knowledged. We thank Johnson-Matthey for a generous loan of precious metals.

Supplementary Material Available: Full spectral characterization of $(C_5H_5)(CO)_2Re(CH_2{=}CH_2)$, **6**, **7**, **8**, *cis*-**9**, and *trans*-**9** (2 pages). Ordering information is given on any current masthead page.

Stereoselective Oxidative Additions of a Carbon-Carbon σ-Bond in Tetrafluorocyclopropene to Iridium(I) Complexes

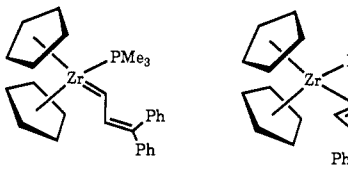
Russell P. Hughes,* Mackenzie E. King, David J. Robinson, and James M. Spotts

Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

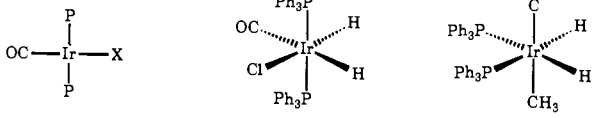
Received July 31, 1989

The stoichiometric and catalytic transition metal promoted reactions of cyclopropenes are of considerable interest and synthetic utility.[1] Opening of the cyclopropene ring by the metal center occurs frequently, to yield putative vinylcarbene intermediates **1** or isomeric metallacyclobutenes **2**. Only two vinylcarbene complexes[2,3] and a single example of a metallacyclobutene complex[4] have actually been isolated from such cyclopropene reactions. The mechanism of ring opening has been unclear, but the recent observation that 3,3-diphenyl-1-cyclopropene reacts with [Zr-$(\eta^5$-$C_5H_5)_2(\eta^2$-1-butene)(PMe_3)] to afford a mixture of isomers **3** and **4**, which do not interconvert thermally, has led to the suggestion by Binger[3] that "vinylcarbene complexes...are formed by direct opening of the cyclopropene ring and not via an η^2-cyclopropene intermediate". Here we confirm that the stereoselectivity of cyclopropene ring opening by Ir(I) complexes is indeed consistent with direct activation of a σ-bond by the metal center.

1 **2**



3 **4**



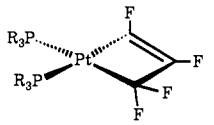
5 a. P = PPh_3, X = Cl
b. P = PPh_3, X = CH_3
c. P = PMe_3, X = Cl

6 **7**

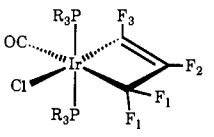
(1) For a review of the transition-metal chemistry of cyclopropenes, see: Binger, P.; Buch, H. M. In *Topics in Current Chemistry*; Meijere, A., Ed.; Springer-Verlag: Berlin, GDR, 1987; pp 77-151.
(2) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205. Valeri, T.; Meier, F.; Weiss, E. *Chem. Ber.* **1988**, *121*, 1093.
(3) Binger, P.; Mueller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610-611.
(4) Hemond, R. C.; Hughes, R. P.; Robinson, D. J.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2239-2241.

Oxidative addition of the σ-bond of the H_2 molecule to square-planar Ir(I) complexes (**5**) has been thoroughly studied.[5,6] Two stereoselective pathways have been defined for kinetically controlled addition; **5a** reacts to give stereoisomer **6**, while **5b** reacts to give **7**. Similar stereoselectivity is obtained for the addition of the R_3Si-H σ-bond to the same Ir(I) substrates, and detailed theoretical rationales for the effect of ancillary ligands on the stereocontrol of these reactions have been published.[5,6]

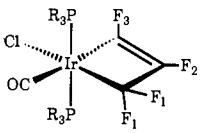
We have shown previously that formal oxidative addition of tetrafluorocyclopropene to the platinum(0) center in [Pt-$(C_2H_4)(PR_3)_2$] occurs rapidly at -78 °C to afford the platinacyclobutene complexes **8**.[4] Similarly, tetrafluorocyclopropene



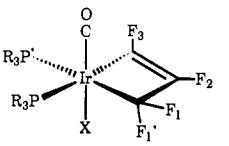
8 a. R = Ph
b. R = Me



9 a. R = Ph
b. R = Me



10 a. R = Ph
b. R = Me



11 a. R = Ph; X = Me
b. R = Me; X = Cl

reacts stereoselectively with **5a** at -78 °C in toluene solution, to yield quantitatively a ca. 1:1 mixture of two isomeric Ir(III) metallacyclobutene complexes. Each isomer exhibits a ^{19}F NMR spectrum containing three resonances of relative intensity 2:1:1 and a ^{31}P NMR spectrum containing a single resonance. The isomers must therefore have structures **9a** and **10a**, each possessing a mirror plane which includes the metallacyclic ring and which relates the phosphine ligands.[7] In contrast, tetrafluorocyclopropene reacts with **5b** to give a quantitative yield of a single isomer, whose ^{19}F NMR spectrum exhibits four equal-intensity resonances and whose ^{31}P NMR spectrum shows two inequivalent phosphorus environments. Accordingly, the structure of this isomer is assigned as **11a**.[7] In contrast to its PPh_3 analogue, the PMe_3 complex **5c** reacts with slightly less stereoselectivity, to give a mixture of **9b** (45%), **10b** (45%), and **11b** (10%).[8] This ratio

(5) Burk, M. J.; McGrath, M. P.; Wheeler, R.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 5034-5039.
(6) Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147-1161.
(7) Satisfactory microanalytical results (C, H; ±0.4% of calculated values) were obtained for all complexes. NMR assignments were confirmed by selective $^{19}F\{^{19}F\}$, $^{19}F\{^{31}P\}$, and $^{31}P\{^{19}F\}$ decoupling experiments. **9a**: ^{19}F NMR ($CDCl_3$) (282 MHz; positive chemical shifts upfield from $CFCl_3$) δ 74.1 (m, 2 F_1), 105.4 (m, F_2), 124.9 (m, F_3), $J_{1,2}$ = 7, $J_{1,3}$ = 20, $J_{2,3}$ = 15, $J_{P\text{-}F3}$ = 4 Hz; $^{31}P\{^1H\}$ NMR ($CDCl_3$) (121 MHz; positive chemical shifts downfield from H_3PO_4) δ 2.1 (m); IR ($CHCl_3$) ν(CO) = 2025 cm^{-1}. **10a**: ^{19}F NMR ($CDCl_3$) δ 86.7 (m, 2 F_1), 106.2 (m, F_3), 112.7 (m, F_2), $J_{1,2}$ = 5, $J_{1,3}$ = 19, $J_{2,3}$ = 11 Hz; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -5.2 (m); IR ($CHCl_3$) ν(CO) = 2057 cm^{-1}. **11a**: ^{19}F NMR ($CDCl_3$) δ 79.7 (m, F_1), 104.2 (m, F_2), 109.3 (m, $F_{1'}$), 118.9 (m, F_3), $J_{1,1'}$ = 205, $J_{1,3}$ = 19, $J_{1,P'}$ = 35, $J_{1,P}$ = 5, $J_{1',3}$ = 20, $J_{1',P'}$ = 36, $J_{1',P}$ = 3, $J_{2,3}$ = 10, $J_{2,P}$ = 22, $J_{2,P'}$ = 22, $J_{3,P}$ = 56, $J_{3,P'}$ = 4 Hz; ^1H NMR ($CDCl_3$) δ 7.5-7.2 (30 H, br m, Ph), 0.34 (3 H, t, $J_{H,P}$ = 15 Hz, Me); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ -2.1 (m, P'), -6.5 (m, P); IR ($CHCl_3$) ν(CO) = 2031 cm^{-1}.

0002-7863/89/1511-8919$01.50/0

remains unchanged in solution at room temperature. Fractional crystallizations resulted in different ratios of the three products. Each ratio remained unchanged after redissolving, confirming that the products are not interconverted and that the initial product mixture is formed under kinetic control. Similarly, compounds **9a**, **10a**, and **11a** remain unchanged in solution for several weeks at room temperature. Therefore, in contrast to analogous reactions of H-H and R_3Si-H bonds, reversible addition of tetrafluorocyclopropene is not observed.

As with our previous Pt chemistry,[4] and in agreement with the suggestion of Binger (vide supra), no spectroscopic evidence for an intermediate η^2-cyclopropene complex could be obtained in any of these reactions. Since the stereoselectivity of tetrafluorocyclopropene addition is identical with that found for kinetically controlled addition of the unambiguously σ-bonds of H-H and R_3Si-H to the same Ir(I) precursors,[5,6] our results provide strongly suggestive evidence that metallacyclobutene formation occurs by analogous direct interaction of a cyclopropene C-C σ-bond with the metal and implicitly support such a pathway for the formation of their vinylcarbene valence tautomers.

Acknowledgment. We are grateful to the Air Force Office of Scientific Research (Grant AFOSR-86-0075) and the National Science Foundation for generous support of our research. National Science Foundation R.E.U. grants to M.E.K. and J.M.S. and a generous loan of iridium salts from Matthey-Bishop Inc. are also gratefully acknowledged.

(8) **9b**: ^{19}F NMR (C_6D_6) δ 77.2 (m, 2 F_1), 103.1 (m, F_2), 126.1 (m, F_3), $J_{1,2}$ = 8, $J_{1,3}$ = 19, $J_{2,3}$ = 12, $J_{1,P}$ = 2, $J_{3,P}$ = 6 Hz; $^{31}P\{^1H\}$ NMR (C_6D_6) δ -31.9 (m). **10b**: ^{19}F NMR (C_6D_6) δ 97.5 (m, 2 F_1), 107.7 (m, F_2), 109.9 (m, F_3), $J_{1,2}$ = 13, $J_{1,3}$ = 18, $J_{2,3}$ = 12, $J_{1,P}$ = 5, $J_{3,P}$ = 6 Hz; $^{31}P\{^1H\}$ NMR (C_6D_6) δ -33.5 (m). **11b**: ^{19}F NMR (C_6D_6) δ 78.3 (m, F_1), 98.1 (m, $F_{1'}$), 98.9 (m, F_2), 122.1 (m, F_3), $J_{1,1'}$ = 205, $J_{1,3}$ = 19, $J_{1',3}$ = 17, $J_{1,P'}$ = 41, $J_{1',P'}$ = 40, $J_{3,P}$ = 70 Hz (due to the low intensities of the peaks for this isomer, other ^{31}P couplings could not be extracted from the spectrum); $^{31}P\{^1H\}$ NMR (C_6D_6) δ -43.8 (m, P'), -47.3 (m, P).

Preparation of Phosphoenolpyruvate from D-(-)-3-Phosphoglyceric Acid for Use in Regeneration of ATP[1]

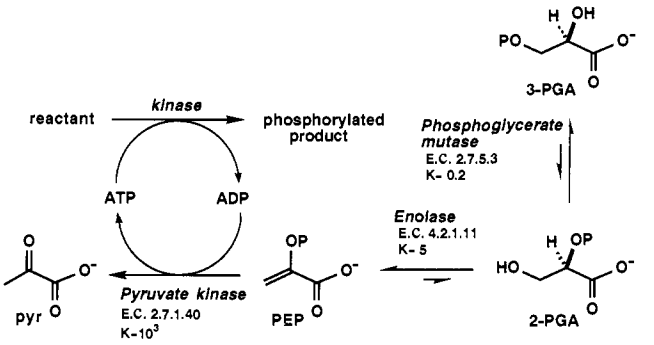
Ethan S. Simon,[2] Sven Grabowski,[3] and George M. Whitesides*

Department of Chemistry, Harvard University Cambridge, Massachusetts 02138

Received July 24, 1989

Adenosine 5'-triphosphate (ATP) is the most useful phosphoryl donor in enzyme-catalyzed synthesis.[4] The most convenient procedure for in situ regeneration of ATP from ADP uses phosphoenolpyruvate (PEP) and pyruvate kinase (Scheme I). Commercial PEP is expensive and must usually be synthesized chemically for use in large-scale synthesis. Here we describe a practical procedure (the PGA method) that uses two inexpensive, commercially available enzymes to generate PEP in situ from the relatively inexpensive D-(-)-3-phosphoglyceric acid (3-PGA) (Scheme I).[6]

Scheme I. Regeneration of ATP Using PEP[a]



[a] PEP can be synthesized in a separate chemical step or generated as shown from 3-PGA. P = phosphate; 3-PGA = D-(-)-3-phosphoglyceric acid; 2-PGA = D-(+)-2-phosphoglyceric acid; PEP = phosphoenolpyruvate; pyr = pyruvate.

Phosphoglycerate mutase[7] converts 3-PGA to D-(+)-2-phosphoglyceric acid (2-PGA); enolase[7] then forms PEP. Consumption of PEP by conversion of ADP to ATP, catalyzed by pyruvate kinase,[7] drives the overall process.[8,9]

We have tested the PGA method by using the reactions shown in Scheme II. CTP, GTP, and UTP are the nucleoside triphosphates needed for the syntheses of the most common nucleoside phosphate sugars used in Leloir pathway biosyntheses (reactions 1-4).[10] Dihydroxyacetone phosphate (reaction 5) is used in reactions catalyzed by aldolases,[11] and arabinose 5-phosphate (reaction 6) is a precursor to 3-deoxy-D-*manno*-2-octulosonic acid 8-phosphate (KDO-8-P).[12] In all cases, procedures based on 3-PGA were as effective as and more convenient than procedures based on chemically synthesized PEP.[5]

The synthesis of CTP from CMP illustrates the PGA method.[13] A suspension of 173 g of 3-PGA (barium salt, dihydrate, ~95%, 461 mmol) in 500 mL of water was stirred vigorously with ~600 mL of ion-exchange resin (Dowex 50W-X8, H^+ form, 20-50 mesh) for 30 min at room temperature. The resin was removed by filtration and washed with four 100-mL portions of water.[14] The combined, clear, pale-yellow filtrates were neutralized with solid KOH and used directly in the next step.

CMP (free acid, 71 g, 220 mmol), ATP·Na_2·$3H_2O$ (1.33 g, 2.20 mmol), $MgCl_2$·$6H_2O$ (51 g, 250 mmol), and triethanolamine (1.9 g, 10 mmol) were added to the solution of 3-PGA, and the pH was adjusted to pH 7.6 with 5 N KOH. The solution (total volume of 1 L) was degassed for 30 min with N_2; 2-mercaptoethanol (0.25 mL, 3 mmol) was added. The enzymes[15] were then added, and

(1) Supported by NIH Grant GM 30367.
(2) Du Pont Fellow 1986-1987.
(3) NATO Postdoctoral Fellow 1988-1989 (administered by the Deutscher Akademischer Austauschdienst).
(4) Chenault, H. K.; Simon, E. S.; Whitesides, G. M. In *Biotechnology & Genetic Engineering Reviews*; Russell, G. E., Ed.; Intercept: Wimborne, Dorset, 1988; Vol. 6, Chapter 6.
(5) Hirschbein, B. L.; Mazenod, F. P.; Whitesides, G. M. *J. Org. Chem.* **1982**, *47*, 3765.
(6) From US Biochemical Corp.: PEP = $4800/mol; 3-PGA = $250/mol.
(7) Phosphoglycerate mutase: Ray, W. J., Jr.; Peck, E. J., Jr. In *The Enzymes*, 3rd ed.; Boyer, P. D., Ed.; Academic: New York, 1972; Vol. VI, Chapter 12. Most commercial preparations of 3-PGA contain 2,3-diphosphoglyceric acid, an activator of phosphoglycerate mutase. Enolase: Wold, F. *Ibid.* Vol. V, Chapter 18. Pyruvate kinase: Kayne, F. J. *Ibid.* Vol. VIII A, Chapter 11.
(8) The isolation of PEP in 15-20% yield from 3-PGA using enzyme preparations from yeast has been reported: Ganti, T.; Csoka, A. *Magy. Kem. Foly.* **1975**, *81*, 335-6; *Chem. Abstr.* **1975**, *83*, 162155v. Csoka, A.; Ganti, T. Hung. Teljes 8,931, 1974; *Chem. Abstr.* **1975**, *82*, 96491c.
(9) The three enzymes required are stable under the conditions used[7] and are inexpensive ($/1000 units): pyruvate kinase (0.3, Biozyme); enolase (4.75, Sigma); phosphoglycerate mutase (4.00, Sigma); 700 units of enzyme will convert 1 mol of reactants to products per day under assay conditions.
(10) Toone, E. J.; Simon, E. S.; Bednarski, M. D.; Whitesides, G. M. *Tetrahedron* **1989**, *45*, 5635.
(11) Bednarski, M. D.; Simon, E. S.; Bischofberger, N.; Fessner, W.-D.; Kim, M.-J.; Lees, W.; Saito, T.; Waldmann, H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 627. Durrwachter, J. R.; Wong, C.-H. *J. Org. Chem.* **1988**, *53*, 4175.
(12) Bednarski, M. D.; Crans, D. C.; Dicosimo, R.; Simon, E. S.; Stein, P. D.; Whitesides, G. M.; Schneider, M. *Tetrahedron Lett.* **1988**, *29*, 427.
(13) CMP is available from Miwon Foods Co., Ltd., Seoul, Korea ($200/kg).
(14) The resin was regenerated with HCl by following the procedure recommended by the manufacturer.

0002-7863/89/1511-8920$01.50/0