These data would seem to indicate that kinetic isotope effects can show the theoretically expected dependence on transition-state structure when the latter is measured by relative reactivity provided that comparison is restricted to a single reaction type. In the present case, this is proton addition to a carbon–carbon double bond activated by a single oxygen atom; protonation of an aromatic ring, a triple bond, or even a double bond bearing other heteroatoms is a sufficiently different process to upset the expected correlation. Each of these other reactions would presumably show a correlation of its own between isotope effect and relative reactivity, but at the present time there are insufficient data to determine whether or not this is so.

N-morpholino-1-isobutylene,[19] cyanoketene dimethyl acetal,[20] dimethylketene dimethyl acetal,[21] and methylbromoketene diethyl acetal[21]) and carbon–carbon triple bonds (ethylthioethyne,[22] 1-ethylthio-3-hydroxy-3-methyl-1-butyne,[23] and 1-(*cis*-propenyloxy)-1-propyne[24]); the hydrolysis of 2-ethoxy-1-cyclopentene-1-carboxylic acid[25] and its anion;[25] the deiodination of 2,4,6-trimethoxyiodobenzene;[26] and the protonation of 1,3,5-trimethoxybenzene.[27]

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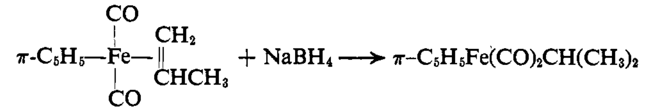
Nuclear Magnetic Resonance Evidence for $\pi \rightarrow \sigma$ Ligand Conversion in Platinum(II) Complexes

Sir:

The catalytic conversion of olefins to functionalized derivatives, *e.g.*, ethylene to acetaldehyde,[1] as well as other olefin reactions carried out in the presence of transition metal complexes, are assumed to all involve olefin coordination *via* a π complex followed by rearrangement to a σ-alkyl complex. The reaction of this type which has received most investigation as to mechanism is the insertion of olefins into metal–hydrogen bonds.[2]

$$RCH{=}CH_2 + M\text{—}H \rightleftharpoons R\text{—}CH_2\text{—}CH_2\text{-}CH_2M$$

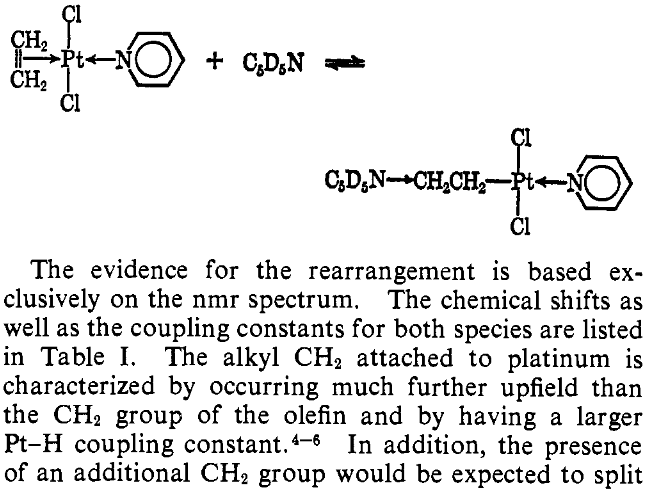
Although the indicated direction of addition is probably the preferred one, and when R and other ligands are large may be the exclusive one,[2] Markovnikov addition followed by elimination of MH is a commonly accepted explanation for transition metal catalysis of olefin isomerization. In the many examples of such isomerization where the hydride cannot be shown to be present as such, it is postulated to be the intermediate. In one important example,[3] a hydride is added externally to the olefin complex to secure the $\pi \rightarrow \sigma$ conversion.



$$\pi\text{-}C_5H_5\text{—}\overset{CO}{\underset{CO}{Fe}}\text{—}\underset{CHCH_3}{\overset{CH_2}{\|}} + NaBH_4 \longrightarrow \pi\text{-}C_5H_5Fe(CO)_2CH(CH_3)_2$$

Although the sequence of steps in the $\pi \rightarrow \sigma$ conversion remains unsettled because intermediates have not been isolated, it is likely that nucleophilic (or hydride) attack occurs on the π complex just prior to the $\pi \rightarrow \sigma$ rearrangement.

We now wish to report that we have secured nmr evidence for the formation of an unstable σ complex at $-50°$ resulting from $\pi \rightarrow \sigma$ rearrangement. The unstable compound is formed when deuterated pyridine is added to a chloroform solution of 1,3-dichloro-2-ethylene-4-pyridineplatinum(II).



The evidence for the rearrangement is based exclusively on the nmr spectrum. The chemical shifts as well as the coupling constants for both species are listed in Table I. The alkyl CH_2 attached to platinum is characterized by occurring much further upfield than the CH_2 group of the olefin and by having a larger Pt-H coupling constant.[4–6] In addition, the presence of an additional CH_2 group would be expected to split the original resonance peak into a triplet and this is observed (Figure 1). The second triplet (not shown) of the CH_2 group attached to pyridine is partially buried in the resonance peak due to platinum–hydrogen coupling in ethylene and can be observed by care-

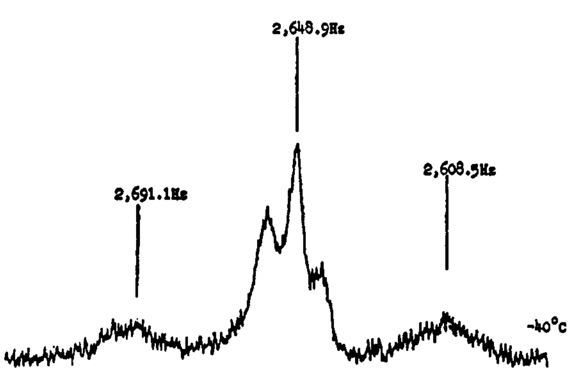


Figure 1. Nmr spectrum of σ complex.

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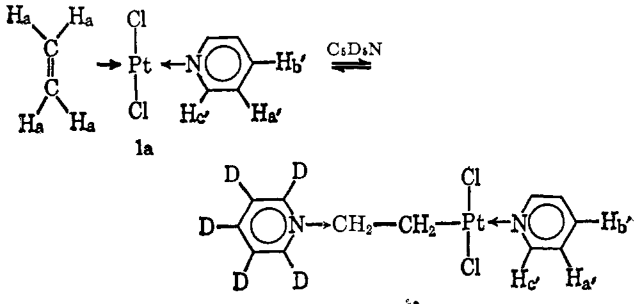
fully varying the temperature to change its chemical shift. The values given here, δ_{CH_2-Pt} = 2.44 ppm and J_{Pt-CH_2} = 83.4 cps, J_{H-H} = 7.1 cps, compare favorably with those for $(CH_3CH_2)_3PtI$, δ_{CH_2-Pt} = 2.23 ppm, J_{Pt-CH_2} = 86.0 cps, J_{H-H} = 7.5 cps;[4] and for those of $Pt(C_3H_5)_2$ at −20°, where δ_{CH_2-Pt} = 2.26 ppm and J_{Pt-CH_2} = 83 cps.[5] Both our triplets display a small deviation from symmetry in the spectra determined over the temperature range −35 to −50°; the spacing between adjacent peak maxima differs by about 0.5 cps. This asymmetry is considered to indicate an AA′XX′ system rather than an A_2X_2 system,[6] possibly because bulky groups on the carbons hinder rotation about the methylene–methylene bond at these low temperatures.

Table I. Chemical Shifts[a] and Coupling Constants[b] (−40°)



1a

1b

Nmr spectrum of **1a**	π complex[c]	Complex plus base[c]	Free base[c]
δ_{H_a}	4.87	4.81	
$\delta_{H_{a'}}$	7.525	7.89	7.36
$\delta_{H_{b'}}$	7.96	7.775	7.76
$\delta_{H_{c'}}$	8.855	8.69	8.69
$J_{Pt^{195}-H^1_a}$	60.6	60.5	
$J_{Pt^{195}-H^1_{c'}}$	35.6	None	
δ_{CH_2-Pt}		2.44	
$J_{Pt^{195}-H^1}$		83.4	
δ_{CH_2-N}		4.55	
$J_{H_1-H_2}$		7.1[d]	

[a] All chemical shifts are given in parts per million from tetramethylsilane (TMS) as an external reference; coupling constants are given in cycles per second. The internal reference was $CHCl_3$. [b] The coupling constants are given in cycles per second. [c] The solutions were prepared in a 10% w/w solute:solvent ratio. The D_5-pyridine was added in approximately a 4:1 ratio of base to complex. [d] The coupling constant between vicinal hydrogens is an average value, since there is some variation in magnitude with temperature.

The π complex was converted to the σ derivative in at least a 30% yield when the pyridine was added to a 10% w/w solution in deuteriochloroform in the temperature range −35 to −50°. The relative concentration of the σ complex was highly dependent on the amount of base used as well as the temperature. Thus, a 1:1 ratio of base to complex produces very little σ complex, although some of the undeuterated pyridine is replaced from the π complex, while a 4:1 ratio of base to complex yielded 30–40% new species. In our experiments the optimum temperature for σ-bond formation appears to be around −50°. At −20 to −30° the new species rapidly disappears, and at −10° the ethylene peak of the π complex broadens, presumably because of an exchange process involving the excess pyridine. Eventually all the ethylene is displaced by pyridine. Whether the normal room-temperature displacement of ethylene by pyridine proceeds by prior π → σ rearrangement remains a provocative but unanswered question.

The chemical shifts of the aromatic protons in the undeuterated pyridine molecule in the solution to which C_5D_5N was added indicate that the major portion of originally complexed C_5H_5N has been replaced by the deuterated species and is present, free, in solution. There are at least two additional pyridine species which, as yet, have not been categorized, owing to the somewhat complex absorption pattern observed in the aromatic region. Further work is in progress.

Synthesis. The ethylene-pyridine complex was prepared by the reaction of pyridine with an aqueous solution of Zeise's salt. The compound was then reprecipitated from chloroform–pentane.

Deuterated pyridine was added to a precooled, 10% w/w, deuteriochloroform solution of the ethylene complex.

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Direct Configurational Correlation of Sulfoxides and Phosphine Oxides by Intersystem Matching of Cotton Effects[1]

Sir:

In the course of studies on the circular dichroism (CD) of phosphine oxides prepared by the Grignard synthesis,[2] we have come upon a remarkable finding which we wish to communicate at this time.

In Figure 1 are displayed the CD curves of three isomeric anisyl *p*-tolyl sulfoxides and anisylmethylphenylphosphine oxides in isooctane. All six compounds were prepared by the Grignard displacement reaction, the sulfoxides from menthyl (*S*)-*p*-toluenesulfinate (**1**),[3] the phosphine oxides from menthyl (*S*)-methylphenylphosphinate (**2**);[2] the sulfoxides and phosphine oxides therefore[2,4] have the *S* configuration at sulfur and phosphorus, respectively.

Because of the richness of their features, the over-all correspondence between the two sets of spectra is apparent upon inspection and is a spectacular confirmation of the *independently* arrived at absolute configurational assignments.[2-4] This intersystem matching of Cotton effects,[5] which we believe to be unprecedented in kind, also provides striking evidence that the lone pair on sulfur in the anisyl *p*-tolyl sulfoxides is not significantly implicated in the generation of the optically

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