toluene for 26 h under D_2 (1.5 atm), followed by the workup described above, led to **8** in 80% yield. Complex **8** was demonstrated to be 83% deuterated by ^1H NMR integration of the hydride resonance against the $C_5(CH_3)_5$ resonance; lack of deuteration on the ring was confirmed by ^2H NMR and IR.[14] Data for **8**: ^2H NMR (C_6H_6) δ −15.34 (s); IR (KBr) 1555 (s), 1545 cm^{-1} (shoulder); $\upsilon_H/\upsilon_D = 1.38$. Interestingly, however, no reaction occurs between **2** and the normally powerful dative ligand $P(CH_3)_3$ under these conditions; only upon elevation of the temperature to 110 °C and heating for 44 h is conversion of tetrahydride **2** to **6** observed. This indicates that the thermal hydrogen exchange reaction must take place by some mechanism (e.g., partial detachment of the Cp ligand; loss of hydrogen atoms in a radical chain process) other than simple reductive elimination of H_2 followed by oxidative addition of D_2.

Both the chemistry and structure of tetrahydride **2** are under further study. It is our hope that the method utilized in the synthesis of **2** will be applicable to other transition-metal systems and that **2** might also be employed as a precursor to additional iridium(V) complexes.

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. We are grateful to the Matthey-Bishop Corp. for a generous loan of iridium trichloride and to Professors P. M. Maitlis and W. A. G. Graham for helpful discussions. The X-ray structure analysis was performed by Dr. F. J. Hollander of the U. C. Berkeley X-ray diffraction facility (CHEXRAY). Funds for the analysis were provided by the above DOE contract; partial funding for the equipment in the facility was provided by NSF Grant CHE 79-007027. R.G.B. acknowledges a Research Professorship (1982–1983) from the Miller Institute for Basic Research at U. C. Berkeley.

Registry No. **1**, 39385-15-4; **2**, 86747-87-7; **3**, 41380-03-4; **4**, 56086-50-1; **5**, 12354-84-6; **6**, 80146-01-6; **7**, 32660-96-1; **8**, 86747-88-8; $LiEt_3BH$, 22560-16-3.

Supplementary Material Available: Experimental writeup by Dr. Hollander, data collection and refinement parameters, positional parameters and their esd's, general temperature factor expressions and their esd's, raw interatomic distances and angles for **2**, listing of F_o and F_c, and packing diagrams for the crystal (27 pages). Ordering information is given on any current masthead page.

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[14] More recent experiments suggest that deuterium may be incorporated into the $C_5(CH_3)_5$ ring when higher pressures or longer reaction times are employed. This result will be considered more fully in future descriptions of this work.

New Evidence in the Iridium(I)-Catalyzed Reaction of *endo*-Tricyclo[3.2.1.$0^{2,4}$]oct-6-ene

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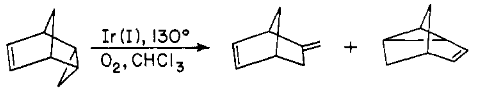
Summary: Tricyclo[3.2.1.$0^{2,7}$]oct-3-ene has been shown to form via a carbocyclic rearrangement from the catalytic reaction of $(Ph_3P)_2IrClCO$ with *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene.

Volger[1] reported in 1969 that *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene reacted with $(Ph_3P)_2IrClCO$ to convert the *exo*-cyclopropane moiety to exocyclic methylene, compound **2**. He also reported that the analogous compounds with an *endo*-cyclopropane moiety, **1**, did not react with Ir(I) to give organic products.

Recently,[2] we found that by changing the reaction solvent from benzene to chloroform that the ring-expanded product **3** was formed in nearly equal quantities with **2**. However, more significantly, under the new reaction conditions, the *endo*-cyclopropane compound was quite reactive and formed products **2** and **3** in 83% yield (eq 1).



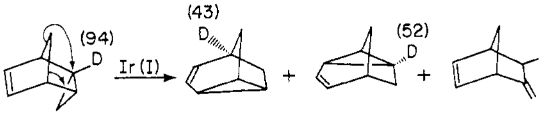
1 2 (72%) 3 (28%)

(1)

In order to provide more details with regard to the mechanism of this reaction, we synthesized two derivatives of **1**: one with a deuterium label at the cyclopropane ring juncture and the other with a methyl at the bridgehead. The results were quite surprising in that they support a carbocyclic rearrangement in the formation of **3**.

Deuterium Results. Compound **1**-*d* was prepared by reacting cyclopentadiene with cyclopropene that had one deuterium atom on the olefinic carbon.[3] Compound **1**-*d* was shown to contain 47% deuterium at the ring juncture positions. However, since there is only one deuterium atom/molecule of **1**-*d*, this means that there is 94% deuterium at one of the ring juncture protons in each molecule.[5] On reaction with the Ir(I) complex, the reaction proceeded as noted with the nondeuterated substrate to provide an 82% yield of exocyclic methylene and ring-expanded products.

Careful analysis by NMR spectroscopy revealed that three products were obtained as shown in eq 2. The



1-d 4 (24%) 5 (29%) 3-d (44%)

(2)

numbers in parentheses represent the amounts of deuterium at each position while the percent yield for each compound is presented below the structure. As can be seen in eq 2, all of the deuterium of **1**-*d*, which proceeds to the ring-expanded products, is accounted for in compounds **4** and **5**.

The deuterium distribution in **4** and **5** cannot be accommodated in a mechanism such as proposed by Katz[4] for the analogous *exo*-cyclopropane compound. Instead, it appears that either the deuterium atom has migrated or that each side of the bridge carbon undergoes a 1,2 shift to the respective cyclopropyl ring juncture carbons as indicated in eq 2. The difference in deuterium concentrations in **4** and **5** is significant and probably reflects an isotope effect in the product-determining step.

Bridgehead Methyl Label Results. To determine whether the reaction involved a carbocyclic or deuterium rearrangement as suggested by the deuterium results, we

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[1] Volger, H. C.; Hogeveen, H.; Gaasbeck, M. M. P. *J. Am. Chem. Soc.* **1969**, *91*, 218, 2137.

[2] Campbell, W. H.; Jennings, P. W. *Organometallics* **1982**, *1*, 1071.

[3] Magid, R. M.; Welch, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 5211.

[4] Katz, T. J.; Cerefire, A. A. *J. Am. Chem. Soc.* **1969**, *91*, 2405, 1971, *93*, 1049.

[5] All deuterium analyses were performed on a Bruker WM 250 NMR spectrometer by measuring the diminished proton integrals. The errors of integration were 2.0%. In addition, the analyses were complimented by analysis on the VG 16 mass spectrometer.

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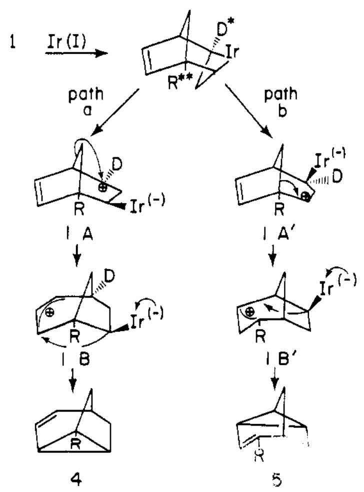
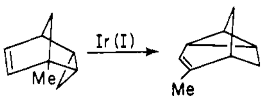
Organometallics **1983**, *2*, 1461-1463 1461

Scheme I[a]



[a] The asterisk means, when D is present, R = H, and the double asterisk means when R = CH_3, D = H.

prepared compound 1 with a methyl group substituted at the bridgehead position, 1-*Me*.[6] On reaction with Ir(I) under the same conditions as used in the above reactions, a 90% yield of 5-*Me* was obtained (eq 3). Methyl analogues of 3 and 4 are conspicuously absent which will be addressed below. This result was quite surprising but when put together with the earlier results provides evidence for the postulated scheme that is shown in Scheme I. In this scheme using 1-*Me*, there are two intermediates labeled as **1B** and **1B′** that would be differentiated by the presence of the methyl group. It is reasonable to suggest that the methyl group would provide added stability to **1B′** and would therefore favor path b. The methyl group also provides additional evidence for the idea that the bridge carbon is migrating.



1-Me 5-Me (90%) (3)

The role of iridium has not been firmly established in that none of the intermediates shown in the scheme have been isolated. However, compound 1 is unreactive to the reaction conditions without Ir(I) present. It is postulated to form the iridacyclobutane complex from circumstantial evidence. First of all, these results are different from reaction of $(Ph_3P)_2IrClCO$ with the exo analogue of 1. In the exo system that has been labeled with deuterium, the reaction path follows a scheme that has been previously elaborated by Katz.[4] In his postulate, Katz suggests that the metal (Rh) forms an intermediate complex in which the metal is in an endo position. Presumably, if the iridium in the system reported herein went by the same intermediate, the same result on labeling would be apparent. It is not.

Further, we feel that the iridium is an iradacycle rather than a π-allyl complex as a result of the deuterium distribution. When the iridacycle cleaves to the cationic intermediate **1A** and **1A′** an α deuterium isotope effect would favor the cleavage to form **1A′** which gives the distribution observed. The isotope effect would have a magnitude of 1.20 which is consistant with a $sp^3 \rightarrow sp^2$ transformation.[8] An alternative iridium complex would be a (π-allyl) metal hydride. Subsequent bridge migration would produce 4 and 5, but the ratio of products would not be consistant with the isotopic distribution observed. This transformation $sp^2 \rightarrow sp^3$ would favor the formation of 1A over 1A′, which is the opposite of what is observed.

Conclusion. The Ir(I)-catalyzed reaction of *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene to form tricyclo[3.2.1.0^{2,7}]oct-3-ene has been shown to proceed via a carbocyclic rearrangement. This conclusion is based on the evidence garnered from both deuterium- and methyl-labeled substrates.

Registry No. 1-*d*, 86766-39-4; 1-Me, 86766-40-7; 3-*d*, 86766-41-8; 4, 86784-83-0; 5, 86766-42-9; 5-Me, 86766-43-0; $(Ph_3P)_2IrClCO$, 14871-41-1.

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(6) Compound 1-*Me* was prepared from the reaction of methyl cyclopentadiene (Aldrich) and cyclopropene.[7] Along with the 1-methyl-*endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene, we obtained the 6-methyl analogue. The overall yield was 10% with the ratio of products being 4.6, respectively. The sample was separated and collected by preparative GC-20% SE30 in Chromosorb W.

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Isolation and Chemical Properties of Ruthenium and Iron Hydroxymethyl Complexes $(\eta^5\text{-}C_5H_5)M(CO)_2CH_2OH$[†]

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Summary: The hydroxymethyl complexes $(\eta^5\text{-}C_5H_5)M(CO)_2(CH_2OH)$ (M = Ru, Fe) were isolated from the reduction of the tricarbonyl cations $(\eta^5\text{-}C_5H_5)M(CO)_3^+$ with 4 equiv of $NaBH_3CN$. They decompose catalytically to $(\eta^5\text{-}C_5H_5)Ru(CO)_2H$ or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and formaldehyde when treated with phosphorus ligands. They react with CH_3OH, $CH_3C(O)Cl/C_5H_5N$, and $(CH_3)_3SiCl/C_5H_5N$ to form methoxymethyl, (acyloxy)methyl, and (trimethylsiloxy)methyl complexes. Only the (trimethylsiloxy)methyl complexes can be hydrolyzed to regenerate the hydroxymethyl precursors. No CO insertion reactions were observed for any of these products at pressures up to 4000 psi at 80 °C.

We have prepared the hydroxymethyl compounds $CpM(CO)_2CH_2OH$ (M = Ru (1), Fe (2); Cp = $\eta^5\text{-}C_5H_5$) by reducing $CpM(CO)_3^+$ with $NaBH_3CN$ in MeOH. Although few hydroxymethyl compounds have been isolated and little is known about their chemistry, they are proposed intermediates in the direct conversion of syn gas to ethylene glycol[1] and the hydroformylation of formaldehyde to glycolaldehyde,[2] an ethylene glycol precursor.

Unsubstituted hydroxymethyl complexes have been isolated from the reactions of hydride donors with $CpRe(NO)(CO)_2^{+}$ [3] and $(\eta^5\text{-}C_5Me_5)Os(CO)_3^+$,[4] acidolysis of

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[†] Contribution no. 3252.

(1) (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (b) Dombeck, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466; **1980**, *102*, 6857; **1981**, *103*, 6508. (c) Knifton, J. F. *J. Catal.* **1982**, *76*, 101.

(2) Roth, J. A.; Orchin, M. *J. Organomet. Chem.* **1979**, *172*, C27.

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