Notes

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Catalysis by Dimanganese Decacarbonyl of the Exchange between Deuterium Gas and Bis(η^5-cyclopentadienyl)dihydridotungsten[1]

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Received October 4, 1978

The exchange between gaseous D_2 and hydrogen bonded to carbon in a variety of hydrocarbon compounds and their derivatives is catalyzed by transition metals under a variety of conditions.[2-4] We report here a unique catalytic system discovered in our study of the reaction of D_2 with the bimetallic cyclometalated derivatives $(\eta^5\text{-}C_5H_5)(CO)M(\mu\text{-}(\eta^5{:}\eta^1\text{-}C_5H_4))Mn(CO)_4$, M = Mo or W.[1b] The products of this reaction were $Mn_2(CO)_{10}$ and $(\eta^5\text{-}C_5H_{5-x}D_x)_2MH_{2-y}D_y$ in which the latter had become extensively exchanged with D_2. This observation led us to check the interaction of nondeuterated metallocenes with $Mn_2(CO)_{10}$ under D_2 atmosphere resulting in a facile method for the deuteration of $(\eta^5\text{-}C_5H_5)_2WH_2$, described here.

Results

Initial treatment of $(\eta^5\text{-}C_5H_5)_2WH_2$ with D_2 at 6.5 atm in benzene solution and in the presence of 21.3 mol % $Mn_2(CO)_{10}$ indicated the deuterium had equilibrated throughout the gas phase and metallocene in solution, *but not with the solvent.* The recovered $(\eta^5\text{-}C_5H_5)_2WH_2\text{-}d_n$ was cycled through 6 M HCl followed by neutralization with NaOH and benzene extraction. This provided a convenient internal ^1H NMR reference against which to compare intensity of the $(\eta^5\text{-}C_5H_5)$ signal in the deuterated product. ^1H NMR of this recovered product showed it to contain 16% H compared to the expected value of 18% in statistical equilibration (see Table I). This result also compares favorably with the 20.2% hydrogen detected in the gas phase at the conclusion of the experiment (see Table I and Figure 1). The rate of exchange followed a typical unimolecular behavior taking into account the loss of an estimated 0.5 atm of pressure at each gas sampling. A mass spectrum of the recovered benzene solvent revealed only trace, i.e., less than 1%, deuteration.

The reaction was repeated at the same pressure but with twice the D_2 volume and only 9.6 mol % $Mn_2(CO)_{10}$. Toluene was employed as solvent so that the CH_3 signal could be used internally to detect any deuteration of the aromatic ring protons. After a 15.7-day reaction, NMR analysis of the toluene indicated only trace deuteration. Table I and Figure 2 show that the $(\eta^5\text{-}C_5H_5)_2WH_2$ in the presence of 9.6% $Mn_2(CO)_{10}$ was 94% deuterated from NMR results and 91.7% deuterated from the mass spectrum of the gas phase at the conclusion of the experiment.

The gas analysis of a blank run with only $Mn_2(CO)_{10}$ and D_2 in toluene showed that $Mn_2(CO)_{10}$ does not catalyze exchange of aromatic hydrogen in toluene (also shown in Table I and Figure 2). Gas analysis of a blank experiment with $(C_5H_5)_2WH_2$ and D_2 in toluene demonstrated that the hydride does self-deuterate, but at a much slower rate than when $Mn_2(CO)_{10}$ is present. The NMR of the recovered product, after exchange with 6 M HCl, indicated no ring deuteration.

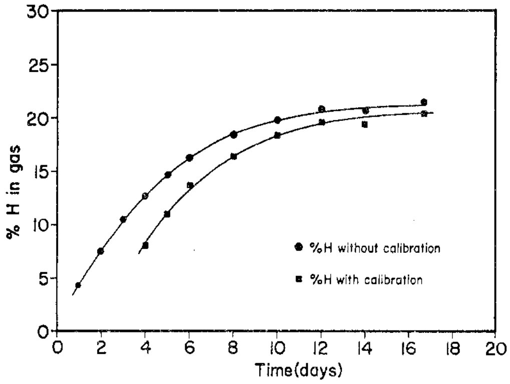

Figure 1. Appearance of hydrogen in the gas phase as a function of time in the deuteration of $(C_5H_5)_2WH_2$ catalyzed by 21.3 mol % $Mn_2(CO)_{10}$ in benzene at 80 °C. Absolute errors are included within the shaded round and square symbols.

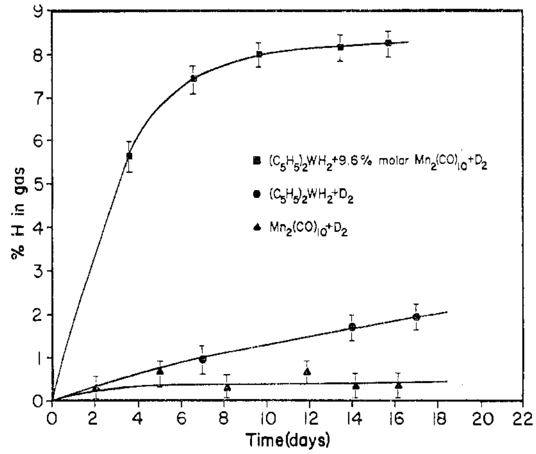

Figure 2. Appearance of hydrogen in the gas phase as a function of time in the deuteration of $(C_5H_5)_2WH_2$ catalyzed by 9.6 mol % $Mn_2(CO)_{10}$ in toluene at 80 °C and for each of the separate components.

Scheme I

$$Cp_2WH_2 \xrightarrow{-H_2} [Cp_2W] \xrightarrow{+ArH} Cp_2W(H)Ar \xrightarrow[-ArD]{+D_2} Cp_2WHD \ldots \text{etc.}$$

Discussion

The observation of trace deuteration of aromatic solvent in the above-mentioned catalytic system and of trace deuteration $(\eta^5\text{-}C_5H_5)WH_2$ without added $Mn_2(CO)_{10}$ suggests at least one of the reactions occurring in this system is that indicated in Scheme I (where Ar–H may be the aromatic solvent or another metallocene).

Such pathways have been amply discussed[2,3,5,6] but obviously require higher activation than a pathway involving $Mn_2(CO)_{10}$ or some species derived from it in the present catalytic system.

One possible role of the $Mn_2(CO)_{10}$ is suggested from the facile reaction of $CH_3Mn(CO)_5$ with $(\eta^5\text{-}C_5H_5)_2WH_2$, which leads to the binuclear derivative A[1c] indicated in Scheme II. It is suggested that $HMn(CO)_5$ formed under equilibration of $Mn_2(CO)_{10}$ with H_2 might lead to such an intermediate. Metallocenes which are not observed to give such bimetallic species fail to participate in this type of exchange pathway:

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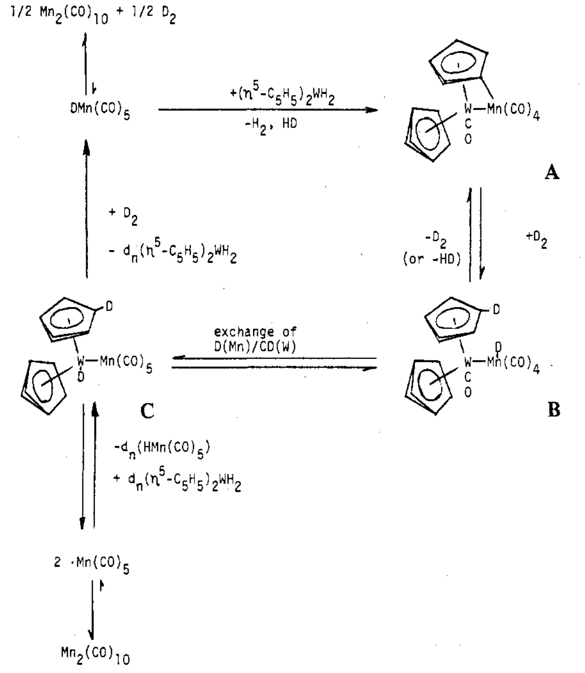
Table I. Mass Spectral and NMR Data for the Deuteration of $(\eta^5\text{-}C_5H_5)_2WH_2$ at 80 °C Catalyzed by $Mn_2(CO)_{10}$

solvent	time of reacn, days	mmol of $(C_5H_5)_2WH_2$	mmol of $Mn_2(CO)_{10}$	mmol of D_2	D_2 press., atm	statist predicted final % H	final % H in gas[a]	% H in $(C_5H_5)_2WH_2$ by NMR
benzene	16.7	2.33	0.500	65	18.8 ± 2	18.0	21.50	16.0
toluene	15.7	1.39	0.133	136	18.7	5.7	8.27	6.0
toluene	17.0	1.36		135	18.6	5.7	1.95	100.0
toluene	16.2		0.515	135	18.7	0.0	0.35	

[a] Without calibration; see Table II (supplementary material); these values were of sufficient accuracy to follow progress of deuteration. Calibration of first value listed led to a corrected value of 20.2%.

Scheme II



two such metallocene derivatives were tested in the presence of $Mn_2(CO)_{10}$, namely, ferrocene and zirconocene dichloride. These metallocenes were chosen because to our knowledge they do not participate in self-exchange pathways. As indicated in the Experimental Section, no exchange is observed under conditions comparable to those observed for exchange of D_2 gas with $(\eta^5\text{-}C_5H_5)_2WH_2$ and $Mn_2(CO)_{10}$. Species B and C have already been discussed in the reaction of A with D_2, which leads to $(\eta^5\text{-}C_5H_5)_2WH_2\text{-}d_n$ in which extensive deuteration is observed.[1c]

Another conceivable entry into the catalytic cycle would be production of species C by attack on metal hydride of $(\eta^5\text{-}C_5H_5)_2WH_2$ by the $Mn(CO)_5$ radical derived from the thermolysis of $Mn_2(CO)_{10}$.[7] Species C is identical with intermediate **i-1** of a companion work[1c] for which spectroscopic evidence was obtained. Species C would have to equilibrate with B and A in order to exchange hydrogen atoms on the ring. Further studies are needed to sort out these possibilities.

Experimental Section

General Procedures. All manipulations were performed in standard Schlenk-type flasks under an inert atmosphere of nitrogen or argon. Reactions with D_2 gas were performed in 310-mL stainless steel Hoke cylinders fitted with a double needle valve arrangement for gas sampling (see Figure 3). The Hoke cylinders were purchased from Castle Controls, Inc., Pasadena, Calif. Teflon tape was used on joints to prevent gas leakage. Gas sampling was effected by evacuating the system outside the Hoke cylinder by opening stopcocks A, B, and C; D remained closed (see Figure 3). While stopcocks A and C were closed, D was opened and then closed again. The high-pressure gas was then trapped between C and D. Stopcock C was then opened, filling the evacuated bulb. After B was closed, a mass spectrum of the gas sample was taken.

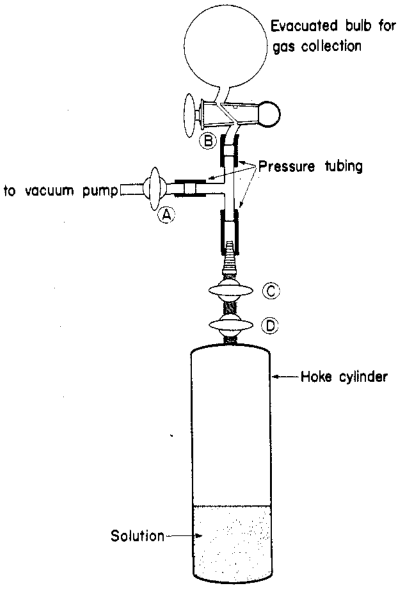


Figure 3. Apparatus for deuteration reactions and gas sampling.

Reagents. The following materials were obtained from the indicated sources: WCl_6, ferrocene and $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, Alfa Inorganics, Beverly, Mass.; $Mn_2(CO)_{10}$, Pressure Chemical Co., Pittsburgh, Pa.; D_2, Liquid Carbonics. All other reagents and solvents are those available from general chemical vendors. The synthesis employed for $(\eta^5\text{-}C_5H_5)_2WH_2$ was that described by King.[8] All solvents were distilled from CaH_2 except for halogenated solvents which were dried over molecular sieves (4A) and deoxygenated by bubbling nitrogen through them for 5–10 min.

Instrumentation. Mass spectra of gases were taken on a Consolidated Engineering Corp. Model 21-620 mass spectrometer. This was calibrated with known pressures of pure D_2 and H_2 gases. The pressures of the gases leaked into the evacuated gas bulb were measured with a manometer. The gas mixtures were stirred with a Teflon paddle fitted inside the bulb, and the D/H height ratio was obtained from the mass spectrum of the gas mixture by using the formula

$$D/H = \frac{(D_2^+\ \text{height}) + \frac{1}{2}(HD^+\ \text{height})}{[(H_2^+ - D^+)\ \text{height}] + \frac{1}{2}(HD^+\ \text{height})}$$

The D/H height ratio was plotted against the percent of H determined from the partial pressure of H_2 (see supplementary Table II and Figure 4). The D^+ height was estimated to be 1.71% of the D_2^+ peak by taking the mass spectrum of pure D_2 as a function of time in the spectrometer. The height intensity of each peak decreased with time (see supplementary Figure 5), but the D^+ peak remained approximately 1.71% of the D_2^+ peak (see supplementary Figure 6).

All mass spectra were taken with an ionizing current of 20 μA and at a gas pressure of 50 (±1) μm. To cancel changes in height due to pressure loss inside the ionizing chamber, we measured the H_2^+ (and D^+) peak of each gas sample approximately 2 min after gas introduction, the HD^+ peak after 4 min, and the D_2^+ peak after 6 min. The decrease in pressure between the H_2^+ (and D^+) and the D_2^+ peaks was very small.

Deuteration of $(C_5H_5)_2WH_2$ by D_2 Gas and 21.3 mol % $Mn_2(CO)_{10}$ in Benzene. A 210-mL benzene solution of $(C_5H_5)_2WH_2$ (0.737 g, 2.33 mmol) and $Mn_2(CO)_{10}$ (0.194 g, 0.497 mmol) was degassed through three successive freeze–thaw cycles in the Hoke cylinder. Then D_2 (6.5 atm, 65 mmol) was drawn into the evacuated cylinder over a period of 0.5 min at approximately −150 °C. Valves C and D were closed, and after thawing to room temperature, the cylinder was placed in an oven maintained at 80 °C. Gas samples were taken periodically. After 16.7 days, the cylinder was opened, and by repeated gradual leaks into a calibrated system, the final pressure was ascertained. The solution was filtered, and the benzene removed under vacuum and retained in a liquid N_2 trap.

Protonation of Metal Hydrogen To Provide an Internal ^1H NMR Reference To Determine the Extent of Ring Deuteration. The solid residue from the experiment above was extracted three times with 20-mL portions of 6 M HCl, and the solution was filtered and stirred for 40 h. The solution was neutralized with aqueous NaOH, and the resultant yellow precipitate was extracted three times with 40-mL portions of benzene, dried over anhydrous $MgSO_4$, and filtered. After removal of benzene under vacuum, the product was sublimed at approximately 100 °C (10^{-2} mm).

Deuteration of $(C_5H_5)_2WH_2$ by D_2 Gas and 9.6 mol % $Mn_2(CO)_{10}$ in Toluene. Toluene (60 mL, 0.565 mol), $(C_5H_5)_2WH_2$ (0.440 g, 1.39 mmol), $Mn_2(CO)_{10}$ (0.052 g, 0.133 mmol), and D_2 (136 mmol) were reacted at 80 °C for 15.7 days. The reaction was monitored by mass spectra. After opening of the bomb, the toluene was removed and collected under vacuum. The residue was metal protonated with 6 M HCl as described above.

Control Experiment of D_2 with $(C_5H_5)_2WH_2$ in Toluene. A 100-mL toluene solution of $(C_5H_5)_2WH_2$ (0.430 g, 1.36 mmol) and D_2 (135 mmol) was heated to 80 °C and reacted for 17.0 days. The toluene was removed under vacuum, and the residue was metal protonated with 6 M HCl as described above.

Control Experiment of D_2 with $Mn_2(CO)_{10}$ in Toluene. Toluene (100 mL, 0.942 mol), $Mn_2(CO)_{10}$ (0.201 g, 0.515 mmol), and D_2 (135 mmol) were reacted at 80 °C for 16.2 days. The reaction was monitored by mass spectra of gas samples and analyzed from the NMR of the toluene recovered.

Reaction of $(C_5H_5)_2Fe$ and 23.7 mol % $Mn_2(CO)_{10}$ and D_2 in Toluene. Ferrocene (0.802 g, 4.31 mmol), $Mn_2(CO)_{10}$ (0.199 g, 0.510 mmol), and D_2 (135 mmol) in 100 mL of toluene were reacted for 6.0 days at 80 °C and 5.2 days at 112 °C. After 6 days at 80 °C, the amount of H in the gas was 0.51% (uncalibrated) out of a possible maximum 14%. After 5.25 days more at 112 °C, the gas was 1.14% H (uncalibrated). There was evidence of some slight reaction in the observation of a small amount of $(C_5H_5)Mn(CO)_3$ in the infrared spectrum of the product, as previously reported by Abel and co-workers in the absence of D_2.[9] It has not been determined whether the hydrogen–deuterium exchange involved the cyclopentadienyl rings of ferrocene or involved solvent.

Reaction of $(C_5H_5)_2ZrCl_2$ and 27.4 mol % $Mn_2(CO)_{10}$ and D_2 in Toluene. A solution of $(C_5H_5)_2ZrCl_2$ (0.751 g, 2.57 mmol) and $Mn_2(CO)_{10}$ (0.137 g, 0.352 mmol) in 150 mL of toluene was reacted with D_2 for 9.7 days at 80 °C and 2.2 days at 110 °C. No H_2, HD, or HCl was detected in the gas phase. The reaction mixture was not further analyzed.

Acknowledgment. We thank the National Science Foundation (Grant GP 23267) for support of this work and the following donors for support of the departmental instruments employed in this study: Varian A-60D NMR spectrometer, E. I. du Pont de Nemours & Co. and NSF Grant G 20207; Beckman IR-4, E. I. du Pont de Nemours & Co.; AEI MS9, NSF Grant GP 3672.

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $(C_5H_5)_2WH_2$, 1271-33-6; $(C_5H_5)_2Fe$, 102-54-5; D, 7782-39-0.

Supplementary Material Available: Table II (mass spectral calibration data) and Figures 4–6 (mass spectral peak heights as functions of % H and time in spectrometer) (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Material taken in part from the Ph.D. dissertation of R. J. Hoxmeier, UCLA, 1972, and the M.S. dissertation of J. R. Blickensderfer, UCLA, 1971. This is part 16 of a series of papers on metalation reactions. (b) Part 15: R. J. Hoxmeier, C. B. Knobler, and H. D. Kaesz, *Inorg. Chem.*, companion article in this issue. (c) Part 14: R. J. Hoxmeier, J. R. Blickensderfer, and H. D. Kaesz, *ibid.*, companion article in this issue.

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Structural Features of Chloro(dimethylphenylphosphonium (trimethylsilyl)methylide)(1,5-cyclooctadiene)palladium(II) Hexafluorophosphate

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Received June 29, 1979

Coordination complexes of ylides have been of interest as examples of compounds containing alkyl ligands which show exceptional stability due to the zwitterionic character of the ylide.[1] Itoh and co-workers have reported the preparation of palladium(II) complexes formed with the prochiral phosphonium (trimethylsilyl)methylide, $PhMe_2P{=}CH(SiMe_3)$.[2] The dimeric complex $[Pd(CH(PPhMe_2)(SiMe_3))Cl_2]_2$ was formed by treating $PdCl_2(PhCN)_2$ with $PhMe_2{=}CH(SiMe_3)$. Abstraction of chloro ligands with $AgPF_6$ in the presence of 1,5-cyclooctadiene produced the diolefin complex $[Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl]PF_6$. For establishment of the mode of coordination of the ylide ligand in this complex a molecular structure analysis was undertaken.

Experimental Section

A crystalline sample of $[Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl]PF_6$ was provided by Dr. Kenji Itoh of Toyohashi University. Preliminary photographs indicated monoclinic symmetry and an extinction pattern consistent with space group $P2_1/c$. A crystal of dimensions 0.31 × 0.27 × 0.22 mm was mounted and aligned on a Syntex $P\bar{1}$ automated diffractometer. Lattice constants of $a = 8.561$ (1) Å, $b = 22.899$ (3) Å, $c = 13.614$ (3) Å, and $\beta = 102.98$ (2)° were obtained from a least-squares refinement of the centered settings of 15 high-angle reflections. A calculated density of 1.581 g cm^{-3} agrees with an experimental value of 1.56 g cm^{-3} calculated for four formula weights per unit cell. Intensity data were collected within the angular range $3° \le 2\theta \le 50°$ by the θ–2θ scan technique by using Mo Kα radiation. A scan rate of 4.0°/min was used. Data were corrected for Lorentz, polarization, and absorption effects ($\mu = 10.2$ cm^{-1}). Of 4711 independent reflections measured, 3186 were found to have $F_o^2 > 3\sigma(F_o^2)$ and were included in the refinement. The structure was solved by the heavy-atom method and refined by using programs and procedures outlined previously.[3] In final cycles of refinement all nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic thermal parameters. Final discrepancy indices of $R = 0.041$ and $R_w = 0.048$ were obtained with the standard deviation of an observation of unit weight at 1.78. Final atomic coordinates and thermal parameters for all nonhydrogen atoms and the ylide hydrogen are contained in Table I. A listing of the final observed and calculated structure factor amplitudes (×10) is available.

Results and Discussion

A view of the $Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ cation is shown in Figure 1. Selected bond distances and angles are contained in Table II. The centrosymmetric unit

0020-1669/79/1318-3608$01.00/0