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; $C_2H_5^+$, 14936-94-8; H^+, 12184-88-2; BH_3, 13283-31-3; CH_3^+, 14531-53-4; CH_4, 74-82-8; BH_2^+, 15194-16-8.

Oxidative Addition of Unactivated Epoxides to Iridium(I) Complexes. Formation of Stable *cis*-Hydridoformylmethyl and -Acylmethyl Complexes[†]

D. Milstein* and J. C. Calabrese

Central Research & Development Department
Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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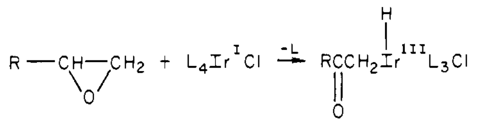
Despite the large number of transition-metal homogeneously catalyzed transformations of epoxides reported and their considerable synthetic utility,[1] little is known about the mechanism of interaction of transition-metal complexes with epoxides. Intermediates resulting from such reactions, although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

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



$$R-\underset{\diagdown O \diagup}{CH-CH_2} + L_4Ir^{I}Cl \xrightarrow{-L} R\underset{\underset{O}{\|}}{C}CH_2\overset{\overset{H}{|}}{Ir^{III}}L_3Cl \quad (1)$$

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 $Ir(C_8H_{14})(PMe_3)_3Cl$[4,5] (**1**) under N_2 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 yield the *cis*-hydridoformylmethyl complex **2** (Chart I) in 85% yield as white needles.[6] Since the hydrido ^1H 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.[7]

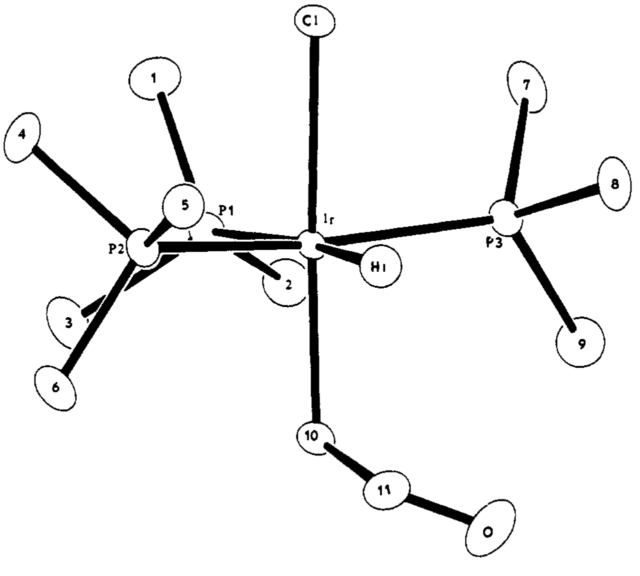
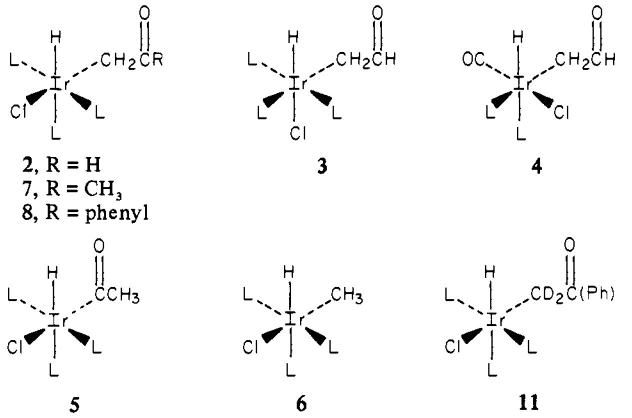


Figure 1. ORTEP drawing of a molecule of **2** showing thermal ellipsoids at 25% probability level. Selected bond distances (Å) and angles (deg) are as follows: Ir–Cl, 2.467 (1); Ir–H, 1.64 (6); Ir–P_1, 2.337 (1); Ir–P_2 2.309 (1); Ir–P_3, 2.312 (1); Ir–C_{10}, 2.127 (6); C_{10}–C_{11}, 1.478 (8); Ir–C_{10}–C_{11}, 106.7 (4); Cl–Ir–C_{10}, 176.1 (2); P_2–Ir–P_3, 163.7 (1).

Chart I[a]



2, R = H
7, R = CH_3
8, R = phenyl

3

4

5

6

11

[a] L = PMe_3.

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.[8] 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

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[†] 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 Deckker: New York, 1971.

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

(3) The two processes known are: (a) Addition of $HCo(CO)_4$ 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 $[Ir(PMe_3)_4]^+Cl^-$ 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_2 drybox using dry, degassed solvents.

(6) **2**: IR (Nujol) 2683 (m, ν_{OC-H}), 2015 (s, ν_{Ir-H}), 1663 cm^{-1} (s, $\nu_{C=O}$); ^1H NMR ($CDCl_3$) δ 1.40 (d, J = 7 Hz, 9 H, PMe_3), 1.56 (t, J = 4 Hz, 18 H, 2 PMe_3), 1.92 (pseudo quintet, J = 6 Hz, 2 H, CH_2–Ir), 8.76 (t, J = 6 Hz, 1 H, CHO), −11.3 (d of t, $J_{H-P,trans}$ = 152, $J_{H-P,cis}$ = 19 Hz, 1 H, Ir–H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 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**: $IrC_{11}H_{31}P_3Cl\cdot O$ space group $P2_1/c$, 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^3, Z = 4, R = 0.026, R_w = 0.034 for 278 parameters, 3570 absorption corrected (μ = 73.441 cm^{-1}) data with $I \geq 2\sigma(I)$. 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.

0002-7863/82/1504-3773$01.25/0

ligand. The Ir-H distance of 1.64 (6) Å is exactly the same as determined in other studies.[9]

Reaction of **1** with ethylene oxide leads to formation of a small amount (ca. 5%) of the isomer **3**, which structure was determined unambiguously by NMR and IR.[10] **2** and **3** are fairly insensitive to oxygen, especially in the solid state, but are very hygroscopic.

2 can be obtained also from reaction of ethylene oxide with $[Ir(PMe_3)_4]^+Cl^-$,[4] although this reaction is somewhat slower. Reaction of $Ir(CO)(PMe_3)_2Cl$[11] with ethylene oxide takes place in a similar fashion, yielding **4**.[12] This reaction is substantially slower (15 h is required for completion) than that of **1** with the epoxide, probably reflecting the lower tendency of the Ir(I) carbonyl complex to undergo oxidative addition. In view of the above observations, it is perhaps not surprising that no reaction at all takes place at 25 °C between $[Ir(PMe_3)_4CO]^+Cl^-$ [11] and ethylene oxide.

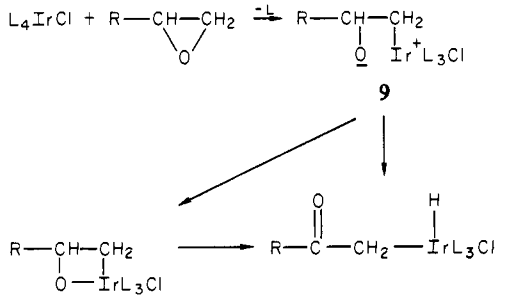
It is interesting to note that **2–4** can be formally regarded as oxidative-addition products of acetaldehyde at the methyl, rather than formyl, C–H bond and are the only transition-metal complexes of this kind reported.

The mere formation of **2–4** is remarkable, since once formed, oxidative addition of the formylmethyl ligand to the unreacted Ir(I) complex is expected to be a facile process. Moreover, stirring a solution of **2** with a 2-fold excess of **1** for 24 h did not result in any reaction. On the other hand, **1** reacts rapidly with acetaldehyde to yield the *cis*-acetylhydridoiridium(III) complex **5**.[13] Although the relatively low reactivity of the formylmethyl ligand can be attributed in part to steric reasons, it seems likely that this is due mainly to a β effect.[8] Nevertheless, under forcing conditions, complex **2** undergoes interesting reactions.[14] One such reaction is the clean decarbonylation of **2** upon heating with $Rh(PMe_3)_3Cl$ at 100 °C for 24 h to give the stable *cis*-hydridomethyl complex **6**[15-17] in 90% yield, in addition to $Rh(CO)(PMe_3)_2Cl$.[18]

Addition of epoxides to (trimethylphosphine)iridium(I) complexes seems to be of a general nature with regard to the epoxide. Propylene oxide reacts with **1** to afford the Ir(III) *cis*-hydrido(acetylmethyl)iridium(III) complex **7** in 88% yield,[19] whereas reaction of **1** with styrene oxide leads to formation of the *cis*-hydrido(benzoylmethyl)iridium(III) complex **8**[20] in 82% yield. The reaction of (trimethylphosphine)iridium(I) complexes with epoxides are regioselective in all of the cases studied, leading only to products in which the terminal oxirane carbon becomes attached to Ir.

2–4 and **6–8** are quite thermally stable. Compounds **2**, **3**, and **6**, for example, can be heated at 100 °C for 24 h under N_2 without any decomposition taking place. This stability, which has also been observed with other *cis*-hydridoalkyl(trimethylphosphine)iridium(III) complexes[16,21] is unusual in view of the generally high tendency of *cis*-hydridoalkyl complexes to undergo reductive elimination of the alkane[22] and is probably due to the reluctance of the trimethylphosphine ligands to dissociate from Ir(III).[23] This can account also for the observation that isomers **2** and **3** do not interconvert even under extent heating at 100 °C.

Mechanistically, the reaction seems to proceed through oxidative addition of the Ir(I) complexes to the epoxide at the least substituted C–O bond, followed by β-H elimination of the dipolar intermediate **9** or metallooxetane[24] **10** to yield the observed *cis*-hydridoalkyliridium(III) complexes (eq 2). Support for this mechanism includes formation of **11**[25] (chart I) as the sole product of the reaction of β,β-dideuteriostyrene oxide and **1**.[26,27]



9

10

(2)

Formation of **2–4**, **7–9**, and **11** sheds light on the mechanism of catalytic reactions of transition-metal complexes with epoxides under neutral conditions. Reductive elimination of analogous complexes, for example, would lead to formation of organic carbonyl compounds, thus pointing out a plausible pathway for the transition-metal-catalyzed isomerization of epoxides. Complexes of the type **2** and **7** have been invoked as intermediates in catalytic transformations of epoxides,[28] but evidence for their formation has been lacking until now.

Acknowledgment. Discussions with Drs. C. A. Tolman, S. S. Wreford, T. Herskovitz, T. H. Tulip, and D. L. Thorn are greatly appreciated. We thank M. A. Cushing, Jr., and L. Lardear for skilled technical assistance.

Supplementary Material Available: Crystal structure analysis summary and tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, interatomic distances, intramolecular angles, and intermolecular distances for $IrC_{11}H_{31}P_3Cl{\cdot}O$ (9 pages). Ordering information is given on any current masthead page.

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(9) See, for example: (a) Cichanourcz, M.; Skapeki, A. C.; Troughton, P. G. H. *Acta Crystallogr., Sect. B.* **1976**, *B32*, 1673. (b) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3252.

(10) **3**: ^1H NMR (C_6D_6) δ 1.30 (m, 27 H, PMe_3), 1.83 (m, 2 H, CH_2), 9.00 (t, J = 6 Hz, 1 H, CHO), –21.5 (d of t, $J_{H\text{-}P,cis}$ = 19 Hz, $J_{H\text{-}P',cis}$ = 13.5 Hz, 1 H, Ir–H, H trans to Cl); IR (Nujol) 2150 ($\nu_{Ir\text{-}H}$, H trans to Cl), 1663 cm^{-1} ($\nu_{HC=O}$).

(11) Preparation of this complex is described by Labinger and Osborn (Labinger, J. A.; osborn, J. A. *Inorg. Synth.* **1978**, *18*, 62.

(12) **4**: ^1H NMR (C_6D_6) δ 1.55 (d, J = 9 Hz, 9 H, PMe_3, trans to Ir–H) 1.75 (t, J = 4 Hz, 18 H, PMe_3 cis to Ir–H), 2.60 (m, 2 H, CH_2), 9.30 (d of d, J_1 = 8 Hz, J_2 = 1 Hz, 1 H, CHO), –8.86 (d of d, $J_{H\text{-}P,trans}$ = 174 Hz, $J_{H\text{-}P,cis}$ = 19.5 Hz); IR (Nujol) 2700 (m, $\nu_{H\text{-}CO}$), 2080 (m, $\nu_{Ir\text{-}H}$), 2010 (vs, $\nu_{Ir\text{-}CO}$), 1660 cm^{-1} (vs, $\nu_{HC=O}$).

(13) **5** has not been isolated pure so far, but its formation is unambiguous based on NMR and IR data: Milstein, D., to be submitted for publication. Not even traces of **2** are formed in the reaction of **1** with acetaldehyde.

(14) Milstein, D., to be submitted for publication.

(15) **6**: ^1H NMR (C_6D_6) δ 1.45 (t, J = 3.6 Hz, 18 H, PMe_3 cis to H), 1.15 (d of d, $J_{H\text{-}P}$ = 7.1 Hz, $J_{H\text{-}H}$ = 1.0 Hz, 9 H, PMe_3, trans to H) 0.20 (d of t of d, $J_{H\text{-}P}$ = 8.3 Hz, $J_{H\text{-}P'}$ = 6.3 Hz, $J_{H\text{-}H}$ = 1.0 Hz, 3 H, Ir–CH_3), –10.48 (d of t, $J_{H\text{-}P,trans}$ = 155.8 Hz, $J_{H\text{-}P,cis}$ = 21.5 Hz, 1 H, Ir–H); IR (Nujol) 1955 cm^{-1} ($\nu_{Ir\text{-}H}$).

(16) A stable cationic *cis*-hydridomethyliridium(III) complex has been reported recently: Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7109.

(17) Other stable *cis*-hydridomethyl compounds have been reported: Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421. Hayter, R. G. *J. Chem. Soc.* **1963**, 6017. Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

(18) IR and NMR spectra are identical with those reported by Jones et al. (Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511).

(19) **7**: ^1H NMR (C_6D_6) δ 1.13 (d, J = 7.2 Hz, 9 H, PMe_3), 1.63 (t, J = 3.5 Hz, 18 H, PMe_3), 2.15 (q, J = 6.5 Hz, 2 H, CH_2–Ir), 2.32 (s, 3 H, CH_3), –11.1 (d of t, $J_{H\text{-}P,trans}$ = 157.5 Hz, $J_{H\text{-}P,cis}$ = 18.8 Hz, 1 H, Ir–H); IR (Nujol) 2020 ($\nu_{Ir\text{-}H}$), 1640 cm^{-1} ($\nu_{C=O}$).

(20) **8**: ^1H NMR (C_6D_6) δ 1.12 (d, J = 7 Hz, 9 H, PMe_3), 1.40 (t, J = 4 Hz, 18 H, PMe_3), 2.50 (t of d, J_1 = 15 Hz, J_2 = 7 Hz) 7.12 (m, 3 H, *m,p*-phenyl H), 7.75 (m, 2 H, *o*-phenyl H), –11.14 (d of t, $J_{H\text{-}P,trans}$ = 160 Hz, $J_{H\text{-}P,cis}$ = 19 Hz, 1 H, Ir–H); IR (Nujol) 2030 ($\nu_{Ir\text{-}H}$), 1630 cm^{-1} ($\nu_{C=O}$).

(21) Thorn, D. L. *Organometallics* **1982**, *1*, 197.

(22) See, e.g.: Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.

(23) It has been suggested that dissociation of a ligand is required to form a "T"-shaped arrangement in dialkyl reductive elimination from square-planar complexes: Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

(24) Tetracyanoethylene oxide reacts with low-valent transition-metal complexes to give tetracyanometallooxetanes; see ref 2.

(25) **12**: ^1H NMR (C_6D_6) δ 0.8–1.2 (m, 27 H, PMe_3), 7.13 (m, 3 H, phenyl, *m,p*-H), 7.73 (m, 2 H, phenyl, *o*-H), –11.3 (d of t, $J_{H\text{-}P,trans}$ = 160 Hz, $J_{H\text{-}P,cis}$ = 18 Hz, 1 H, Ir–H) (the triplet of doublets at 2.50 ppm in the ^1H NMR of **8** assigned to Ir–CH_2 is completely absent here); IR (Nujol) 2160 (m, $\nu_{C\text{-}D}$), 2030 (s, $\nu_{Ir\text{-}H}$), 1625 cm^{-1} (s, $\nu_{C=O}$).

(26) 99% pure styrene-β,β-d_2 oxide was prepared by reaction of β,β-dideuteriostyrene with *m*-chloroperbenzoic acid.

(27) A Lewis acid type mechanism in which coordination of the metal to oxygen followed by β elimination takes place would lead to scrambling.

(28) See, for example, ref 1c,d.