


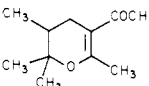
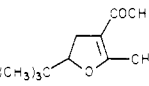
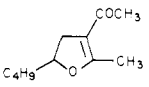

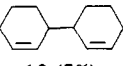


Table I. Benzophenone-Sensitized Photoreduction of  $\text{Cu}(\text{acac})_2$  in the Presence of Various Olefins

|   |   |  |
|---|---|--|
|  |  |     |
| <b>2 (24%)</b>  | <b>3 (6%)</b>   |  |
| $(\text{CH}_3)_3\text{CCH}=\text{CH}_2$   | $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{CH}(\text{COCH}_3)_2$                | $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}(\text{COCH}_3)_2$ |
| <b>4 (35%)</b>  | <b>6 (3%)</b>   |  |
|  |  |  |
| <b>5 (11%)</b>  | <b>7 (12%)</b>  |  |
| $\text{C}_4\text{H}_9\text{CH}=\text{CH}_2$                                       | $\text{C}_4\text{H}_9\text{CH}_2\text{CH}_2\text{CH}(\text{COCH}_3)_2$            | $\text{C}_3\text{H}_7\text{CH}=\text{CHCH}_2\text{CH}(\text{COCH}_3)_2$              |
| <b>8 (16%)</b>  | <b>9 (4%)</b>   |  |
|  |   |  |
| <b>10 (13%)</b>   |   |  |
|  |  |  |
| <b>11 (48%)</b>   | <b>12 (7%)</b>  |  |

by the triplet signal of the methine proton. The formation of **5** and **6** suggests the intervention of carbenium ion intermediates<sup>10</sup> by electron transfer as shown in eq 10:  $\text{Cu}(\text{OAc})_2$  is known to be a better oxidizing species<sup>3</sup> than  $\text{Cu}(\text{acac})_2$ .

The product pattern indicates that, besides abstracting a hydrogen, the acetylacetyl radical also adds to  $\pi$  bonds regio-specifically and exclusively as the C radical. This is in good agreement with the report that 77% of the spin density in the acetylacetyl radical resides at  $\text{C}_3$  and the O-radical structure is unimportant.<sup>6</sup> With poor hydrogen-donating substrates such as norbornene and neohexene the acetylacetyl radical attacks the double bonds without showing any sign of hydrogen abstraction. The cyclohexenyl radical is much more easily oxidized than the acyclic radical to the corresponding carbenium ion under the reaction conditions, and the 2-norbornyl radical is surprisingly resistant to the oxidation. In view of the ease of solvolytic formation of norbornyl cations,<sup>11</sup> the tendency for radical oxidation must be related to, among other factors, the extent of the s character of the orbital containing the unpaired electron. The oxidative addition, as represented by eq 2 and 6-8, involves reduction to copper(I) and then to copper metal, which would slowly retard the photoreaction. Owing to the reduction process, the addition reaction of the acetylacetyl radical cannot be schemed into a catalytic cycle at the present stage.

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Research Council of Canada for generous operating grants. Y.L.C. is much indebted to Professor A. Rassat and his colleagues of LEDSS, Université Scientifique et Médicale de Grenoble, for lively discussion and hospitality.

**Registry No.** **1**, 77350-15-3; *exo-2*, 81769-99-5; *exo-3*, 25121-32-8; **4**, 81770-00-5; **5**, 81770-01-6; **6**, 81770-02-7; **7**, 81770-03-8; **8**, 64122-32-3; **9**, 81770-04-9; **10**, 81770-05-0; **11**, 14447-34-8; **12**, 1541-20-4;  $(\text{CH}_3)_3\text{CCH}=\text{CH}_2$ , 558-37-2;  $\text{C}_4\text{H}_9\text{CH}=\text{CH}_2$ , 592-41-6;  $\text{Cu}(\text{acac})_2$ , 46369-53-3; benzophenone, 119-61-9; 2-norbornene, 498-66-8; cyclohexene, 110-83-8; acetylacetyl radical, 17374-75-3; 2-nitroso-2-methylpropane, 917-95-3.

**Supplementary Material Available:** Photolysis conditions and isolation of the products and the NMR, IR, and MS data of products **2-11** (5 pages). Ordering information is given on any current masthead page.

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## Carbenium-Carbonium Structures, $\text{H}_2\text{C}^+-\text{CH}_4^+$ , for the Ethane Dication

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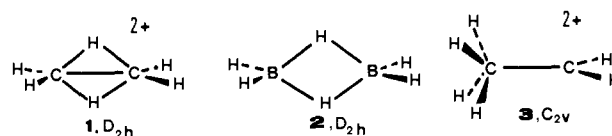
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Olah and Simonetta's theoretical reexamination of the ethane dication,  $\text{C}_2\text{H}_6^{2+}$ , favored a doubly bridged form, **1** ( $D_{2h}$ ), similar



to **2**, the structure of the isoelectronic analogue diborane.<sup>1</sup> Despite being highly unstable electrostatically toward dissociation into two methyl cations, **1** was indicated to be a minimum on the potential-energy surface. As part of an extensive theoretical survey of dications,<sup>2</sup> we have also examined a variety of  $\text{C}_2\text{H}_6^{2+}$  structures and states. The results extend the findings of Olah and Simonetta significantly. Surprisingly, the carbenium-carbonium dication geometry, **3**, is significantly more stable than **1**. We also conclude that  $\text{C}_2\text{H}_6^{2+}$  might be observable experimentally, e.g., by charge-stripping mass spectroscopy.<sup>3</sup>

Various fixed points on the  $\text{C}_2\text{H}_6^{2+}$  potential-energy surface were first located and characterized by the number of negative eigenvectors in the force-constant matrix at the 3-21G//3-21G split valence ab initio basis set level (Table I).<sup>4</sup> Some of the geometries were further optimized with a d orbital augmented basis set (6-31G\*\*//6-31G\*\*).<sup>5</sup> Because of the importance of electron correlation in describing the dimerization of borane<sup>6</sup> and the bridging of the ethyl cation,<sup>7</sup> final calculations at the 6-31G\* geometries were carried out at the fourth-order Møller-Plesset level (including all single, double, and quadruple excitations) with a larger basis set, including p-type polarization functions on hydrogen (MP4SDQ/6-31G\*\*//6-31G\*\*).<sup>5,8</sup> Correlation does decrease the energy of **1** relative to **3**, but not decisively (Table I). A large number of geometries were explored, but only the lowest energy forms are listed in Table I. In particular, triplet states were found not to be competitive, and singlet structures

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(5) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209-213.  
(6) See: (a) Redmon, L. T.; Purvis, G. D., III; Bartlett, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 2856-2862. (b) Dill, J. D.; Schleyer, P. v. R.; Pople, J. A. *Ibid.* **1975**, *97*, 3402-3409.

(7) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649-5657.

(8) Krishnan, R.; Pople, J. A. *Int. J. Quant. Chem.* **1978**, *14*, 91-100.

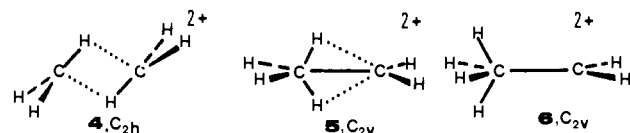
Table I. Calculated Total (au) and Relative Energies (kcal/mol, in Parentheses)

| species   | 3-21G//3-21G                   | 6-31G**//6-31G*                | MP2/6-31G**//6-31G*            | MP4SDQ/6-31G**//6-31G* |
|---|--------------------------------|--------------------------------|--------------------------------|------------------------|
| 1, $D_{3h}$   | -77.762 15 (34.0) <sup>a</sup> | -78.231 51 (15.8) <sup>a</sup> | -78.475 66 (9.7)               | -78.553 03 (9.0)       |
| 3, $C_{2v}$   | -77.816 26 (0.0) <sup>a</sup>  | -78.256 70 (0.0)               | -78.491 17 (0.0)               | -78.567 35 (0.0)       |
| 4, $C_{2h}$   | -77.757 23 (37.0) <sup>b</sup> | -78.213 94 (26.8)              |                                | -78.524 62 (26.8)      |
| 5, $C_{2v}$   | -77.759 00 (35.9) <sup>c</sup> |                                |                                |                        |
| 6, $C_{2v}$   | -77.815 07 (0.7) <sup>b</sup>  | -78.255 28 (0.9)               | -78.488 69 (1.6)               |                        |
| 2CH <sub>3</sub> <sup>+</sup>                                   | -78.018 26 (-126.8)            | -78.461 28 (-128.4)            | -78.650 28 (-99.8)             | -78.734 74 (-105.0)    |
| C <sub>2</sub> H <sub>6</sub> <sup>2+</sup> + (H <sup>+</sup> ) | -77.872 60 (-35.3)             | -78.311 23 (-34.2)             | -78.551 84 (-38.1)             | -78.620 65 (-33.4)     |
| C <sub>2</sub> H <sub>6</sub>                                   | -78.793 95 (-613.5)            | -79.228 75 (-610.0)            | -79.494 74 (-629.7)            |                        |
| 7, $C_{2v}$   | -65.314 54 (0.0)               | -65.692 60 (0.0) <sup>d</sup>  | -65.896 21 (0.0) <sup>d</sup>  |                        |
| 8, $C_{2v}$   | -65.263 09 (32.3)              | -65.634 18 (36.7) <sup>d</sup> | -65.849 32 (29.4) <sup>d</sup> |                        |
| BH <sub>3</sub> + CH <sub>3</sub> <sup>+</sup>                  | -65.246 43 (42.7)              | -65.620 65 (45.1)              | -65.789 38 (67.0)              |                        |
| CH <sub>4</sub> + BH <sub>2</sub> <sup>+</sup>                  | -65.295 42 (12.0)              | -65.665 97 (16.7)              |                                |                        |
| 2, $D_{3h}$   | -52.497 81 (0.0)               | -52.812 40 (0.0)               | -52.992 82 (0.0) <sup>e</sup>  |                        |
| 9, $C_{2v}$   | -52.387 42 (69.3)              | -52.691 20 (76.1) <sup>d</sup> | -52.882 97 (68.8) <sup>d</sup> |                        |
| 2BH <sub>3</sub>  | -52.474 60 (14.6)              | -52.780 02 (20.3)              | -52.928 46 (40.4) <sup>e</sup> |                        |

<sup>a</sup> No negative eigenvalues in the force constant matrix. <sup>b</sup> One negative eigenvalue. <sup>c</sup> Two negative eigenvalues. <sup>d</sup> 3-21G geometries. <sup>e</sup> MP2/6-31G\* geometries.

based on ethane-like symmetries ( $D_{3d}$  or  $D_{3h}$ ) dissociated upon geometry optimization.

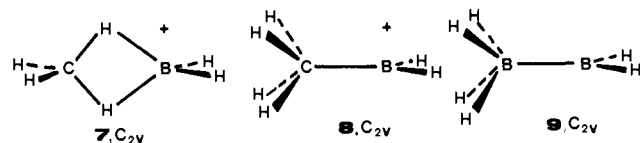
In agreement with Olah and Simonetta, the diborane-like geometry (1) was found to be a local minimum (no negative eigenvalues) on both the 3-21G and the 6-31G\* potential-energy surfaces. A transition structure for dissociation of 1 into two methyl cations (4,  $C_{2h}$ , with one negative eigenvalue) was 17.8



kcal/mol higher in energy (MP4SDQ/6-31G\*\*//6-31G\*). However, a  $C_{2v}$  geometry (5), only 2.0 kcal/mol higher in energy than 1, characterizes a process whereby the two bridging hydrogens move simultaneously<sup>9</sup> to give the carbenium-carbonium dication, 6, which is substantially more stable than 1 at all levels studied. With one negative eigenvalue, 6 is not a local minimum but rather the transition structure for rotation into a second  $C_{2v}$  form, 3, the global  $C_2H_6^{2+}$  minimum. The rotation barrier is small.<sup>10</sup>

While 3 still is unstable thermodynamically toward dissociation into two methyl cations (by 105 kcal/mol) or toward loss of a proton (by 38 kcal/mol), both these processes should require considerable activation. With the assumption that 4 is the transition structure for the dissociation of 3, 26.8 kcal/mol activation would be needed to give two methyl cations. Preliminary calculations at the 3-21G level indicate that the loss of a proton from 3 would involve a large activation energy. In this respect,  $C_2H_6^{2+}$  should be similar to  $CH_4^{2+}$ ,<sup>2c</sup> an experimentally observable carbocation.<sup>3</sup>

Structures for the isoelectronic  $BCH_6^+$  cation, which models a species for which there is experimental evidence,<sup>1</sup> also were examined. In this case, the diborane-like geometry, 7, the global



minimum, was found to be 29.4 kcal/mol (MP2/6-31G\*\*//3-21G) more stable than 8 (the form analogous to 3). For  $B_2H_6$ , the

similar energy difference favoring 2 over 9 increases to 69.2 kcal/mol at the same level.

In contrast to  $C_2H_6^{2+}$ ,  $CBH_6^+$  is stable toward dissociation into  $CH_3^+$  and  $BH_3$  by 67.0 kcal/mol (MP2/6-31G\*\*//3-21G). However, a second dissociation mode, to give  $BH_2^+$  and  $CH_4$ , is somewhat less unfavorable (38.6 kcal/mol). For comparison at a similar theoretical level (MP2/6-31G\*\*//MP2/6-31G\*), the dissociation of diborane into two  $BH_3$ 's requires 40.4 kcal/mol. This value is only a little above the best theoretical estimates.<sup>6</sup>

Why is the structural preference of  $C_2H_6^{2+}$  so exceptional? What effects are responsible for the greater stability of 3 over 1? In the first place, the B-B bond is inherently weaker than the C-C bond. Thus, the B...B distance in diborane, 1.77 Å,<sup>6</sup> is considerably longer than the standard B-B single bond length (1.64 Å),<sup>6b</sup> but the C-C distance in 1, 1.563 Å, is only slightly longer than that of a typical C-C single bond (1.53 Å). In 3, the shortened C-C distance, 1.477 Å, indicates hyperconjugative stabilization between the nominally vacant carbenium p orbital and the pyramidal  $CH_4$  moiety.

The second effect is electrostatic. The population analysis indicates that the positive charges are primarily located on the hydrogen atoms, since hydrogen is more electropositive than carbon. In 3, the hydrogens on the average are farther apart than in 1, and intramolecular electrostatic repulsion is reduced.

**Conclusions.** 1. The structures of the two minima on the  $C_2H_6^{2+}$  potential-energy surface can easily be understood as products of formal proton addition, either symmetrically to the bridged ethyl cation to give 1 or to the methyl group of the classical ethyl cation to give 3.

2. Unlike the isoelectronic  $B_2H_6$  and  $CBH_6^+$  species, the unprecedented carbenium-carbonium dication structure for  $C_2H_6^{2+}$ , 3, is preferred over the diborane-like alternative, 1, which, at best, represents a shallow minimum easily converted into 3. This preference is due to reduced electrostatic repulsion and stronger C-C bonding in 3.

3. Although 3 is unstable thermodynamically, the rather high barriers toward loss of a proton or dissociation into two methyl cations should permit observation of  $C_2H_6^{2+}$  under appropriate experimental conditions, e.g., by charge-stripping mass spectroscopy.<sup>3,11</sup>

**Acknowledgment.** This work was supported at Erlangen by the Fonds der Chemischen Industrie and at Pittsburgh by the National

(9) Since 5 has two negative eigenvalues, it is not the true transition structure separating the two minima 1 and 3. The true transition structure, which cannot have  $C_{2v}$  symmetry, must have somewhat less energy than 5.

(10) In general, semiempirical calculations perform tolerably well. MNDO, known to disfavor bridged forms (Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899, 4907), finds 6 to be about 35 kcal/mol more stable than 1. MINDO/3 gives the opposite stability order but a smaller energy difference (ca. 5 kcal/mol). Association of the 2-propyl cation and  $BH_3$  to give  $(CH_3)_2CH_2BH_2^+$  (see 7)<sup>1</sup> is 9.4 kcal/mol exothermic (MNDO). M. J. S. Dewar (private communication) also has examined  $C_2H_6^{2+}$  at these semiempirical levels.

(11) There is one report of the fleeting experimental observation of  $C_2H_6^{2+}$  by Auger spectroscopy: Spohr, R.; Bergmark, T.; Magnusson, N.; Werme, L. O.; Nordling, C.; Siegbahn, K. *Phys. Scr.* 1970, 2, 31-37. However, the reported dissociation energy (into  $C_2H_5^+$  and  $H^+$ ), about -8 eV, for  $C_2H_6^{2+}$ , is in gross disagreement with our calculated value (-1.6 eV, Table I). The calculated double ionization potential of  $C_2H_6$ , 27.3 eV at MP2/6-31G\*, likewise is far less than the reported experimental value,  $34.8 \pm 0.8$  eV.  $C_2H_6^{2+}$  has not been observed by electron impact; see: Jones, B. E.; Abbey, L. E.; Chatham, H. L.; Hanner, A. W.; Teleshefsky, L. A.; Burgess, E. M.; Moran, T. F. *Org. Mass Spectrosc.* 1982, 17, 10; Meyerson, S.; Ihrig, P. J., private communication.

Science Foundation (Grant CHE-79-01061) and was facilitated by a NATO grant. We thank Professor Olah for a preprint of ref 1 and are indebted to Professor Beynon and Professor Ast for helpful information.

Registry No. 1, 81702-60-5; 2, 19287-45-7; 3, 5, 6, 81643-07-4; 4, 80181-26-6; C<sub>2</sub>H<sub>5</sub><sup>+</sup>, 14936-94-8; H<sup>+</sup>, 12184-88-2; BH<sub>3</sub>, 13283-31-3; CH<sub>3</sub><sup>+</sup>, 14531-53-4; CH<sub>4</sub>, 74-82-8; BH<sub>2</sub><sup>+</sup>, 15194-16-8.

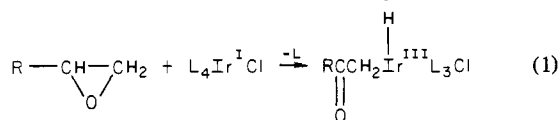
### Oxidative Addition of Unactivated Epoxides to Iridium(I) Complexes. Formation of Stable *cis*-Hyridoformylmethyl and -Acylmethyl Complexes<sup>†</sup>

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Despite the large number of transition-metal homogeneously catalyzed transformations of epoxides reported and their considerable synthetic utility,<sup>1</sup> little is known about the mechanism of interaction of transition-metal complexes with epoxides. Intermediates resulting from such reactions, although highly desirable for mechanistic understanding, are exceedingly scarce and have been isolated only with the very electron-deficient tetracyanoethylene oxide<sup>2</sup> and in two cases where ligand-initiated reactions take place leading to complexes that are stabilized by carbonylation to the corresponding acyl complexes.<sup>3</sup>

We have recently found that a series of stable Ir(III) *cis*-hydridoacylmethyl complexes can be easily obtained from reactions of epoxides with Ir(I) trimethylphosphine complexes (eq 1). In



addition to providing the first examples of unassisted oxidative addition of simple epoxides to transition-metal complexes, the reaction sheds more light on the mechanism of the transition-metal-catalyzed transformations of epoxides and leads to formation of complexes that are of interest in their own right.

Addition of excess ethylene oxide to an orange solution of Ir(C<sub>8</sub>H<sub>14</sub>)(PMe<sub>3</sub>)<sub>3</sub>Cl<sup>4,5</sup> (1) under N<sub>2</sub> at -10 °C followed by warming to room temperature over 45 min results in decoloration. Removal of the solvent and excess epoxide and crystallization of the resulting oil from toluene by the vapor diffusion of hexane

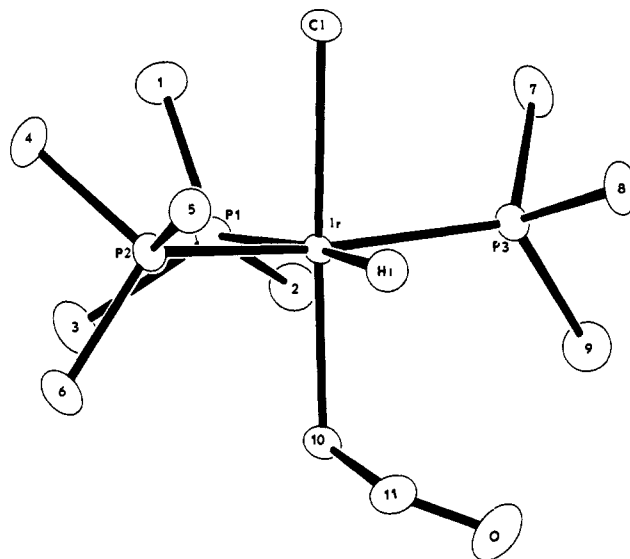
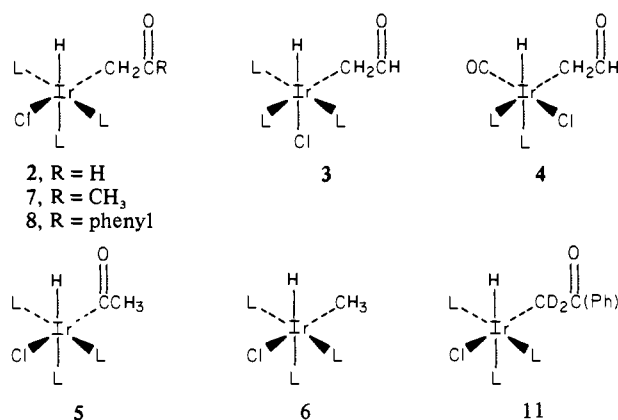


Figure 1. ORTEP drawing of a molecule of 2 showing thermal ellipsoids at 25% probability level. Selected bond distances (Å) and angles (deg) are as follows: Ir-Cl, 2.467 (1); Ir-H, 1.64 (6); Ir-P<sub>1</sub>, 2.337 (1); Ir-P<sub>2</sub>, 2.309 (1); Ir-P<sub>3</sub>, 2.312 (1); Ir-C<sub>10</sub>, 2.127 (6); C<sub>10</sub>-C<sub>11</sub>, 1.478 (8); Ir-C<sub>10</sub>-C<sub>11</sub>, 106.7 (4); Cl-Ir-C<sub>10</sub>, 176.1 (2); P<sub>2</sub>-Ir-P<sub>3</sub>, 163.7 (1).

#### Chart I<sup>a</sup>



<sup>a</sup> L = PMe<sub>3</sub>.

yield the *cis*-hydridoformylmethyl complex 2 (Chart I) in 85% yield as white needles.<sup>6</sup> Since the hydrido <sup>1</sup>H NMR signal is consistent only with a structure containing a trimethylphosphine ligand trans to the hydride ligand and having two identical *cis*-trimethylphosphine ligands, the hydrido and formylmethyl ligands have to be in mutually *cis* positions. This structural assignment of 2 has been confirmed by a single-crystal X-ray diffraction study, shown in Figure 1.<sup>7</sup>

Coordination about the iridium is octahedral with expected deviations arising from the decreased steric bulk of the hydride ligand. The C(10)-C(11) bond length of 1.478 (8) Å is slightly shorter than a normal C-C bond because of the expected β effect.<sup>8</sup> The Ir-P trans to the hydride is 0.03 Å longer than the Ir-P bond *cis* to it, thus reflecting the large trans effect exerted by the hydride

(6) 2: IR (Nujol) 2683 (m, ν<sub>OC-H</sub>), 2015 (s, ν<sub>Ir-H</sub>), 1663 cm<sup>-1</sup> (s, ν<sub>C=O</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.40 (d, J = 7 Hz, 9 H, PMe<sub>3</sub>), 1.56 (t, J = 4 Hz, 18 H, 2 PMe<sub>3</sub>), 1.92 (pseudo quintet, J = 6 Hz, 2 H, CH<sub>2</sub>-Ir), 8.76 (t, J = 6 Hz, 1 H, CHO), -11.3 (d of t, J<sub>H-P,trans</sub> = 152, J<sub>H-P,cis</sub> = 19 Hz, 1 H, Ir-H); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ -52.4 (t, J = 21 Hz, 1 P), -45.2 (d, J = 21 Hz, 2 P). Satisfactory C and H analyses were obtained for 2-4, 6-8, and 11.

(7) Crystal data for 2: IrC<sub>11</sub>H<sub>13</sub>P<sub>3</sub>ClO space group P2<sub>1</sub>/c, cell dimensions (-100 °C) a = 13.691 (3) Å, b = 9.307 (2) Å, c = 15.184 (2) Å, β = 99.29 (1)°, V = 1909 Å<sup>3</sup>, Z = 4, R = 0.026, R<sub>w</sub> = 0.034 for 278 parameters, 3570 absorption corrected (μ = 73.441 cm<sup>-1</sup>) data with I ≥ 2σ(I). All details are included in the supplementary material.

(8) For a similar effect in (acylalkyl)manganese complexes, see: Engelbrecht, J.; Greiser, T.; Weiss, E. *J. Organomet. Chem.* 1981, 204, 79.

<sup>†</sup> Contribution No. 3022.

(1) Transition-metal complexes have been reported to catalyze isomerization, hydrogenation, hydroformylation, carboxylation, carbonylation, hydrogenolysis, dimerization, and deoxygenation reactions of epoxides: (a) Milstein, D.; Buchman, O.; Blum, J. *J. Org. Chem.* 1977, 42, 2299 and references therein. (b) Blum, J.; Zinger, B.; Milstein, D.; Buchman, O. *Ibid.* 1978, 43, 2961. (c) Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* 1979, 101, 1623. (d) Suzuki, M.; Watanabe, A.; Noyori, R. *Ibid.* 1980, 102, 2095. (e) Fujitsu, H.; Shirahama, S.; Matsumura, E.; Takenshita, K.; Mochida, I. *J. Org. Chem.* 1981, 46, 2287. (f) Kamiya, Y.; Kawato, K.; Ohta, H. *Chem. Lett.* 1980, 1549. (g) Hayashi, Y.; Schwartz, J. *Inorg. Chem.*, 1981, 20, 3473. (h) Thompson, D. T.; Whyman, R. In "Transition Metals in Homogeneous Catalysis"; G. N. Schrauzer, Ed.; Marcel Dekker: New York, 1971.

(2) (a) Schlotter, R.; Ibers, J. A.; Lenarda, M.; Graziani, M. *J. Am. Chem. Soc.* 1974, 96, 6893. (b) Lenarda, M.; Ros, R.; Travsero, O.; Pitts, W. D.; Baddley, W. H.; Graziani, M. *Inorg. Chem.* 1977, 16, 3178.

(3) The two processes known are: (a) Addition of HCo(CO)<sub>4</sub> to epoxides, which is proton promoted: Heck, R. F. *J. Am. Chem. Soc.* 1963, 85, 1460. (b) The trimethylsilyl-initiated reaction of (trimethylsilyl)manganese pentacarbonyl with ethylene oxide: Brinkman, K. C.; Gladysz, J. *J. Chem. Soc., Chem. Commun.* 1980, 1260. In both these reactions, stable product complexes could be obtained only after reaction with CO.

(4) Preparation of 1 and [Ir(PMe<sub>3</sub>)<sub>4</sub>]<sup>+</sup>Cl<sup>-</sup> is reported by Herskovitz (Herskovitz, T. *Inorg. Synth.*, in press).

(5) The Ir(I) complexes employed are very oxygen sensitive, and all operations were carried out in a N<sub>2</sub> drybox using dry, degassed solvents.