

Figure 1. ORTEP diagram of $\text{Cp}^*(\text{L})\text{Ir}(\text{CH}=\text{CH}_2)(\text{H})$ (**1**). Selected distances and angles: Ir-C₁₁, 2.054 (4); Ir-H₁, 1.61 (5); C₁₁-C₁₂, 1.296 (6); Ir-Cp*, 1.899 Å; H₁-Ir-C₁₁, 86.2 (17)°; P-Ir-C₁₁, 85.8 (1)°.

This demonstrates that both products are completely stable to the reaction conditions. Above 170 °C, however, in either cyclohexane or benzene solvent, **1** was completely converted to **2** without any formation of solvent C-H insertion products. These observations require the following conclusions: (a) the invariant 66:34 mixture of **1** and **2** represents the true kinetic product ratio for the thermal reaction of **3** with ethylene; (b) the η^2 -ethylene complex **2** is the thermodynamic product of the reaction; (c) because **2** is stable to the ethylene reaction conditions, the olefin complex **2** cannot be an intermediate in the formation of C-H insertion product **1**—i.e., there must be two independent transition states leading to these two products;⁹ (d) given that the transient intermediate “Cp*IrL” reacts with ethylene and benzene at similar rates,¹⁰ the absence of Cp*(L)Ir(Ph)(H) (which control experiments demonstrated was completely stable under these conditions) in the conversion of **1** to **2** above 170 °C requires that this reaction proceeds without reversion to ethylene and the reactive intermediate—i.e., it must proceed through a third transition state distinct from those leading from the intermediate to **1** and **2**.

To account for our results we propose the reaction mechanism illustrated in Scheme I. The separate transition states required for the formation of hydrido vinyl complex **1** and π -complex **2** from the reactive intermediate Cp*Ir(L) and ethylene are suggested to have structures similar to A and B. The third transition state, required for thermal conversion of **1** to **2** at temperatures above 170 °C, should have a structure similar to C, intermediate between A and B. It is startling that the rate of formation of C-H insertion transition state A is so similar to that (B) required for simple coordination of the metal center to the loosely held π -electrons of the alkene. The C-H insertion process may be assisted by prior coordination of the metal to the C-H bond in some way, perhaps in the linear fashion suggested by Hoffmann.¹¹ This possibility is illustrated in Scheme I but further studies will be required to determine whether such “ σ -complexes” are truly involved as intermediates in these and other¹² C-H insertion reactions.

(9) Another possibility is that interaction of Cp*IrL with ethylene leads to only one transition state, and partitioning to **1** and **2** occurs at a branch located beyond this point on the reaction energy surface (for an example of the use of this type of surface, see: Salem, L. “Electrons in Chemical Reactions”; Wiley-Interscience: New York, 1982; p 55). These two alternatives are very difficult to distinguish, but we hope to obtain some information on this question by using deuterium isotope effects.

(10) Thermolysis of **3** in cyclohexane-*d*₁₂ in the presence of known amounts of benzene and ethylene gives both **1** and Cp*(L)Ir(C₆H₅)(H) (in addition to **3-d**₁₂ and **2**). The relative yield of these two products can be used to estimate that the rate of attack on one C-H bond in benzene, relative to that in ethylene, is ca. 1.0.

(11) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006-2026.

(12) Periana, R. A.; Stryker, J. M.; Buchanan, J. M.; Bergman, R. G., unpublished results.

As pointed out earlier, it has been almost universally assumed that π -complexes are intermediates in the many known reactions of alkenes with transition metals.¹³ Our results demonstrate that in at least one case, even though π -coordination occurs, the coordinated complex does *not* lie on the pathway for activation of the alkene. It must be concluded that prior coordination in other processes cannot be taken for granted, even when the coordinated complex is isolated or detected spectroscopically. Evidence must be provided which demonstrates that complex formation is not simply a “dead end” but actually lies on the pathway for reaction.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098. The crystal structure analyses were performed by Dr. F. J. Hollander, staff crystallographer at the UC Berkeley X-ray Crystallographic Facility (CHEXRAY).

Supplementary Material Available: ¹H NMR, ¹³C NMR, IR, MS, melting point, and elemental analysis data for complexes **1**, **2**, and (η^5 -C₅Me₅)(PMe₃)Ir(CH=CH₂)(Br) and experimental details of the X-ray diffraction study, including tables of crystal and data collection parameters, intramolecular distances and angles, and general temperature factor expressions (*B*'s) and a table of positional parameters and their esd's (32 pages). Ordering information is given on any current masthead page.

(13) See, for example: (a) Reference 2c. (b) Pino, P.; Piacenti, F.; Bianchi, M. In “Organic Synthesis via Metal Carbonyls”; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2. (c) James, B. R. “Homogeneous Hydrogenation”; Wiley-Interscience: New York, 1973. (d) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (e) Tolman, C. A. In “Transition Metal Hydrides”; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; Vol. 1. (f) Hartley, F. R. *Chem. Rev.* **1969**, *69*, 799. (g) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. (h) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (i) Ugo, R., Ed. “Aspects of Homogeneous Catalysis”; Reidel: Holland, 1974. (j) Boor, J., Jr. “Ziegler-Natta Catalysts and Polymerizations”; Academic Press: New York, 1979. (k) Ziegler, C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

Formation of Novel, Dimeric Epdioxides from the Lewis Acid Catalyzed Oxygenation of 1-*tert*-Butylcyclohexa-1,3-diene

Munawar F. Arain,[†] Richard K. Haynes,*[‡]
Simone C. Vonwiller,[†] and Trevor W. Hambley[†]

*Departments of Organic Chemistry and
Inorganic Chemistry, University of Sydney
Sydney 2006, New South Wales, Australia*

Received September 26, 1984

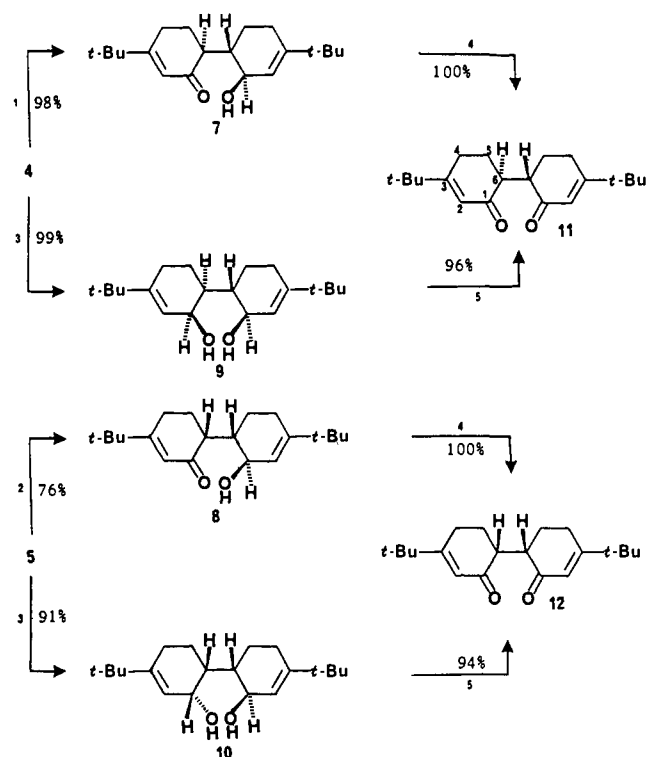
1,1-Diarylethylenes are converted into 3,3,6,6-tetraaryl-1,2-dioxanes by O₂ and SbCl₅ in CH₂Cl₂ at -78 °C.¹ In these and related² reactions, the lifetime of the cation radical formed from the ethylene and the Lewis acid is presumably too short to allow reaction with O₂, and it is the longer lived, hindered dimer cation radical derived from the monomer cation radical and the ethylene which gives the dioxane.¹ If we consider a 1-alkylcyclohexa-1,3-diene cation radical, it will react through C-4 with the parent

[†] Department of Organic Chemistry.

[‡] Department of Inorganic Chemistry.

(1) Haynes, R. K.; Probert, M. K. S.; Wilmot, I. D. *Aust. J. Chem.* **1978**, *31*, 1737.

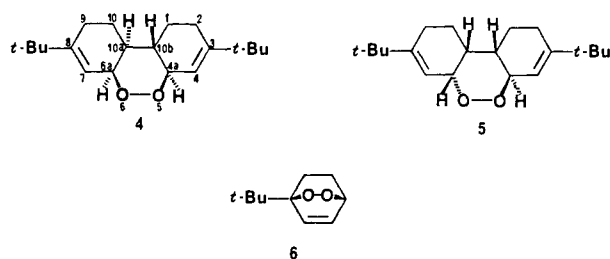
(2) Hisatome, M.; Namiki, T.; Yamakawa, K. *J. Organomet. Chem.* **1976**, *117*, C23. Hisatome, M.; Koshikawa, S.; Chimura, K.; Hashimoto, H.; Yamakawa, K. *J. Organomet. Chem.* **1978**, *145*, 225. Mattes, S. L.; Farid, S. In “Organic Photochemistry”; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, pp 300, 301. Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1983**, *103*, 1386. Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1984**, *25*, 185. Gollnick, K.; Schnatterer, A. *Tetrahedron Lett.* **1984**, *25*, 2735.

Scheme I^a

^a Reagents: (1) Et₃N in CH₂Cl₂, reflux 48 h. (2) DMAP in CH₂Cl₂, reflux 72 h. (3) Zn in THF-HOAc, 65 °C. (4) MnO₂ in CH₂Cl₂, reflux 6 h. (5) CrO₃·2pyr in CH₂Cl₂, 0 °C.

diene³ to give a dimer cation radical (see Scheme II) providing pericyclic processes^{3a,4} do not intervene. Consequently the dimer cation radical, like that from the diarylethylene, may become receptive to oxygenation. We have therefore examined the oxygenation of 1-*tert*-butylcyclohexa-1,3-diene (**1**)⁵ under conditions which give monomeric endoperoxides from other 1,3-dienes.⁷

Irradiation (tungsten lamp, 600 W) of **1** (1.5 mmol) in CH₂Cl₂ (50 mL) with Ph₃C⁺BF₄⁻ (0.15 mmol) in a Pyrex flask for 2 h at -78 °C under O₂ gave **1** (10–20%), several oxygen-free products, a mixture (30–40%) of the epidioxides **4** (52%) and **5** (43%)⁹



(3) (a) Belville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 2665. Extended STO-3G* calculations on 1-methylcyclohexa-1,3-diene and its cation radical indicate if steric effects prevent reaction through C-1, reaction will take place through C-4, whether this proceeds by a charge- or an FMO-controlled process involving a SOMO (cation radical)-HOMO (diene) interaction. The results of these calculations are given in the supplementary material. (b) That diene cation radicals react in a 1,4-sense with the parent dienes is, in the case of cation radical-induced polymerization of 1,3-dienes, well-known: see Shiga, T.; Matsuyama, T.; Yamaoka, H.; Okamura, S. *Makromol. Chem.* **1974**, *175*, 217 and references therein.

(4) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718. Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 5158.

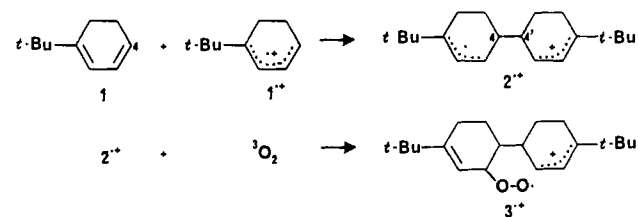
(5) **1**, bp 120 °C (110 mm), was prepared in 65% yield from the benzenesulfonylhydrazone of 3-*tert*-butylcyclohex-2-en-1-one⁶ and LDA (4 equiv) in THF at -78 to 0 °C.

(6) Piers, E.; Nagakura, I. *J. Org. Chem.* **1975**, *40*, 2694.

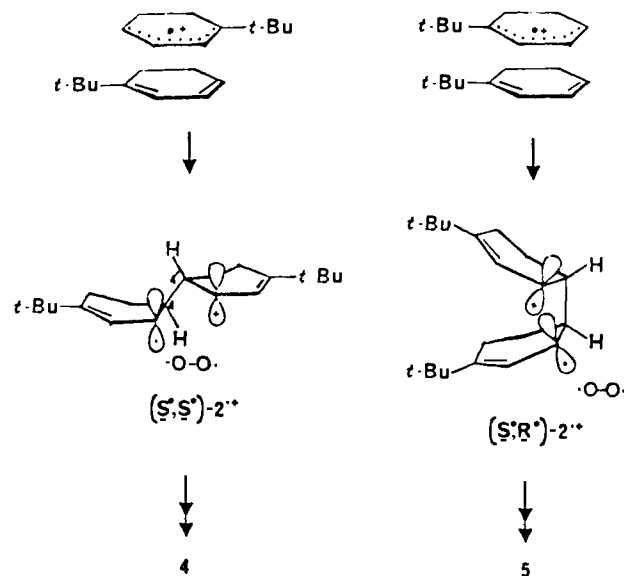
(7) Haynes, R. K. *Aust. J. Chem.* **1978**, *31*, 121. Haynes, R. K. *Aust. J. Chem.* **1978**, *31*, 131. Haynes, R. K.; Peters, J. M.; Wilmot, I. D. *Aust. J. Chem.* **1980**, *33*, 2653.

(8) Use of SnCl₄, BF₃, TiF₄, etc.⁷ results in inferior yields of **4** and **5**.

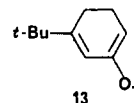
Scheme II



Scheme III



and traces of four other unidentified epidioxides, and the endoperoxide **6** (5–10%). **4** and **5**¹⁰ were converted via the ketols **7** and **8** or the dialcohols **9** and **10** into the diketones **11** and **12**¹⁰ according to Scheme I. **11** was also prepared by oxidative dimerization¹¹ [Cu(OSO₂CF₃)₂, *i*-PrCN-THF; 50%] of the dienolate **13** of 3-*tert*-butylcyclohex-2-en-1-one. As a single-crystal



X-ray structural determination of **11**¹² indicated that it is the *R*^{*},*R*^{*} diastereomer, diketone **12** is the *R*^{*},*S*^{*} or meso diastereomer. Thus epidioxide **4**, which yields **11**, has H-10a and H-10b trans. The trans and cis ring junctions follow from coupling constants of 9.2 Hz for H-4a and H-10b and 5.0 Hz for H-6a and H-10a and from NOE enhancements (4–6%) of H-10a induced by preirradiation of each of H-6a and H-4a. Epidioxide **5**, which gives **12**, has H-10a and H-10b cis. Coupling constants of 9.8 Hz for H-4a and H-10b and 2.6 Hz for H-6a and H-10a indicate trans and cis fusions, which also follow from NOE enhancements (4–6%) of H-10a and H-10b induced upon preirradiation of H-6a. Thus **4** has a trans-anti-cis and **5** a trans-syn-cis backbone.

Oxygenation of **1** is likely to proceed via cation radicals. Endoperoxide **6** than arises from **1**⁺ and O₂ as discussed for related cases.⁷ The preferred reaction of **1**⁺ is with **1** to give **2**⁺. Reaction

(9) **4** and **5** were separated by HPLC (Waters 6000A pump, U6K injector, R401 RI detector, semi-prep μ -Porasil column, 0.25% ethyl acetate in hexane, flow rate 3.5 mL min⁻¹ at 1000 psi) and recrystallized from methanol. **4** is (4 α ,6 α ,10 α ,10 β)-3,8-di-*tert*-butyl-1,2,4a,6a,9,10,10a,10b-octahydrodibenzo[*c,e*][1,2]dioxin, needles mp 141–143 °C. **5** is (4 α ,6 α ,10 α ,10 β)-3,8-di-*tert*-butyl-1,2,4a,6a,9,10,10a,10b-octahydrodibenzo[*c,e*][1,2]dioxin, prisms, mp 157–159 °C.

(10) 400-MHz ¹H NMR data for **4**, **5**, **11**, and **12** are given in the supplementary material.

(11) Kobayashi, Y.; Taguchi, T.; Morikawa, T.; Tokuno, E.; Sekiguchi, S. *Chem. Pharm. Bull.* **1980**, *28*, 264.

(12) Crystals of **4**, **5**, and **7–10** are unsuitable for X-ray analysis. Crystal data for **11** are given in the supplementary material.

of 2^+ with O_2 to form the peroxy cation radical 3^+ (Scheme II) and back electron transfer from the Lewis acid, or **1**, will lead to **4** and **5**. The intriguing aspect of the reaction is, however, the preference for formation of the trans-anti-cis and trans-syn-cis epidioxides.¹³ It is likely that formation of 2^+ proceeds when **1** and 1^+ lie above one another in approximately parallel planes, as would be required by an FMO-controlled process.^{3,14} Thus, two such orientations of the reactants which are approximately equivalent in terms of FMO overlap will give the diastereomeric cation radicals (S^*,S^*)- 2^+ and (S^*,R^*)- 2^+ in each of which the bridging C4-C4' bond is pseudoaxial to both rings (Scheme III). Addition of O_2 to the allyl radical in each dimer cation radical is constrained for steric reasons to the lower, or *si*, face. In the reaction leading to **4**, ring closure can only proceed through the lower, or *re*, face of the second ring to deliver the trans-anti-cis epidioxide. In that reaction leading to **5**, ring closure can only proceed through the *si* face to give the trans-syn-cis epidioxide.

These reactions afford a type of product not encountered in singlet oxygen reactions,¹⁵ and which, as carbon-carbon bond formation is associated with the oxygenation process, offer considerable mechanistic and synthetic appeal. As far as we can ascertain, compounds related to **4** and **5** have not previously been described.

Acknowledgment. We thank the Australian Research Grants Scheme for financial support.

Supplementary Material Available: Frontier orbital coefficients in 1-methylcyclohexa-1,3-diene and its cation radical and spin densities and charge distributions in the cation radical, 1H NMR and HRMS data for **4**, **5**, **11**, and **12**, and ORTEP diagram, angles, bond lengths, least-squares coordinates, and thermal parameters for **11** (8 pages). Ordering information is given on any current masthead page.

(13) The four other epidioxides that can be formed will possess respectively cis-syn-cis, trans-syn-trans, cis-anti-cis, and trans-anti-trans configurations.

(14) Association of the benzene cation radical with benzene takes place in such a manner: Milosevich, S. A.; Saichek, K.; Hinchey, L.; England, W. B.; Kovacic, P. *J. Am. Chem. Soc.* **1983**, *105*, 1088 and references therein.

(15) Reaction of **1** with 1O_2 generated by means of methylene blue on alumina in CH_2Cl_2 at $-78^\circ C$ gave quantitatively the endoperoxide **6**.

Surface Conversion of Benzene to Acetylene

W. L. Parker* and R. M. Hexter

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

A. R. Siedle*

Science Research Laboratory
3M Central Research Laboratories
St. Paul, Minnesota 55144

Received February 4, 1985

Benzene is well-known to be a quite stable molecule and its chemistry is dominated by C-H substitution processes in which the C_6 aromatic ring is preserved. Cyclization of acetylenes to arenes is catalyzed by numerous molecular organometallic compounds¹ and also proceeds on metal surfaces, notably Pd(111).²⁻⁴ These observations suggest that these two hydrocarbons may be in equilibrium and the reverse process, decyclotrimerization of

(1) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. In *New Pathways for Organic Syntheses*; Plenum Press: New York, 1984; p 105.

(2) Gentle, T. M.; Muettterties, E. L. *J. Phys. Chem.* **1983**, *87*, 2469.

(3) Tysoc, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1983**, 623.

(4) Sesselman, W.; Woratschek, B.; Ertl, G.; Kuppers, J. *Surf. Sci.* **1983**, *130*, 245.

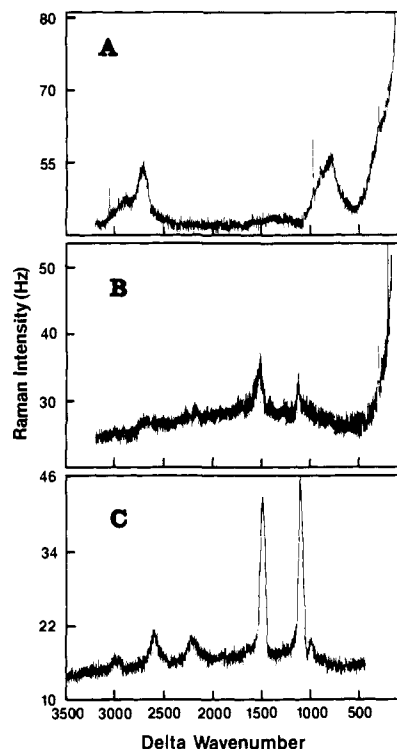


Figure 1. Raman spectrum of (A) benzene, (B) benzene plus CO, and (C) acetylene on 10% Rh on alumina obtained with 4880-Å laser excitation, 100-mW power input.

benzene to acetylene, may be possible. We wish to report results which demonstrate that, in the presence of certain coadsorbates, conversion of benzene to acetylene occurs on metallic rhodium catalysts, a reaction that appears to be without precedent.

The analytical probe in our experiments is Raman spectroscopy which we have previously shown to be useful for surface chemical characterization on supported catalysts and metal particles.^{5,6} The catalyst is 10% rhodium supported on α -alumina, reactions on which were carried out in an ultrahigh vacuum combination reactor and Raman cell.⁷

Benzene was admitted to the cell to ca. 60 torr. The Raman spectrum at this stage, Figure 1A, shows broad lines near 2960 and 1000 cm^{-1} due to chemisorbed benzene and sharp peaks at 3063 and 992 cm^{-1} which correspond to the most intense lines in the spectrum of liquid benzene. The latter are assigned to a physisorbed multilayer phase as inferred from earlier infrared data,¹² they are not apparent when the laser beam is focused on the sample holder instead of the catalyst sample. The lines due to physisorbed benzene disappear upon evacuation of the cell. The Raman spectrum of chemisorbed benzene on Rh/ Al_2O_3 is consistent with a η_6 bonding mode found on single crystal metal

(5) Parker, W. L.; Hexter, R. M.; Siedle, A. R. *Chem. Phys. Lett.* **1984**, *107*, 96.

(6) Parker, W. L.; Hexter, R. M.; Siedle, A. R. *J. Am. Chem. Soc.* **1985**, *107*, 264.

(7) The supported catalyst was prepared by the method of Yang and Garland⁸ according to which alumina impregnated with $RhCl_3$ is reduced with 100 torr of hydrogen at $150^\circ C$. The reduction is performed in a combination ultrahigh vacuum reactor-spectrometer cell after which the cell is evacuated to 5×10^{-7} torr and baked at $150^\circ C$ for 8 h and then cooled prior to introduction of adsorbates. It is known⁹ that, at 10% loading, the average metal particle size is ca. 2.6 nm and has a raftlike morphology. Infrared spectroscopy of CO on such particles indicates that the group frequencies and bridge:terminal CO ratio are similar to those on Rh(111).¹⁰ Pure alumina exhibits an intense luminescence¹¹ which frustrates collection of background spectra and which is effectively quenched in the presence of metallic rhodium.

(8) Yang, A. C.; Garland, C. W. *J. Phys. Chem.* **1957**, *61*, 1504.

(9) Yates, D. J. C.; Murell, L. L.; Prestridge, E. B. *J. Catal.* **1979**, *57*, 41.

(10) Cavanagh, R. R.; Yates, J. T., Jr. *J. Chem. Phys.* **1981**, *74*, 4150.

(11) Jeziorowski, H.; Knozinger, H. *Chem. Phys. Lett.* **1977**, *51*, 519.

(12) Little, L. H. "Infrared Spectra of Adsorbed Species"; Academic Press: New York, 1966.