

Preparation of Organoaluminum Compounds by Hydrozirconation-Transmetalation

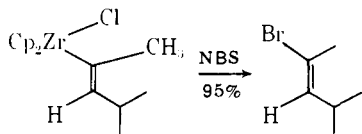
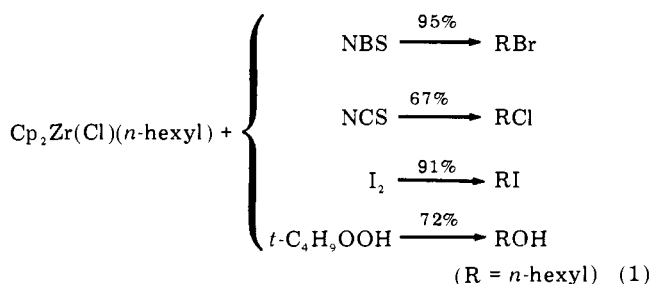
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Abstract: Organozirconium(IV) complexes produced by hydrozirconation of olefins or acetylenes with $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) are precursors of organoaluminum compounds. By stoichiometric transmetalation, the η^1 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 $\text{Cp}_2\text{Zr}(\text{Cl})(\text{acyl})$ 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 D_2O results in an aldehyde which is at least 83% $\text{-C}(\text{O})\text{-D}$. 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).

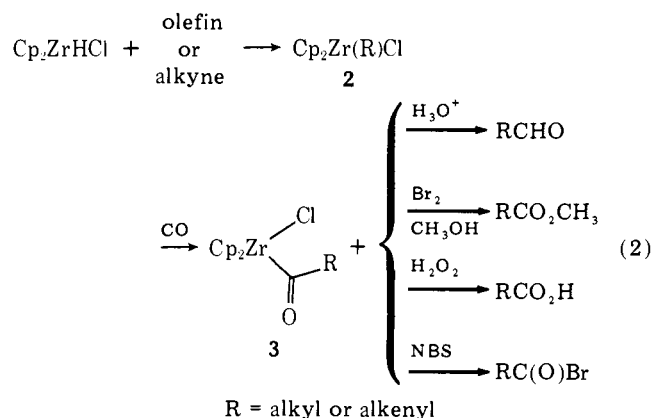
Introduction

Organozirconium(IV) complexes, produced by hydrozirconation¹ of olefins² or acetylenes³ with $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (**1**), are intermediates of demonstrated value in organic synthesis. A variety of organic products may be obtained from them stereospecifically⁴ by electrophilic cleavage of the carbon-zirconium bond. For example, these organometallic species (**2**) react with electrophilic halogenation reagents (Br_2 , I_2 , *N*-bromo- or *N*-chlorosuccinimide) to give the corresponding organic halides, and with *t*- $\text{C}_4\text{H}_9\text{OOH}$ to give alcohols (reaction 1). However, organozirconium complexes have not yet



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.⁵

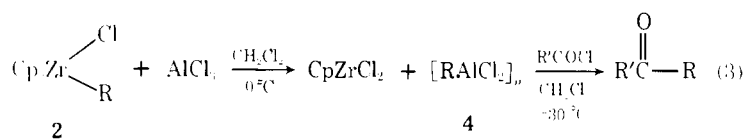
The specificity of hydrozirconation is noteworthy. The bulky size of the $\text{Cp}_2\text{Zr}(\text{Cl})$ - group ensures that it will become attached to the least hindered position of an acyclic olefin either by regioselective addition of Zr-H to a terminal olefin or addition to an internal olefin 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, tetrahydropyranoxy, or silyl ether groups, which are labile toward hydroalumination.^{6,7} 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.⁴ 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).⁸ 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 $(\text{Cp}_2\text{ZrCl})^+$ 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

Chart I



	olefin/ acetylene	→ RAlCl ₂	product	yield, % (based on RZr) ^a	
				Zr only	Zr → Al
a				60 (29 h)	98 (30 min)
b	<i>n</i> -octenes ^c		2-decanone	80 (>2 days)	98 (60 min)
c				{ 8 (48 h) } { R = CH ₃ }	{ 64 ^b (45 min) } { R = Ph }
d	$\text{+} \equiv \text{-H}$				97 (45 min)
e					98 (45 min)

^a Yield determined by VPC. ^b Isolated yield. ^c 1-Octene, *cis*-2-octene, *trans*-2-octene, *cis*-4-octene, *trans*-4-octene (1:0.5:0.5:1:1).

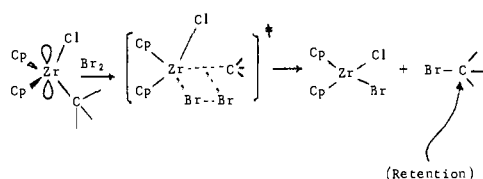


Figure 1. Closed transition state for electrophilic cleavage of the C-Zr bond.

transition state. It is therefore proposed that organozirconium complexes do not react with most carbon electrophiles for the following reason. A closed transition state would require C-C bond formation by "frontside" reaction of both C-X and C-Zr bonds. Those carbon species possessing nucleophilic (to Zr) counterions are weak electrophiles; stronger carbon electrophiles (e.g., methyl fluorosulfonate) do not contain nucleophilic counterions which could coordinate effectively to Zr in the 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 η^1 -bound organic ligand in **2** can be transferred stereospecifically to a metal which, with its complement of ligands, is more electronegative than is the $\text{Cp}_2\text{Zr}(\text{Cl})$ moiety.⁹ 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,¹⁰ AlCl_3 was chosen as the electrophilic metal halide to initiate a detailed study of transmetalation. We have further developed the concept of transmetalation to include the transfer of alkyl, alkenyl, and acyl groups from **2** to AlCl_3 to give organoaluminum dichlorides and the transfer of alkenyl groups from **2** to chloroalanes to give alkenylalanes.

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 I. A solution of the organozirconium complex in CH_2Cl_2 is added to a

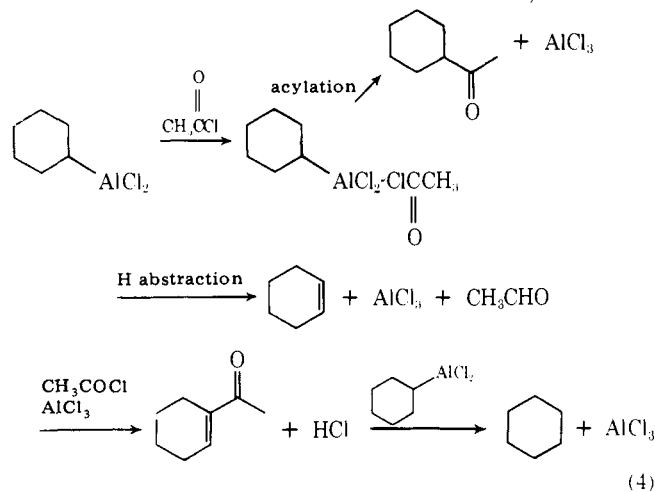
suspension (in CH_2Cl_2 , 0°C) of AlCl_3 . Transmetalation, which is usually rapid and accompanied by an instantaneous color change, can be conveniently monitored by NMR analysis. The initial organometallic product of transmetalation depends on the amount of AlCl_3 present relative to **2**. A stoichiometric amount of AlCl_3 reacts with **2** to give free Cp_2ZrCl_2 . If an excess of AlCl_3 is used (less than 100% excess), free Cp_2ZrCl_2 is not produced; the product obtained is a rapidly interconverting mixture of free Cp_2ZrCl_2 and AlCl_3 -complexed Cp_2ZrCl_2 . For varying amounts of excess AlCl_3 only a single sharp Cp resonance is observed (at 35°C); the position of this resonance with regard to free Cp_2ZrCl_2 (δ 6.52) and the deep orange complex (δ 7.10) formed from equal amounts of AlCl_3 and Cp_2ZrCl_2 depends on the amount of excess AlCl_3 present.⁴⁴

Organoaluminum 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.¹¹ 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 organoaluminum compound is rapid and can also be conveniently monitored by NMR; it gives AlCl_3 -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 isomeric olefins 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 alkenylaluminum 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 organometallic species; regioselectivity in the ketone product is the same as that observed in its Zr precursor.

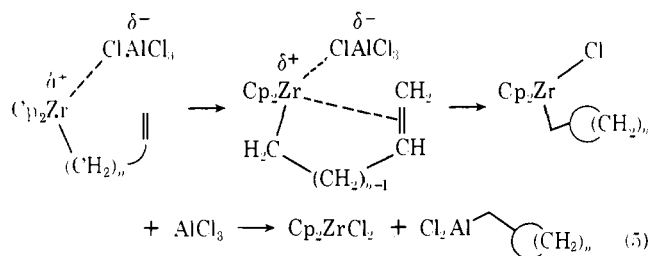
Reports of the formation of ketones from organoaluminum dichlorides and acid chlorides had been almost exclusively limited to primary saturated alkylaluminum dichlorides.¹¹ In this investigation it was found that acylation proceeds well only for these and for alkenylaluminum dichlorides. Secondary

alkylaluminum dichlorides react with aliphatic acid chlorides to give low yields of the desired products. When **2c** was treated with AlCl_3 , the expected transmetalation reaction occurred, but subsequent treatment of the product **4c** with acetyl chloride gave cyclohexane 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 Al results in attack by activated acetyl chloride, *not* by acylation, but rather by hydride abstraction to give cyclohexene, acetaldehyde, and AlCl_3 . β -Hydride abstraction from this alkane may parallel other routes to β -hydride abstractions which have been found for organotin¹² or -zirconium compounds.¹³ The conversion of cyclohexene, AlCl_3 , and acetyl chloride to the observed ketone and HCl is well-known.¹⁴ As shown in reaction 4, conversion



of (cyclohexyl)aluminum dichloride and acetyl chloride to the observed product mixture may be catalyzed by AlCl_3 , 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, $\text{Cp}_2\text{Zr}(\text{Cl})(3\text{-pentenyl})$ (**2f**), upon treatment with AlCl_3 followed by acetyl chloride, affords 3-cyclopropyl-3-methylpropan-2-one (79%) (also present in less than 10% yield was *trans*-5-hepten-2-one, the ketone resulting from unrearranged organoaluminum dichloride). It was also found, by low-temperature NMR studies (-46 to 24°C) of transmetalation between $\text{Cp}_2\text{Zr}(\text{Cl})(5\text{-hexenyl})$ (**2g**) and AlCl_3 , that complete cyclization to (cyclopentylmethyl)aluminum dichloride had occurred. Trialkylaluminum compounds, in which one alkyl group contains a remote double bond, have been noted to undergo similar cyclizations, usually, however, at high temperature.¹⁵ It is possible that facile cyclization at the low temperature noted for these transmetalation products compared with previously known cases results simply from the greater electronegativity of Al in (5-hexenyl) AlCl_2 (which would foster remote double coordination to Al) compared with that in (alkyl) $_2\text{Al}(5\text{-hexenyl})$. It is worthwhile speculating, though, that this cyclization involves both Zr and Al species (eq 5). Here, AlCl_3 would first coordinate to the organozirconium compound via the chloride ligand of the latter to create a partial positive charge on Zr. This would facilitate coordination of the remote olefinic bond to Zr. An analogous reaction involving Cp_2ZrCl_2 -catalyzed addition of Me_3Al to acetylenes has been proposed¹⁶ to proceed through "insertion" of Zr-CH₃ into the triple bond of coordinated acetylene. Treatment of



$\text{Cp}_2\text{ZrCl}(\text{7-octenyl})$ (**2h**) with AlCl_3 gives mainly uncyclized product, (7-octenyl) AlCl_2 (**4h**). Oxygenation of **4g** or **4h** followed by hydrolysis gives the corresponding alcohols in yields comparable to those obtained by oxygenation and hydrolysis of an authentic sample of EtAlCl_2 (28%).

B. Transmetalation of Alkyl and Alkenyl Groups from Zr to Al. Catalytic Considerations. The sequence shown in reaction 3 suggests that acylation of **2** by acid chlorides could be catalyzed by AlCl_3 . Transmetalation succeeds readily, however, only if AlCl_3 is not complexed with a Lewis base. Unfortunately, the ketonic product of acylation is a strong enough Lewis base to coordinate an equivalent amount of AlCl_3 ; this slows further transmetalation. Using 15% AlCl_3 (based on **2a**, 0°C , 10 h), a 40% yield of ketone is produced; heating this reaction mixture (70°C , 0.5 h) results in a higher yield (83%). Transmetalation does not proceed readily in Lewis basic solvents (such as ethers), presumably for similar reasons.

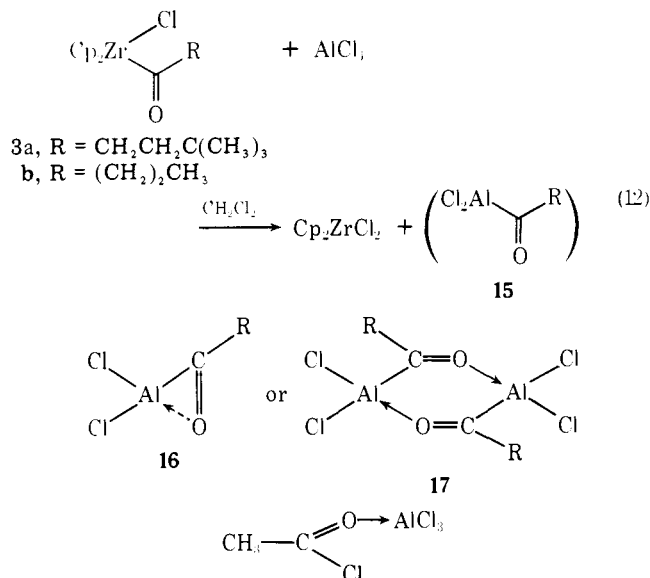
C. Transmetalation of Alkyl and Alkenyl Groups from Zr to Al. Mechanistic Considerations. The mechanism of transmetalation from Zr to Al was investigated in order to determine whether it in fact proceeded through a closed transition state, analogous to the one shown in Figure 1, in which an organic group bridges Zr and Al. Since it is known that vinyl and substituted vinylic aluminum compounds exhibit a greater tendency toward association through alkenyl "bridges" than do comparable alkyl derivatives (through alkyl "bridges"),¹⁷ it was expected that the transfer of an alkenyl group from Zr to Al would be a more facile process than transfer of an alkyl group would be if such bridging intermediates were involved. In a competitive procedure involving equimolar amounts of alkyl complex **2a**, alkenyl species **2d**, and 0.5 equiv of AlCl_3 , it was found that transmetalation occurred faster for the vinylic substituent than for the alkyl one. It was also shown that transmetalation of alkenyl groups to Al can proceed with a different stoichiometry than that observed for alkyl group transfer. All of **2d** was consumed even though 0.5 equiv of AlCl_3 had been used. By employing a ratio of **2d** to AlCl_3 of 3:1, the tris(alkenyl) species can be formed; for each alkyl complex examined, on the other hand, varying ratios of Zr to Al resulted in a transmetalation stoichiometry of only 1:1.

The mechanism of transmetalation was further investigated by employing specifically dideuterated zirconium complex **5** in a transmetalation reaction with AlCl_3 . It was found that transmetalation from Zr to Al proceeded predominantly with retention of configuration at carbon (as it does with vinylic substrates). The ^2H -decoupled 100-MHz ^1H NMR spectrum of **6** revealed a value $^3J_{\text{HH}} = 9$ Hz for the erythro diastereomer. 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 AlCl_3 could give tris(alkenylalanes); it was therefore of interest to determine whether alkenylalanes would be available through

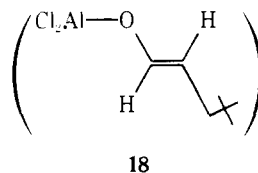
condensation. The reactivity of such a species as an acyl anion equivalent could then be tested. The method of transmetalation of an acyl group from a stable transition metal complex to an electronegative metal halide seemed to be particularly amenable to these requirements.

Di(cyclopentadienyl)chlorozirconium(IV)-acyl complexes are readily available by "insertion" of CO into the Zr-R bond⁵ (R = alkyl, cycloalkyl, alkenyl, and benzyl)²² 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



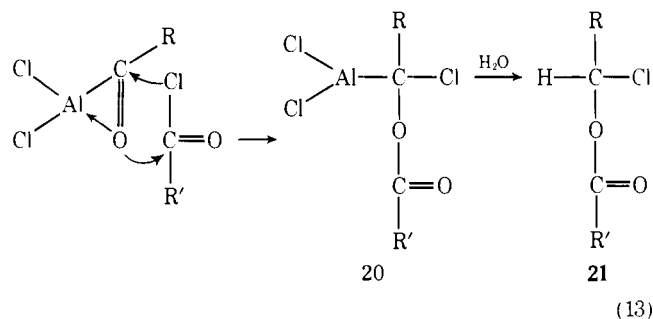
CH₂Cl₂ was added to a suspension of AlCl₃ in CH₂Cl₂ at -20 °C. Low-temperature NMR analysis (at -20 °C) after 10 min indicated the complete absence of **3a**, the presence of Cp₂ZrCl₂, and resonances at δ (ppm) 0.9 (s), 1.57 (m), and 3.38 (m) attributed to **15a**. Warming the NMR sample to room temperature resulted in deterioration of the spectrum, particularly as evidenced by the broadening of the singlet (δ 0.9) corresponding to the *tert*-butyl 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 (ν_{CO} 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**, ν_{CO} = 1550 cm⁻¹. An X-ray structural determination for the compound Cp₂Zr(COCH₃)CH₃ (ν_{CO} 1545 cm⁻¹) indicates that the acyl ligand bonds to zirconium via both the carbon and oxygen atoms.²² It is probable that a similar explanation accounts for the observed ν_{CO} 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.)²³

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)AlCl₂ (**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-nonanone. In order to prove that **15a** is a "direct" acyl metallic species and not an enolate (**18**), 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 α 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)-D.

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 I. 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 α-diketone **19** was formed; however, the major product in each case examined was the α-chloroalkyl acetate **21**. The origin of **21** is proposed in reaction 13, in which it is



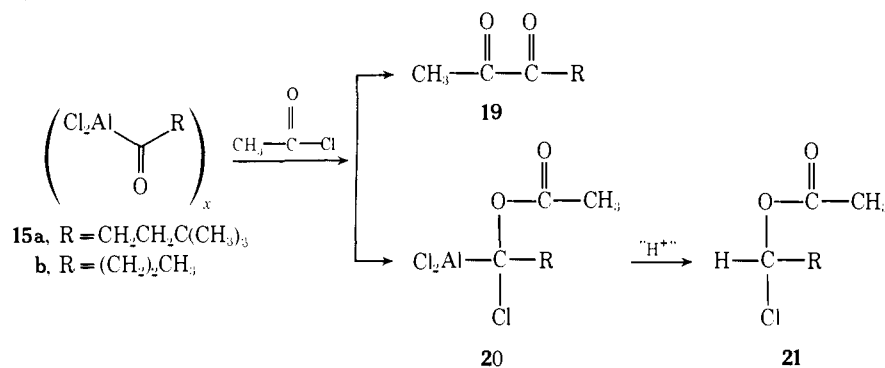
suggested that acetyl chloride attacks **15a** either at the acyl carbon or at oxygen (hydrolysis may proceed through a similar route). Side products reported in Table I result from hydrolysis of unreacted **15** or from hydrolysis of **4a**. It is interesting to note that D₂O workup gave **21** which was only 22% d₁ as shown by NMR integration. The origin of the remaining proton is unknown. Lewis acids such as AlCl₃ are known to catalyze the reaction between aldehydes (which could be formed by hydrolysis of the aluminum acyl) and acetyl chloride to produce α-chloroalkyl acetates such as **21**. However, NMR spectral analysis of unhydrolyzed reaction mixtures indicates that treatment of **15** with acetyl chloride proceeds to give **20** (and **21**) before hydrolysis. That **21** is not formed during workup is further substantiated by the observation that added aldehyde survives intact under the reaction and workup conditions employed.

The acyl group of **3b** failed to transfer to diisobutylaluminum chloride, even at room temperature (in CH₂Cl₂). Instead the two species formed a weak complex. This was indicated by the fact that the only change in the NMR spectrum of the reaction mixture was a slight downfield shift of the Cp resonance from its position in free **3b**. This complex was readily dissociated by ether, which caused the Cp resonance to return to its usual position.

Conclusions

Organozirconium(IV) complexes were shown to be extremely convenient precursors of organoaluminum dichlorides and of alkenylalanes by transmetalation. Both of these aluminum species find broad use in organic synthesis. Transmetalation was also shown to be a viable method for the formation of at least one type of main group acyl metallic derivative from

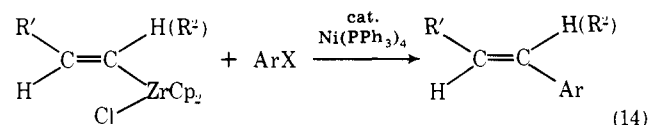
Table I



R	reaction temp, °C	reaction time, h	major product	minor product	side products	workup
a	-20	1.5				H ₂ O
a	5	1.5	21	19		H ₂ O
a	-20 to -5	1	21	19		H ₂ O
b	-15	1.5	21 (32%)	19		H ₂ O
b	-20 to 5	3	21 (32%)			D ₂ O

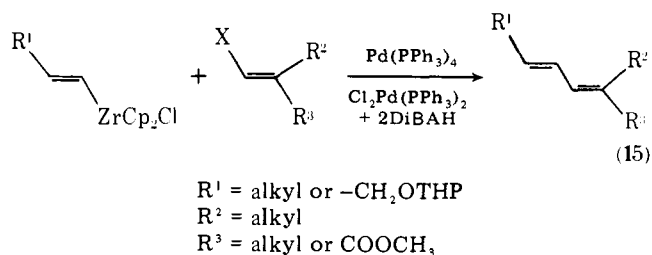
a transition metal acyl complex. The findings noted herein may perhaps lead to new strategies which could be applied to similar systems for the preparation of main group acyl metallic species which function in organic synthesis as acyl anion equivalents.

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 alkyllithium compounds will alkylate Cp₂ZrCl₂. Therefore, the following order of alkylating abilities of organometallic alkyls toward metal halides may be developed: RLi, RMgX, or R₃Al > Cp₂Zr(Cl)R > RAlCl₂ (R = alkyl). It has also been found in the course of these investigations that Cp₂Zr(Cl)R (R = alkenyl) will transfer its alkenyl group to R₂AlCl, ZnCl₂,²⁴ CuCl,²⁵ PdCl₂,²⁵ and SnCl₄.²⁴ Negishi and co-workers have studied several coupling reactions of organometallics⁶ with organic halides, 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 alkenyl 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



RLi). They, combined with the reactions studied in the present investigation, in which the organic group is transferred from the transition-metal center to a main-group center, provide strong evidence for the utility of tandem metal systems for organic synthesis; by using a *sequence* of organometallic reagents, it becomes possible to exploit the best features of each metallic component in the design of overall synthetic routes.

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 ¹³C NMR were obtained with a Varian XL-100 spec-

rometer 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). Elemental analyses were performed by the analytical laboratories of A. Bernhardt (Elbach, West Germany).

Analytical thin layer chromatography (TLC) was performed on Whatman K5 silica strips and preparative TLC on Whatman K5 20 × 20 cm plates. Preparative liquid chromatography was performed by using a Waters Associates refractive index detector R403 and a Fluids Metering Inc. solvent delivery system. Samples were run through two 310 × 25 mm EM Laboratories silica gel columns with varying percentages of hexane and ethyl acetate.

Analytical vapor phase chromatography (VPC) was performed on a Hewlett-Packard 402 instrument equipped with a flame ionization detector. Preparative gas chromatography was carried out on a Perkin-Elmer 3920 thermal conductivity instrument. The following columns, all aluminum, were used: A, 3/8 in. × 9 ft 10% Carbowax 20M on Chromosorb P NAW 60-80; B, 1/4 in. × 8 ft 5% Carbowax 20M on Chromosorb P NAW 60-80; C, 1/4 in. × 8 ft 5% DEGS on Chromosorb P NAW 80-100; D, 1/4 in. × 8 ft 5% Carbowax 1540 on Chromosorb P NAW 60-80; E, 3/8 in. × 8 ft 10% DEGS on Chromosorb P NAW 60-80. VPC yields were derived from the weights of peak areas of products vs. that of internal standards and were adjusted with the appropriate response factors. Response factors were determined by using standard solutions of known compounds or compounds prepared specifically for that purpose. Products were identified by coinjection with known samples unless otherwise specified.

Dichlorobis(η^5 -cyclopentadienyl)zirconium (Cp_2ZrCl_2) was obtained from ROC/RIC or from Boulder Scientific. Chlorobis(η^5 -cyclopentadienyl)hydrido-zirconium (Cp_2ZrHCl) (**1**) was made from Cp_2ZrCl_2 by the procedure of Wailes,²⁶ except that a benzene solution of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ (Vitride) was used as the hydride source. Zirconocene hydrido-chloride (**1**), thus prepared as a precipitate, is 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 oils and were normally used immediately after preparation.

Aluminum trichloride (AlCl_3) was obtained 99.5% pure (anhydrous) from ROC/RIC. Acetyl chloride was purified by refluxing with PCl_5 for several hours and distillation from quinoline directly before each use. Benzoyl chloride was purified by distillation from SOCl_2 .

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

Analysis of Precipitated Cp_2ZrHCl for Purity. To a suspension of 0.5164 g of NaCl-contaminated Cp_2ZrHCl in 10 mL of THF in a flask connected to a gas buret was added 10 mL of a 25% aqueous solution of H_2SO_4 . After the reaction mixture had returned to room temperature, the amount of hydrogen gas evolved was measured on the gas buret. Gas evolved was calculated (assuming ideal gas behavior) to be 1.4 mmol. The composition of the prepared reagent was therefore determined to be 70% Cp_2ZrHCl . Small amounts of Cp_2ZrH_2 contamination result in some inaccuracy in this determination (vide infra).

The purity of Cp_2ZrHCl may be further ascertained by mixing a weighed quantity with a slight excess of acetone. NMR integration of the residual acetone resonance vs. that for $\text{Cp}_2\text{ZrCl}(\text{OPr-}i)$ provides a rapid means of analysis. Cp_2ZrH_2 can be measured by this acetone-based analysis, too, by quantitative NMR comparison of relative amounts of the resulting $\text{Cp}_2\text{ZrCl}(\text{OPr-}i)$ and $\text{Cp}_2\text{Zr}(\text{OPr-}i)_2$.

Preparation of Chlorobis(η^5 -cyclopentadienyl)-3,3-dimethylbutylzirconium (2a**).** To 3.9632 g (15.4 mmol) of **1** suspended in 25 mL of benzene was added 2 mL (15.4 mmol) of 3,3-dimethylbutene. After stirring for several hours, the reaction mixture was filtered and the benzene removed to give yellow crystals (88% yield) identified as **2a**: $^1\text{H NMR}$ (CH_2Cl_2) δ 0.92 (s, 9), 1.09 (m, 2), 1.54 (m, 2), 6.27 (s, 10).

In similar fashion **2i** was prepared (95% yield) from methylene-cyclohexane. Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{ClZr}$: (**2i**) C, 57.67; H, 6.54; Cl, 10.02. Found: C, 57.61; H, 6.53; Cl, 10.25.

Preparation of (*E*)-Chlorobis(η^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-dimethylbutyne. 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 **2b**: $^1\text{H NMR}$ (CH_2Cl_2) δ 1.00 (s, 9), 5.86 (d, 1, $J = 19$ Hz), 6.31 (s, 10), 6.79 (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. Calcd for $\text{C}_{16}\text{H}_{21}\text{ClZr}$: Cl, 10.43; C, 56.62; H, 6.23. Found: Cl, 10.33; C, 56.33; H, 6.12.

Reaction of Cp_2ZrHCl (1**) with 4-Methyl-2-pentyne.** 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-pentyne. After stirring for several hours, the benzene and volatiles were removed to afford an oil which was 55% chlorobis(η^5 -cyclopentadienyl)-2-(4-methyl-2-pentyl)zirconium (**2e**) and 45% its isomer, chlorobis(η^5 -cyclopentadienyl)-3-(4-methyl-2-pentyl)zirconium. A few milligrams of Cp_2ZrHCl were added to the oil, 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%): $^1\text{H NMR}$ (benzene) of **2e** δ 1.26 (d, 6, $J = 7$ Hz), 2.12 (d, 3, $J = 2$ Hz), 2.83 (septet, 1, $J = 7$ Hz), vinylic H obscured by solvent; $^1\text{H NMR}$ (benzene) of isomer δ 1.32 (d, 6, $J = 7$ Hz), 1.77 (d, 3, $J = 2$ Hz), 2.83 (septet, 1, $J = 7$ Hz), vinylic H obscured by solvent.

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

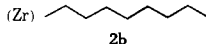
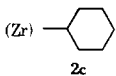
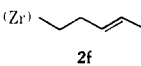
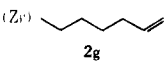
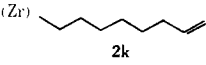
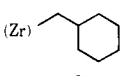

Preparation of 5,5-Dimethyl-2-hexanone by Transmetalation from Zr to Al. To a suspension of 0.775 g (5.8 mmol) of AlCl_3 in 5 mL of CH_2Cl_2 at 0 °C was added a solution of 1.37 g (4.0 mmol) of **2a** and 0.4984 g (2.87 mmol) of dodecane (standard) in CH_2Cl_2 . An instantaneous color change from yellow to orange indicated the formation of 3,3-dimethylbutylaluminum dichloride (**4a**): $^1\text{H NMR}$ (CH_2Cl_2) δ 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_2SO_4 . The product, 5,5-dimethyl-2-hexanone,²⁷ was found to be present in 98% yield (column B, 110 °C).

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_2Cl_2 at -30 °C was added a solution of 7.85 mmol of **2b** and 0.547 g (5.53 mmol) of dichloroethane (standard) in CH_2Cl_2 . An instantaneous color change from yellow to dark orange indicated the formation of *n*-octylaluminum dichloride (**4b**): $^1\text{H NMR}$ (CH_2Cl_2) δ 0.35 (m, 2), 0.90 (t, 3, $J = 5.5$ Hz), 1.32 (m, 12). Then 1.23 g (9.25 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_2Cl_2 at 0 °C was added a solution of 4.38 mmol of **2c**. An instantaneous color change from orange to yellow indicated the formation of cyclohexylaluminum dichloride (**4c**): $^1\text{H NMR}$ (CH_2Cl_2) δ 0.70 (m, 1), 1.10-2.20 (m, broad, 10). Then 0.72 g (5.15 mmol) of benzoyl 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.²⁸ 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_2Cl_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 3,3-dimethylbutenylaluminum dichloride (**4d**): $^1\text{H NMR}$ (CH_2Cl_2) δ 1.08 (s, 9), 6.04 (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

Table II

olefin or acetylene	Zr adduct	isolated yield, %	NMR spectrum, δ (CH ₂ Cl ₂ or CD ₂ Cl ₂)
1-octene, <i>cis</i> - and <i>trans</i> - 2-octenes, <i>cis</i> - and <i>trans</i> - 4-octenes	(Zr)  2b	96	0.93 (t, 3, $J = 5.5$ Hz), 1.30 (m, 14), 6.27 (s, 10)
cyclohexene	(Zr)  2c	90	0.98–2.15 (m, broad, 11), 6.23 (s, 10)
<i>trans</i> -1,3-pentadiene	(Zr)  2f	73	1.05 (t, 3, $J = 8$ Hz), 1.57–1.95 (m, 4), 6.30 (s, 10), vinylic H's obscured by solvent and Cp resonance
1,5-hexadiene	(Zr)  2g	92	1.37 (m, 6), 2.10 (q, 2, $J = 6$ Hz) 4.92 and 5.20 (m, 3), 6.27 (s, 10)
1,7-octadiene	(Zr)  2k	98	1.53 (m, 10), 2.15 (q, 2, $J = 5.5$ Hz), 5.17–5.54 (m, 3), 6.45 (s, 10)
methylene-cyclohexane	(Zr)  2i	95	1.03 (d, 2, $J = 6$ Hz), 1.10–2.03 (m, 11), 6.28 (s, 10)
3-hexyne	(Zr)  10	93	0.88 (t, 3, $J = 7$ Hz), 1.05 (t, 3, $J = 7$ Hz), 1.99 (broad quintet, 2, $J_{\text{obsd}} = 7$ Hz), 2.56 (broad quartet, 2, $J_{\text{obsd}} = 7$ Hz), 5.83 (broad, t, 1, $J_{\text{obsd}} = 6$ Hz), 6.18 (s, 10)

mixture allowed to stir for 45 min at that temperature before standard workup. The product, 5,5-dimethyl-3-hexen-2-one,²⁹ was present in 97% yield (column D, 105 °C).

Preparation of (*E*)-3,5-Dimethyl-3-hexen-2-one by Transmetalation from Zr to Al. To 0.46 g (3.44 mmol) of AlCl₃ in CH₂Cl₂ 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-pentyl)aluminum dichloride (**4e**) was formed: ¹H NMR (CH₂Cl₂) δ 1.00 (d, 6, $J = 7$ Hz), 1.85 (d, 3, $J = 2$ Hz), other resonances not visible because of dilution. Then 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).³⁰

Preparation of 3-Cyclopropyl-2-butanone by Transmetalation from Zr to Al. To 0.91 g (6.80 mmol) of AlCl₃ in CH₂Cl₂ at 0 °C was added a solution of 3.47 mmol of **2f** and 0.5591 g (5.65 mmol) of dichloroethane (standard). A color change from orange to yellow indicated the formation of 1-(1-cyclopropylethyl)aluminum dichloride (**4f**): ¹H NMR (CH₂Cl₂) δ 0.0–0.68 (m, broad, 6, cyclopropyl and Al–CH), 1.02 (m, 3). Then 0.55 mL (7.73 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 E, 90 °C). The major product, 3-cyclopropyl-2-butanone, was present in 79% yield (column E, 90 °C): IR (neat) CO 1710 cm⁻¹; ¹H NMR (CCl₄) δ 0.0–0.8 (m, broad, 5), 1.14 (d, 3, $J = 6.5$ Hz), 1.67 (q, 1, $J = 6.5$ Hz), 2.15 (s, 3); ¹³C NMR (CCl₄) δ 3.64, 4.71, 14.47, 15.56, 27.89, C=O not observed; M⁺, *m/e* 112 (0.68), 43 (1.00), 41 (0.82), 69 (0.68), 39 (0.21). The minor product, *trans*-5-hepten-2-one,³¹ was present in less than 10% yield.

Reaction of Chlorobis(η^5 -cyclopentadienyl)-5-hexenylzirconium (2g) with Aluminum Chloride. To 1.17 g (8.77 mmol) of AlCl₃ in 5 mL of CD₂Cl₂ at 0 °C were added 4.67 mmol of **2g** and 0.5327 g (5.38 mmol) of dichloroethane (standard). An instantaneous color change from yellow to a lighter yellow indicated the formation of (cyclopentylmethyl)aluminum dichloride (**4g**): ¹H NMR (CD₂Cl₂) δ 0.25 (t, 2, $J = 5.5$ Hz), 0.55–2.38 (m, 9). (Note: A separate low-temperature NMR study was made of this reaction and it was found that no change in the spectrum occurred between –46 and 24 °C.) The reaction mixture was worked up in two different manners. In workup A, a small excess of acetyl chloride was added to the reaction mixture

at 0 °C and, after 30 min, hydrolysis was carried out. The major product was identified as 1-cyclopentyl-2-propanone (column B, 90 °C).³² In workup B, CaCl₂-dried air was bubbled through the reaction mixture at 0 °C for 30 min and at 10 °C for 30 min. Pure, dry O₂ was then bubbled through at 10 °C for 30 min and at room temperature for 30 min. The reaction mixture was hydrolyzed with dilute aqueous HCl and subjected to standard workup. Two organic products were collected by preparative GC (column A, 100 °C). The major product, cyclopentylmethanol, was present in 26% yield (column D, 100 °C).³³

Reaction of Chlorobis(η^5 -cyclopentadienyl)-7-octenylzirconium (2h) and Aluminum Chloride. To 1.23 g (9.20 mmol) of AlCl₃ in 5 mL of CD₂Cl₂ at 0 °C were added 5.21 mmol of **2h** and 0.5136 g (5.19 mmol) of dichloroethane (standard). The product was 7-octenylaluminum dichloride (**4h**): ¹H NMR (CD₂Cl₂) δ 0.43 (t, 2, AlCH₂, $J = 6.5$ Hz), 1.40 (m, 8), 2.03 (q, 2, $J = 6.5$ Hz), 4.87–5.15 (m, 3). Then CaCl₂-dried air was bubbled through the reaction mixture at 0 °C for 30 min. Dry oxygen was bubbled through at 0 °C for 40 min and at room temperature for 30 min. The reaction mixture was hydrolyzed with dilute aqueous HCl and worked up in the standard fashion. The product, 7-octen-1-ol, was identified.³⁴

Reaction of Chlorobis(η^5 -cyclopentadienyl)cyclohexylmethylzirconium (2i) with Aluminum Chloride. To 0.69 g (5.19 mmol) of AlCl₃ in 5 mL of CH₂Cl₂ at 0 °C was added a solution of 4.02 mmol of **2i** and 0.5533 g (5.59 mmol) of dichloroethane (standard). An immediate color change from dark yellow to light yellow indicated the formation of cyclohexylmethylaluminum dichloride (**4i**): ¹H NMR (CH₂Cl₂) δ 0.40 (d, 2, AlCH₂, $J = 6$ Hz), 0.62–2.00 (m, 11). The reaction mixture was worked up by two different methods. In workup A, a small excess of acetyl chloride was added at –30 °C and the reaction mixture allowed to stir for 30 min before standard workup and hydrolysis. The two major products were collected by preparative GC (column E, 110 °C). The major product, 1-cyclohexyl-2-propanone, was present in 41% yield (column F, 90 °C).³⁵ The minor product, 1-cyclohexen-1-yl-2-propanone, was present in 18% yield (column F, 90 °C).³⁶ In workup B, dry oxygen was bubbled through the reaction mixture at 0 °C for 20 min and at room temperature for 30 min. The reaction mixture was then hydrolyzed with dilute aqueous HCl. The major organic product, cyclohexylmethanol, coincided with an authentic sample (column E, 100 °C) and was present in 32% yield.

Reaction of erythro-(CHDCHDC(CH₃)₃)Zr(Cl)(η^5 -C₅H₅)₂ (5) with

Aluminum Chloride. To a solution of 4.26 g (14.58 mmol) of Cp_2ZrCl_2 in 30 mL of THF was added 0.15 g (3.54 mmol) of LiAlD_4 . After 45 min of stirring, the reaction mixture was filtered, washed with THF (4×15 mL), and dried under vacuum to give $\text{Cp}_2\text{Zr}(\text{D})\text{Cl}$. This was dissolved in 8 mL of benzene and combined with 3.30 mmol of (*E*)- $\text{CHD}=\text{C}(\text{CH}_3)_3$.^{4b} 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 (CH_2Cl_2) δ 0.87 (s, 9), 1.21 (d, 1, $J = 12.9$), 6.23 (s, 10), H_A obscured by *tert*-butyl. A CH_2Cl_2 solution of *erythro*-**5** was added to 0.61 g (4.60 mmol) of AlCl_3 in CH_2Cl_2 at 0 °C to give *erythro*-((CH_3)₃- CCHDCHD) AlCl_2 (**6**): ^1H NMR (CH_2Cl_2) δ 0.35 (d, 1, AlCHD), 0.88 (s, 9), 1.27 (d, 1 CHD [*tert*-butyl]). Deuterium decoupled 100-MHz NMR spectral analysis of the methylene protons in **6** showed $^3J_{\text{HH}} = 9$ Hz (Figure 2).

Preparation of Dimethyl(3,3-dimethylbutenyl)aluminum (9a) by Transmetalation from Zr to Al. To 0.56 g (1.65 mmol) of **2d** in CH_2Cl_2 at 0 °C was added 0.12 g (1.30 mmol) of Me_2AlCl in CH_2Cl_2 . The product, formed after a few minutes, was dimethyl(3,3-dimethylbutenyl)aluminum (**9a**): ^1H NMR (CH_2Cl_2) δ -0.35 (s, 6, AlCH_3), 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-dimethylbutenyl)aluminum (9b) by Transmetalation from Zr to Al. To 0.46 g (1.35 mmol) of **2d** suspended in a few milliliters of pentane at 0 °C were added 0.24 g (1.36 mmol) of *i*- Bu_2AlCl and 0.1872 g (1.89 mmol) of dichloroethane (standard). The reaction mixture was allowed to stir at 0 °C for 1 h and at room temperature for 1 h. The product, diisobutyl(3,3-dimethylbutenyl)aluminum (**9b**), was present in 97% yield based on NMR integration with respect to standard: ^1H NMR (CH_2Cl_2) δ 0.11 (d, 4, AlCH_2 , $J = 7$ Hz), 0.90 (d, 12, $J = 6$ Hz), 1.08 (s, 9), 1.82 (septet, 2, $J = 6$ Hz), 5.73 (d, 1, $J = 20.5$ Hz), 7.49 (d, 1, $J = 20.5$ Hz). The reaction mixture was filtered to remove Cp_2ZrCl_2 and the pentane removed in vacuo to leave crystals which corresponded to a 90% yield (0.27 g) of pure **9b**.³⁷

Preparation of Diisobutyl(3,3-dimethylbutenyl)aluminum (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 over 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 Transmetalation from Zr to Al. To 0.14 g (0.82 mmol) of diisobutylaluminum chloride in CH_2Cl_2 at -40 °C was added 0.37 g (1.09 mmol) of **10** in CH_2Cl_2 . The reaction mixture was allowed to stir for 0.5 h at -40 °C and analyzed by NMR at that temperature. The product was (*E*)-diisobutyl-3-hexenylaluminum (**11**): ^1H NMR (CH_2Cl_2) δ 0.37 (d, 4, AlCH_2 , $J = 7$ Hz), 1.00 (d, 12, $J = 6$ Hz), 0.97 (m, 6), 1.55–2.50 (m, 6), 6.98 (t, 1, $J = 6$ Hz).

Preparation of (*E*)-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 corresponded with the one reported above for **11**.

Preparation of Chlorobis(η^5 -cyclopentadienyl)acylzirconium 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), 5.63 (s, 10); IR (CH_2Cl_2) 1550 cm^{-1} (ν_{CO}).

In similar fashion, **2i** was carbonylated to the corresponding acyl (90%), ν_{CO} 1545 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{23}\text{OClZr}$: C, 56.69; H, 6.07; Cl, 9.27. Found: C, 56.50; H, 6.06; Cl, 9.37.

Preparation of Chlorobis(η^5 -cyclopentadienyl)acylzirconium Complex 3b. To 3.29 g (12.8 mmol) of **1** in 20 mL of toluene was added about 4 mL of condensed propylene through a dropping funnel. The reaction mixture was allowed to stir overnight, during which time it became a clear yellow solution. This was placed in a Fischer-Porter bottle and charged with 40 psi of CO gas. The reaction mixture was allowed to stir overnight and filtered, and the benzene and volatiles

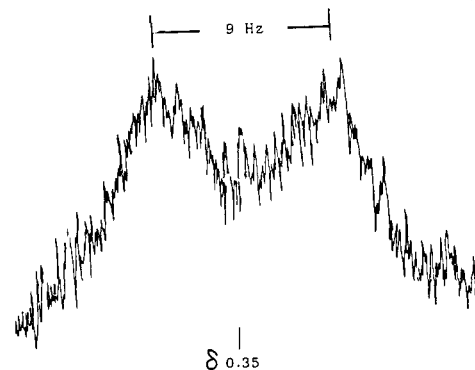


Figure 2. ^2H -Decoupled ^1H spectrum (100 MHz) for $\text{C}_2\text{AlCHDCHD}[t\text{-Bu}]$.

were removed in vacuo to give a white powder. This was washed thoroughly with hexane to give **3b**: ^1H NMR (CH_2Cl_2) δ 1.10 (t, 3, $J = 6.5$ Hz), 1.92 (sextet, 2, $J = 7$ Hz), 3.22 (t, 2, $J = 7$ Hz), 5.92 (s, 10); IR (CH_2Cl_2) 1550 cm^{-1} (ν_{CO}).

Preparation of Acylaluminum Dichloride (15a) from 3a. To 0.30 g (2.25 mmol) of AlCl_3 suspended in 5 mL of CH_2Cl_2 at -20 °C was added a CH_2Cl_2 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 (CH_2Cl_2) δ 0.90 (s, 9), 1.57 (m, 2), 3.38 (t, 2, $J = 7$ Hz). An IR spectrum of the carbonyl region, recorded before the sample could warm significantly above -78 °C, showed ν_{CO} 1530 cm^{-1} .

Preparation of Deuterated 4,4-Dimethylpentanal (22) from 15a. To 1.25 mmol of **15a** at -20 °C in CH_2Cl_2 was added 0.02 mL (1.25 mmol) of D_2O . The reaction mixture turned from 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-dimethylbutenylbenzene³⁸ and 2,2,8,8-tetra-methyl-5-nonanone.³⁹

Determination of the Position of Deuterium Incorporation in 4,4-Dimethylpentanal (22) Obtained by Treatment of 31a by D_2O . 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**.⁵

For undeuterated **22**: IR (CCl_4) 1722, 2720 cm^{-1} .⁴⁰ For deuterated **22**: IR (CCl_4) 1722, 2060 cm^{-1} . For undeuterated **22**: ^1H (CCl_4) 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 δ 2.33 to be 74% H and 26% D and the resonance at δ 9.85 to be 82% D and 18% H.

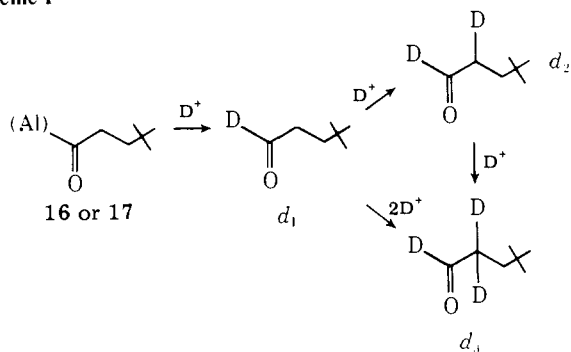
For undeuterated **22**: M^+ m/e 114 (0.00), 57 (1.00), 43 (0.32), 41 (0.32), 81 (0.28), $\text{M} - 15$ 99 (0.02). For deuterated **22**: M^+ m/e 115 (0.001), 57 (1.00), 41 (0.41), 43 (0.23), 82 (0.22). These samples were also studied by chemical ionization GC-MS to determine percent deuterium incorporation in **22**. The $\text{M} + 29$ region, rather than the $\text{M} + 1$ region, was used for the calculations since the loss of H and H_2 from the $\text{M} + 29$ ion is much less than the same losses for the $\text{M} + 1$ 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 I may arise. From structure **18** the products shown in Scheme II may arise. It is therefore possible to obtain d_3 , d_2 , and d_1 products from structures **16** or **17**. It is possible to obtain d_2 , d_1 , and d_0 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 d_0 . The NMR integration shows that 18% of the $d_0 + d_1 + d_2$ 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 $d_0 + d_1 + d_2$ 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-

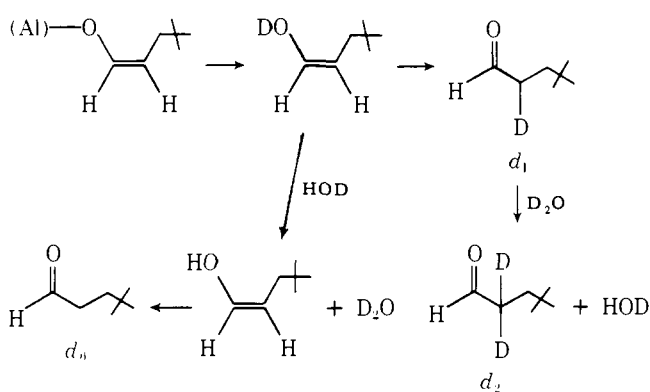
Table III

<i>m/e</i>	labeled aldehyde	unlabeled aldehyde		deuterium incorporation in pentanal	% <i>d</i>
	obsd rel abundance (mean of 3 samples)	obsd rel abundance (mean of 3 samples)	isotopically corrected		
142	1.89				
143	100.0	12.70	10.81	<i>d</i> ₀	6.24
144	9.98	100.00	97.90	<i>d</i> ₁	56.54
145	0.65	63.74	53.59	<i>d</i> ₂	30.95
146		16.56	10.85	<i>d</i> ₃	6.27

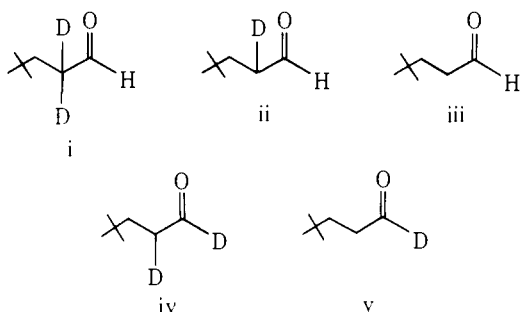
Scheme I



Scheme II



spends to d_3 , which must arise from **16** or **17**. Therefore, the total percentage of product which was derived from a direct acyl metallic species is 83%.



Reaction of Acylaluminum Dichloride Complex 15a with Acetyl Chloride. To 2.58 mmol of **15a** at $-20^\circ C$ in 5 mL of CH_2Cl_2 was added 0.25 mL (3.5 mmol) of acetyl chloride. The reaction mixture was allowed to stir between $-20^\circ C$ and $-5^\circ C$ for 1 h, hydrolyzed with aqueous $NaHCO_3$, 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, $85^\circ C$): IR (CH_2Cl_2) 1759, 1207, 740 cm^{-1} ; 1H NMR (CH_2Cl_2) δ 0.92 (s, 9), 1.45 (m, 2), 2.02 (m, 2), 2.13 (s, 3), 6.40 (t, 1, $J = 5.5$ 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-nonane, and 6,6-dimethyl-2,3-heptandione (**19a**): IR (CH_2Cl_2) 1725 cm^{-1} ; 1H NMR (CH_2Cl_2) 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).

Reaction of Acylaluminum Dichloride Complex 15b with Acetyl Chloride. To 1.48 g (11.1 mmol) of $AlCl_3$ in 5 mL of CH_2Cl_2 at $-20^\circ C$ were added 8.42 mmol of $Cp_2Zr(Cl)(COCH_2CH_2CH_3)$ (**3b**) and 0.2842 g (2.87 mmol) of dichloroethane as a standard. After 15 min at $-20^\circ C$ the product **15b** was analyzed: 1H NMR (CH_2Cl_2) δ 1.05 (m, 3), 1.78 (m, 2), 3.28 (m, 2); IR (CH_2Cl_2 , low temperature) 1530 cm^{-1} (ν_{CO}). The temperature of the bath was raised to $-15^\circ C$ and 0.70 mL (8.92 mmol) of acetyl chloride was added. After stirring for 1.5 h at $-15^\circ C$, the reaction mixture was worked up in the usual manner. The major product, 1-acetoxy-1-chlorobutane, was collected by preparative GC (column E, $110^\circ C$) and was present in a yield of 32%: IR (CCl_4) 1770, 1210, 738 cm^{-1} ; 1H NMR (CCl_4) δ 0.98 (t, 3, $J = 6.5$ Hz), 1.52 (m, 2), 1.92 (q, 2, $J = 6.5$ Hz), 2.05 (s, 3), 6.38 (t, 1, $J = 6$ Hz); ^{13}C NMR (CCl_4) 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).⁴¹ Also present were small amounts of *n*-propylbenzene⁴² and 2,3-hexanedione.⁴³

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 (44) For example, the Cp position in the reaction between $Cp_2Zr(Cl)(3,3\text{-dimethylbutyl})$ and a 40% excess of $AlCl_3$ appears approximately 40% of the way between the positions of free Cp_2ZrCl_2 and the complex $Cp_2ZrCl_2 \cdot AlCl_3$. This complex is weak; it is readily destroyed (as evidenced by NMR) by weak Lewis bases such as ethers, acyl chlorides, or ketones.
 (45) When transmetalation was performed between 0 and 25 °C, a small amount of isobutylene was generated as a side product; when the reaction was performed at -40 °C, no isobutylene was produced.

Resonance Raman Spectra, Excitation Profiles and Excited State Geometry of Bispyridine Iron(II) Heme

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Abstract: Totally symmetric bound pyridine vibrational modes are observed in the resonance Raman spectra of $(py)_2Fe^{II}MP$ (py = pyridine, MP = mesoporphyrin IX dimethyl ester) and the pyridine- d_5 analogue. The frequencies and their deuterium shifts are satisfactorily calculated using a benzene force field and an Fe-N stretching force constant of $1.96 \text{ mdyn } \text{Å}^{-1}$. 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 $d_{\pi(Fe)} \rightarrow \pi^*(py)$ charge transfer.

Introduction

Recently we reported¹ resonance-enhanced Raman scattering by bound pyridine, as well as porphyrin, modes (RR modes) of $(py)_2Fe^{II}MP$ and $(4\text{-Mepy})_2Fe^{II}MP$ (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 $\sim 490 \text{ nm}$, which might plausibly be an $Fe^{II} \rightarrow py$ charge transfer (CT) transition. This assignment had been suggested² for a shoulder in the $(py)_2Fe^{II}TPP$ (TPP = tetraphenylporphyrin) 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 oxyhemoglobin⁵ and a "picket fence" porphyrin analogue³ for iron(III) octaethylporphyrin halides^{6,7} and for methemoglobin complexes.⁸ The bispyridine Fe^{II} 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 $(py)_2Fe^{II}MP$ and in its $py\text{-}d_5$ 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- h_5 was distilled and stored over KOH. Pyridine- d_5 was purchased from Merck Sharp and Dohme and used without further purification. Dichloromethane was distilled and stored over molecular sieve.

The preparation of $(F^-)Fe^{II}MP$ has been described previously.¹ The preparation of $(py)_2Fe^{II}MP$ was carried out in a modified Spex spinning cell sealed with a Teflon stopper. A solution of $(F^-)Fe^{II}MP$ and excess pyridine in dichloromethane was covered with a water layer. After nitrogen gas had been bubbled through the solution for $\sim 5 \text{ min}$, 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 $(py)_2Fe^{II}MP$ in dichloromethane was $\sim 1 \text{ mg/mL}$.

Spectra were excited with various lines of an Ar^+ laser, and recorded with a Spex 1401 double monochromator equipped with a cooled ITT FW 130 photomultiplier and photon counting electronics. Frequencies were internally calibrated against the solvent bands and are believed to be accurate to $\pm 1 \text{ cm}^{-1}$ for the strong bands.

Results and Discussion

Figure 1 shows RR spectra of $(py)_2Fe^{II}MP$ and $(py\text{-}d_5)_2Fe^{II}MP$ 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 I.

Normal Coordinate Analysis. A normal coordinate analysis, using available computer programs,⁹ was carried out on a linear $py\text{-}Fe\text{-}py$ model to obtain a qualitative picture of the