

(46) Cirelli, G.; Graf, F.; Günthard, H. H. *Chem. Phys. Lett.* **1974**, *28*, 494.

(47) See, for example, Robertson, G. B.; Whimf, P. O. *J. Am. Chem. Soc.* **1975**, *97*, 1051.

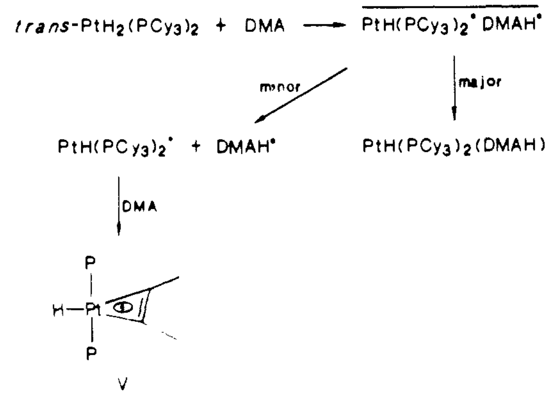
(48) Klinger, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147.

G), no additional hyperfine splitting was resolved except in some cases where an additional pair of lines was assigned to ^{195}Pt splitting (14–60 G). The g values were in the range 1.98–1.996. If in the structure U proposed above the unpaired electron is to some degree delocalized also over the carboalkoxyl group, the observed high g values and lower ^{195}Pt splittings can be accounted for, e.g.,



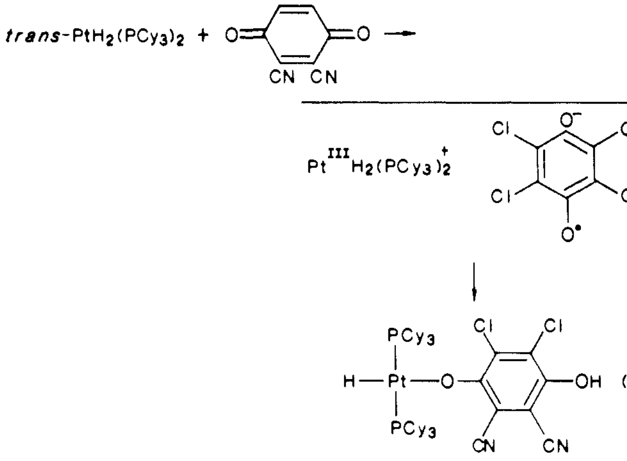
The overall evidence, therefore, and particularly the ESR parameters convincingly argue that the observed radicals have structure U and that they constitute the first example of such unsaturated metallacycle radicals to be observed.

Although this radical is a secondary product and does not participate directly in the insertion process, it remains to explain its formation in these reactions. We postulate that the observed radical arises from the caged radical pair $\overline{\mathrm{PtH(PCy_3)_2{}^{\bullet}DMAH^{\bullet}}}$ (IV above). The radical $\mathrm{HPt(PCy_3)_2{}^{\bullet}}$, after escaping from the cage, can then be scavenged by another molecule of acetylene to give V. In simplified format, leaving aside details of the electron- and proton-transfer process, the overall reaction can then be described as follows



Finally, with regard to mechanism, these proposals require the ready participation of the Pt(II) dihydride in an electron-transfer process; no direct evidence has yet been presented that such participation is likely. We initially considered that the observance at low temperature of a charge-transfer absorption at 515 nm provided such direct evidence for a charge-transfer insertion mechanism. If, however, the rate constant derived from the kinetic data is applied to the reaction of DMA with *trans*-$\mathrm{PtH_2(PCy_3)_2}$ at known concentration, it can be readily calculated that the reaction is 99% complete with 0.4 s. Since the absorption at 515 nm has a half-life considerably in excess of this, and, indeed, since the rate of decay of this absorption is approximately of the same order of magnitude as the decay of the ESR signal, we conclude that this 515-nm absorption is characteristic of the radical U. The most direct evidence for the participation by Pt(II) dihydrides in an electron-transfer process, therefore, comes from the reaction of *trans*-$\mathrm{PtH_2(PCy_3)_2}$ with dichlorodicyanoquinone. This reaction in $\mathrm{C_6D_6}$, initiated with a stoichiometric excess of the dihydride, is characterized by the immediate appearance of an intense dark green color which fades to yellow over 4–5 min. This is accompanied by the appearance in the ^{1}H NMR spectrum of a new hydride resonance at δ −17.7 ppm [J(PtH) = 1159 Hz]. As more of the quinone is added stepwise, this cycle of appearance of the dark green color which then rapidly fades is repeated, until with molar equivalents of dihydride and quinone, the original dihydride resonance at δ −3.0 has completely diasppeared, and only the new resonance at δ −17.7 remains. This value established that the product cannot be *trans*-$\mathrm{PtHCl(PCy_3)_2}$ (δ −17.95, J(PtH) 1270), nor does it correspond to a product containing σ-C trans to H. The data are, however, consistent with those of comparable phenoxy derivatives:[49] *trans*-$\mathrm{PtH(PCy_3)_2(OC_6H_5)}$ δ −16.7 and *trans*-$\mathrm{PtH(PCy_3)_2(OC_6F_5)}$ δ −24.86.

The ESR spectrum of a benzene solution containing equimolar amounts of dihydride and the quinone consisted of a single broad (3G) line, as might be expected for a quinone radical anion; the ESR signal decayed at approximately the same rate as the intensity of the dark green coloration. It is reasonable to conclude, therefore, that the overall reaction can be described by eq 6, illustrating clearly the participation of the dihydride in an electron-transfer process.



(6)

There is thus an interesting transition from the Pt(II) monohydrides to the corresponding dihydrides. The former undergo facile insertion reactions with olefins and acetylenes involving a four-centered cyclic transition state,[50,51] although under appropriate solvent conditions a slower radical chain process may occur. The dihydrides, on the other hand, while undergoing similarly facile insertion reactions, apparently do so through electron-transfer processes. The cause of this different behavior presumably lies in the different charge distributions in the mono- and dihydrides. By using ab initio molecular orbital theory, Noell and Hay[52] calculated the distribution of charge in the species *trans*-$\mathrm{PtCl_2(PH_3)_2}$, *trans*-$\mathrm{PtHCl(PH_3)_2}$, and *trans*-$\mathrm{PtH_2(PH_3)_2}$; within this series, the charge on Pt decreases from +1.18 for the dichloride to +1.01 for the dihydride, the charge on phosphorus becomes somewhat more negative (from +0.17 to +0.06 to −0.01), but most significantly the charge on H in the monohydride is −0.28 but 0.50 in the dihydride. Moreover, the hydrogen is markedly more anionic in the trans isomer of the dihydride compared with the cis, while the difference between trans and cis isomers of the monohydride is much less. Certainly these calculations indicate a markedly more anionic character for the hydride ligand in the dihydride than in the monohydride. It seems reasonable, then, that the dihydride should preferentially react through charge-transfer processes, although of course steric effects may also well play a role.

Finally, there remains the question as to why the remaining Pt–H bond of the alkenyl products, formed from the dihydride

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(49) Forries, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006.
(50) Thom, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.
(51) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.
(52) Noell, J. A.; Hay, P. J. *Inorg. Chem.* **1982**, *21*, 14.

and acetylenes, should itself be unreactive toward further insertion of acetylene. Such behavior is not uncommon; most studies with dihydrides have similarly reported insertion into only one M–H bond, for example, the work of Otsuka et al.[1,2,53] with the dihydrides Cp_2MH_2, M = Mo or W.

More recently, however, it has been pointed out[54] that insertion into both M–H bonds of these hydrides can be observed with alkynes of low steric hindrance. Clearly, with the Pt(II) dihydrides used in our investigations, steric effects must be particularly important. The stereochemistry of tricyclohexylphosphine Pt(II) complexes will be discussed in detail elsewhere, and it is sufficient here to point out that the tricyclohexylphosphine behaves like a bulky conic cog, with cone angle[55] values determined from crystal structure studies in the range 163–181°.[56] It is also likely that in the monoalkenyl product, the P–Pt–P angle containing the second hydride ligand will be less than 180°; in the hydridoalkenyl product described here and containing the P-*t*-Bu_2-*n*-Bu ligand of comparable size, this angle is 163.5 (1)°. The second hydride ligand is, therefore, essentially "lined" and protected by the two cis tricyclohexyl phosphines; its lack of reactivity toward alkyne insertion is then attributed entirely to steric effects.

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Registry No. DMA, 762-42-5; *trans*-PtH(*trans*-$CH_3OOCC{=}CHCOOCH_3)(PCy_3)_2$, 104215-64-7; *trans*-PtH(*trans*-$CF_3C{=}CHCF_3)(PCy_3)_2$, 104215-65-8; *trans*-PtH(*trans*-$CH_3OOC{=}CHCH_3)(PCy_3)_2$, 104215-66-9; *trans*-PtH(*trans*-$CH_3OOC{=}CHPh)(PCy_3)_2$, 104215-67-0; *trans*-PtH(*trans*-$NCC{=}CHCH_3)(PCy_3)_2$, 104215-68-1; *trans*-PtH(*trans*-$NCC{=}CHPh)(PCy_3)_2$, 104215-69-2; *trans*-PtH(*trans*-$CF_3C{=}CHPh)(PCy_3)_2$, 104215-70-5; *trans*-PtH($CH_3OOCC{=}CH_2)(PCy_3)_2$, 104215-71-6; *trans*-PtH($NCC{=}CH_2)(PCy_3)_2$, 104215-72-7; *trans*-PtH($CF_3C{=}CH_2)(PCy_3)_2$, 104215-73-8; *trans*-PtH($CH_2{=}CHCH_2OOCC{=}CH_2)(PCy_3)_2$, 104215-74-9; *trans*-PtH($CH{\equiv}CCH_2OOCC{=}CH_2)(PCy_3)_2$, 104215-75-0; *trans*-PtH(*trans*-(4-$O_2NC_6H_4)C{=}CHPh)(PCy_3)_2$, 104240-24-6; *trans*-PtH(*trans*-$CH_3OOCC{=}CHCOOCH_3$)(P-*i*-$Pr_3)_2$, 104215-76-1; *trans*-PtH(*trans*-$CF_3C{=}CHCF_3$)(P-*i*-$Pr_3)_2$, 104215-77-2; *trans*-PtH(*trans*-$CH_3OOCC{=}CHCOOCH_3$)(P-*t*-Bu_2-*n*-Bu), 104215-58-9; *trans*-PtH(*trans*-$CF_3C{=}CHCF_3$)(P-*t*-Bu_2-*n*-$Bu)_2$, 104215-59-0; *trans*-PtH(*trans*-$CH_3OOCC{=}CHCOOCH_3$)(P-*t*-$Bu_2Me)_2$, 104215-60-3; *trans*-PtH(*trans*-$CF_3C{=}CHCF_3$)(P-*t*-$Bu_2Me)_2$, 104215-61-4; *trans*-$PtD_2(PCy_3)_2$, 104215-62-5; *trans*-$PtCl_2(PCy_3)_2$, 60158-99-8; *cis*-$Pt(PEt_3)_2Cl$(*trans*-$CH_3OOCC{=}CHCOOCH_3$), 65059-02-1; *trans*-$Pt(PEt_3)_2Cl$(*cis*-$CH_3OOCC{=}CHCOOCH_3$), 65059-01-0; *trans*-$Pt(PEt_3)_2Cl$(*trans*-$CH_3OOCC{=}CHCOOCH_3$), 65059-03-2; *cis*-$Pt(PEt_3)_2Cl$(*cis*-$CH_3OOCC{=}CHCOOCH_3$), 57127-81-8; *trans*-$PtH(PCy_3)_2$(DMA), 104240-19-9; *trans*-$PtH(PCy_3)_2(HC{\equiv}CCOOCH_3)$, 104240-20-2; *trans*-$PtH(PCy_3)_2(DC{\equiv}CCOOCH_3)$, 104240-21-3; *trans*-$PtH(PCy_3)_2(C_6H_5C{\equiv}CCOOCH_3)$, 104240-22-4; *trans*-$PtH(PCy_3)_2(C_6H_5C{\equiv}CCF_3)$, 104240-23-5; *trans*-PtH(P-*t*-$Bu_2Me)_2(CH_3OOCC{\equiv}CCOOCH_3)$, 104215-63-6; PCy_3, 2622-14-2; P-*i*-Pr_3, 6476-36-4; *p*-*t*-Bu_2-*n*-Bu, 29949-72-2; P-*t*-Bu_2Me, 6002-40-0; $CF_3C{\equiv}CCF_3$, 692-50-2; $CH_3C{\equiv}CCOOCH_3$, 23326-27-4; $C_6H_5C{\equiv}CCOOCH_3$, 4891-38-7; $CH_3C{\equiv}CCN$, 13752-78-8; C_6H_5-$C{\equiv}CCN$, 935-02-4; $C_6H_5C{\equiv}CCF_3$, 772-62-3; $HC{\equiv}CCOOCH_3$, 922-67-8; $HC{\equiv}CCN$, 1070-71-9; $HC{\equiv}CCF_3$, 661-54-1; $HC{\equiv}CCOOCH_2CH{=}CH_2$, 14447-00-8; $C_6H_5C{\equiv}C$(*p*-$C_6H_4NO_2$), 1942-30-9; $HC{\equiv}CCOOCH_2C{\equiv}CH$, 4383-39-5; D_2, 7782-39-0.

Supplementary Material Available: A listing of calculated hydrogen coordinates, thermal parameters, and bond angles (6 pages); tables of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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Comparison of the Photochemical and Photophysical Properties of Clays, Pillared Clays, and Zeolites[†]

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Abstract: Uranyl-containing pillared clays, uranyl-exchanged clays, and zeolites have been used to photooxidize solutions of ethanol and diethyl ether. Product analysis indicates that uranyl ions in the clay pillars produce a more selective catalyst than materials obtained by inserting uranyl ion in the interlamellar spacings of the clay. Mechanisms are proposed to distinguish reactivity and selectivity differences of these photocatalysts. Incorporation of uranyl ions does not significantly affect the cracking properties of pillared clay catalysts.

I. Introduction

Photochemical methods,[1-11] such as luminescence excitation, emission, and lifetime experiments on organic[1-4] and inorganic dopants,[3,5-10] have been proven useful in understanding processes that occur during electron transfer,[8] energy transfer[9,10] and photoassisted catalysis on solid surfaces.[2,3,7] Luminescence can provide information concerning excited-state species that occur on aluminosilicate surfaces and changes that these species undergo

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