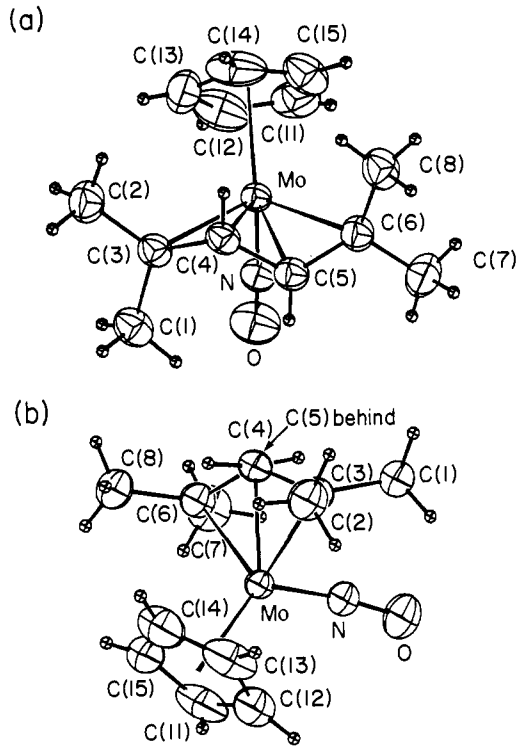

Figure 1. Views of the molecular structure of **1c** (a) along the axis bisecting the Cp-Mo-NO angle and (b) down the C(4)-C(5) bond. Selected bond lengths (Å) and angles (deg): Mo-N = 1.767 (2), N-O = 1.213 (3), Mo-N-O = 172.2 (2), C(3)-C(4) = 1.418 (4), C(4)-C(5) = 1.408 (4), C(5)-C(6) = 1.401 (4), Mo-C(3) = 2.390 (3), Mo-C(4) = 2.209 (3), Mo-C(5) = 2.234 (3), Mo-C(6) = 2.365 (3), C(Me)-C(av) = 1.510 (7), C(3)-C(4)-C(5) = 122.3 (3), C(4)-C(5)-C(6) = 122.1 (3), C(1)-C(3)-C(2) = 112.7 (3), C(1)-C(3)-C(4) = 121.7 (3), C(2)-C(3)-C(4) = 118.1 (3), C(3)-C(4)-H(4) = 115 (2), C(4)-C(5)-H(5) = 117 (2), C(5)-C(4)-H(4) = 120 (2), C(6)-C(5)-H(5) = 118 (2), C(5)-C(6)-C(7) = 117.9 (3), C(5)-C(6)-C(8) = 120.7 (3), C(7)-C(6)-C(8) = 112.6 (3).

complexes of Cp_2Zr ($^3J_{HH} \sim 10$–11 Hz) than their *trans*-diene analogues ($^3J_{HH} \sim 15$–16 Hz). This spectroscopic property thus reaffirms the partial double-bond character of the coordinated diene's central C-C link in **1c**.[19] There is, however, no evidence in any case for isomerization of the bound dienes in **1** to their cis forms as occurs with $Cp_2Zr(\eta^4$-diene) species.[10] Since there appears to be no steric restriction to such isomerization,[23] the factors responsible for the preferred linkage of dienes to the CpMo(NO) fragment in a twisted, transoidal fashion must be electronic in nature. Confirmation of this inference must obviously await a detailed theoretical analysis of the intramolecular bonding. In the interim, the characteristic reactivity of the bound dienes in **1** toward representative nucleophiles and electrophiles is currently under investigation.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and a graduate scholarship to A.D.H. We also thank The University of British Columbia for the award of a graduate fellowship to C.R.N. and a referee for constructive comments.

Supplementary Material Available: Elemental analysis and spectroscopic (IR, ^{1}H and ^{13}C NMR, mass spectral) data for **1a** and **1b** and tables of fractional coordinates and isotropic and anisotropic thermal parameters for **1c** (7 pages). Ordering information is given on any current masthead page.

(23) Indeed, this lack of steric crowding permits the isolation of complexes **1a** and **1b** which contain dienes that are sterically prohibited from attaining a trans configuration when coordinated to Cp_2Zr.[19]

Specific Long-Range Effects on Relaxation of Local Stress during a Solid-State Reaction

Mark D. Hollingsworth and J. Michael McBride*

Department of Chemistry, Yale University
New Haven, Connecticut 06511

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Discussions of organic solid-state reactions have tended to stress the importance of the static structure of a reactant molecule and its environment. The environment's local mechanical properties should also be important, since some accommodation to reactant motion is essential. If it were adequate to approximate the medium as an isotropic continuum, one could treat mechanical properties with simple elasticity theory. But if the specific molecular mechanism by which stress is transmitted should be important, anisotropy would invalidate such a treatment. Here we report observations on the influence of crystal defects which demonstrate that mechanical effects can be both specific and of long range.

We have used FTIR spectroscopy to study pairs of CO_2 molecules generated by photolyzing single crystals of diundecanoyl peroxide (UP) at low temperature.[1] We previously found a characteristic sequence of IR patterns as stress resulting from bond cleavage was annealed.[2] The present work concerns UP crystals that were made defective by introducing 11.8% of decanoyl undecanoyl peroxide (DUP) as a solid solute.[3] This means that 5.9% of the alkyl chains in the crystal were one-carbon short, leaving holes at the chain ends. Labeling one of the carboxyl carbons of DUP with ^{13}C made it possible to distinguish by FTIR spectroscopy between CO_2 pairs derived from DUP and those derived from UP.

Figure 1A shows $^{12}CO_2$ asymmetric stretching vibrations in such a crystal. There are 10 absorptions from 2329.3 to 2352.3 cm^{-1}. Nine of these can be assigned unambiguously to the first four stages of relaxation previously observed in pure UP crystals.[4] We assign the new peak at 2330.9 cm^{-1} to the ^{12}C member of the $^{12}CO_2/^{13}CO_2$ pair from DUP. The isolated $^{13}CO_2$ peak at 2265.3 cm^{-1} (Figure 1B) is due to the other member of this pair. The assignment was confirmed by an analogous experiment in which the other carboxyl carbon of DUP was labeled. In this spectrum the guest $^{12}CO_2$ peak shifted down by 0.5 cm^{-1} to 2330.5 cm^{-1}, while the $^{13}CO_2$ peak shifted up by 0.5 cm^{-1} to 2265.8 cm^{-1}, as expected for isotopic exchange between CO_2 sites with frequencies differing by 0.5 cm^{-1}.

Under these conditions where CO_2 pairs from UP show a variety of structures, those from DUP guests show a single structure in which the CO_2 molecules do not exchange positions over a period of hours. Spectra of host and guest pairs remained distinct through further annealing, although CO_2s in the guest sites began to exchange positions at higher temperature. Only after completing relaxation above 150 K did the strong peak from the host CO_2 (2333.7 cm^{-1}) correspond to that from the guest (2268.4 cm^{-1}). Until then the host always had at least one peak above 2338 cm^{-1}, higher than any guest peak.

(1) A Nicolet 7199 FTIR spectrometer was used with nominal resolution of 0.24 cm^{-1} to measure transmission through a sandwich of two crystal plates each about 5 mm wide and 0.1 mm thick. Absorbance subtraction was used to observe the effect of photolysis (<0.1% conversion, Osram 200W/2 Hg arc, $CuSO_4$ filter). Background absorption in the 2200–2400-cm^{-1} region was weak enough to give a reasonable base line, although the weak "triplet" near 2668 cm^{-1} in Figure 1B is probably artifactual. The crystals were held in vacuum and cooled from the edges by a Displex CS-202 cryostat.

(2) For a preliminary account, see: McBride, J. M. *Acc. Chem. Res.* **1983**, *16*, 304.

(3) Crystals grown from methanol solution at 22 °C were shown to be single by examination with a polarizing microscope and to be solid solutions by their melting in a single exotherm upon differential scanning calorimetry. By X-ray diffractometry lattice constants were within 0.1% of those for pure UP. The concentration of DUP was estimated by 125.7-MHz ^{13}C NMR spectra in CD_2Cl_2 solution.

(4) There are 16 host absorptions some of which overlap or are too weak to observe. These arise because each stage consists of two slowly equilibrating structures, each with two different CO_2 molecules. Four stages are present simultaneously because of substantial temperature gradients in these crystals.

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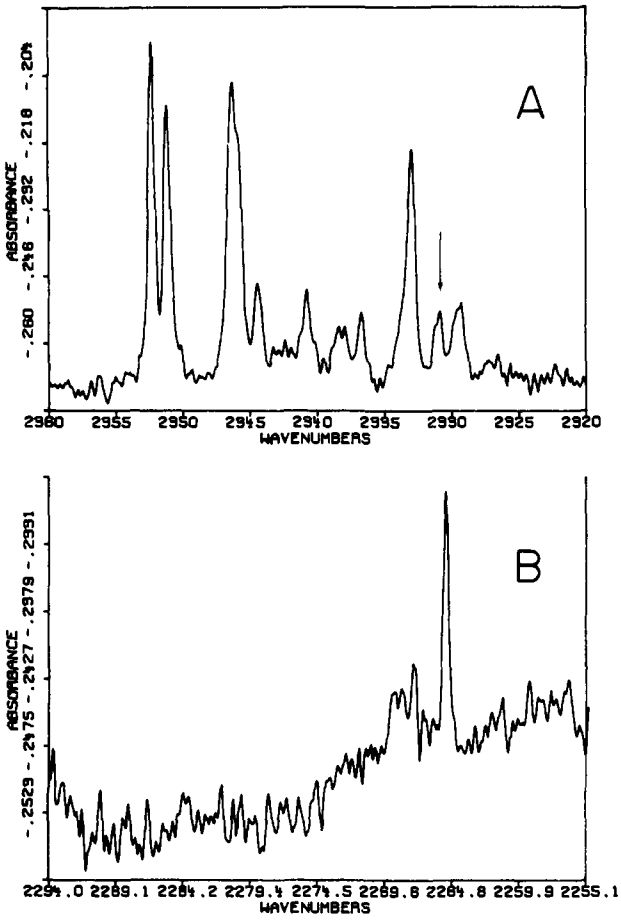


Figure 1. FTIR difference spectrum of R· CO_2 CO_2 ·R near 30 K, from partially photolyzed UP crystals that contain 11.8% of DUP with 92% ^{13}C in the short-chain carbonyl. (A) $^{12}CO_2$ asymmetric stretches. The arrow marks the $^{12}CO_2$ peak from DUP. (B) $^{13}CO_2$ asymmetric stretch from DUP. 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.

Acknowledgment. We thank Dr. B. E. Segmuller for her help in this work, which was supported by the NSF Division of Materials Research (Grant DMR-8203662) and by a Dox Fellowship to M.D.H. We acknowledge an NSF instrument grant for the FTIR spectrometer and NSF support for the Northeast Regional NMR Facility at Yale University.

(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.

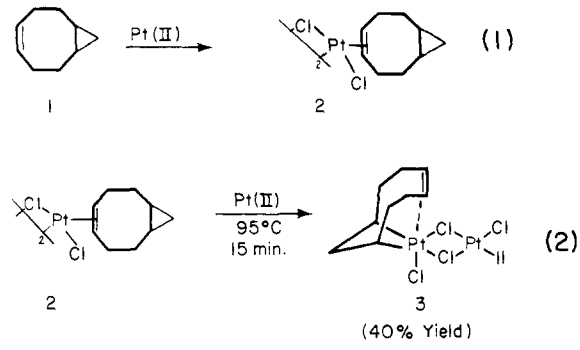
Synthesis and Characterization of the First Example of an Organoplatinum Complex Containing a Platinum(IV)–Olefin Bond

Edith J. Parsons, Raymond D. Larsen, and P. W. Jennings*

Gaines Hall, Department of Chemistry
Montana State University, Bozemen, Montana 59717
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

(1) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.
(2) Johnson, T. H.; Cheng, S. S. *Synth. Commun.* **1980**, *10*, 381.

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