shift data much better when we reverse the methyl assignments, Table I. This assignment is, however, clearly incorrect, and we must conclude that the apparent success, which many pseudocontact shift calculations have had, needs to be viewed with caution.

Table I. $Eu(dpm)_3$ Induced Shifts for Sulfoxide **1** in $CDCl_3$

	Protons				
	H_{cis}	H_{trans}	Me	Me	R,[c] %
Observed shifts	236	137	79	64	
Correct assignment[a]	222	138	77 (trans)	78 (cis)	6.21
Incorrect assignment[b]	234	133	83 (cis)	66 (trans)	2.25

[a] For the unshifted spectra δ[12,15] $H_{trans} > H_{cis} > Me_{cis} > Me_{trans}$ while for spectra with $[Eu(dpm)_3]/[\mathbf{1}] > 0.15$ $\delta H_{cis} > H_{trans} > Me_{trans} > Me_{cis}$. [b] The methyl assignments are the reverse of the above. [c] R^2 = (calculated shift − observed shift)^2/(observed shift)^2; R(%) = $100R$; calculated for the equatorial-oxygen conformation.[17]

(17) Since in solution **1** is known to exist in the equatorial-oxygen conformation,[12] and since this also is the conformation of the sulfoxide ring in the $Eu(dpm)_3$ adduct, we used the X-ray determined coordinates for these calculations. Fits with either assignment using a planar ring or a combination of equatorial and axial conformations were considerably poorer.

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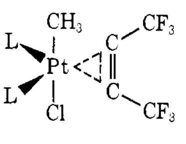
Mechanism of the Insertion of an Acetylene into a Methylplatinum(II) Bond

Sir:

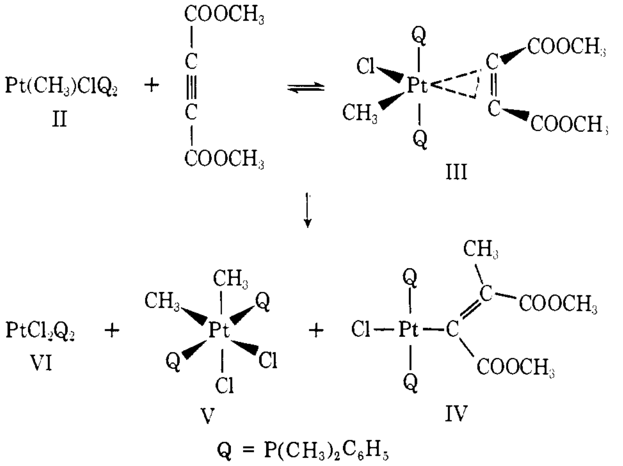
Initial coordination of an unsaturated molecule followed by insertion into a metal–hydrogen or metal–carbon bond is believed to form the basis of most metal-catalyzed hydrogenation and polymerization reactions of olefins and acetylenes.[1,2] The 1:1 adducts $PtCl(CH_3)(CF_3C{\equiv}CCF_3)L_2$, I,[3-6] where L = a *tert*-phosphine or arsine, formed in the methylplatinum insertion reaction of $CF_3C{\equiv}CCF_3$ with *trans*-$PtCl(CH_3)L_2$, present a rare[7] example of the isolation of a π intermediate.



However, further reaction of I in benzene led, in addition to the insertion product *trans*-$PtCl\{CCF_3{=}C(CH_3)CF_3\}L_2$ expected from an intramolecular rearrangement of I, to the formation of $Pt(CF_3C{\equiv}CCF_3)L_2$ and $PtCl_2(CH_3)_2L_2$.[4,5] The role played by the π complex I in these reactions remained uncertain.

We have now studied an analogous reaction between dimethyl acetylenedicarboxylate, $CH_3OOCC{\equiv}CCOOCH_3$, and *trans*-$PtCl(CH_3)\{P(CH_3)_2C_6H_5\}_2$, II, in chloroform. Contrary to our expectations, we find that insertion into the platinum–methyl bond to give $PtCl\{CCOOCH_3{=}C(CH_3)COOCH_3\}\{P(CH_3)_2C_6H_5\}_2$, IV, does not proceed by a simple intramolecular rearrangement of the 1:1 adduct $PtCl(CH_3)(CH_3OOCC{\equiv}CCOOCH_3)\{P(CH_3)_2C_6H_5\}_2$, III, but rather by a free-radical mechanism involving both II and III. Other products from this reaction are $Pt(CH_3)_2Cl_2\{P(CH_3)_2C_6H_5\}_2$, V, and $PtCl_2\{P(CH_3)_2C_6H_5\}_2$, VI (see Scheme I).[8]

Scheme I



We find that the reaction is very dependent on the particular sample of II. For some samples reaction proceeded as above (see Figure 1), but for others only the π complex III was formed, no insertion or disproportionation occurring over several weeks. Furthermore, addition of an "unreactive" solution to a "reactive" one immediately stopped the insertion and "disproportionation" reactions. On the other hand, these reactions occurred after addition of a small amount of the free-radical initiator $C_6H_5COO_2OCC_6H_5$ to an "unreactive" solution. This is illustrated in Figure 2 for an "unreactive" sample of II. These findings clearly show that the reaction proceeds by a free-radical mechanism. "Unreactive" samples of II must contain a trace of a radical scavenger (whose nature is unknown and which could not be removed by chromatography or recrystallization).

These reactions were followed by nmr spectroscopy (100 MHz). For a given concentration of radical initiator, the results are consistent with the rate law (1) for insertion.

$$\frac{d[\text{insertion}]}{dt} = k_{\text{ins}}[\text{PtClMeQ}_2][\text{PtClMeQ}_2(\text{acetylene})] \qquad (1)$$

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(1) M. L. H. Green, "Organometallic Compounds," Vol. 11, Methuen, London, 1968, p 312.

(2) L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Polymer Reviews 12, Interscience, New York, N. Y., 1966.

(3) H. C. Clark and R. J. Puddephatt, *Chem. Commun.*, 92 (1970).

(4) H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **9**, 2670 (1970).

(5) H. C. Clark and R. J. Puddephatt, *ibid.*, **10**, 18 (1971).

(6) B. R. Davies, N. C. Payne, and R. J. Puddephatt, *Can. J. Chem.*, **50**, 2276 (1972).

(7) For related π-coordinated intermediates, see H. A. Tayim and J. C. Bailar, *J. Amer. Chem. Soc.*, **89**, 4330 (1967), and W. H. Bradley and M. S. Frazer, *ibid.*, **91**, 3661 (1969).

(8) The stereochemistry of III (as shown in Scheme I) is deduced from the phosphinemethyl proton resonances of II which appear as overlapping triplets showing (i) the presence of mutually *trans*-phosphine ligands and (ii) the absence of a plane of symmetry within the P–Pt–P axis. Furthermore, we observed two well-separated methoxy proton resonances in III.

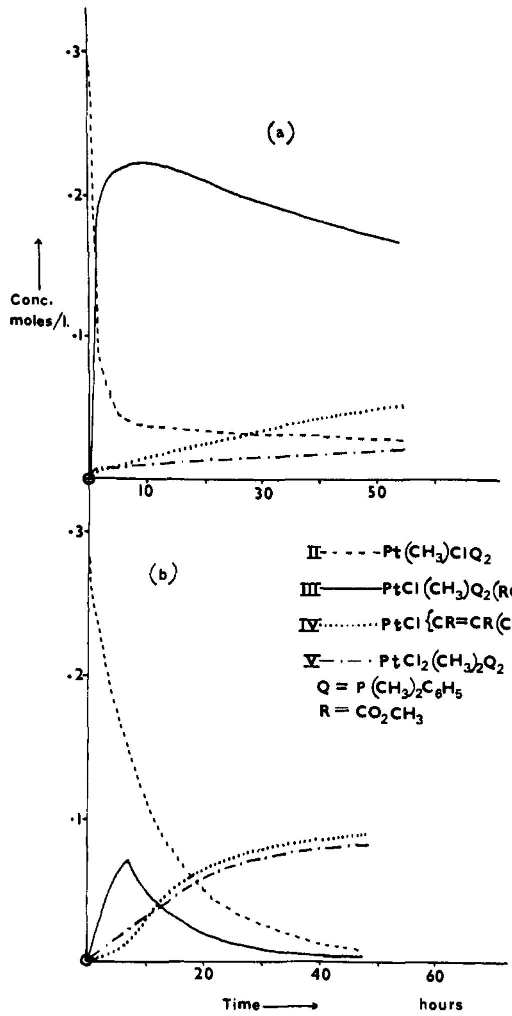

Figure 1. Plot of concentrations of reactants in $CHCl_3$ with time for initial ratio of $CH_3O_2CC{\equiv}CCO_2CH_3$/"reactive" $PtCl(CH_3)Q_2$ = 4.8 (a) and 0.65 (b).

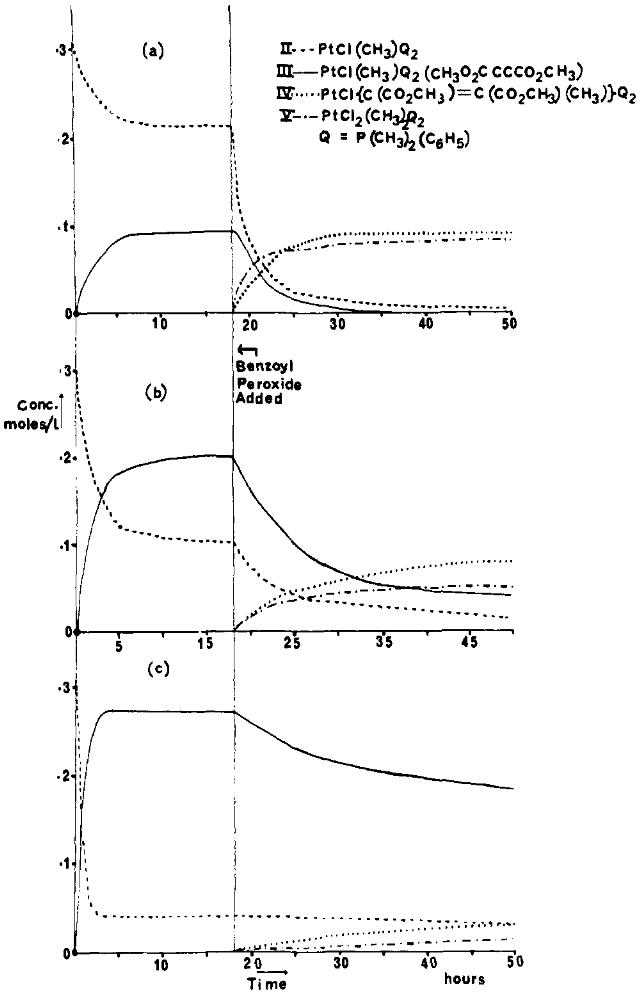

Figure 2. Plot of concentrations of reactants in $CHCl_3$ with time for initial ratio of $CH_3O_2CC{\equiv}CCO_2CH_3$/"unreactive" $PtCl(CH_3)Q_2$ = 7 (a), 2.2 (b), and 0.56 (c). Benzoyl peroxide (0.0093 g) in $CHCl_3$ was added to the solutions after 18 hr.

Chloroform solutions of II, on the addition of a radical initiator or on ultraviolet irradiation, undergo a free-radical reaction in the absence of acetylene to give $PtCl_2Me_2Q_2$ and $PtCl_2Q_2$. Our kinetic data suggest that in the presence of acetylene, the formation of the Pt(IV) compound from II follows the rate law (2).

$$\frac{d[PtCl_2Me_2Q_2]}{dt} = k_{1_{\mathrm{diff}}}[PtClMeQ_2]^2 + k_{2_{\mathrm{diff}}}[PtClMeQ_2][PtClMeQ_2(\text{acetylene})] \quad (2)$$

A consequence of these rate laws, and of the relatively large equilibrium constant for formation of III (K = 5.2 mol^{-1} l.), is that these reactions are hindered by a large initial ratio of acetylene to II, as illustrated by Figures 1 and 2. The results are consistent with a reaction sequence, in which the formation of the radical $[\dot{P}t(CH_3)Q_2]$ from II plays a vital role. This clearly requires reaction of this radical with the π complex III according to (3) followed by rearrangement of the resulting radical to give the insertion product. Significantly, the Pt–Cl bond in III must be less susceptible toward homolytic fission than that in II. As implied from our observations, the reaction is solvent dependent. Different reactions occur in other solvents; for example, in acetone π complex is formed and very little insertion occurs at high concentrations while at lower concentrations slow insertion is favored *via* a cationic mechanism.[9] Similar behavior occurs in methanol at high concentrations while in more dilute solutions the methyl vinyl ether derivative is formed.[10] In benzene neither insertion nor π-complex formation is observed, while in methylene chloride π-complex formation and insertion takes place together with a more complex reaction. Clearly chloroform is particularly efficient in propagating the insertion reaction; these solvent effects are being further investigated.

$$[\dot{P}t(CH_3)Q_2] + Pt(CH_3)Q_2Cl(RC{\equiv}CR) \longrightarrow \dot{P}t(CH_3)Q_2(RC{\equiv}CR) + Pt(CH_3)Q_2Cl \quad (3)$$

It is clear from these results that insertion into a metal–carbon bond does not necessarily proceed *via* a simple intramolecular rearrangement of 5-coordinate π complexes similar to I and III. Indeed, all our observations show that acetylenes are activated toward (i) Pt–C insertion, (ii) rearrangements, and (iii) nucleophilic attack by coordination to a relatively electron-deficient metal as in $[PtX(RC{\equiv}CR')L_2]^+$ [9] and [$\dot{P}$t-

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(9) M. H. Chisholm, H. C. Clark, and D. H. Hunter, *Chem. Commun.*, 809 (1971), and M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, **94**, 1532 (1972), and references cited therein.

(10) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **10**, 2557 (1971).

$CH_3(RC{\equiv}CR')L_2]$ and deactivated toward these reactions by coordination to a relatively electron-rich metal such as I and III.

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Can Molecular Conformation Control Photochemical Behavior?[1]

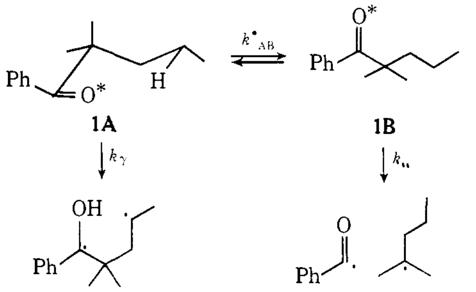
Sir:

The effect of ground-state conformation on photochemical reactivity[2,3] and product composition[4] is a topic of considerable current interest. When two conformers can give rise to different photoproducts (eq 1),

$$\begin{tikzcd}
 & A \arrow[r, shift left, "k_{AB}"] \arrow[d, "h\nu"] & B \arrow[l, shift left] \arrow[d, "h\nu"] & \\
X & A^* \arrow[l, "k_A"'] \arrow[r, shift left, "k^*_{AB}"] & B^* \arrow[l, shift left] \arrow[r, "k_B"] & Y
\end{tikzcd} \qquad (1)$$

two limiting cases should be possible. In case I the energy barrier for excited state conformational isomerization[5] is *lower* than the activation energies for formation of X or Y ($k^*_{AB} \gg k_A, k_B$). In this case the ratio of products will depend on the difference in energy for the transition states leading to X and Y (Curtin–Hammett principle[6]) and the lifetimes of both excited state conformers will be the same ($\tau^*_A = \tau^*_B = (k_A + k_B)^{-1}$).[7] In case II the energy barrier for excited state conformational isomerization is *higher* than the activation energy for formation of X or Y ($k^*_{AB} \ll k_A, k_B$). In this case the ratio of products depends upon the relative population of A* and B* and the lifetimes of the excited state conformers need not be the same ($\tau^*_A = k_A^{-1}$, $\tau^*_B = k_B^{-1}$). Since electronic excitation is much faster than nuclear motion (Franck–Condon principle[8]), the initial population of A* and B* will be determined by ground-state conformational populations and extinction coefficients. We wish to present the first quantitative evidence that both case I and case II do occur.

We[2,9] and Wagner and McGrath[10] recently reported that *tert*-alkyl phenyl ketones such as α,α-dimethylvalerophenone (**1**) undergo competitive photochemical α cleavage and γ-hydrogen abstraction (eq 2). γ-Hydrogen abstraction requires a six-membered transition state (**1A**), whereas α cleavage should occur from all conformations (**1A**, **1B**, etc.).[11,12] Since bond rotations for acyclic compounds ($k^*_{AB} \geq 10^{10}$ sec^{-1}) are much more rapid than k_γ for valerophenone (**2**) or k_α for pivalophenone (**3**) (Table I),[13] ketone **1** should provide an example of case I. That this is indeed the case is shown by the observations that (a) Stern–Volmer plots ($\Phi_0/\Phi = 1 + k_q\tau[Q]$) for quenching α cleavage and γ-hydrogen abstraction products have identical slopes ($\tau^*_A = \tau^*_B$) and (b) the ratio of products is roughly similar to the ratio of rate constants for the model compounds **2** and **3**.[9,10,16]



(2)

Table I. Quantum Yields and Kinetic Data[a]

Ketone	Φ_α[b]	Φ_γ[c]	$k_q\tau$,[d] M^{-1}	$1/\tau$[e] $\times 10^{-8}$ sec^{-1}
1[f]	0.06	0.11 0.45[g]	44	1.1
2[f]		0.42	36	1.4
3[f]	0.30		447	0.11
4	0.03	0.19	380[h,i]	0.13[h,i]
5	0.20	0.045	200[h]	0.25[h]
		0.21[j]	29[i]	1.7[i]

[a] Benzophenone–benzhydrol actinometry with 313- or 365-nm irradiation. [b] Quantum yield for benzaldehyde formation in degassed benzene containing 10^{-2} M dodecanethiol. [c] Total quantum yield for photocyclization and elimination products in degassed benzene. [d] Slope of linear Stern–Volmer plots for naphthalene quenching using 365-nm irradiation. [e] Calculated assuming $k_q = 5 \times 10^9$ M^{-1} sec^{-1}. [f] Values from ref 9. [g] Value from ref 10 for 1-propanol solvent. [h] Values for quenching of benzaldehyde formation. [i] Values for quenching bicyclic alcohol formation. [j] Value for 1-propanol solvent.

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(1) The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and PPG Industries for support of this research.

(2) F. D. Lewis, R. W. Johnson, and R. A. Ruden, *J. Amer. Chem. Soc.*, **94**, 4292 (1972).

(3) A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969).

(4) (a) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *ibid.*, **87**, 3406 (1965); (b) J. E. Baldwin and S. M. Kruger, *ibid.*, **91**, 6444 (1969); (c) C. W. Spangler and R. P. Hennis, *J. Chem. Soc., Chem. Commun.*, 24 (1972); (d) W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, and P. H. Wendschuh, *J. Amer. Chem. Soc.*, **94**, 4285 (1972); (e) R. M. Moriarty and R. C. Reardon, *Tetrahedron*, 1379 (1970).

(5) Ground- and excited-state energy barriers for conformational isomerization need not be the same. For the systems studied electronic excitation should not have a large effect on conformational mobility ($k_{AB} \approx k^*_{AB}$). This is probably not the case when the chromophore is part of the conformationally mobile system (*cf.* ref 4).

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 151, 237.

(7) Other excited state processes including nonradiative decay are neglected for the purposes of clarity and simplicity.

(8) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 30.

(9) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **94**, 3852 (1972).

(10) P. J. Wagner and J. M. McGrath, *ibid.*, **94**, 3849 (1972).

(11) Since γ-hydrogen abstraction from a secondary alkyl center is approximately ten times more rapid than α cleavage of *tert*-alkyl phenyl ketones,[9,10] the simplifying assumption that $k_\gamma > k_\alpha$ when γ-hydrogen abstraction is geometrically feasible will be made.

(12) Walling and Padwa have suggested that the analogous intramolecular hydrogen abstraction and β-cleavage reactions of alkoxy radicals might be faster than alkyl side-chain conformation changes: C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1597 (1963).

(13) The energy barrier for alkane bond rotation which does not involve alkyl–alkyl eclipsing is ~3.4 kcal/mol.[14] The Arrhenius activation energy for valerophenone γ-hydrogen abstraction is 5–6 kcal/mol.[15] The activation energy for α cleavage of pivalophenone has not been measured, but probably is slightly larger than that for valerophenone γ-hydrogen abstraction.[9]

(14) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 9.

(15) (a) J. C. Scaiano, J. Grotewold, and C. M. Previtali, *Chem. Commun.*, 390 (1972); (b) F. D. Lewis, *Mol. Photochem.*, in press.

(16) Both biradical and radical pair intermediates can revert to ground-state ketone.[2,9,10] Addition of alcohols to the solvent often increases biradical product quantum yields.[10] We have recently observed ~50% cage recombination following α cleavage of an optically active alkyl phenyl ketone (F. D. Lewis and J. G. Magyar, unpublished results). Further discussion of this topic will be deferred to our full paper.