Preparation of Organoaluminum Compounds by Hydrozirconation–Transmetalation

Denise B. Carr and Jeffrey Schwartz*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. Received November 27, 1978

Abstract: Organozirconium(IV) complexes produced by hydrozirconation of olefins or acetylenes with Cp2Zr(H)Cl (Cp = η5-C5H5) are precursors of organoaluminum compounds. By stoichiometric transmetalation, the n1 organic ligand can be transferred stereospecifically from zirconium to aluminum by treatment with aluminum halides. Organoaluminum dichlorides can act as mild alkylating agents; they are precursors of ketones through acylation with acid chlorides (this acylation has been found to proceed well for primary, saturated alkyl- and alkenylaluminum dichlorides). Transmetalation from Zr to Al occurs faster for vinylic substituents than for alkyl ones and proceeds predominantly with retention of configuration at carbon. A mechanism for transmetalation is postulated in which the transition state (or intermediate) involves a transition metal–main group metal complex containing a bridging alkyl (or vinylic) group. This mechanism is analogous to the one reported for electrophilic cleavage of alkylzirconium complexes. Acylaluminum dichlorides have been formed by transmetalation between Cp2ZrCl(acyl) and aluminum chloride. They have been shown to be reactive toward electrophiles at both the carbon and the oxygen of the acyl group. Treatment of an acylaluminum dichloride with D2O results in an aldehyde which is at least 83% – C(O)D. However, treatment with acetyl chloride gives an α-chloroalkyl acetate as the major product (attack at O) and an α-diketone as a minor product (attack at C).

Introduction

Organozirconium(IV) complexes, produced by hydrozirconation of olefins or acetylenes with Cp2Zr(H)Cl (I), are intermediates of demonstrated value in organic synthesis. A variety of organic products may be obtained from them stereospecifically by electrophilic cleavage of the carbon–zirconium bond. For example, these organometallic species (2) react with electrophilic halogenation reagents (Br2, I2, NBS, N-bromo- or N-chlorosuccinimide) to give the corresponding organic halides, and with t-C4H9OOH to give alcohols (reaction 1). However, organozirconium complexes have not been found to be effective reagents for routine formation of carbon–carbon bonds: 2 has never been observed to add to the carbonyl group of aldehydes or ketones or to react with common alkylating agents such as alkyl halides, sulfates, or fluorosulfonates. Several of them undergo acylation by acyl halides, but very slowly and in good yield only if steric congestion is minimal. In fact, the only useful direct C–C bond-forming reaction observed thus far for 2, alone, is carbon monoxide “insertion” (reaction 2) which enables the preparation of homologous aldehydes of carboxylic acid derivatives.

The specificity of hydrozirconation is noteworthy. The bulky size of the Cp2ZrCl(–) group ensures that it will become attached to the least hindered position of an acyclic olefin either by regiospecific addition of Zr–H to a terminal olefin or addition to an internal olefin followed by migration past primary or secondary carbons to the least hindered terminus of the alkyl chain. Hydrozirconation of disubstituted acetylenes is also governed by steric effects and proceeds stereospecifically with high regioselectivity to yield the cis addition product in which Zr is attached to the less hindered carbon atom. As well, hydrozirconation can tolerate ether functionalities such as ethoxy, tetrahydropranoxy, or silyl ether groups, which are labile toward hydroalumination. The specificity of hydrozirconation enables the direct conversion of an olefin or an acetylene to a reactive organometallic compound; to adapt organozirconium complexes for use in carbon–carbon bond formation reactions was therefore an attractive goal.

That organozirconium compounds react readily with a variety of heteroatom electrophiles but only rarely with carbon electrophiles may be understood by considering the proposed mechanism for electrophilic cleavage of the C–Zr bond. In insight into the nature of this process was obtained by examination of cleavage reactions employing deuterium-labeled compound 3. The observation of retention of configuration at carbon (once attached to zirconium) in the cleavage products suggests a closed transition state similar to the one proposed for halogenation of organomercurials (Figure 1). Presumably the electrophilic reagent coordinates to Zr by donation of a pair of electrons to the vacant, low-lying orbital of the metal atom, thus facilitating frontside attack on the C–Zr bond. Coordination of X–Y to the metal in the transition state avoids the formation of 14-electron species (Cp2ZrCl)4 which would be generated by an “open” transition state geometry. The fact that acyl halides do react, albeit sluggishly, with zirconium alkyls may be due to carbonyl oxygen coordination to Zr in the...
complexes do not react with most carbon electrophiles for the bonds, those carbon species possessing nucleophilic (to Zr) bond formation by "frontside" reaction of both C-X and C-Zr counterions which could coordinate effectively to Zr in the durens, it was possible to develop the means to overcome what transition state. it is therefore proposed that organozirconium whose use in C-C bond formation processes is well established, transition state for C-Zr cleavage.

Through consideration of successful C-Zr cleavage procedures, it was possible to develop the means to overcome what appeared to be a built-in limitation on the utility of organozirconium species as reagents for C-C bond formation. We have found that the π-bound organic ligand in 2 can be transferred stereospecifically to a metal which, with its complement of ligands, is more electronegative than is the Cp₂Zr(II) moiety. Therefore, by selecting halides of metals whose use in C-C bond formation processes is well established, it is possible to take advantage of the ease and selectivity of hydrozirconation and of the known C-C bond forming propensity of this other metallic element in an essentially "one-pot" reaction. Since there is a large body of evidence indicating that redistribution reactions of mixtures of organoalanes occur through four-centered alkyl-bridged intermediates, AlCl₃ is used (less than 100% excess), free Cp₂ZrCl₂ is not produced; the product obtained is a rapidly interconverting mixture of free Cp₂ZrCl₂ and AlCl₃-complexed Cp₂ZrCl₂. For varying amounts of excess AlCl₃ only a single sharp Cp resonance is observed (at 35 °C); the position of this resonance with regard to free Cp₂ZrCl₂ (δ 6.52) and the deep orange complex (δ 7.10) formed from equal amounts of AlCl₃ and Cp₂ZrCl₂ depends on the amount of excess AlCl₃ present.

Organoa1um dichlorides can act as mild alkylating agents; for example, several of them have been reported to be preferred precursors of ketones through acylation with acid chlorides. To effect ketone synthesis, the reaction mixture containing 3 is cooled to −30 °C and a small excess of acyl chloride is slowly added. Acylation of the organoa1um compound is rapid and can also be conveniently monitored by NMR; it gives AlCl₃-coordinated ketone from which free ketone can be obtained by hydrolysis and extraction.

Several features of the hydrozirconation-transmetalation sequence deserve comment. First, it is noteworthy that, since hydrozirconation of internal (or terminal) acyclic olefins gives the terminal zirconium alkyl exclusively, this sequence provides a simple method for converting a mixture of double-bond isomers of organoa1anes to a single ketonic product (for example, see 2b). Secondly, attempts to directly acylate vinylic complexes 2d and 2e failed. By transmetalation, however, it was possible to produce organoa1um dichlorides (which cannot themselves be prepared directly from acetylenes) and to acylate these aluminum species to obtain high yields of α,β-unsaturated ketones. Ketone is thus formed in this sequence by overall stereospecific cis addition of acyl H to an alkyne by means of two reactive organoa1um species; regioselectivity in the ketone product is the same as that observed in its Zr precursor.

Reports of the formation of ketones from organoa1um dichlorides and acid chlorides had been almost exclusively limited to primary saturated organoa1um dichlorides. In this investigation it was found that acylation proceeds well only for these and for organoa1um dichlorides. Secondary

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**Chart 1**

![Chart 1](image-url)

**Figure 1.** Closed transition state for electrophilic cleavage of the C-Zr bond.

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### Results and Discussion

**A. Transmetalation of Alkyl and Alkenyl Groups from Zr to Al. Stoichiometric Considerations.** Transmetalation from Zr to Al is accomplished as shown in reaction 3, Chart 1. A solution of the organozirconium complex in CH₂Cl₂ is added to a suspension (in CH₂Cl₂, 0°C) of AlCl₃. Transmetalation, which is usually rapid and accompanied by an instantaneous color change, can be conveniently monitored by NMR analysis. The initial organometallic product of transmetalation depends on the amount of AlCl₃ present relative to 2. A stoichiometric amount of AlCl₃ reacts with 2 to give free Cp₂ZrCl₂. If an excess of AlCl₃ is used (less than 100% excess), free Cp₂ZrCl₂ is not produced; the product obtained is a rapidly interconverting mixture of free Cp₂ZrCl₂ and AlCl₃-complexed Cp₂ZrCl₂. For varying amounts of excess AlCl₃ only a single sharp Cp resonance is observed (at 35 °C); the position of this resonance with regard to free Cp₂ZrCl₂ (δ 6.52) and the deep orange complex (δ 7.10) formed from equal amounts of AlCl₃ and Cp₂ZrCl₂ depends on the amount of excess AlCl₃ present.

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### Table 1

<table>
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<tr>
<th>olefin/acylene</th>
<th>RAICl₂</th>
<th>product</th>
<th>Zr yield, % (based on RZr)</th>
<th>Zr → Al yield, %</th>
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<tr>
<td>a</td>
<td></td>
<td></td>
<td>60 (29 h)</td>
<td>98 (30 min)</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td></td>
<td>80 (&gt;2 days)</td>
<td>98 (60 min)</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td></td>
<td>8 (48 h)</td>
<td>64 (45 min)</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td></td>
<td>97 (45 min)</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td></td>
<td></td>
<td>98 (45 min)</td>
<td></td>
</tr>
</tbody>
</table>

*a Yield determined by VPC. * Isolated yield. 1-Octene, cis-2-octene, trans-2-octene, cis-4-octene, trans-4-octene (1:0.5:0.5:1:1).
alkylaluminum dichlorides react with aliphatic acid chlorides to give low yields of the desired products. When 2c was treated with AlCl3, the expected transmetatlation reaction occurred, but subsequent treatment of the product 4c with acetyl chloride gave cyclohexylketone as a major product. GC-mass spectral analysis of the reaction mixture also revealed a substantial amount of methyl 1-cyclohexenyl ketone and very small amounts of its isomers, methyl 2-cyclohexenyl ketone and methyl 3-cyclohexenyl ketone. An almost negligible amount of the desired methyl cyclohexyl ketone was formed. It is possible that steric congestion at AI results in attack by activated acetyl chloride, not by acylation, but rather by hydride abstraction to give cyclohexyl, acetaldehyde, and AlCl3. β-Hydride abstraction from this alane may parallel other routes to β-hydride abstractions which have been found for organotin12 or -zirconium compounds.13 The conversion of cyclohexene, AlCl3, and acetyl chloride to the observed ketone and HCl is well-known.14 As shown in reaction 4, conversion

\[
\text{AlCl}_3 + \text{CH}_2\text{COCl} \rightarrow \text{CH}_3\text{C}=\text{O} + \text{HCl} + \text{AlCl}_3
\]

of cyclohexylaluminum dichloride and acetyl chloride to the observed product mixture may be catalyzed by AlCl3, which is generated in the initial sequence depicted.

Another significant finding of this study is that organoaluminum dichlorides, in which the alkyl group contains a remote double bond, can undergo intramolecular cyclization. (See reaction 6, Chart II.) This cyclization may be analogous to the one observed for dialkyl(5-hexenyl)aluminum complexes.15 Thus, Cp2ZrCl(3-pentenyl) (2f), upon treatment with AlCl3 followed by acetyl chloride, affords a 3-cyclopropyl-1-methylpropan-2-one (79%) (also present in less than 10% yield was 3-cyclopropyl-2-methylpropan-2-one) which would foster transmetalation to give tris(alkenyl)alanes; it was therefore of interest to determine whether alkenylalanes would be available through such intermediate species found in Zr-Al chemistry.18

The mechanism of transmetatlation of alkenyl groups to Al was investigated in order to determine whether it in fact proceeded through a closed transition state, analogous to the one observed in reaction 6, Chart II. This cyclization may be analogous to the one observed for dialkyl(5-hexenyl)aluminum complexes.15 Thus, Cp2ZrCl(3-pentenyl) (2f), upon treatment with AlCl3 followed by acetyl chloride, affords a 3-cyclopropyl-1-methylpropan-2-one (79%) (also present in less than 10% yield was 3-cyclopropyl-2-methylpropan-2-one) which would foster transmetalation to give tris(alkenyl)alanes; it was therefore of interest to determine whether alkenylalanes would be available through such intermediate species found in Zr-Al chemistry.18

**C. Transmetatlation of Alkyl and Alkenyl Groups from Zr to Al. Mechanistic Considerations.** The mechanism of transmetalation was further investigated by employing specifically deuterated zirconium complex 5 in an intramolecular reaction with AlCl3. It was found that transmetalation from Zr to Al proceeded predominantly with retention of configuration at carbon (as does with vinylic substrates). The 2H-decoupled 100-MHz 1H NMR spectrum of 6 revealed a value of J\text{CH}=\text{CH} = 9 Hz for the ethyl diastereomers. Because of broadening of lines in the spectrum of 6 (due to the quadrupolar moment of Al), it was not possible to determine quantitatively to what extent racemization at carbon (if any) occurred. The observation of retention of configuration at carbon supports the hypothesis of a four-centered intermediate or transition state such as 7. Bridging alkyl and alkenyl groups have previously been postulated to occur in intermediates or in isolable species found in Zr-Al chemistry.18

**D. Preparation of Alkenylalanes.** It had been shown that reaction between alkenylzirconium species and AlCl3 could give tris(alkenylalanes); it was therefore of interest to determine whether alkenylalanes would be available through
transmetalation involving alkenylzirconium complexes and dialkylaluminum chlorides. Indeed, it was found that addition of 2d to an equimolar amount of diisobutylaluminum chloride resulted in the instantaneous formation of Cp₂ZrCl₂ and the appropriate dialkylalkynylaluminum compound. It is interesting to compare this result with that in which a trialkylaluminum is observed to alkylate Cp₂ZrCl₂. It is possible that in reaction 8, at equilibrium, the alkenylalane is favored because, as the reaction compared favorably with that of an authentic sample obtained by addition of DiBAH to 3-hexyne. Alkenylalanes prepared by transmetalation and separated from Cp₂ZrCl₂ can be used in known synthetic procedures which have been developed for such compounds prepared through conventional routes. It was discovered, however, that, when the reaction mixture still containing Cp₂ZrCl₂ was warmed, isobutylene formation ensued. This can be explained as follows. Transfer of an isobutyl group from the diisobutylalkynylalane back to Cp₂ZrCl₂ gives an isobutylzirconium complex. Reversible β-hydride elimination from the alkenyl Zr(IV) species could be displaced by simultaneous trapping of the resulting zirconium hydride in a stable Zr–H–Al bridge. Ultimately, polyhydride species such as the known aggregate 12 would be formed. It is noteworthy, therefore, that, when 12 is treated with 3-hexyne at room temperature in benzene, isobutylene is evolved. The resulting mixed-metal species has not been isolated. It is possible that, as hydride bridges are consumed by M–H addition to 3-hexyne, hydride abstraction from the β-position of an isobutyl group (and elimination of isobutylene from the aggregate) occurs.

E. Transmetalation of Acyl Groups from Zr to Al. Main group acylmetallic derivatives are of particular interest because they may function as “acyl anion equivalents” (or nucleophilic acylation reagents). However, acyl derivatives of main-group metals have not been readily available since routes to their preparation (see reaction 11) are hampered by condensation side reactions (in 11a the acylmetallic species formed can attack the starting aldehyde while in 11b the acyl metal can add R–M). One approach to circumventing the problems encountered in the formation of a main-group acylmetallic is to attempt to generate such a species in the absence of a substrate (aldehyde or metal alkyl) which could destroy it through
condensation. The reactivity of such a species as an acyl anion equivalent could then be tested. The method of transmetalation of an acyl group from a stable transition metal complex to an electronegative metal halide seemed to be particularly amenable to these requirements.

Di(cyclopentadienyl)chlorozirconium(IV)-acyl complexes are readily available by "insertion" of CO into the Zr-R bond (R = alkyl, cycloalkyl, alkenyl, and benzyl) as shown by eq 2. It was found that simply combining 3a or 3b with AlCl₃ for a few minutes, at low temperature, resulted in the preparation of the first examples of acylaluminum dichlorides (15) as shown in reaction 12. In typical procedures a solution of 3a in CH₂Cl₂ was added to a suspension of AlCl₃ in CH₂Cl₂ at -20 °C. Low-temperature NMR analysis (at -20 °C) after 10 min indicated the complete absence of 3a, with resonances at δ (ppm) 0.9 (s), 1.57 (m), and 3.38 (m) attributed to 15a. Warming the NMR sample to room temperature resulted in deterioration of the spectrum, particularly as evidenced by the broadening of the singlet (δ 0.9) corresponding to the terti-buty1 group. Infrared analysis was also obtained for 15a. The carbonyl region of the cold reaction mixture in each case revealed a strong absorbance assigned to the acyl carbonyl group (νCO 1530 cm⁻¹). It was shown that this absorbance was not attributable to Cp₂ZrCl₂. Once again, warming the infrared sample resulted in the deterioration of the spectrum. It is interesting to note that, for 3a, νCO = 1550 cm⁻¹. An X-ray structural determination for the compound Cp₂Zr(COCH₃)CH₃ (νCO 1545 cm⁻¹) indicates that the acyl ligand bonds to zirconium via both the carbon and oxygen atoms. It is probable that a similar explanation accounts for the observed νCO in both 3a and 15a. Possible structures for the aluminum acyl (16 or 17) are shown in reaction 12. (The structure of a donor-acceptor addition compound formed between acetyl chloride and aluminum trichloride was assigned as indicated partially on the basis of a strong absorbance at 1560 cm⁻¹ attributed to the coordinated carbonyl group.)

Hydrolysis of the reaction mixture containing 15a gives 4,4-dimethylpentanal (45%). The only other organic products detectable by GC analysis derive from decarbonylation of 15a to give (neohexyl)AlCl₃ (4b). Carbon monoxide evolution from a mixture of 3a and AlCl₃ at -15 °C was found to be 0.11 equiv (based on Zr) after 12 h. Also produced was an extremely small amount of 2,2,8,8-tetramethyl-5-norane. In order to prove that 15a is a "direct" acyl metallic species and not an enolate, it was treated with D₂O and the resultant aldehyde was analyzed for deuterium content and position of substitution. If the product of transmetalation were an enolate (18), most of the deuterium label would be incorporated in the a position of the aldehyde. If, on the other hand, this product were a direct acyl metallic species, most of the deuterium would be incorporated in the aldehydic position. NMR integration data, correlated with chemical ionization mass spectral data, indicated that the aldehyde formed is at least 83% -C(O)-D₂.

After we determined that 15a was indeed a "direct" acylaluminum species, it was reasonable to test its reactivity as a possible "acyl anion equivalent" by examining its reaction with acetyl chloride. Results of this experiment are shown in Table 1. It was found that the reaction between 15 and acetyl chloride did not proceed to any appreciable extent at -20 °C. When the reaction was performed at higher temperatures, some of the desired a-diketone 19 was formed; however, the major product in each case examined was the a-chloroalkyl acetate 21. The origin of 21 is proposed in reaction 13, in which it is
transmetalation of the alkenyl group from Zr to Pd(II), and reductive elimination of the coupled alkenyl halides (eq 14 and 15). These reactions most likely involve reactions of alkenylzirconium derivatives with aryl and alkyl halides, all of which involve transmetalation steps. Of particular pertinence here are the Ni- and Pd-catalyzed cross-coupling reactions of organometallics with organic halides, which function in organic synthesis as acyl anion equivalents.

It should be emphasized that the importance of the work described herein transcends that of simply finding new routes to organoaluminum species, notwithstanding the utility of these species in their own right. This study demonstrates, rather, that an easily prepared transition-metal complex can serve as the precursor of other reactive organometallic species; it suggests that sequential organometallic reagent systems can be developed in a rational manner through consideration of transmetalation reactivity series. For example, it is known that trialkylaluminum, alkylmagnesium halide, or alkyl lithium compounds will alkylate Cp2ZrCl2. Therefore, the following order of alkylating abilities of organometallic alkyls toward metal halides may be developed: RLi, RMgX, or R3Al. It has also been found in the course of these investigations that Cp2ZrCl2 is a useful reagent for the transfer of an alkenyl group to R2AI, ZrCl2, CuCl2, and SnCl4. Negishi and co-workers have studied several coupling reactions of organometallics with organohalides, all of which involve transmetalation steps. Of particular pertinence here are the Ni- and Pd-catalyzed cross-coupling reactions of alkenylzirconium derivatives with aryl and alkyl halides (eq 14 and 15). These reactions most likely proceed through oxidative addition of organic halide to Ni(0) or Pd(0), transmetalation of the alkenyl group from Zr to Ni(II) or Pd(II), and reductive elimination of the coupled product.

Reactions of species such as RLi, RMgX, and R3Al with transition-metal salts are commonly encountered transmetalation reactions (e.g., the preparation of organocuprates from a transition metal acyl complex. The findings noted herein may perhaps lead to new strategies which could be applied to similar systems for the preparation of main group acyl metallic species which function in organic synthesis as acyl anion equivalents.

Experimental Section

All experiments were performed under an atmosphere of nitrogen or argon from which oxygen was removed by passing through a bed of BTS catalyst in reduced form (previously heated under a CO stream) and from which water was removed by passing through a column of Matheson site 4A molecular sieves. The atmosphere was introduced by repeated evacuation and addition of gas to thoroughly dried glassware. Liquid transfers were performed by syringe, and solid transfers were performed under a stream of inert gas or in a drybox. All ether and routinely used hydrocarbon solvents were distilled, just prior to use, under argon or nitrogen, from sodium/benzophenone ketyl. Approximately 5% tetraglyme was added to hydrocarbon solvents to ensure solubility of the ketyl. All other solvents were distilled under argon or nitrogen from the proper drying agent (calcium hydride or lithium aluminum hydride). Commercially obtained organic compounds were dried by the appropriate method and, if liquid, distilled under argon or nitrogen directly prior to use. All pressure reactions were carried out in a Fischer-Porter glass pressure apparatus.

Infrared (IR) spectra were obtained with either a Perkin-Elmer 237B or a Perkin-Elmer 283 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were taken on a Varian A-60A spectrometer and are reported downfield from tetramethylsilane (Me4Si) in units of δ in the order multiplicity, intensity (and identity); 100-MHz 1H and 233C NMR were obtained with a Varian XL-100 spec-

<table>
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<th>reaction time, h</th>
<th>major product</th>
<th>minor product</th>
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trometer equipped with a pulsed Fourier transform system. Mass spectra were recorded on an A.E.I.-MS 9 and gas chromatographic mass spectra on a Du Pont 21-490 GC mass spectrometer. Chemical ionization mass spectra of labeled aldehydes was performed by Dr. Timothy Wachs at Cornell University. GC–mass spectra are reported in the order molecular ion (intensity), four highest peaks (intensities).

Preparation of (E)-Chlorobis(n$^\text{5}$-cyclopentadienyl)-3,3-dimethylbutenylzirconium (2d). To 1.2397 g (4.81 mmol) of 1 suspended in 13 mL of benzene was added 0.8 mL (6.50 mmol) of 3,3-dimethylbutylene. After stirring for 5 h, the reaction mixture was filtered and the benzene removed in vacuo. The resulting yellow oil was washed with hexane until colorless to afford a white powder identified as 2d. NMR (CDCl$_3$) $\delta$ 1.00 (s, 9), 1.86 (d, 3, $J = 7$ Hz), 6.39 (d, 1, $J = 19$ Hz), 6.67 (d, 1, $J = 19$ Hz). The white powder was recrystallized by dissolving in toluene, followed by the addition of sufficient hexane to render the solution cloudy. The suspension was redissolved in toluene and placed in the refrigerator to crystallize. It was filtered at low temperature and thoroughly dried under vacuum (89% yield). Anal. Caled for C$_{27}$H$_{28}$Zr: Cl: 10.43; C: 56.62; H: 6.23. Found: Cl: 10.33; C: 56.33; H: 6.12.

Reaction of Cp$_2$ZrHCl (1) with 4-Methyl-2-pentene. To 3.3865 g (13.1 mmol) of 1 suspended in 25 mL of benzene was added 2 mL (16.2 mmol) of 4-methyl-2-pentene. After stirring for several hours, the benzene and volatiles were removed to afford an oil which was 55% chlorobis(n$^\text{5}$-cyclopentadienyl)-2-(4-methyl-2-pentyl)zirconium (2e) and 45% its isomer, chlorobis(n$^\text{5}$-cyclopentadienyl)-3-(4-methyl-2-pentenyl)zirconium. A few milligrams of Cp$_2$ZrHCl were added to a 5 mL, redissolved in benzene, and after overnight stirring the reaction mixture was filtered and the benzene removed to afford an orange oil which was >93% 2e and <7% of its isomer (total yield 80%): $^1$H NMR (benzene) of 2e $\delta$ 1.26 (d, 6, $J = 7$ Hz), 2.12 (d, 3, $J = 2$ Hz), 2.83 (septet, 1, $J = 7$ Hz), vinyl H, H, 6.12. $^1$H NMR (benzene) of isomer $\delta$ 1.32 (d, 6, $J = 7$ Hz), 1.77 (d, 3, $J = 2$ Hz), 2.83 (septet, 1, $J = 7$ Hz), vinyl H, 6.12. 

In a manner similar to that described for 2a, 2d, and 2e, the following chlorobis(n$^\text{5}$-cyclopentadienyl)zirconium (IV) adducts were synthesized. These are reported, together with their NMR spectra, in Table II.

Preparation of 5,5-Dimethyl-2-hexanone by Transmetalation from Zr to Al. To a suspension of 0.775 g (5.8 mmol) of AlCl$_3$ in 5 mL of CH$_2$Cl$_2$ at 0°C was added a solution of 1.37 g (4.0 mmol) of 2a and 0.4984 g (2.87 mmol) of dodecane (standard) in CH$_2$Cl$_2$. An instantaneous yellow color change from yellow to orange indicated the formation of a precipitate, which was always contaminated with some NaCl (which, however, has never been found to impede its subsequent reactions). Since 1 is only very slightly soluble in all organic solvents examined, rigorous purification was not possible. Analysis of preparations of 1 is described below. Organozirconium compounds are red, orange, or yellow solids or liquids and were normally used immediately after preparation.

Aluminum chloride (AlCl$_3$) was obtained 99.8% pure (anhydrous from ROC/RIC). Acetyl chloride, with PCl$_3$ for several hours and distillation from quinoline directly before each use. Benzyl chloride was purified by distillation from S0Cl$_2$.

All reactions were performed at room temperature unless otherwise stated. Literature references following spectral data indicate reported spectra of the compound in question.

Preparation of 5,5-Dimethyl-3-hexen-2-one by Transmetalation from Zr to Al. To 1.23 g (9.25 mmol) of AlCl$_3$ in 10 mL of CH$_2$Cl$_2$ at 0°C was added a solution of 7.845 mL of 2b and 0.547 g (5.53 mmol) of dichloroethane (standard) in CH$_2$Cl$_2$. An instantaneous yellow color change from yellow to orange indicated the formation of 3,3-dimethylbutylaluminum dichloride (4a). $^1$H NMR (CDCl$_3$) $\delta$ 0.25 (m, 2), 0.83 (s, 9), 1.33 (m, 2). The reaction mixture was cooled to −30°C and a small excess of acetyl chloride was added. After stirring at −30°C for 30 min, the reaction mixture was hydrolyzed. The organic layer was washed with aqueous NaHCO$_3$ (saturated), extracted with ether, and dried with Na$_2$SO$_4$. The product, 5,5-dimethyl-2-hexanone, was found to be present in 98% yield. Analysis is described below.

Preparation of 2-Decanone by Transmetalation from Zr to Al. To a suspension of 1.23 g (9.25 mmol) of AlCl$_3$ in 10 mL of CH$_2$Cl$_2$ at −30°C was added a solution of 7.85 mL of 2b and 0.547 g (5.53 mmol) of dichloroethane (standard) in CH$_2$Cl$_2$. An instantaneous color change from yellow to dark orange indicated the formation of 4a: $^1$H NMR (CDCl$_3$) $\delta$ 0.35 (m, 2), 0.93 (d, $J = 5.5$ Hz), 1.33 (d, $J = 5.5$ Hz). Then 22 g (455 mmol) of acetyl chloride was added, and after stirring at −30°C for 60 min the reaction mixture was hydrolyzed and worked up as described above. The product, 2-decanone, was found to be identical with an authentic sample and was present in 98% yield (column C, 40°C).

Preparation of Cyclohexyl Phenyl Ketone by Transmetalation from Zr to Al. To 0.54 g (4.08 mmol) of AlCl$_3$ in 10 mL of CH$_2$Cl$_2$ at 0°C was added a solution of 4.38 mmol of 2c. An instantaneous color change from orange to yellow-orange indicated the formation of 4b: $^1$H NMR (CDCl$_3$) $\delta$ 0.70 (m, 1), 1.10–2.20 (m, broad, 10). Then 0.72 g (5.15 mmol) of benzyl chloride was added at −15°C and the reaction mixture allowed to stir for 45 min. It was worked up as described above and rotary evaporated, and the major organic product, cyclohexyl phenyl ketone, was collected by liquid chromatography. The yield of cyclohexyl phenyl ketone was 64%. A small amount of cyclohexane was also found to be present.

Preparation of 5,5-Dimethyl-3-hexen-2-one by Transmetalation from Zr to Al. To 0.58 g (4.32 mmol) of AlCl$_3$ in 10 mL of CH$_2$Cl$_2$ at −5°C was added a solution of 4.40 mmol of 2d and 0.725 g (7.33 mmol) of dichloroethane (standard). The color of the solution immediately changed from yellow to orange, indicating the formation of 4b: $^1$H NMR (CDCl$_3$) $\delta$ 0.60 (s, 9), 0.64 (d, 1, $J = 23$ Hz), 7.04 (d, 1, $J = 23$ Hz). Then 0.44 g (5.54 mmol) of acetyl chloride was added at −30°C and the reaction...
mixture allowed to stir for 45 min at that temperature before standard workup. The product, 5,5-dimethyl-3-hexen-2-one,\(^{25}\) was present in 97% yield (column D, 105 °C).

**Preparation of \((E)-3,5\text{-Dimethyl-3-hexen-2-one}\) by Transmetalation from \(\text{Zr} \text{to Al}\).**

To 0.46 g (3.44 mmol) of \(\text{AlCl}_3\) in \(\text{CH}_2\text{Cl}_2\) at 0 °C was added a solution of 2.72 mmol of 2e and 0.3850 g (3.89 mmol) of dichloroethane (standard). After the mixture was stirred for 15 min at 0 °C, 2-(4-methyl-2-pentenyl)aluminum dichloride (4e) was formed:

\[ \text{H NMR (CD}_2\text{Cl}_2\text{) } \delta \text{ 0.43 g (5.42 mmol) of acetyl chloride was added at -30 °C and the reaction mixture allowed to stir at that temperature for 45 min before hydrolysis and standard workup. The product, (E)-3,5-dimethyl-3-hexen-2-one, was present in 98% yield (column A, 100 °C).} \]

**Preparation of \(3\text{-Cyclopropyl-2-butanone}\) by Transmetalation from \(\text{Zr} \text{to Al}\).**

To 1.17 g (8.77 mmol) of \(\text{AlCl}_3\) in \(\text{CH}_2\text{Cl}_2\) at 0 °C was present in 97% yield (column D, 105 °C).

**Preparation of \(3\text{-Cyclopropyl-2-butanone}\) by Transmetalation from \(\text{Zr} \text{to Al}\).**

To 0.69 g (5.19 mmol) of \(\text{AlCl}_3\) in 5 mL of \(\text{CD}_2\text{Cl}_2\) at 0 °C was added a solution of 4.02 mmol of 2i and 0.533 g (5.39 mmol) of dichloroethane (standard). The product was 7-octenylaluminum dichloride (4h):

\[ \text{H NMR (CD}_2\text{Cl}_2\text{) } \delta \text{ 0.40 g (5.16 mmol) of acetyl chloride was added at -30 °C and the reaction mixture allowed to stir at that temperature for 45 min before hydrolysis and standard workup. Two organic products were collected by preparative GC (column A, 100 °C). The major product, cyclopentenylmethylaluminum dichloride (4i), was present in 26% yield (column D, 100 °C).} \]

**Preparation of \(3\text{-Cyclopropyl-2-butanone}\) by Transmetalation from \(\text{Zr} \text{to Al}\).**

To 0.46 g (3.44 mmol) of \(\text{AlCl}_3\) in \(\text{CH}_2\text{Cl}_2\) at 0 °C was added a solution of 2.72 mmol of 2e and 0.3850 g (3.89 mmol) of dichloroethane (standard). After the mixture was stirred for 15 min at 0 °C, 2-(4-methyl-2-pentenyl)aluminum dichloride (4e) was formed:

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**Preparation of \(3\text{-Cyclopropyl-2-butanone}\) by Transmetalation from \(\text{Zr} \text{to Al}\).**

To 0.46 g (3.44 mmol) of \(\text{AlCl}_3\) in \(\text{CH}_2\text{Cl}_2\) at 0 °C was added a solution of 2.72 mmol of 2e and 0.3850 g (3.89 mmol) of dichloroethane (standard). After the mixture was stirred for 15 min at 0 °C, 2-(4-methyl-2-pentenyl)aluminum dichloride (4e) was formed:

\[ \text{H NMR (CD}_2\text{Cl}_2\text{) } \delta \text{ 0.43 g (5.42 mmol) of acetyl chloride was added at -30 °C and the reaction mixture allowed to stir at that temperature for 45 min before hydrolysis and standard workup. The product, (E)-3,5-dimethyl-3-hexen-2-one, was present in 98% yield (column A, 100 °C).} \]
Aluminum Chloride. To a solution of 4.26 g (14.58 mmol) of Cp₂ZrCl₂ in 30 mL of THF was added 0.15 g (3.54 mmol) of LiAlD₄. After 45 min of stirring, the reaction mixture was filtered, washed with THF (4 × 15 mL), and dried under vacuum to give Cp₂Zr(THF). This was dissolved in 8 mL of benzene and combined with 3.30 mmol of (E)-CHD=CH(C₂H₅)₂. After stirring for 5 h, the reaction mixture was filtered and the benzene removed to give a yellow oil, which was recrystallized from 4 mL of hexane to give an essentially quantitative yield of yellow crystals identified as erythro-5: ¹H NMR (CDCl₃) δ 0.87 (s, 9), 1.01 (d, 1, J = 2.9), 2.63 (s, 10), H₂O obscured by tert-butyl. A CH₂Cl₂ solution of erythro-5 was added to 0.61 g (4.60 mmol) of AlCl₃ in CH₂Cl₂ at 0 °C to give erythro-(CH₂Cl)₂.CHClCDHClD.AICl₃ (6): ¹H NMR (CDCl₃) δ 0.35 (d, 1, CHD/CD), 0.88 (s, 9), 1.27 (d, 1 CHD [tert-butyl]). Deuterium abundant. 100-MHz NMR spectral analysis of the methylene protons in 6 showed J₁HH = 9 Hz (Figure 2).

Preparation of Dimethyl-3,3-dimethylbutenyl)aluminum (9a) by Transmethylation from Zr to Al. To 0.56 g (1.65 mmol) of 2d in CH₂Cl₂ at 0 °C was added 0.12 g (1.30 mmol) of Me₂AlCl in CH₂Cl₂. The product, formed after a few minutes, was dimethyl-3,3-dimethylbutenylaluminum (9a): ¹H NMR (CDCl₃) δ 0.85 (s, 6, AlCH₃), 1.13 (s, 9), 5.88 (d, 1, J = 20.5 Hz, 7.44 (d, 1, J = 20.5 Hz).

Preparation of Diisobutyl-3,3-dimethylbutenylaluminum (9b) by Transmethylation from Zr to Al. To 0.46 g (1.35 mmol) of 2d suspended in a few milliliters of pentane at 0 °C was added 0.24 g (2.05 mmol) of LiAlD₄ in pentane. After 1 h, the reaction mixture was filtered, washed with THF (2 × 5 mL), and allowed to stir at 45 °C for 1 day. To 4.8 mL (40 mmol) of diisobutyl(3,3-dimethylbutenyl)aluminum (9b), was present in 97% yield based on NMR integration with respect to standard: ¹H NMR (CDCl₃) δ 0.11 (d, 4, AlCH₃), 7.07 (s, 1), 9.09 (d, 12, J = 6.0 Hz), 1.08 (s, 9), 1.82 (septet, 2, J = 6.0 Hz). 5.73 (d, 1, J = 20.5 Hz), 7.49 (d, 1, J = 20.5 Hz). The reaction mixture was filtered to remove Cp₂ZrCl₂ and the pentane removed in vacuo to leave crystals which corresponded to a 90% yield (0.27 g) of pure 9b.

Preparation of Diisobutyl-3,3-dimethylbutenylaluminum (9b) by Reaction of Diisobutylaluminum Hydride and 3,3-Dimethylbutyne. A solution of 12.8 g (90 mmol) of diisobutylaluminum hydride in 50 mL of hexane was added dropwise to 1 h to 19 mL (155 mmol) of 3,3-dimethylbutyne in 70 mL of hexane in a three-necked flask fitted with a reflux condenser and dropping funnel. The reaction mixture was allowed to reflux overnight, and the hexane and volatiles were removed in vacuo to give white crystals of 9b. The ¹H NMR spectrum was identical with that reported above.

Preparation of (E)-Diisobutyl-3-hexenylaluminum (11) by Transmethylation from Zr to Al. To 0.14 g (0.82 mmol) of diisobutylaluminum chloride in CH₂Cl₂ at -40 °C was added 0.37 (1.09 mmol) of 10 in CH₂Cl₂. The mixture was allowed to stir for 0.5 h at -40 °C and analyzed by NMR at that temperature. The product, (E)-diisobutyl-3-hexenylaluminum (11): ¹H NMR (CDCl₃) δ 0.37 (d, 4, AlCH₃), 7.11 (s, 1), 3.00 (s, 12, J = 6.3 Hz). 0.97 (m, 6), 1.55–2.50 (m, 6), 6.98 (t, 1, J = 6.5 Hz).

Preparation of (1S)-Diisobutyl-3-hexenylaluminum (11) by the Reaction of Diisobutylaluminum Hydride and 3-Hexyne. To 4.8 mL (40 mmol) of 3-hexyne (neat) was added 3.5 mL (20 mmol) of diisobutylaluminum hydride (neat). The reaction mixture was allowed to stir at 45 °C for 1 day, the excess 3-hexyne removed, and the product, a colorless liquid, dried under vacuum overnight. Its ¹H NMR spectrum corresponded with the one reported above for 11.

Preparation of Chloro(thiy)pentadienyl)acetylboration Complex 3a. To 2.25 g (6.60 mmol) of 2a in 15 mL of THF in a Fischer-Porter bottle was added 50 psi of CO gas. After approximately 1 h, 20 psi of CO had been consumed and the reaction mixture was filtered and the benzene removed to give pale yellow crystals identified as 3a: ¹H NMR (benzene) δ 0.83 (s, 9), 2.10 (t, 2, J = 7 Hz), 2.85 (t, 2, J = 7 Hz). 3.10 (m, 10), 1.55–2.50 (m, 6), 6.98 (t, 1, J = 6.5 Hz).

In similar fashion, 3b was carbonylated to the corresponding acyl chloride, CH₂Cl₂ solution of 1.25 mmol of 3a and 0.2675 g (2.70 mmol) of dichloroethane (standard). A low-temperature NMR spectrum (-20 °C) after 10 min showed the product to be 15a: ¹H NMR (DCl₃) δ 0.90 (s, 9), 1.57 (m, 2), 3.38 (t, 1, J = 7 Hz). An IR spectrum of the carbonyl region, recorded before the sample could warm significantly above -78 °C, showed νCO 1530 cm⁻¹.

Preparation of Deuterated 4,4-Dimethylpentanal (22) from 15a. To 1.25 mmol of 15a at -20 °C in CH₂Cl₂ was added 0.02 mL (1.25 mmol) of D₂O. The reaction mixture turned yellow to green upon this addition and was allowed to stir at 20 °C overnight. The major product, deuterated 4,4-dimethylpentanal, was collected by preparative GC (column E, 80 °C). Its yield was found to be 43% (column C, 65 °C). Spectral analysis of this product will be presented in the next paragraph. Also collected from the reaction mixture were two minor products, 3,3-dimethylbutylbenzene and 2,2,8,8-tetramethyl-5-nonanone.

Determination of the Position of Deuterium Incorporation in 4,4-Dimethylpentanal (22) Obtained by Treatment of 31a by D₂O. Deuterated 4,4-dimethylpentanal was analyzed by IR. ¹H NMR, and chemical ionization GC–MS and compared with undeuterated 4,4-dimethylpentanal obtained by acid hydrolysis of 3a.

For undeuterated 22: IR (CCl₄) 1722, 2720 cm⁻¹. For deuterated 22: IR (CCl₄) 1722, 2606 cm⁻¹. For undeuterated 22: ¹H (CCl₄) δ 0.90 (s, 9), 1.50 (t, 2, J = 6.5 Hz). For deuterated 22, chemical shifts are the same as the preceding numbers. Integration shows the resonance at 8.23 to 33% H and 26% D and the resonance at 9.85 to 82% D and 18% H.

For undeuterated 22: M+ 114 (0.00), 57 (1.00), 43 (0.32), 41 (0.32), 81 (0.28), M – 15.99 (0.02). For deuterated 22: M+ 115 (0.001), 57 (1.00), 43 (0.41), 43 (0.23), 82 (0.22). These samples were also studied by chemical ionization GC–MS to determine percent deuterium incorporation in 22. The M + 29 region, rather than the M + 1 region, was used for the calculations since the loss of H₂ from the M + 29 ion is much less than the same losses for the M + 1 ion. The abundance of each ion was obtained by integration over the complete GC peak and includes about 40 mass scans. Results are shown in Table III.

The method used for calculation of position of deuterium incorporation in 22 was as follows. From structure 16 or 17 the products shown in Scheme 1 may arise. From structure 18 the products shown in Scheme II may arise. It is therefore possible to obtain d₁, d₂, and d₃ products from structures 16 or 17. It is therefore possible to obtain d₁, d₂, and d₃ products from structure 18. The mass spectral data shows that, at most, 94% of the product could have arisen from 16 or 17 since 6% of the aldehyde formed is d₂. The NMR integration shows that 18% of the d₁, d₂, and d₃ total (6.24% + 56.54% + 30.95% = 94%) arises from structure 18. Compounds i–iii are represented in this 18%. By taking 82% of 94%, one arrives at the percentage of the d₁, d₂, and d₃ total which must be represented by iv and v. This figure is 77%. In order to arrive at the total percentage of aldehyde which could arise from 16 or 17, one must add 77% to the 6% of the total which corre-
Hsponds to with aqueous NaHCO₃, extracted with ether, and filtered. The organic was allowed to stir between -20 °C and products were distilled. The major product, 1-acetoxy-1-chlorotanal, CI 157 (0.02), Hz); M+. 192 E, (5-nonanone, and 1725 cm⁻¹; 'H NMR (CH₂Cl₂)

\[ 16 \text{ or 17} \]

Scheme II

**(a)** -0

(w, 1.11 mmol) of AlCl₃ in 5 mL of CH₂Cl₂ at -20 ºC were added 8.42 mmol of Cp₂Zr(Cl)(COCH₂CH₂CH₃) (3b) and 0.2642 g (2.87 mmol) of dichlorehete as a standard. After 15 min at -20 ºC the product 1b was analyzed: 'H NMR (CH₂Cl₂) δ 0.98 (t, J = 6.5 Hz), 1.52 (m, 2), 1.92 (q, J = 6.5 Hz), 2.05 (s, 3), 6.38 (1, J = 6 Hz); ¹³C NMR (CCL₄) δ 13.18, 18.07, 20.21, 39.99, 83.19, 166.76; M + m/e 150 (0.00), 43 (1.00, 71 (0.11), 55 (0.06), 107 (0.05). M – Cl 115 (0.05). Also present were small amounts of n-propylbenzene⁴ⁿ and 2,3-hexanedione⁴ⁿ.

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**References and Notes**


**Table III**

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</table>

**Scheme I**

\[ 16 \text{ or 17} \]

\[ d₁, d₂, d₃ \]

sponds to d₃, which must arise from 16 or 17. Therefore, the total percentage of product which was derived from a direct alkyl metallic species is 83%.

**Reaction of Acylchlorine Dihloride Complex 15a with Acetyl Chloride.** To 2.58 mmol of 15a at -20 ºC in 5 mL of CH₂Cl₂ was added 0.25 mL (3.5 mmol) of acetyl chloride. The reaction mixture was allowed to stir between -20 ºC and -5 ºC for 1 h, hydrolyzed with aqueous NaHCO₃, extracted with ether, and filtered. The organic products were distilled. The major product, 1-acetoxy-1-chloro-4,4-dimethylpentanal (21a), was collected by preparative GC (column E, 85 ºC): IR (CH₂Cl₂) 1759, 1207, 740 cm⁻¹; ¹H NMR (CH₂Cl₂) δ 0.92 (s, 9), 1.45 (m, 2), 2.02 (m, 2), 2.13 (s, 3), 6.40 (t, J = 5.5 Hz); M + 192 (0.00), 43 (1.00, 57 (0.74), 41 (0.25), 81 (0.21); M – Cl 157 (0.02). Also present were small amounts of 4,4-dimethylpentanal, (E)-3,3-dimethyl-1-butenyl)benzene, 2,2,8,8-tetramethyl-5-nonanone, and 6,6-dimethyl-2,3-heptadiene (19a): IR (CH₂Cl₂) 1725 cm⁻¹; ¹H NMR (CH₂Cl₂) δ 0.93 (s, 9), 1.23 (m, 2), 2.45 (m, 2), 2.13 (s, 3); M + m/e 154 (0.4), 43 (1.00), 57 (0.80), 41 (0.26), 100 (0.18).
Resonance Raman Spectra, Excitation Profiles and Excited (Iron → Pyidine Charge Transfer) State Geometry of Bispyridine Iron(II) Heme

P. G. Wright, P. Stein, J. M. Burke, and T. G. Spiro*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. Received July 3, 1978

Abstract: Totally symmetric bound pyridine vibrational modes are observed in the resonance Raman spectra of (py)2FeII-MP (py = pyridine, MP = mesoporphyrin IX dimethyl ester) and the pyridine-d5 analogue. The frequencies and their deuterium shifts are satisfactorily calculated using a benzene force field and an Fe-N stretching force constant of 1.96 mdyn Å−1. The Fe-py stretching mode is at 179 cm−1. Excitation profiles show all py modes maximizing at 496.5 nm, close to a bump in the absorption spectrum at 490 nm. Approximate origin shifts are obtained from the relative Raman intensities of the py modes and are combined with the calculated eigenvectors to provide a qualitative picture of the geometry in the resonant excited state, which is assigned to \( \pi \rightarrow \pi^* \) charge transfer.

Introduction

Recently we reported1 resonance-enhanced Raman scattering by bound pyridine, as well as porphyrin, modes (RR modes) of (py)2FeII-MP and (4-Mepy)2FeII-MP (py = pyridine, 4-Mepy = 4-methylpyridine, MP = mesoporphyrin IX dimethyl ester). The pyridine modes appeared to be resonant with a bump in the absorption spectrum at \( \sim 490 \) nm, which might plausibly be an FeII → py charge transfer (CT) transition. This assignment had been suggested2 for a shoulder in the (py)2FeII-TPP (TPP = tetraphenylporphine) absorption spectrum at 476 nm, and RR modes of bound pyridine have also been observed for this complex.3 While metalloporphyrin RR spectra are dominated by in-plane vibrational modes of the porphyrin ring,4 low-frequency modes assignable to iron-axial ligand vibrations have been observed for oxyhemoglobin3 and a "picket fence" porphyrin analogue5 for iron(III) octaethylporphine halides6,7 and for methemoglobin complexes.8 The bispyridine FeII hemes, however, appear to be the only reported instance where bound ligand modes are enhanced. It seemed of interest to characterize the process in greater detail. We present here results of a normal coordinate and intensity analysis of the bound pyridine modes in (py)2FeII-MP and in its py-d5 analogue, which give a satisfying account of the eigenvectors and of the likely geometry of the CT excited state.

Experimental Section

Mesoporphyrin IX dimethyl ester was purchased from Sigma Chemical Co. and used without further purification. Pyridine-d5 was distilled and stored over KOH. Pyridine-d5 was purchased from Merck Sharp and Dohme and used without further purification. Dichloromethane was distilled and stored over molecular sieve.

The preparation of (F-)FeII-MP has been described previously.1 The preparation of (py)2Fex2MP was carried out in a modified Spex spinning cell sealed with a Teflon stopper. A solution of (F-)FeII-MP and excess pyridine in dichloromethane was covered with a water layer. After nitrogen gas had been bubbled through the solution for \( \sim 5 \) min, a small amount of sodium dithionite was added. The cell was quickly sealed and vigorously shaken until the dichloromethane layer changed from red-brown to orange. The concentration of (py)2FeII-MP in dichloromethane was \( \sim 1 \) mg/mL.

Spectra were excited with various lines of an Ar+ laser, and recorded with a Spex 1401 double monochromator equipped with a cooled ITT F130 photomultiplier and photon counting electronics. Frequencies were internally calibrated against the solvent bands and are believed to be accurate to \( \pm 1 \) cm−1 for the strong bands.

Results and Discussion

Figure 1 shows RR spectra of (py)2FeII-MP and (py-d5)2FeII-MP excited at 476.5 nm. The bound pyridine bands, labeled in Figure 1, are readily identified by the deuteration shifts as well as from the excitation profiles (vide infra). All of these bands are polarized and therefore arise from totally symmetric vibrations. Their frequencies are listed in Table 1.

Normal Coordinate Analysis. A normal coordinate analysis, using available computer programs,6 was carried out on a linear py→Fe model to obtain a qualitative picture of the...