Figure 1. FTIR difference spectrum of R· CO_2 CO_2 ·R near 30 K, from partially photolyzed UP crystals that contain 11.8% of DUP with 92% ^{13}C in the short-chain carbonyl. (A) $^{12}CO_2$ asymmetric stretches. The arrow marks the $^{12}CO_2$ peak from DUP. (B) $^{13}CO_2$ asymmetric stretch from DUP. The frequency scale of (B) is shifted from that of (A),[9] so that peaks with the same force constant are displaced vertically between (A) and (B). The $^{12}CO_2$ and $^{13}CO_2$ peaks from DUP have similar absorbance, about 0.015.

These differences demonstrate strong influence from a crystal defect 14.2 Å from the reaction center.[5] The influence must be relayed specifically through the carbon chain of the free radical. Otherwise the reaction center should have been perturbed by defects in neighboring molecules. In the herringbone packing of crystalline UP there are 42 terminal methyl groups of neighboring molecules that are closer to a molecule's reaction center than its own methyls are; the closest is at 10 Å.[5,6] In a random solid solution with 5.9% methyl defects, the percentages of UP centers having zero–seven defects within 14.2 Å are 7.8, 20.5, 26.3, 22.0, 13.5, 6.4, 2.5, and 0.8, respectively. The same probabilities hold for one–eight defects near a DUP center with its additional intramolecular defect. Comparison of these series shows that 74% of the host CO_2 pairs should have as many methyl defects within 14.2 Å as 74% of the guest pairs do.[7] Since only guest spectra show the defect's influence,[8] it must be transmitted only through the nine-carbon chain.

These observations confirm Segmuller's mechanism for relaxing the local stress generated by photolysis of crystalline UP. On the basis of X-ray diffraction and radical-pair EPR studies she proposed that the principal relaxations involve successive rotational

translation of the two decyl radicals.[2,5] Each of the first nine carbons replaces its neighbor, and the terminal methyl is driven into the soft region between layers of molecules.[6] For DUP guests the terminal methyl is replaced by a hole. This should facilitate the initial rotational translation, which is complete after the third relaxation step in UP. The spectrum of Figure 1 shows host pairs in several structures waiting to undergo the first rotational translation and a single guest pair that has completed this process.

After rotational translation the C_9 radical is accommodated better than the C_{10} radical would be. This reduces the driving force for subsequent motion of the longer radical from guest as compared to that from host. FTIR support for this and other aspects of the mechanism will appear in a full paper.

Synthesis and Characterization of the First Example of an Organoplatinum Complex Containing a Platinum(IV)–Olefin Bond

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Received October 5, 1984

Interest in platinacylobutane chemistry is garnered from their potential importance to olefin metathesis, carbon–carbon bond forming reactions, and various catalytic processes.[1,2]

In order to facilitate the seemingly rich area of platinacyclobutane chemistry, a project has been launched to investigate the preparation and chemistry of platinacyclobutanes from bicyclo[N.1.0]hydrocarbons. These hydrocarbons may contain an olefinic moiety. The latter functinality is of particular importance because Pt(II) prefers to complex with the double bond rather than react with the cyclopropane. Thus, in this paper, we wish to report results which show that platinacyclobutanes can be prepared in the presence of olefins and that the product is a very novel complex. The reactions are shown in eq 1 and 2.
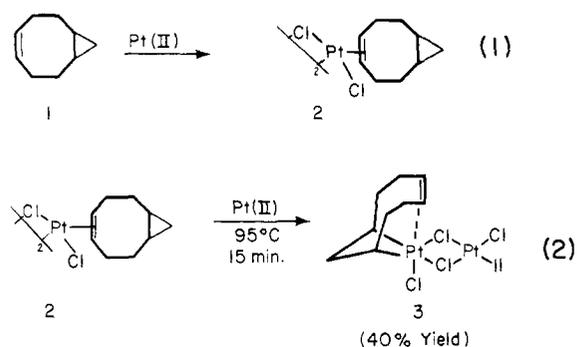
It is clear from the results shown in eq 1 that Pt(II) prefers to react with the olefin. Complex **2** is a yellow solid which exhibits platinum couling to the olefinic protons (Δ 5.57, d d, $J_{Pt,H}$ = 66.5 Hz) and the olefinic carbons (Δ 89.9, d, $J_{Pt,C}$ = 162 Hz). With the olefinic moiety essentially encumbered as in **2**, it was surmised that excess Pt(II) would subsequently react with the cyclopropane portion. At room temperature, there was no reaction. Likewise on heating to 60 °C there was no reaction. However, upon heating a nitrogen-purged solution of **2** in $CHCl_3$ with excess Zeise's dimer

(5) The crystal structure of UP and a mechanistic study of the reaction are reported in: Segmuller, B. E. Ph.D. Dissertation, Yale University, New Haven, CT, 1982.

(6) McBride, J. M. *Mol. Cryst. Liq. Cryst.* **1983**, *96*, 19.

(7) This "overlap" is equivalent to 1 − *x*, where *x* is the fraction of the most abundant species.

(8) Some host peaks are slightly broadened.

(9) By a factor of 1/0.97204. I. Suzuki, *J. Mol. Spectrosc.* **1968**, *25*, 479.

(1) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

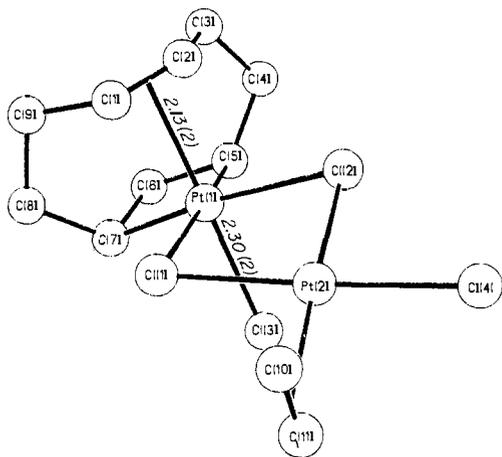(2) Johnson, T. H.; Cheng, S. S. *Synth. Commun.* **1980**, *10*, 381.

Figure 1. computer-generated view of the non-hydrogen atoms of complex **3**.
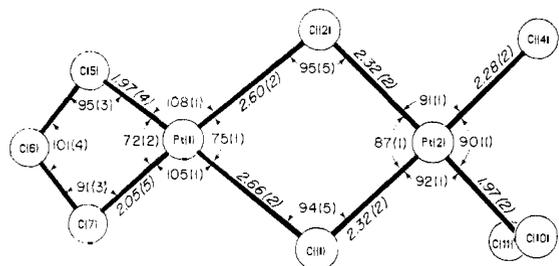

Figure 2. Computer-generated view of the platinacyclobutane ring and dichlorodiplatinum ring system with corresponding bond lengths and angles.

to 95 °C for 5–15 min, reaction occurred as shown in eq 2.

The following are most significant features of the NMR spectra for complex **3**: (a) there is a proton resonance at 7.4 ppm integrating for 2 H and coupled to ^{195}Pt by 60 Hz, these are assigned to the olefinic protons; (b) there is a carbon resonance at 120 ppm which is coupled to these protons and to ^{195}Pt by 94 Hz; (c) in addition, there are two carbons with doublet multiplicity coupled to ^{195}Pt by 338 Hz which indicates a σ bond; (d) finally, there are only five carbon resonances for the nine-carbon structure indicating symmetrical magnetic environments for the hydrocarbon portion.[3] **X-ray Analysis.**[5] Even though the NMR spectral data were consistant with the organic portion of **3**, the platinum NMR spectrum consisted of two resonances at 2184.4 and 2795.8 ppm downfield relative to $Na_2Pt(CN)_4$ as an external standard. Thus, an X-ray crystal structure was sought to elaborate the inorganic portion. The results of the analysis are shown in Figures 1 and

(3) For previous results on the NMR spectral assignments for platinacyclobutanes, see: Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 1370; **1983**, *2*, 1269.

(4) Ling, S. S. M.; Puddephatt, R. J. *J. Organomet. Chem.* **1983**, 255.

(5) X-ray Determination of Complex **3**: Yellow-orange crystals of **3** were grown by allowing heptane to diffuse into a chloroform solution. A specimen suitable for X-ray analysis (0.16 × 0.22 × 0.33 mm) was mounted on a glass fiber and data collection was carried out on a Nicolet R3ME automated diffractometer using $\theta/2\theta$ scans and graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Unit cell constants of a = 10.963 (3) Å, b = 13.606 (3) Å, and c = 21.170 (7) Å were determined by a least-squares fit of 25 2θ values from diffractometer measurements in the range 19 < 2θ < 33.[6] The space group was found to be *pbca*, on the basis of systematic extinctions, and the calculated density is 2.88 g/cm^3 for $C_{22}H_{18}Cl_4Pt_2$ in the assymetric unit. Intensity data were collected for all unique reflections in the range 3 < 2θ < 50, and 1174 were observed with $I \geq 3\sigma(I)$. Absorption corrections were made by the Gaussian integration method using crystal dimensions between indexed crystal faces. The structure was refined to an R value of 0.080. Carbon positions were refined with isotropic thermal parameters. All structure determinations and refinement calculations were carried out with the SHELXTL package of programs on the Nicolet R3mE crystallographic system.[6]

(6) Programs used for centering of reflections, autoindexing, refinement of cell parameters, axial photographs, and data collections were those described in: "Nicolet P3/R3 Data Collection Manual"; Calabrese, J. C., Ed.; Nicolet XRD Corp.: Madison, WI, 1983.

2, which also contain data on selected bond angles and distances. In this complex, it appears that one platinum atom exists as a typical 4-coordinate, square-planar Pt(II) and the other as a 6-coordinate, octahedral Pt(IV). Since the resonance lines are sharp in the ^{1}H, ^{13}C, and ^{195}Pt spectra, it is apparent that **3** is a mixed-valent complex.[4] The dichlorodiplatinum ring is puckered by 28 (1)° and the platinacyclobutane ring is puckered by 11 (3)° from linearity. Moreover, the C(5)–C(7) bond distance is 2.37 (6) Å, which preclues any thoughts that the cyclopropane exists and that an edge complex is present. Due to the excessive electron density of the platinum and chlorine atoms it was necessary to constrain the C–C bond lengths to idealized values. No constraints were imposed on nonbonded carbon atoms or on the platinum and chlorine atoms.

Since the olefin appears by NMR and X-ray data to be bonded to the Pt(IV), it would be expected to be subject to nucleophilic attack. Thus, on treatment with LAH, a nearly quantitative yield of the hydrogenated analogue of **1** was obtained. This structure was determined by comparison with an authentic sample with NMR and mass spectroscopy.

While the Pt(IV)–olefin bond is new, it is important to note that this platinacyclobutane ring is also the first example of a *cis*-2,4-dialkyl-substituted system. This is significant since this type product has been proposed but never observed.

Supplementary Material Available: Tables of atomic coordinates, isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

Flash Photolysis Investigations of RhCl(CO)(PPh$_3$)$_2$: Reaction Dynamics of the Wilkinson's Catalysis Intermediate "RhCl(PPh$_3$)$_2$"

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Received October 23, 1984

The catalysis chemistry of rhodium(I) phosphine complexes continues to hold much interest 2 decades since the description of such reactions by Wilkinson.[1] However, despite considerable quantitative scrutiny,[1–3] the mechanistic details of key catalytic steps for even the original Wilkinson's catalyst RhCl(PPh$_3$)$_3$ are not fully resolved.[3] The reason lies within the very nature of catalytic processes, namely, that the activation of substrates often involves reactions of unstable transient species, the properties of which can only be inferred from kinetic rate laws or from spectral studies under conditions considerably different from those of an operating catalyst. In some cases it may be possible to use flash photolysis to generate significant concentrations of such a transient and to investigate the reactions of that species more directly. In the present case we report the flash photolysis of the metal car-

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(2) (a) Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629–630. (b) Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P.; *J. Am. Chem. Soc.* **1974**, *96*, 2762–2774. (c) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 65–69.

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