

509. *Nuclear Magnetic Resonance and Infrared Spectroscopic Evidence for the Structure of Some Metal-Olefin Complexes.*

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A band near 1500  $\text{cm}^{-1}$  in the infrared spectra of ethylene-platinum co-ordination complexes has been assigned to a C-C stretching frequency or alternatively to a bending mode of the  $\text{CH}_2$  group by different authors. This ambiguity has been resolved in favour of the first assignment by a demonstration that this band persists in the infrared spectrum of  $\text{K}[\text{Pt}(\text{cis-CH}_3\text{-CH}\cdot\text{CH}\cdot\text{CH}_3)_2\text{Cl}_2]$  where the C- $\text{CH}_2$  group is not present.

Hydrogen nuclear magnetic resonance spectra of several complexes of olefins with platinum and silver show chemical shifts of the ethylenic CH bonds which are little different from the general range for ethylenic CH in simple molecules. It is concluded that the co-ordinated hydrocarbon groups have electronic properties much closer to those of the parent olefins than to structures of the type  $\overline{\text{X}\cdot\text{CH}_2\cdot\text{CH}_2}$  with single C-C and C-X bonds.

In a recent analysis of the infrared spectrum of ethylene co-ordinated to platinum in a series of complexes we concluded that many of the vibration frequencies of the free ethylene molecule are only slightly changed in the co-ordination compounds.<sup>1</sup> This implies that, apart from a change in the symmetry, the ethylene molecule is not greatly perturbed on formation of the co-ordination linkage. On the other hand, Babushkin, Gribov, and Helman<sup>2</sup> have concluded from similar spectroscopic evidence that a 3-membered ring is formed from the two carbon and the platinum atoms and that all three bonds in this ring are essentially single bonds. The most important difference in the two assignments of the infrared bands is that we have, following Chatt and Duncanson,<sup>3</sup> assigned a band at

<sup>1</sup> Powell and Sheppard, *Spectrochim. Acta*, 1958, **13**, 69.

<sup>2</sup> Babushkin, Gribov, and Helman, *Doklady Acad. Sci. U.R.S.S.*, 1958, **123**, 461.

<sup>3</sup> Chatt and Duncanson, *J.*, 1953, 2939.

about 1500  $\text{cm}^{-1}$  to a perturbed C:C stretching frequency, whereas Babushkin *et al.* consider this to be a  $\text{CH}_2$  scissors (deformation) vibration.

If the latter assignment is correct, the band near 1500  $\text{cm}^{-1}$  should be absent for any complex formed from an olefin which does not contain a C: $\text{CH}_2$  group. In fact, Jonassen and Kirsch<sup>4</sup> had previously recorded frequencies near 1505 and 1520  $\text{cm}^{-1}$ , respectively, for complexes containing *cis*- and *trans*-but-2-ene. We have confirmed this result by studying the spectrum of another complex of *cis*-but-2-ene, *viz.*,  $\text{K}[\text{Pt}(\text{cis-CH}_3\text{-CH:CH-CH}_3\text{)Cl}_3]$ , and also find the C:C band at 1505  $\text{cm}^{-1}$  with the expected intensity.†

We have also studied the high-resolution nuclear magnetic resonance spectrum of some olefin co-ordination compounds to see whether the chemical shifts observed for the hydrogen resonance are consistent or not with slightly perturbed olefinic structures. The compounds actually studied by nuclear magnetic resonance were Zeise's salt  $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$ ,\* the *cis*-but-2-ene platinum complex mentioned above, and the complexes formed in aqueous solution between *cis*-but-2-ene and cyclohexene with silver nitrate. The Raman spectra of the silver nitrate olefinic complexes have been discussed by Taufen, Murray, and Cleveland.<sup>5</sup>

The hydrogen chemical shifts were obtained in deuterium oxide solution and were measured relative to the sharp resonance of the residual hydrogen atoms in the solvent. They are therefore expressed on the water scale, where  $\sigma = 10^6(H - H_r)/H_r$ ,  $H$  is the magnetic field at which the specified hydrogen atoms give resonance at 40 Mc., and  $H_r$  is the corresponding field for resonance of the water hydrogen atoms.

A Varian Associates V 4300-B spectrometer and 12 in. electromagnet were used with sample spinning. The experimental chemical shift results are listed below and some of the spectra obtained are shown in the Figure. The assignment of the different resonances of the butene and cyclohexene complexes follows from their relative intensities.

*Chemical shifts,  $\sigma$ , of the hydrogen atoms in some metal-olefin complexes.*

Compound	$\sigma$
Pt-ethylene complex (Zeise's salt)	
CH resonance .....	+0.05 †
Pt- <i>cis</i> -but-2-ene complex	
{ CH resonance .....	-0.7 (broad)
{ $\text{CH}_2$ resonance * .....	+3.1 (poorly resolved doublet)
Ag- <i>cis</i> -but-2-ene complex	
{ CH resonance .....	-1.3 (quartet)
{ $\text{CH}_2$ resonance * .....	+3.0 (2 close doublets)
Ag-cyclohexene complex	
{ CH resonance .....	-1.6 (narrow)
{ $\text{CH}_2$ resonances .....	+2.6 ‡ (broad triplet)
{ $\text{CH}_2$ resonances .....	+3.0 (broad triplet)

\* *cis*-But-2-ene itself dissolved in deuterium oxide showed this resonance at  $\sigma = 3.35$ .

† The satellites, separated by 17 c./s., on either side of the main resonance of the ethylene complex (see Figure) are caused by spin-spin splitting due to the platinum-195 nucleus of spin  $\frac{1}{2}$  and natural abundance 34%. The  $\text{H-}^{195}\text{Pt}$  coupling constant is hence 34 c./s.

‡ This is probably the resonance of the methylene group adjacent to C=C (see later discussion).

As olefinic CH bonds commonly occur at chemical shift values on this scale between  $-1$  and  $+0.5$ ,<sup>6</sup> it can be seen that the hydrogen atoms originally attached to the C:C

\* In the course of this work we were informed by Dr. J. A. S. Smith, of Leeds University, that he had also examined the high resolution nuclear magnetic resonance spectrum of solutions of Zeise's salt.

† Note added in proof.—This same point has been made by Adams and Chatt (*Chem. and Ind.*, 1960, 149) who studied the infrared spectra of  $[\text{Pt}(4\text{-methylpent-2-ene})_2\text{Cl}_2]$  with the olefin in the *cis*- and the *trans*-form.

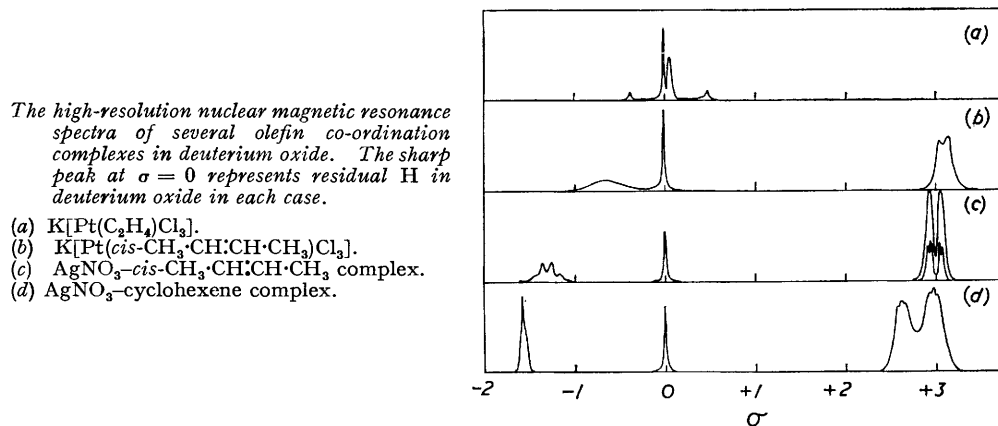
<sup>4</sup> Jonassen and Kirsch, *J. Amer. Chem. Soc.*, 1957, **79**, 1279.

<sup>5</sup> Taufen, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 3502.

<sup>6</sup> Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance Spectroscopy," McGraw-Hill, London, 1959, Chap. XI.

double bonds still give resonance close to the typical olefinic range when incorporated in the complexes.

For comparison, the chemical shifts of  $\text{CH}_2$  groups in cyclopropane and ethylene sulphide have the markedly different values of  $+4.4$  and  $+2.4$  on the same scale.\* Furthermore the methyl and methylene resonances of the co-ordination complexes occur at values similar to those found for such groups in olefinic hydrocarbons ( $\sigma = 2.5-3.5$  for  $\text{CH}_2$  and  $\text{CH}_3$  adjacent to  $\text{C}:\text{C}$ ;  $\sigma = 3.5-4.0$  for ring  $\text{CH}_2$ ).<sup>6</sup>



The  $\text{CH}$  and  $\text{CH}_3$  resonances of co-ordinated *cis*-but-2-ene show structure due to spin-spin interaction between the two types of hydrogen nucleus. Although in principle these spectra can be rather complex, the most pronounced splitting pattern is expected to be a quartet for the  $\text{CH}$  group and a doublet for the  $\text{CH}_3$ . The platinum compound gave rather broad hydrogen resonances consistent with the expected intensity contours. The hydrogen resonances of the silver complex gave more detailed fine structure of the expected type, with a principal coupling constant of  $4.5$  c./s.

These results, obtained by using high resolution nuclear magnetic resonance spectroscopy, are quite consistent with the evidence from the infrared spectra, namely, that the nature of the  $\text{C}-\text{C}$  bond in these complexes is that of a perturbed double bond, rather than of a single bond, although the observed  $\text{H}-^{195}\text{Pt}$  coupling constant for ethylene does indicate that the olefinic molecule is firmly bound to platinum.

The simple olefins studied here all give resonances in the range  $+0.1$  to  $-1.7$ . However it should be mentioned that a few nuclear magnetic resonance spectra of the more complex ligands cyclopentene,<sup>7</sup> cyclopentadiene,<sup>7</sup> and cyclo-octatetraene,<sup>8,9</sup> co-ordinated to other metals, give resonances in the range  $0.0$  to  $+1.0$  when recalculated on this same scale. These latter compounds all have additional  $\text{CO}$  ligands to the metal atom.

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\* Actually measured relative to *t*-butyl alcohol ( $\sigma = +3.54$ ) as an internal standard.

<sup>7</sup> Green and Wilkinson, *J.*, 1958, 4314.

<sup>8</sup> Manuel and Stone, *Proc. Chem. Soc.*, 1959, 90.

<sup>9</sup> Rausch and Schrauzer, *Chem. and Ind.*, 1959, 957.