the proton-transfer reactions studied here have been established by all standard criteria[16] to be true equilibria. In particular, the present experimental data suggest either that the benzyl anion is (kinetically) the favored reprotonation site or, alternatively that rearrangement from an initially metal reprotonated species to the thermodynamically more stable ligand reprotonated form, i.e., (toluene)chromium tricarbonyl, is rapid on the ICR time scale.

Experimental Section

Perfluorobenzene was purchased from Alfa Ventron and used without further purification. Toluene and *m*- and *p*-xylene were vacuum distilled prior to use. Chromium arenes were prepared by using a metal atom reactor.[17] Typical experimental conditions: 3.1 g of toluene and 6.1 g of perfluorobenzene were degassed and cocondensed with chromium vapor (produced by resistive heating of 0.32 g of chromium powder (from MCB) in a molybdenum boat) onto the 77 K walls of the reactor over a period of approximately 30 min. Upon warming to room temperature, the initial reddish brown matrix yielded a brownish yellow solution. This was filtered (under argon), the solvent removed in vacuo, and the resulting fine yellow powder exposed to air to oxidize any bis(toluene)chromium.[18] Yellow crystals resulted from sublimation at 60 °C and recrystallization from benzene–diethylether.

Gas-phase acidities were established relative to several "standard" acids. While, due to experimental constraints,[19] it was not always possible to bracket the acidities of the chromium arene complexes, the acidity of each compound was established with respect to at least two standards. The experimental free energies and error limits are provided in Tables II and III. The corresponding enthalpies, presented in Table I, have been obtained from the free energy data by assuming entropy changes due to symmetry-number effects alone,[20] and a temperature of 300 K.

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Note Added in Proof. A recent negative ion mass spectral study of (arene)$Cr(CO)_3$ compounds[21] has reached the conclusion that $Cr(CO)_3$ is a strong electron-withdrawing group in the gas phase. In this case stabilization is with respect to the radical anion ($M^{-}\cdot$) and not, as discussed here, to the deprotonated form $(M-H)^-$.

Registry No. $(C_6H_5CH_3)Cr(C_6F_6)$, 91711-70-5; $(1,3\text{-}C_6H_4(CH_3)_2)Cr(C_6F_6)$, 91711-71-6; $(1,4\text{-}C_6H_4(CH_3)_2)Cr(C_6F_6)$, 91711-72-7; $C_6H_5CH_3$, 108-88-3; *m*-$C_6H_4(CH_3)_2$, 108-38-3; *p*-$C_6H_4(CH_3)_2$, 106-42-3; *p*-$C_6H_4(CH_3)(CHO)$, 104-87-0; *p*-$C_6H_4(CH_3)(CN)$, 104-85-8.

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[19] The low volatility of the chromium complexes reduced the working partial pressures into the range of (1–5) × 10^{-7} torr. Under these conditions the introduction of standards that were even slightly more acidic led to unacceptable reductions in signal strength.

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Purification of Air-Sensitive Organometallic Compounds by a Modified Flash Chromatography Procedure

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Still's "flash chromatography" procedure has been modified to permit the routine purification of organometallic compounds that would rapidly decompose under normal aerobic chromatographic conditions. In order to maintain an inert atmosphere during sample purification, appropriate changes have been made in the design of the glass apparatus and in the techniques for packing and elution of the column. A key component of the modified chromatographic apparatus is a specially designed flow controller. Two specific examples of the procedure are given.

A very commonly encountered problem in organometallic chemistry is the purification of air-sensitive compounds.[1] For this purpose, we have developed a modified form of the flash chromatography technique reported by Still[2] that permits the entire procedure to be performed under an inert atmosphere. We have found this technique to be a fast and convenient method for the purification of a number of organometallic compounds, including the iron complexes involved in our earlier work.[3] The total time required for packing, preparation, and elution of the column is only 1–2 h. We recommend, though, that before attempting the use of the techniques described below, the user should first become familiar with Still's original procedure.

In comparison with the apparatus described by Still,[2] we have designed a special solvent reservoir and we have redesigned the flow controller and chromatography columns (Figure 1).[4] The solvent with which the column is eluted is stored under nitrogen in solvent reservoirs of 2-L capacity.[5] These reservoirs are easily constructed from

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[1] Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

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[4] As used in our laboratory, all of the glassware depicted in this paper is fitted with 24/40 ground glass joints and nos. 2 and 4 Teflon stopcocks.

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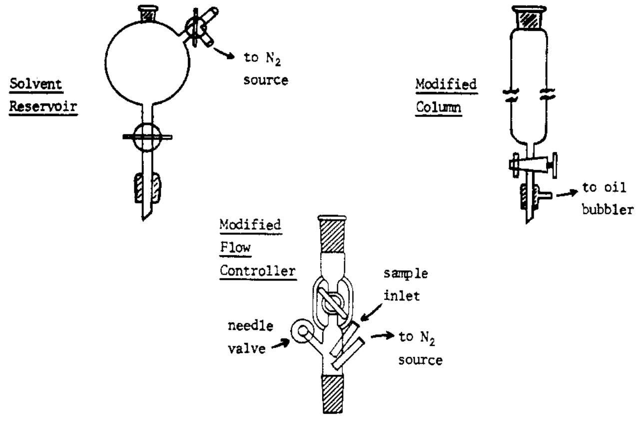

Figure 1.

2-L flasks to which the two-way and three-way stopcocks are attached. Having more than one of these reservoirs on hand is desirable when the compounds to be purified exceed about 1 g, in which case the contents of more than one reservoir may be needed for elution. Smaller solvent reservoirs may also be used, but, on the other hand, those of larger capacity may be too bulky and heavy to be conveniently handled.

The flow controller (drawn to scale in Figure 1), which is needed for maintaining proper pressurization of the chromatography column under nitrogen, has been redesigned in several ways. An additional ground glass joint at the top permits the convenient connection and rapid interchange of solvent reservoirs. Two heavy-walled (7 mm) glass struts between the upper and lower portions of the controller provide the structural integrity necessary to support the weight of the solvent reservoirs. The two-way stopcock in the middle of the controller serves two functions. First, it controls the amount and rate of flow of solvent into the column, and second, when closed, it prevents nitrogen pressure that is applied to the column from pushing dangerously upwards into the solvent reservoir. At the base of the flow controller is an extra tubular inlet for sample injection under nitrogen. This inlet is fashioned with a lip at its upper end so that an overlaid rubber septum tightly bound with wire will not slip off under pressure. All three inlets at the base of the controller are oriented upwards at an angle of approximately 45° to prevent back-flooding of solvent and to ease the application of sample by syringe onto the adsorbent bed.

The chromatography columns have been modified to include a ground glass joint with a pressure relief outlet below the Teflon stopcock. Receiving flasks previously placed under nitrogen may quickly be attached and replaced as needed. The fact that organometallic compounds are most often colored greatly assists in deciding when to change receivers to collect new fractions.

The procedure for dry-packing the column follows that of Still.[2] After the flow controller (needle valve open) and the filled solvent reservoir[6] have been stacked and secured with clamps atop the packed column, the system is degassed by flushing nitrogen (pressure controlled by adjusting the needle valve) through the column for several minutes. The nitrogen source and then the needle valve are closed.[7] Alternatively, the column may be degassed by evacuation and careful refilling with nitrogen.

After the system has attained atmospheric pressure, solvent is allowed to flow into and fill the column. The stopcocks on the flow controller and the solvent reservoir are then closed, the needle valve is opened slightly, and nitrogen pressure[8] is applied to flush the solvent through the silica gel, thereby conditioning the column in the same manner as Still[2] and also removing residual air from the adsorbent. The column may be refilled with solvent as needed after excess nitrogen pressure is vented.[9]

After the desired volume of solvent[10] has been flushed through the column, one should simultaneously close the stopcock at the bottom of the column, open the needle valve, and reduce the nitrogen pressure. The sample is then applied to the column through the septum inlet with a syringe. After the sample is washed into the top of the adsorbent bed with a few small portions of solvent from the reservoir, the column is filled with further solvent as described above. The stopcocks on the flow controller and solvent reservoir are then closed, and the column is eluted under nitrogen pressure.[8] Appropriate adjustment of the needle valve on the flow controller determines the rate of elution, the flow rate being chosen in accordance with Still's guidelines.[2] Receiving flasks are changed as needed. An alternative method for collection of fractions under an inert atmosphere is to employ a "cow-type" adapter of the style often used for distillations. In this manner, the risk of exposing very sensitive materials to the air is minimized. Whatever collection method is employed, excess pressure is vented out of the collectors via a bubbler connected to the pressure relief outlet at the bottom of the column.

Still has noted that the sample size can be increased considerably for mixtures having components separated by R_f values greater than 0.4. We have found this point to be true for air-sensitive compounds as well. Alternatively, a longer bed of silica gel may be packed into the column to increase the resolution and sample capacity, and the column may be longer or wider (e.g., 60 mm) than those

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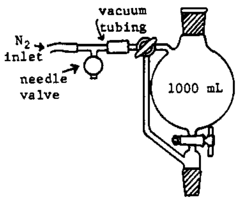
(5) The solvent may either be degassed (repeated cycles of evacuation and refilling with nitrogen is usually adequate) after being placed in the reservoir or may be distilled directly into the reservoir under a nitrogen atmosphere. If the former procedure is employed, note that the Teflon stopcock may be subject to leakage under vacuum, but this problem may be minimized by placing a flask on the joint below the stopcock.

(6) The solvent reservoir is connected to a nitrogen source by way of either a mineral oil bubbler or a nitrogen-filled balloon in order to maintain positive pressure within the container while solvent is drained into the column.

(7) The needle valve is closed lastly so that the column may attain atmospheric pressure. Connection of the open end of the needle valve to a mineral oil bubbler is desirable to prevent back-diffusion of air into the system.

(8) Although we do not monitor the nitrogen pressure in the column precisely, it is probably not necessary to exceed about 10 psi at any point in our procedure. As a safety precaution, the pressurized apparatus should be handled behind an appropriate shield.

(9) Professor J. A. Gladysz, Dr. Danny E. Smith, and Mr. Kerry C. Brinkman (University of Utah) have noted that with our apparatus in order to add further solvent to the column from the reservoir, the column must be depressurized and the chromatography interrupted. However, in our experience, this need has never posed any problems, and indeed, the same need holds for other common chromatography procedures carried out under pressure, including Still's original procedure.[2] Nevertheless, if depressurization were to pose a problem, the Utah researchers have kindly suggested the use of the alternative design for the solvent reservoir shown.



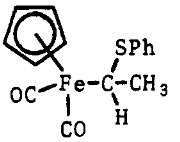
(10) This point is judged by noting the cessation of formation of gas bubbles in the solvent exiting the bottom of the column and by a uniformly packed appearance of the adsorbent. Typically, for a 250 × 60 mm bed of silica gel, the initial flushing requires on the order of 500 mL of solvent.

suggested by Still. These modifications are useful for chromatographic separations involving sample sizes of several grams.

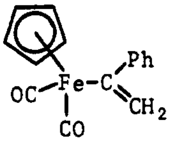
In summary, we have found this modified flash chromatography procedure to be a straightforward, fast, and effective means of purifying air-sensitive compounds.

Experimental Section

Two representative examples of purifications using the technique described in this paper are given below for the iron-containing compounds 1 and 2.



1



2

Purification of Compound 1. Crude 1[3a] (4.5 g) was dissolved in methylene chloride (10–15 mL) and chromatographed according to our procedure using a 1.5:1 mixture of hexanes and methylene chloride (700–1000 mL for elution of the sample in addition to the ca. 500 mL required to set up the column initially) on a 250 × 60 mm column of silica gel (E. Merck No. 9385, 0.040–0.063-mm particle size) with a flow rate of ca. 12 mm/min. An orange band was collected that after concentration in vacuo gave 3.9 g (86% recovery) of 1 as yellow crystals.[3a]

Purification of Compound 2. A sample of highly impure 2[3b] (ca. 5 g) was dissolved in methylene chloride and chromatographed as above by using 4:1 pentane–methylene chloride to give 2.8 g of 2 as a yellow-brown oil.[3b]

Acknowledgment. We wish to thank Professor J. A. Gladysz, Dr. Danny E. Smith, and Mr. Kerry C. Brinkman (University of Utah) for their very thoughtful and constructive comments regarding this work and Mr. Edward J. O'Connor (SUNY, Stony Brook) for some experimental work. We are grateful for the generous financial support provided by the National Science Foundation (Grant CHE 8120466) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 77418-50-9; 2, 83096-21-3.

1,4-Diene-Derived (η^3-Allyl)palladium Complexes. Palladium-Initiated Nucleophilic Addition of Methanol to Dimethyl-1,4-cyclohexadienes

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Dimethyl-1,4-cyclohexadienes in the presence of bis(acetonitrile)palladium dichloride in methanol are stereospecifically converted to (5-methoxy-1–3-η^3-cyclohexenyl)palladium complexes. 1,2-Dimethyl-1,4-cyclohexadiene affords bis(5-methoxy-1,2-dimethyl-1–3-η^3-cyclohexenyl)palladium chloride (1) in the presence or absence of potassium bicarbonate, but the yield improves with the base. In contrast, 1,4-dimethyl-1,4-cyclohexadiene yields bis(5-methoxy-2,5-dimethyl-1–3-η^3-cyclohexenyl)palladium chloride (2) in good yield with base and bis(5-methoxy-1,4-dimethyl-1–3-η^3-cyclohexenyl)palladium chloride (3) without base. 1,5-Dimethyl-1,4-cyclohexadiene affords a mixture of bis(5-methoxy-1,5-dimethyl-1–3-η^3-cyclohexenyl)palladium chloride (4), bis(5-methoxy-2,4-dimethyl-1–3-η^3-cyclohexenyl)palladium chloride (5), and bis(4-methoxy-2,4-dimethyl-1–3-η^3-cyclohexenyl)palladium chloride (6) in base; however, only 5 is formed in the absence of base. Configuration and conformation assignments are based on NMR studies. A mechanism for the formation of the (η^3-allyl)palladium complexes is suggested.

Introduction

With palladium(II) as the promoter, 1,3-dienes are generally difunctionalized by a 1,4 addition of nucleophiles.[2] This synthetically useful reaction, which is stereospecific, is extremely versatile since various functionalities may be introduced by the selection of appropriate nucleophiles and have included alcohols,[3] amines,[3,4] carboxylates,[5] chloride,[6] enolates,[7] and malonate anions.[8] This two-step process involves the intermediacy of a (η^3-allyl)palladium complex, which in certain cases can be isolated and characterized. Since rather complex alkyl-substituted 1,4-cyclohexadienes can be prepared by our tandem alkylation–reduction procedures,[9] as well as by simple Birch metal–ammonia reduction of aromatic compounds,[10] it was of interest to examine whether (η^3-al-

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