analysis of variance showed no unusual trends. In the last cycle of refinement, the shifts for all parameters were less than 0.007σ, except for H and cyclooctene parameters. A final difference Fourier map showed a residual electron density of 0.7 e/Å^3 near disordered cyclooctenes. All calculations were performed on a VAX-11/730 DEC computer.

The final fractional atomic coordinates are listed in Table IV.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes for $5\cdot(C_8H_{14})_2$ (16 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Rhenocene Derivatives

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Summary: An improved preparation of Cp_2ReH (1) is reported, which employs the reaction of $ReCl_5$ with Na(C_5H_5) and a borohydride reducing agent in dimethoxyethane, affording 1 in 40% yield. Lithiation of 1 with BuLi in THF gives Cp_2ReLi. Alkylation of Cp_2ReLi with primary alkyl halides affords the alkyl derivatives Cp_2Re–R in excellent yields and high purity. The alkyl derivatives react with protic acids to afford thermally labile Re(V) alkyl hydrides, which readily eliminate the corresponding alkane.

The attempt to synthesize the rhenium analogue of manganocene by Wilkinson and Birmingham in 1955[1] led to the isolation of Cp_2ReH (1) (Cp = η^5-C_5H_5). The isolation of 1 was of some importance in the early development of transition-metal organometallic chemistry, since it was the first hydride complex not containing carbonyl coligands and was the first such complex to be characterized by ^{1}H NMR spectroscopy. Perhaps as a consequence of the difficult synthesis[2] of 1, relatively few studies of 1 and its derivatives have been reported.[3] In this paper, we report an improved preparation of 1, which allows for a convenient entry into the chemistry of rhenocene derivatives.

The rhenocene alkyls Cp_2Re–R are found to be thermally stable (with the exception of R = benzyl) but reactive species. We have found that the alkyls react with protic acids to afford thermally labile cationic Re(V) alkyl hydride complexes, which can in some cases be isolated as microcrystalline solids at low temperature. The alkyl hydride complexes are found to readily undergo reductive elimination in the solid state or in solution to give the corresponding alkane. With chloride as the counterion, the final product is Cp_2ReCl.

Experimental Section

General Considerations. All reactions were carried out by standard Schlenk, drybox, or vacuum line techniques. An inert atmosphere was provided by purified argon. All solvents were dried and distilled from Na/K benzophenone or activated 4-Å molecular sieves. Rhenium metal (powder, 30–200 mesh) was purchased from Rhenium Alloys Inc., Elyria, OH. Chlorine gas (UHP) was purchased from Matheson. Alkyl halides were freshly distilled from 4-Å molecular sieves. Elemental analyses were performed by Galbraith Analytical Laboratory and by Mikroanalytisches Labor Pascher.

Synthesis of Cp_2ReH from $ReCl_5$. Rhenium pentachloride was prepared by the method of Lincoln and Wilkinson.[11] The product of chlorination of 18.6 g (0.1 mol) of Re metal was collected in a 2-L flask fitted with a 24/40 taper joint and a sidearm with a vacuum valve. The collection flask was flame-sealed under reduced pressure. The flask was cooled to −78 °C and 100 mL of 1,2-dimethoxyethane (DME) was added. The mixture was stirred while being warmed to 0 °C. A suspension of 0.6 mol of Na(C_5H_5) in DME (1 L) at 0 °C was added. The dark purple mixture was stirred for 1 h at room temperature. The flask was fitted with a reflux condenser and heated to reflux for 12 h. At this point 100 mL of KBH(i-OPr)$_3$ solution (1 M in THF) was added and heating continued for 12 h. The mixture was transferred while hot through a wide-bore cannula to a 2-L flask equipped with a vacuum valve and a large O-ring flange. Volatiles were removed by pumping, resulting in a dark purple residue. The flask was fitted with a heating mantle and gently heated with continuous pumping until yellow crystals were observed on the upper surfaces of the flask. A large cold finger was fitted to the O-ring joint. Sublimation at 100–120 °C (10^{-4} mmHg) gave 12.1 g of 1 (40% based on Re metal). The material can be recrystallized from Et_2O/heptane (1:5) to remove traces of triisopropoxyborane and resublimed at 60 °C. Anal. Calc for $C_{10}H_{11}Re$: C, 37.84; H, 3.49. Found: C, 38.05; H, 3.50. ^{1}H NMR, δ: (CD_2Cl_2) 4.38 (d, J = 1 Hz, Cp, 10 H), −13.41 (br s, Re–H, 1 H); (C_6D_6) 4.20 (d, J = 1 Hz, Cp, 10 H), −12.92 (br m, Re–H, 1 H).

Synthesis of 1 from $ReCl_4(THF)_2$. To a solution of K(C_5H_5) (20 mmol) in 100 mL of DME at 0 °C was added 3.2 g (6.7 mmol) of $ReCl_4(THF)_2$.[6] After stirring at 0 °C for 1 h, $LiBH_4$ (0.147 g, 6.7 mmol) was added and the mixture was warmed to room temperature for 3 h. Volatiles were removed by pumping and 1 was isolated by sublimation (80 °C, 10^{-4} mmHg). Yield: 0.86 g (40%).

Synthesis of 1 from Cp_2ReCl. To a solution of 0.100 g of Cp_2ReCl in 20 mL of DME at 0 °C was added 3 mL of a 1 M solution of tris(isopropoxy)borohydride. The solution was stirred at room temperature for 3 h. The volatiles were removed, and compound 1 was recovered by vacuum sublimation. Yield: 0.51 g (57% based on Cp_2ReCl).

Synthesis of Rhenocene Alkyls. The procedures are exemplified by that adopted for the methyl complex. A solution of

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Cp_2ReLi in ca. 30 mL of THF was prepared by the reaction of 1 (0.482 g, 1.52 mmol) with BuLi (0.65 mL of a 2.4 M solution in hexane) at 0 °C and frozen with liquid nitrogen. Methyl chloride (0.8 g, 9 mmol) was vacuum-transferred into the reactor from activated 4-Å molecular sieves. The mixture was warmed to 0 °C with stirring and turned a deep orange as all precipitates dissolved. After stirring at 0 °C for 20 min, volatiles were removed. Vacuum sublimation, (40 °C, 10^{-6} mmHg) gave Cp_2Re-CH_3 as orange crystals (0.452 g, 90%). The use of CH_3I in this procedure gives yields of 50–60%. Anal. Calc for $C_{11}H_{13}Re$: C, 39.86; H, 3.85. Found: C, 39.74; H, 3.95. ^1H NMR, δ: (CD_2Cl_2) 4.23 (s, Cp, 10 H) 0.32 (s, $Re-CH_3$, 3 H); (C_6D_6) 3.97, 0.77. No ^1H NMR resonances for 1 were detected. $^{13}C\{^1H\}$ NMR, δ: (C_6D_6) 71.6 (Cp), −35.4 ($Re-CH_3$).

$Cp_2Re-CH_2CH_3$ was similarly prepared by using ethyl iodide and isolated as light orange crystals (yield 80% based on 1). Anal. Calc for $C_{12}H_{15}Re$: C, 41.72; H, 4.38. Found: C, 41.05; H, 4.05. ^1H NMR, δ: (C_6D_6) 3.96 (s, Cp, 10 H), 1.70 (t, CH_3, 3 H), 1.58 (q, CH_2, 2 H). $^{13}C\{^1H\}$ NMR, δ: (C_6D_6) 71.1 (Cp), 24.9 (CH_3), −18.6 ($Re-CH_2$).

A similar procedure using *n*-Pr–Cl affords $Cp_2Re-CH_2CH_2CH_3$ as light orange crystals in 78% yield. Anal. Calc for $C_{13}H_{17}Re$: C, 43.41; H, 4.73. Found: C, 43.02; H, 4.60. ^1H NMR, δ: (CD_3CN, 500 MHz) 4.21 (s, Cp, 10 H), 1.3–1.2 (m, $Re-CH_2CH_2-$, 4 H), 0.72 (t, CH_3, 3 H). $^{13}C\{^1H\}$ NMR, δ: 71.9 (Cp), 34.4 ($-CH_2-$), 22,8 ($-CH_3$), −7.7 ($Re-CH_2-$).

$Cp_2ReCH_2Si(CH_3)_3$ was isolated as orange crystals in 69% yield by using $(CH_3)_3SiCH_2Cl$. Anal. Calc for $C_{14}H_{21}SiRe$: C, 41.68; H, 5.25. Found: C, 41.25; H, 5.02. ^1H NMR, δ: (CD_3CN, 250 MHz) 4.24 (s, C_5H_5, 10 H), −0.11 (s, $-Si(CH_3)_3$, 9 H), −0.19 (s, $Re-CH_2-$, 2 H). $^{13}C\{^1H\}$ NMR, δ: (CD_3CN) 72.3 (Cp), 3.09 ($-Si(CH_3)_3$). The methylene carbon resonance could not be located.

The benzyl complex Cp_2ReCH_2Ph was prepared by reaction of 1 equiv of benzyl bromide with Cp_2ReLi in THF at −30 °C. Stirring was continued at this temperature for 1.5 h. After warming to room temperature and removal of volatiles, the residue was extracted with 25 mL of toluene. After filtration and concentration to ca. 3–4 mL, 20 mL of heptane was added, affording a dark red-brown precipitate. Cooling to −78 °C completed the precipitation of the product, which was recrystallized from acetonitrile to give the product as dark red-orange needles (30% yield). The benzyl complex suffers slight decomposition upon vacuum sublimation at 60 °C. ^1H NMR, δ: (CD_3CN, 250 MHz) 7.1–6.75 (m, $-C_6H_5$, 5 H), 4.25 (s, Cp, 10 H), 2.70 (s, $Re-CH_2-$, 2 H).

Protonation of Rhenocene Alkyl Complexes. Due to the thermal lability of the alkyl hydride complexes, samples were prepared in a Schlenk tube reactor with a 5-mm NMR tube attached directly to the side or in a 5-mm NMR tube sealed to a Kontes 4-mm high-vacuum valve. All solvents were added via vacuum-transfer techniques, while manipulations by syringe were carried out against a counterflow of argon. The procedure employed for the methyl hydride complex is typical: Cp_2ReCH_3 (4.5 mg) was placed in a 5-mm NMR tube containing a stir bar. After addition of 0.5 mL of Et_2O at −78 °C, $HBF_4{\cdot}Et_2O$ (1.2 equiv) was added via syringe. After 10 min of stirring, the supernatant was removed by syringe, and the colorless precipitate was washed twice with small portions of Et_2O and dried by pumping at −30 °C. The NMR solvent (CD_2Cl_2, 0.4 mL) was added, and the stir bar removed. The solution was frozen in liquid nitrogen, and the tube was flame-sealed under dynamic vacuum. ^1H NMR, δ: (CD_2Cl_2, 250 MHz, 272 K) 5.45 (s, Cp, 10 H), 0.59 (s, $Re-CH_3$, 3 H), −12.12 (s, Re–H, 1 H). Other alkyl hydride complexes were similarly prepared and their ^1H NMR spectra (δ) recorded in CD_2Cl_2 at 272 K: $[Cp_2Re(H)CH_2CH_3]BF_4$ 5.41 (s, Cp, 10 H), 1.58 (q, $Re-CH_2$, 2 H), 1.36 (t, $-CH_3$, 3 H), −12.11, (s, Re–H, 1 H); $[Cp_2Re(H)CH_2CH_2CH_3]BF_4$ 5.41 (s, Cp, 10 H), 1.48 −1.15 (m, $Re-CH_2CH_2-$, 4 H), 0.81 (br t, $-CH_3$, 3 H), −12.07 (s, Re–H, 1 H); $[Cp_2Re(H)CH_2Ph]BF_4$ 7.25–7.0 (m, $-C_6H_5$, 5 H), 5.40 (s, Cp, 10 H), 3.10 (s, $Re-CH_2$, 2 H), −12.05 (s, Re–H, 1 H).

Results and Discussion

Preparation of Cp_2ReH (1). Compound 1 has been prepared from $ReCl_5$, $Na(C_5H_5)$, and a borohydride reducing agent (eq 1) in 1,2-dimethoxyethane (DME). After removal of volatiles, compound 1 is conveniently isolated

$$ReCl_5 + 6Na(C_5H_5) + KBH(i\text{-}OPr)_3 \rightarrow Cp_2ReH \quad (1)$$

by sublimation. The yield of 1 by this process is 40%. The preparation of 1 reported here differs from the original method primarily in that DME has been substituted for THF as the reaction solvent. It is known that THF reacts with $ReCl_5$ to give $ReCl_4(THF)_2$.[6] The organic products of this reaction have not been identified, but presumably they are not beneficial in the preparation of 1. Thus the original preparative conditions likely involve a competition between reduction of $ReCl_5$ by the cyclopentadienide anion and reduction by THF. DME does not react with $ReCl_5$ at lower temperatures but still provides a polar environment ensuring at least partial solubility of the reagents. The conditions reported here provide a convenient one-pot synthesis of 1, from which other derivatives of the rhenocene system are readily accessible.

In an attempt to ascertain the nature of the intermediates involved in eq 1, the reaction of $ReCl_5$ with $Na(C_5H_5)$ in DME at room temperature was undertaken on a small scale and the products were analyzed by ^1H NMR spectroscopy. A small amount of Cp_2ReCl was formed, as determined by comparison of the ^1H NMR resonance with an authentic sample.[7] Additional chloride complex was formed upon refluxing the solution. In a separate experiment, authentic Cp_2ReCl was reacted with $KBH(i\text{-}OPr)_3$, giving 1 in 60% yield. Thus the intermediacy of the chloride complex in the synthesis of 1 is plausible. Another possible intermediate in the reaction is the rhenocene dimer, $[Cp_2Re]_2$, recently reported by Pasman and Snell.[8] It was reported that thermolysis of this dimer affords 1 (eq 2). Since the theoretical maximum yield of 1 from such a process would be 50%, this could be a factor in the relatively low yields of 1.

$$2[Cp_2Re]_2 \rightarrow 2Cp_2ReH + (\eta\text{-}C_5H_5)_2(C_5H_4)_2Re_2 \quad (2)$$

We have also investigated the use of Re(IV) complexes as starting materials for rhenocene chemistry. Thus the reaction of $ReCl_4(THF)_2$ with $Na(C_5H_5)$, followed by borohydride reduction was carried out and found to give a 40% yield of 1. The intermediacy of Cp_2ReCl was established by ^1H NMR monitoring of the reaction mixture. This preparation is actually less convenient than the one-pot procedure starting from $ReCl_5$, since $ReCl_4(THF)_2$ must be prepared from $ReCl_5$.[6]

Preparation of Alkyl Derivatives Cp_2Re-R. Previous reports of the alkyl derivatives of rhenocene have indicated some difficulty in their preparation in a pure state. For example, Baudry and Ephritikine reported that treatment of 1 with BuLi in hexane affords a white precipitate of Cp_2ReLi, which could be alkylated to give Cp_2Re-R (R = CH_3, $CH_2CH{=}CH_2$). These alkyls were obtained as orange oils.[7] Stucky and co-workers employed lithiation of 1 with BuLi/PMDT followed by alkylation and were able to obtain these and other alkyls as solid materials, but considerable difficulty with contamination of the products with the starting hydride was encountered.[9]

The procedure that we have adopted involves lithiation of 1 with 1 equiv of BuLi in THF at 0 °C. The solution of the lithiated intermediate was immediately reacted with an appropriate primary alkyl halide, to afford the alkyl derivatives Cp_2Re-R. Removal of the volatiles followed by vacuum sublimation affords the alkyls as orange-red crystalline solids, free of detectable amounts of 1. The alkyl complexes are very soluble in hydrocarbon solvents, quite air sensitive in the solid state, and extremely air sensitive in solution, which makes their subsequent manipulation difficult. The procedure reported here employs

THF as solvent and allows for rapid reaction with the alkyl halides under homogeneous conditions. A possible explanation for the success of the current procedure is found in the report by Ephritikine and Baudry that Cp_2ReCH_3 reacts with methyl halides to afford the cationic dimethyl complex $[Cp_2Re(CH_3)_2]^+$.[7] We have found that this complex can act as a proton donor to Cp_2ReLi to afford **1**. The nature of the other rhenium-containing products has not been determined, but it is clear that in the preparation of the rhenocene alkyl complexes, where an excess of alkyl halide has typically been employed, the formation of the dialkyl complexes should be avoided. The heterogeneous conditions employed by previous workers may have accentuated this problem, since the alkyls are freely soluble in hexane, while the lithiated intermediates have very limited solubility.

Reaction of Rhenocene Alkyls with Acids. We have previously reported[10] that Cp_2ReCH_3 reacts with protic acids (HCl or $HBF_4{\cdot}Et_2O$) to afford the thermally unstable methyl hydride complex $[Cp_2Re(H)CH_3]^+$. Reductive elimination of methane from this complex is facile in solution and in the solid state at room temperature, but the cation can be isolated by protonation in diethyl ether at low temperature. Careful removal of the supernatant solution by syringe followed by vacuum drying at temperatures ≤0 °C affords the product as a colorless powder. The proton NMR spectrum obtained at low temperatures in CD_2Cl_2 exhibits a Cp resonance, a methyl signal, and a resonance for the hydride proton at δ −12.10. Reductive elimination of methane from the chloride salt leads to clean formation of Cp_2ReCl.

Similar protonation reactions have been carried out with the ethyl, *n*-propyl, and benzyl complexes. The products were identified as alkyl hydride complexes by their low-temperature ^1H NMR spectra (see Experimental Section). Reductive elimination of the corresponding alkane was observed under conditions similar to those noted above for the methyl case. The qualitative trend in rates of reductive elimination observed was *n*-propyl > ethyl > methyl ≅ benzyl. In the case of the (trimethylsilyl)methyl derivative, protonation led to very rapid formation of TMS, and the presumed alkyl hydride intermediate could not be observed directly.

These observations establish that the rhenocene alkyls act as bases toward protic acids, as noted in the initial reports on the reactivity of the parent hydride.[2] In contrast to the thermal stability[2] of the dihydride cation $[Cp_2Re(H)_2]^+$ with respect to reductive elimination of hydrogen, the corresponding alkyl hydrides eliminate readily to afford alkanes and the rhenocene cation.

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Is the Haptotropic Rearrangement in Bis(tributylphosphine)(anthracene)nickel Inter- or Intramolecular? Determination of the Molecularity by a Spin Saturation Transfer Approach[1]

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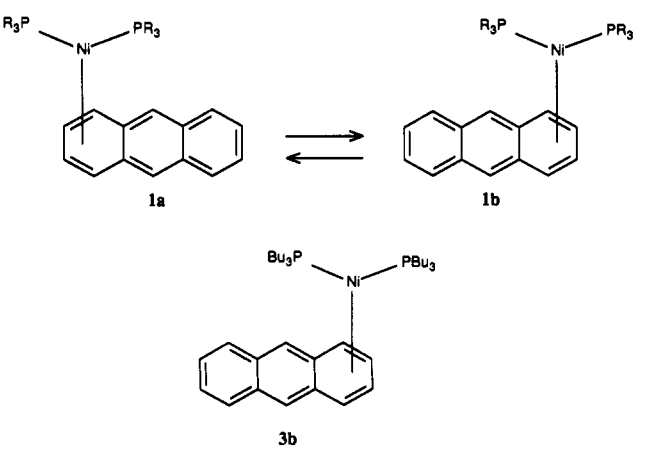
Summary: A simple, fast, and inexpensive method for the determination of the molecularity of a reaction is presented. The method is based on spin saturation transfer technique coupled with VTNMR spectroscopy. A sample containing the complex under study and the ligand, with which a possible exchange might take place, is brought to a temperature at which saturation transfer can be observed. Which of the nuclei in the mixture is coupled to a saturated nucleus is then determined by magnetization transfer. The rearrangement **1a** ⇄ **1b** was studied as a test case. A mixture of **3b** and free anthracene was cooled to −70 °C, and H_2 and H_3 were saturated. No change in the other resonances was observed. The experiment was repeated at −50 °C, where the diminishing of H_5 and H_6 was clearly observed, but the free anthracene's resonances stayed unchanged. It is thus concluded that the rearrangement **1a** ⇄ **1b** is intramolecular. The advantages and disadvantages of the method as compared to crossover methodology and 2D EXSY experiments are discussed.



The investigation of mechanisms in organometallic chemistry is a complex task. In many cases, several competing reaction paths of similar activation energies might take place simultaneously, creating multichannel processes that are difficult to study. One of the most important

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