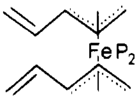
is somewhat larger, 127.3 (3)°.

The hypothetical coupling of the pentadienyl groups in **3** to produce the iron analogue of **2** requires an eclipsed orientation for the two *syn*-η^3-pentadienyl ligands. A simple rotation of one pentadienyl group about an axis drawn from the center of the allylic moiety to the iron atom will not bring the two pentadienyl ligands in **3** into register, neither will the twist mechanism proposed by Green et al.[17] to account for the observed left-to-right exchange process in bis(η^3-2-methylallyl)bis(trimethyl phosphite)ruthenium.



3 after rotation about Fe-(allyl group) axis

However, several mechanisms which will enable the two pentadienyl ligands to assume the eclipsed configuration can be envisaged. The first (Scheme II) commences with a *syn*-η^3- → *anti*-η^3-pentadienyl ligand isomerization. Subsequent loss of a phosphine ligand enables the uncomplexed double bond (C_4–C_5) of the *anti*-η^3-pentadienyl ligand to coordinate to the iron atom, producing an (η^5-pentadienyl)(η^3-pentadienyl)(trimethylphosphine)iron intermediate. Dissociation of C_1–C_2 (η^5-pentadienyl ligand) from the iron atom, recoordination of $P(CH_3)_3$, and isomerization of the *anti*-η^3-pentadienyl ligand back to the syn form produce *syn,syn*-bis(η^3-pentadienyl)bis(trimethylphosphine)iron with the desired eclipsed geometry. A second mechanism (Scheme III) involves a $\pi \rightarrow \sigma$ pentadienyl isomerization, affording a C_3-bound σ-pentadienyl ligand. Coordination of the C_4–C_5 double bond then yields *syn,syn*-bis(η^3-pentadienyl)bis(trimethylphosphine)iron with eclipsed pentadienyl ligands. A variation on this mechanism involves sliding the Fe atom in a concerted fashion from one end of a pentadienyl ligand (C_1, C_2, C_3) to the other end (C_3, C_4, C_5). In this case, the iron atom would remain π-bonded to the pentadienyl ligand throughout.[18] The stability of **3** with respect to pentadienyl coupling suggests that none of these postulated mechanisms for rearranging the pentadienyl ligands is facile in the iron system.[19] In the manganese system, on the other hand, a low-energy mechanism for bringing the pentadienyl ligands into register does exist and is responsible for the observed coupling reaction.

We are continuing to study this and other pentadienylmetal–phosphine reaction systems.

Acknowledgment. We thank the Research Corporation for providing funding for an inert-atmosphere drybox. Additional support was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by BRSG S07 RR07054-17, awarded by the Biomedical Research Support Grant Program, Division of Research Resources, National Institues of Health. We thank Professor G. G. Stanley for assistance with the single-crystal X-ray diffraction study of **3** and Dennis Moore for synthetic help.

Registry No. 3, 88765-93-9; $FeCl_2[P(CH_3)_3]_2$, 55853-16-2; KC_5H_7, 51391-25-4; $FeCl_2$, 7758-94-3; $P(CH_3)_3$, 594-09-2; bis(pentadienyl)iron, 74910-62-6.

Supplementary Material Available: A complete listing of final atomic coordinates, thermal parameters, bond lengths, bond angles, and observed and calculated structure factor amplitudes, as well as a table of several significant least-squares planes including subtended dihedral angles (15 pages). Ordering information is given on any current masthead page.

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[17] Cooke, M.; Goodfellow, R. J.; Green, M.; Parker, G. *J. Chem. Soc. A* **1971**, 16.

[18] Other mechanisms, such as those involving initial formation of a C_1-bound σ-pentadienyl–metal intermediate, can be envisaged.

[19] ^1H and ^{13}C NMR studies give no indication that either process is occurring up to the decomposition temperature of **3**.

Oxidative Addition of Rhodium to Alkane C–H Bonds: Enhancement in Selectivity and Alkyl Group Functionalization

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Summary: UV irradiation of (η^5-C_5Me_5)$RhPMe_3H_2$ (**2**) in alkanes below −30 °C results in the formation of (η^5-C_5Me_5)$RhPMe_3$(R)(H) (**4**) with significantly greater selectivity toward different C–H bonds than the iridium analogue. Treatment of the thermally labile complexes **4** with $CHBr_3$ gave the corresponding halides (η^5-C_5Me_5)$RhPMe_3$(R)(Br) (**5**); reaction of **5** with Br_2 at 25 °C results in the formation of (η^5-C_5Me_5)$RhPMe_3Br_2$ (**7**) and bromoalkane.

Recently several examples of homogeneous oxidative addition of alkane C–H bonds to iridium centers have been discovered.[1] Jones and Feher[2] recently reported the use of the rhodium complex (η^5-C_5Me_5)$Rh(PMe_3)H_2$ (compound **2** in Scheme I) to activate the C–H bonds in benzene and *n*-propane. We have been independently examining this rhodium system, in order to compare its generality, selectivity, and functionalizing ability with those of the iridium system we reported earlier.[1a,c] Accordingly, we have irradiated **2** in a number of liquid hydrocarbons. As in the Ir case, the reaction is quite general, and no hydrocarbon has yet been found whose C–H bonds are unreactive. Our results demonstrate that the selectivity of the Rh system is greater than that of the Ir system and that at least one alkane functionalization method is more effective. In addition, we have obtained several haloalkylrhodium derivatives of the C–H activation products in analytically pure form and have succeeded in determining the structure of one of these by X-ray diffraction.

Dihydride **2** was prepared[3,4] in 85% yield and analytical purity as shown in Scheme I. Irradiation of **2** at room temperature resulted in loss of H_2 and formation of a dark, as yet unidentified, product (presumably a cluster complex), but no new hydrides. However, when irradiation was carried out below −30 °C, the formation of new alkyl hydrides **4** (Scheme I) was observed by ^1H NMR. Cyclopropane is an especially efficient substrate despite the very high dissociation energy (106 kcal/mol)[5] of its C–H bonds.

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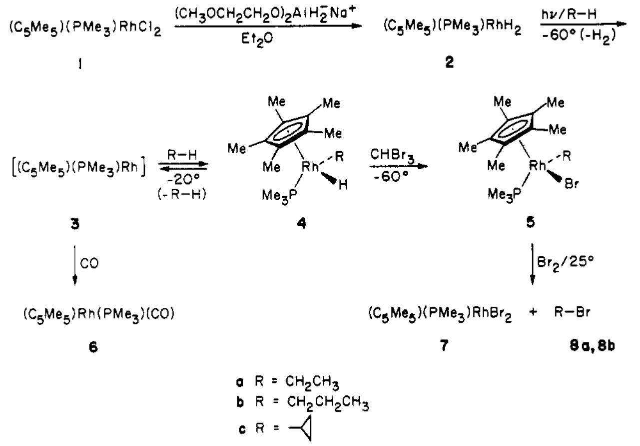
[1] (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723. (c) Janowicz, A. H.; Bergman, R. G. *Ibid.* **1983**, *105*, 3929.

[2] Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562.

[3] Spectral data on this material have also been reported in ref 2 and by: Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003.

[4] Supplementary information provided with this paper includes (a) low-temperature ^1H NMR data for hydridoalkylrhodium complexes **4a**, **4b**, and **4c**; (b) spectral and analytical data for complexes **2**, **5a**, **5b**, and **5c**; and (c) details of the X-ray structure determination of complex **5c**.

Scheme I



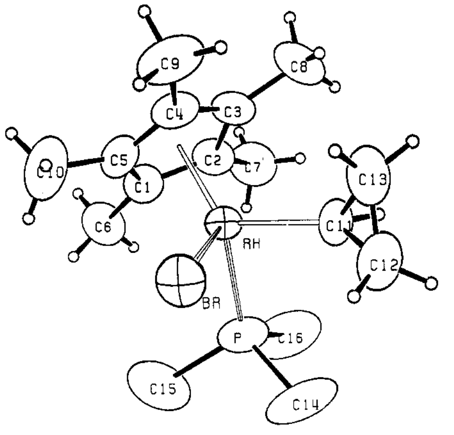


Figure 1. ORTEP diagram illustrating the structure of $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(C_3H_5)Br$ (**5c**).

The C–H insertion product is formed quantitatively on irradiation of **2** in this solvent at −60 °C, with no sign of any products formed by C–C insertion.[6] We have been able to characterize several of the hydridoalkyl complexes **4** by ^1H NMR,[4] but all attempts at isolation have failed. However, treatment of the hydrides with a twofold excess of $CHBr_3$ at −60 °C converted them to the corresponding bromoalkylrhodium complexes **5**. These, too, are sensitive materials, decomposing slowly in solution at room temperature or on attempted chromatography. However, in at least certain cases they can be isolated by rapid evaporation of solvent, extraction into *n*-hexane, and recrystallization from Et_2O/hexane. In this way pure samples of the bromoethyl (**5a**), bromopropyl (**5b**), and bromocyclopropyl (**5c**) complexes have been obtained and characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy.[4] After several attempts, we were successful in obtaining X-ray quality crystals of the bromocyclopropyl complex **5c** by slow recrystallization from a 25% mixture of THF in hexane. An ORTEP diagram is reproduced in Figure 1; it shows clearly the intact cyclopropyl ring and its σ-bonding to the metal. X-ray structural data are supplied as supplementary material.

Table I. Relative Rate Constants[a] for Attack at a Single C-H Bond in Different Molecules by $(\eta^5\text{-}C_5Me_5)(PMe_3)M$, M = Rh and Ir, at -60 °C

C-H bond	k_{rel}(Rh)	k_{rel}(Ir)
benzene	19.5	3.9
cyclopropane	10.4	2.1
n-hexane (1°)	5.9	2.7
n-hexane (2°)[b]	0[c]	0.2
propane (1°)	2.6	1.5
propane (2°)	0[c]	0.3
cyclopentane	1.8	1.1
cyclohexane	1.0	1.0

[a] Relative rate constants are determined from competition experiments (see text) carried out with each individual metal complex in mixtures of two solvents and are normalized by arbitrarily setting the rate constant for cyclohexane equal to 1.0 in each case. [b] Average k_{rel} for attack on both types of secondary hydrogens. [c] A k_{rel} larger than 0.1 could have been detected.

Experimental support for the C–H oxidative addition mechanism outlined in Scheme I is provided by the following experiments: (1) irradiation of **2** in a mixture of cyclopropane and perdeuterated methylcyclohexane resulted only in the formation of $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(C_3H_5)H$ and $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(C_7D_{13})D$ after 30% conversion of starting material; (2) low-temperature irradiation of **2** in solutions containing CO gave $(\eta^5\text{-}C_5Me_5)Rh(CO)(PMe_3)$[7] (**6**); (3) when a mixture of **2** and complex **4b** was warmed to −20 °C in liquid cyclopropane, conversion of **4b** to the corresponding hydridocyclopropyl complex **4c** was observed. Thus the presumed intermediate $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh$, regenerated on thermal decomposition of **4**, can be trapped by an alkane as well as by an aromatic hydrocarbon, as demonstrated earlier.[2]

The relative reactivity of intermediate **3** toward different hydrocarbons was obtained by irradiation of **2** in mixtures of hydrocarbons (as well as in hydrocarbons containing more than one type of C–H bond), followed by integration of signals due to each hydride in the NMR spectra of the C–H addition photolysis mixtures (Table I). In order to make a careful comparison of Rh and Ir selectivities, competition experiments done earlier[1c] at 0–10 °C with $(C_5Me_5)(PMe_3)IrH_2$ were redone at −60 °C, the temperature used for the Rh experiments. The two reactive intermediates differ strikingly in their degree of selectivity. In all cases, the rhodium complex is significantly more discriminating, particularly between C–H bonds in the same molecule. Indeed, with acyclic alkanes the Rh complex apparently inserts *only* into primary C–H bonds, while the Ir complex favors primary insertion over secondary relatively weakly. In no instance has insertion into tertiary C–H bonds been observed for either system. The greater selectivity of the rhodium system (as well as the higher propensity of its hydridoalkyl complexes toward reductive elimination) correlates nicely with the presumably lower exothermicity of its C–H insertion reactions.

Finally, we have obtained some promising preliminary results on conversion of the alkyl groups in these rhodium complexes to organic molecules. In the iridium system, we were not able to convert the haloalkyl–metal complexes to organic bromides by direct treatment with Br_2; it was necessary to first effect alkyl transfer to mercury. In contrast, treatment of bromoalkylrhodium complexes **5a** and **5b** with Br_2 results in conversion to $(\eta^5\text{-}C_5Me_5)(PMe_3)Br_2$ (**7**) and RBr (**8a** and **8b**) in 70–85% yield. We are continuing to search for other differences in func-

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(5) Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838.

(6) **Note Added in Proof.** In contrast to the behavior of the other hydridoalkylrhodium complexes (see below), hydridocyclopropyl complex **4c** undergoes rearrangement, rather than reductive elimination, on warming to 20 °C. Preliminary results indicate that the product of this rearrangement is the rhodacyclobutane complex which results from C–C insertion. This suggests the interesting (and reasonable) conclusion that C–H insertion is favored kinetically in this system, but C–C insertion is favored thermodynamically. The details of this and related investigations are currently under investigation.

(7) Werner, H.; Klingert, B. *J. Organomet. Chem.* **1981**, *218*, 395.

tionalization behavior between rhodium and iridium; we are especially interested in developing sequences which will produce oxygenated derivatives, perhaps via the intermediacy of (alkoxy)(alkyl)metal complexes.

Acknowledgment. We are grateful to Professor W. D. Jones and Frank J. Feher for disclosing the results of their work prior to publication and for many helpful discussions. 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 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 obtained from NSF Grant CHE 79-007027. R.G.B. acknowledges a Research Professorship (1982–83) from the Miller Institute for Basic Research at U.C. Berkeley.

Registry No. **2**, 84624-03-3; **3**, 88825-24-5; **4a**, 88825-25-6; **4b**, 84624-04-4; **4c**, 88825-26-7; **5a**, 88825-27-8; **5b**, 84624-05-5; **5c**, 88825-28-9; **6**, 80182-11-2; **7**, 88704-26-1; **8a**, 74-96-4; **8b**, 106-94-5; $(\eta^5\text{-}C_5Me_5)(PMe_3)Ir$, 88825-29-0; $(\eta^5\text{-}C_5Me_5)(PMe_3)Rh(C_7D_{13})D$, 88825-30-3; perdeuterated methylcyclohexane, 10120-28-2; benzene, 71-43-2; cyclopropane, 75-19-4; *n*-hexane, 110-54-3; propane, 74-98-6; cyclopentane, 287-92-3; cyclohexane, 110-82-7.

Supplementary Material Available: Spectral, analytical, and X-ray diffraction data as discussed in the text (25 pages). Ordering information is given on any current masthead page.

Book Reviews

Chemicals from Synthesis Gas. By R. A. Sheldon. Volume 3 of Catalysis by Metal Complexes. R. Ugo and B. R. James, Editors. D. Reidel Publishing Co., Dordrecht. 1983. xix–216 pages. $48.00

In his preface, the author sets out two goals for this book: "to provide an overview of the reactions of syn gas, many of which have been developed in the last few years" and "to cultivate a deeper understanding and stimulate a wider utilization of transition-metal catalysis in organic synthesis". With one reservation, the author has achieved these goals.

This easily readable text begins with a glossary in which seven types of carbonylation reactions, in addition to a number of other terms used throughout the text, are defined. The introductory chapter contains a brief but complete description of how a barrel of oil is converted into key chemical raw materials. A good case is also made for the increasing importance of syn gas as a feedstock for the future. Following this introduction, the mechanistic principles for the key catalytic steps are clearly described with appropriate literature references. Recent concepts, such as the potential importance of formaldehyde as a key intermediate, are included.

With this foundation, direct hydrocarbon synthesis from syn gas or methanol and olefin hydroformylation chemistry are developed. What these chapters lack in depth on individual topics they make up for in breadth. As the author promised, everything from the synthesis of lower olefins from Fischer–Tropsch to the synthesis of butadiene from ethanol and a short discussion of hydroformamination is covered. Recent developments from both the patent and scientific literature are referenced so that those who choose to explore further, may do so.

The next two chapters are devoted to methanol carbonylation chemistry. Recent important developments in topics such as asymmetric carbonylation, phase-transfer catalysis, and the multitude of synthetic routes to ethylene glycol are included.

A very important feature of this book is the discussion of the carbonylation reactions of nitrogen-containing compounds. Organic amide, amine, and nitro compound carbonylation chemistry is summarized. The author shows his chemical expertise in this chapter by transmuting selenium into an honorary transition metal useful for the oxidative carbonylation of amines. The chapter closes with an interesting description of the effect of ammonia addition on Fischer–Tropsch chemistry.

Recent developments in the direct conversion of syn gas to oxygenates are examined before the book closes with the author's thoughts on the future directions of syn gas chemistry. Potential new research ideas are identified here as well as in numerous additional places throughout the book.

This book would make an excellent addition to the library of anyone interested in transition-metal-catalyzed organic synthesis. My single reservation is the price. The $48.00 cost may be too high for many who would profit from having it close at hand.

Ralph J. Spohn, *Exxon Chemical Company*

Gmelin Handbook of Inorganic Chemistry. 8th Edition. Tellurium. Supplemental Volume A2. L. Berg, V. Haase, I. Hinz, G. Kirschstein, H.-J. Richter-Ditten, and J. Wagner, authors. G. Czack, D. Koschel, and H. K. Kugler, editors. G. Kirschstein, editor in chief. Gmelin-Institute für Anorganische Chemie der Max-Planck-Gesellschaft zur Förderung der Wissenschaften, Springer-Verlag, Berlin/Heidelberg/New York/Tokyo. 1983. XIV + 395 pages. 144 illustrations. Cloth DM 1285, $510.

The Supplemental Volume A2 for system number 11, tellurium, covers the literature on crystallography, physical properties, electrochemistry, and the chemical behavior of tellurium, which appeared during the period 1939 to the end of 1981. In some cases even more recent data were incorporated. The seven chapters are devoted to the crystallographic properties of tellurium (70 pages), its mechanical and thermal properties (34 pages), electrical and magnetic properties (98 pages), optical properties (21 pages), electrochemical behavior (143 pages), the chemical reactions of tellurium (23 pages), and the properties of the molecular cations Te_4^{2+} and Te_6^{4+} (4 pages).

Each chapter provides a wealth of information in a well-organized manner not only for crystalline tellurium but also for amorphous and molten tellurium and for tellurium–selenium alloys. Difficult-to-find data on the phase diagram, the growth and structure of crystals, the preparation and characterization of thin films, the surface structures, the bonding, and the lattice dynamics and imperfections are summarized in a compact and easily understandable form. Questions concerning the density, hardness, critical constants, thermodynamic functions, core electron energies, energy bands and gaps, Mössbauer parameters, nuclear magnetic resonance data, and microwave, infrared, and UV–visible spectra, and optically active tellurium are now easily answered without long hours in the library.

Of special interest to chemists are data for the standard potentials of various tellurium couples and the polarographic and voltammetric behavior of Te^{2-}, Te^0, Te_2^{2+}, and Te(IV) and Te(VI) compounds. The reactions of tellurium with hydrogen, oxygen, nitrogen, chalcogens, halogens, other non-metals, and many metals are described in sufficient detail for a good understanding of the chemistry of tellurium. The organic tellurium chemist will appreciate the sections summarizing the interactions of alkali metals and alkali hydroxide solutions with tellurium. These reactions produce alkali-metal tellurides, which combine with organic halides to produce organic tellurium compounds.