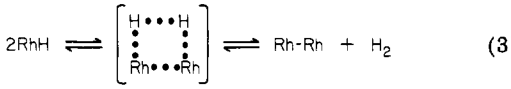

$$2RhH \rightleftharpoons \left[\begin{array}{ccc} H & \cdots & H \\ \vdots & & \vdots \\ Rh & \cdots & Rh \end{array}\right] \rightleftharpoons Rh\text{-}Rh + H_2 \quad (3)$$

Presumably, since the precursor hydrides $RhH(P\text{-}P)_2$ do not spontaneously evolve H_2, reaction 2 probably occurs via dimerization of $RhH(CO)(P\text{-}P)$ species to generate $[Rh(CO)(P\text{-}P)]_2$ and H_2, followed by addition of CO ligands. The corresponding $RhH(CO)(PPh_3)_2$ complex can certainly form **2** via this route, in which the intermediate metal–metal bonded orange dimer $[Rh(CO)(PPh_3)_2]_2$ with no bridging ligands, **3**, has been isolated.[37] The related solvated complex $[Rh(CO)(PPh_3)_2]_2\cdot 2CH_2Cl_2$ that contains two bridging carbonyls[34,37] (vide supra) can be formed by loss of CO from solutions of **2**. Our carbonyl diphosphine dimers such as **1** also lose CO under vacuum, but the product(s) have not yet been characterized.

No crystallographic or ^{31}P NMR data have been reported for the carbonyl bis(triphenylphosphine) dimers **2** and **3**, but the IR data for **2** (2017, 1992, 1800, 1770 cm^{-1}, Nujol)[37] showed the presence of both terminal and bridging carbonyls, and presumably the structure is analogous to that described here for **1**. The higher frequency of the carbonyls in **2** compared to **1** probably reflects the stronger π-acceptor/weaker σ-donor ability of two PPh_3 ligands relative to the diphosphine.

Preliminary experiments reveal that, like the triphenylphosphine analogues, the carbonyl bis(diphosphine) dimers such as **1** are effective under mild conditions (50 °C, 1 atm in benzene) for hydrogenation, isomerization, and hydroformylation of terminal olefins.[41]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of British Columbia Computing Centre for financial support, Dr. J. Trotter for use of the departmental X-ray facilities, Johnson, Matthey Ltd for the loan of rhodium, and Dr. T. W. Dekleva for valuable discussions.

Registry No. $[Rh(CO)(dppp)]_2(\mu\text{-}CO)_2\cdot{}^1/_2C_6H_6$, 86853-77-2; $[Rh(CO)(dppe)]_2(\mu\text{-}CO)_2$, 86853-78-3; $[Rh(CO)(diop)]_2(\mu\text{-}CO)_2$, 86862-66-0; $RhH(dppp)_2$, 70196-25-7; $RhH(dppe)_2$, 29189-87-5; $RhH(diop)_2$, 51222-55-0; carbon monoxide, 630-08-0; Rh, 7440-16-6.

Supplementary Material Available: Table VI, selected bond lengths (Å) and angles (deg) for the coordinated dppp ligands, Table VII, intraannular torsion angles, Table VIII, calculated coordinates and thermal parameters for non-group hydrogen atoms; Table IX, anistropic thermal parameters; Table X, torsion angles; and Table XI, observed and calculated structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

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[41] James, B. R.; Williams, G. M.; Young, C. G., work in progress.

Communications

Preparation and Reactions of Tetrahydrido(pentamethylcyclopentadienyl)iridium: A Novel Iridium(V) Polyhydride

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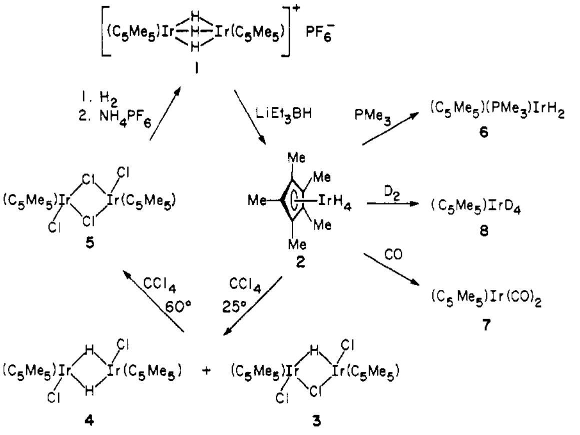
Received July 6, 1983

Summary: The complex $(C_5(CH_3)_5)IrH_4$ (**2**) has been synthesized and characterized by spectroscopic and analytical methods, including a single-crystal X-ray diffraction study. This compound is a rare example of a formal iridium(V) species; it can be converted to $[C_5(CH_3)_5](PMe_3)IrH_2$ on irradiation in the presence of PMe_3, leads to $C_5(CH_3)_5$-substituted chloro- and hydridochloroiridium dimers on treatment with CCl_4, gives $[C_5(CH_3)_5]Ir(CO)_2$ with CO, and undergoes thermal and photochemical H/D exchange in the presence of D_2 gas.

Few examples exist of organometallic complexes of late transition metals in high oxidation states. Comparison with high-valent complexes of early transition metals suggests that such compounds, especially those of group 8B, might be expected to possess unique properties and reactivities.

Phosphine-stabilized iridium(V) hydrides have been known since the early 1970s[1] and were shown somewhat later to catalyze H/D exchange with deuterated solvents at elevated temperatures.[2] Recently, Maitlis and coworkers demonstrated the accessibility of pentamethylcyclopentadienyl-substituted organoiridium(V)[3] and organorhodium(V)[4] complexes, noting intriguing products upon pyrolysis of the former. However, examples of this

Scheme I



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[1] Mann, B. E.; Masters, C.; Shaw, B. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2195.

[2] Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.

[3] (a) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 808; (b) Fernandez, M. J.; Maitlis, P. M. *Organometallics* **1983**, *2*, 164. (c) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 809.

[4] Fernandez, M. J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 310.

type of complex are still relatively rare.

As part of continuing studies of the synthesis and reactivity of iridium hydride complexes,[5] we wish to report the synthesis of the photoactive complex $(C_5(CH_3)_5)IrH_4$ (2, Scheme I). This material represents an unusual example of an iridium(V) organometallic polyhydride, and exhibits several interesting thermal and photochemical reactions.

A search of the available literature indicated that no neutral iridium compounds containing only pentamethylcyclopentadienyl and hydride ligands were known. In 1973, however, White, Oliver, and Maitlis[6] reported the synthesis of the cationic salt $[(C_5(CH_3)_5)Ir]_2H_3PF_6$ (1), which seemed a viable precursor for a neutral complex of the proper formula. Accordingly, we treated a hexane/benzene slurry of the cation at ambient temperature with 5.6 equiv of $LiEt_3BH$[7] and allowed the resulting orange-red solution to stir overnight. Rapid chromatography through alumina III (air-free conditions) followed by removal of solvent gave a yellow-white residue, from which a colorless, moderately air-sensitive solid could be sublimed (40 °C, 30 mtorr) in 55% yield. Spectroscopic and elemental analysis data for this compound indicate it to be the monomeric $(C_5(CH_3)_5)IrH_4$ (2). Data for 2: ^1H NMR (C_6D_6) δ 1.99 (s, $C_5(CH_3)_5$), −15.43 (s, IrH); ^{13}C NMR (C_6D_6, ^1H decoupled) δ 96.5 ($C_5(CH_3)_5$), 10.0 ($C_5(CH_3)_5$); IR (KBr) 2150 (s), 2140 cm^{-1} (shoulder); MS, *m/e* 332, 330, 328, 326, 324, 322; molecular weight (Signer isothermal distillation method,[8] CH_3OCH_3 solvent, 25 °C) 327 ± 15, calcd 331. Anal. Calcd for $C_{10}H_{19}Ir$: C, 36.24; H, 5.78. Found: C, 35.98; H, 5.83.

The polyhydride 2 is highly soluble in most common solvents, which hampered the isolation of X-ray diffraction-quality crystals. However, extremely slow sublimation (5 mtorr) on a warmed surface in a Pyrex NMR tube yielded crystals suitable for a diffraction study.

The single-crystal X-ray structure determination was performed at −150 °C.[9] Even at this temperature, complex decomposition was observed in the X-ray beam over the data collection period. Three data sets were collected. An initial low angle set was discarded during refinement due to difficulties caused by the decomposition. Both a high-angle and a low-angle set were taken on a second crystal; of these, the high-angle data set proved most amenable to a reasonable solution of the structure. The atoms were located through a combination of Fourier and search techniques, and their positions determined accurately through several full-matrix least-squares cycles. Refining two iridium atoms and 20 carbon atoms with anisotropic thermal parameters (199 parameters, 1446 observations), the final residuals are $R = 3.65\%$, $wR = 4.63\%$.

The crystal structure consists of two independent molecules of $(C_5(CH_3)_5)IrH_4$ in the asymmetric unit (Figure 1). The average Ir–C distance is 2.244 (19) Å (range 2.224 (10)–2.271 (11) Å). Although the crystal decomposition problems mentioned above prevented our locating the hydrogen atoms directly, it is clear that they must lie on the "open" side of the Ir atoms. The closest intermolecular contacts to the Ir atoms are in the range 4.4–4.6 Å to the methyl groups of neighboring molecules.

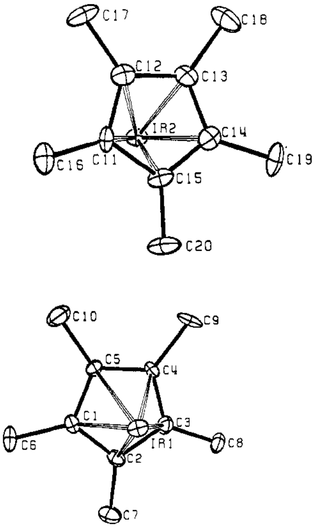

Figure 1. ORTEP drawing of $(\eta^5\text{-}C_5(CH_3)_5)IrH_4$ (2).

Treatment of a benzene solution of 2 with excess CCl_4 at ambient temperature immediately caused the colorless solution to become bright purple; analysis of the ^1H NMR spectrum of the reaction mixture demonstrated that the compounds 3[10] and 4[11] were present. Heating the mixture to 60 °C for 14 h gave the well-known dimer 5,[12] which was isolated in 92% yield and characterized by ^1H NMR.

The polyhydride complex shows high photoactivity under reaction conditions similar to those described by Janowicz and Bergman.[5] Irradiation ($\lambda \geq 275$ nm; high-pressure Hg lamp, Pyrex filter) of 2 in the presence of $P(CH_3)_3$ in toluene smoothly generates 6 in quantitative ^1H NMR yield. Continued irradiation results in extrusion of dihydrogen and insertion of the intermediate into the carbon–hydrogen bonds of the solvent.[5] A similar irradiation of 2 in the presence of CO leads to $(C_5(CH_3)_5)Ir(CO)_2$[12] (7) as demonstrated by ^1H NMR and IR. An intermediate was seen in the ^1H NMR during this experiment, which spectral analysis indicated might be $(C_5(CH_3)_5)Ir(CO)H_2$,[13] corresponding to the phosphine complex discussed above. These two experiments suggest that complex 2 extrudes dihydrogen upon irradiation, leading to the intermediate "$(C_5(CH_3)_5)IrH_2$", which is then trapped by the dative ligand.

The complex is capable of undergoing H/D exchange under photolysis conditions. Irradiation of 2 in toluene under 5 atm of D_2 for 2 h, followed by removal of solvent and sublimation of the reaction mixture led to a colorless compound, which spectral analysis indicated was a partially (ca. 57% by ^1H NMR integration) deuterated analogue of 2, in 76% yield. The extent of deuteration is limited by competitive formation of a burgundy material during irradiation; this material seems to be a hydride-deficient iridium species but as yet has defied isolation due to its extreme solubility.

A more highly deuterated analogue of 2 may be prepared through thermal H/D exchange. Heating 2 at 60 °C in

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(5) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.

(6) White, C.; Oliver, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1901.

(7) Use of less than 5 equiv of hydride reagent results in incomplete consumption of starting material and decreased yields of 2; no other product is isolated under such conditions.

(8) (a) Signer, R. *Justus Liebigs Ann. Chem.* **1930**, *478*, 246. (b) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

(9) Crystal data: monoclinic, $P2_1/n$, $a = 16.7466$ (25) Å, $b = 7.6224$ (15) Å, $c = 17.0821$ (30) Å, $\beta = 101.406$ (13)°, $V = 2137.5$ (12) Å^3, $Z = 8$, d(calcd) = 2.060 g/cm^3 at −150 °C; Mo Kα radiation, $\lambda = 0.71073$ Å, 45° $\leq 2\theta_{max} \leq$ 55°, 2103 reflections, $1446F^2 > 3\sigma(F^2)$; corrected for decay; empirically corrected for absorption.

(10) White, C.; Oliver, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton. Trans.* **1973**, 3322.

(11) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359.

(12) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(13) Hoyano, J. K.; Graham, W. A. G., personal communication.

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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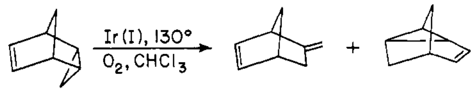
Summary: Tricyclo[3.2.1.0^{2,7}]oct-3-ene has been shown to form via a carbocyclic rearrangement from the catalytic reaction of $(Ph_3P)_2IrClCO$ with *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene.

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).



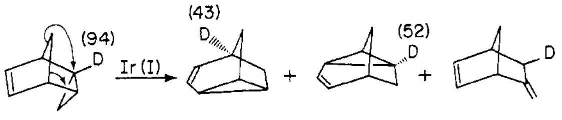
(1)

1 2 (72%) 3 (28%)

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



(2)

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

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.

0276-7333/83/2302-1460$01.50/0