through a quartz photolysis well. After 43 h, ^{19}F NMR spectroscopy indicated no further conversion to **19**. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (60 × 2 cm) at −40 °C. Elution with hexane/CH_2Cl_2 (80:30) (total amount of solvent = 150 mL) produced a yellow band containing **7b** (0.030 g, 46%). Elution with CH_2Cl_2 (total amount of solvent = 50 mL) eluted a second yellow band containing **19** (0.030 g, 35%) which was characterized as described above.

Reaction of [Rh(η^5-C_9H_7)(1,2,5,6-η-C_8F_8)] (3) with *tert*-Butyl Isocyanide. To a solution of **5** (0.010 g, 0.02 mmol) in $CDCl_3$ (0.5 mL) in a 5-mm NMR tube was added *tert*-butyl isocyanide (0.18 μL, 0.02 mmol). The mixture was photolyzed, and the reaction was monitored by ^{19}F NMR spectroscopy. After 5.5 h, resonances corresponding to **23** were observed [δ 107.7, 113.1, 174.5, 182.6 (an analysis of the coupling constants for an isostructural complex **19** appears above, and inspection reveals a similar coupling pattern for **23**)]. After 60 h of photolysis, the ^{19}F NMR spectrum of the solution indicated complete conversion to the ring-closed product **24**. ^{19}F NMR (THF): δ 140.4 (m, F_3, F_5), 164.3 (m, F_4), 195.9 (m, F_1), 202.7 (m, F_2).

Reaction of Rh(η^5-C_9H_7)(1,2,5,6-η-C_8H_8) (25) with *tert*-Butyl Isocyanide. To a stirred solution of **25** (0.020 g, 0.06 mmol) in hexane (10 mL) was added *tert*-butyl isocyanide (0.007 mL, 0.06 mmol). The solution was allowed to stir for 24 h, and the solvent was removed under reduced pressure. The residue was crystallized from hexane at −20 °C to afford Rh(η^5-C_9H_7)(*t*-BuNC)$_2$ as an orange solid (0.009 g) identified by comparison of its spectroscopic properties with the reported literature values.[14]

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Facile Intramolecular Coupling of Alkyl and Acyl Ligands Induced by Lewis Acids: Mechanistic Studies on the Formation of Zirconium Ketone Complexes

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Bis(cyclopentadienyl)zirconium acyl complexes $Cp_2Zr(X)COR$ (X = Cl, Me) react rapidly with alkylaluminum reagents R'_2AlY (Y = R′, Cl) to give alkylaluminum adducts of zirconium ketone complexes $Cp_2Zr(\mu$-η^2-$OCRR')(\mu$-$Cl)AlR'_2$. Zirconium aldehyde complexes $Cp_2Zr(\mu$-η^2-$OC(H)R)(\mu$-$Cl)AlR_2$ are prepared analogously by treating the acyl complexes with diisobutylaluminum hydride. Mechanistic investigations, including isotopic labeling and crossover experiments, indicate that aluminum reagents induce the intramolecular coupling of zirconium alkyl and acyl ligands to give ketone complexes.

Introduction

The effect of Lewis acid cocatalysts and Lewis acidic oxide supports on the activity of transition-metal catalysts is of considerable theoretical and practical interest.[1,2] Main-group Lewis acids are important cocatalysts for industrial processes such as Ziegler–Natta polymerization[3] and olefin metathesis.[4] Lewis acidic oxides, such as silica and alumina, are used as supports for heterogeneous polymerization, metathesis, and CO reduction catalysts.[5] However, the role of Lewis acidic sites in catalytic reactions remains poorly understood.[1]

Interactions between transition-metal complexes and Lewis acidic reagents[6] can reveal important information regarding the effects of Lewis acidic sites on the reactivity of transition-metal centers and coordinated ligands. Shriver[6] and others[7] have demonstrated that Lewis acids can have a dramatic effect on the rate of CO migratory insertion reactions. These studies provide a model for the interactions between transition-metal catalysts and Lewis acidic supports and the cooperativity that may be an important feature of the catalyst-support interface.[8]

Transition-metal acyl complexes occupy a central role in catalytic reactions involving carbon monoxide. Few studies have investigated the effect of coordinated Lewis acids on the reactivity of these intermediates, although

Table I. Preparation of Zirconium Ketone Complexes

acyl	R	reagent	product	R′	yield (%)
1a	Me	$AlMe_3$	**2a**	Me	71
1b	Et	$AlMe_3$	**2b**	Me	85
1c	$CH_2CH_2CMe_3$	$AlMe_3$	**2c**	Me	68
1c	$CH_2CH_2CMe_3$	$AlEt_3$	**2d**	Et	65
1d	c-C_6H_{11}	$AlMe_3$	**2e**	Me	91

† Contribution no. 7727.

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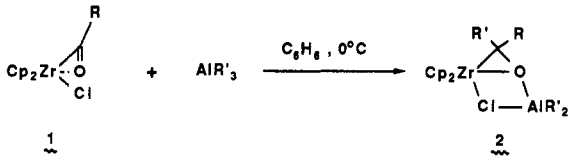
reactions of later transition-metal acyl complexes with electrophiles is a common route to Fischer-type carbenes.[9] In this paper, we report details[10] of a series of novel reactions between zirconium acyl complexes and alkylaluminum reagents. These reactions provide an efficient route to alkylaluminum adducts of zirconium ketone complexes. Mechanistic studies have revealed that aluminum reagents induce the intramolecular coupling of a zirconium acyl ligand and a cis alkyl ligand to give ketone complexes.

Results and Discussion

Preparation of Zirconium Ketone and Aldehyde Complexes. Treatment of bis(cyclopentadienyl)zirconium chloro acyl complexes **1a–d** with trialkylaluminum reagents[11] in aromatic solvents affords the complexes $Cp_2Zr(\mu\text{-}\eta^2\text{-}OCRR')(\mu\text{-}Cl)AlR_2$ (**2a–e**) in isolated yields of 65–90% (Table I, eq 1). The reaction of the acyl com-



(1)

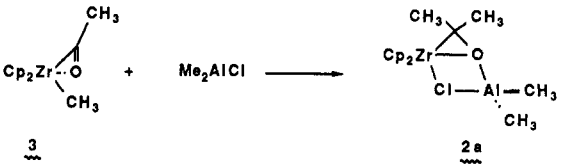
1 2

plexes **1a–d** with alkylaluminum reagents is exothermic; significant decomposition of the ketone complexes is observed unless the reaction is carried out at reduced temperatures (<0 °C). Complexes **2a–e** are thermally sensitive, decomposing in solution or in the solid state at temperatures >30 °C, but can be isolated as pale yellow or colorless powders that are stable under an inert atmosphere below 25 °C. They are moderately air-stable but hydrolyze readily to secondary alcohols and unidentified zirconium products.

Complexes **2a–e** are formally 1:1 adducts between a zirconium ketone complex and $AlMe_2Cl$. Attempts to obtain crystals suitable for an X-ray analysis were unsuccessful; nevertheless, spectroscopic and analytical data indicate that $AlMe_2Cl$ remains coordinated to the ketone ligand, presumably via reciprocal Zr–O–Al and Al–Cl–Zr bridging interactions. For example, resonances due to the $AlMe_2$ moiety of **2a** appear at –0.28 and –6.32 ppm in the ^1H and ^{13}C NMR spectra, respectively. Moreover, $AlMe_2Cl$ remains coordinated to the ketone ligand even in the presence of strong Lewis bases such as pyridine. Treatment of **2a** with pyridine leads to the formation of the pyridine adduct **4**, which can be recrystallized from a mixture of pyridine and ether (eq 2).

$$\underset{\mathbf{2a}}{Cp_2Zr(OCMe_2)\cdot AlMe_2Cl} + py \rightarrow \underset{\mathbf{4}}{Cp_2Zr(OCMe_2)\cdot AlMe_2Cl\cdot py} \quad (2)$$

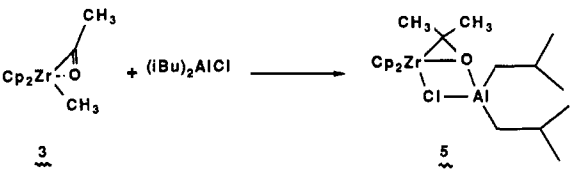
Ketone complexes can also be prepared by treating $Cp_2Zr(Me)COMe$ (**3**) with dialkylaluminum chloride reagents. Addition of an equimolar[12] amount of Me_2AlCl to a toluene-d_8 solution of the acyl complex **3** at –30 °C (eq 3) produced a mixture of products, of which the major product was identified as the ketone complex **2a** (60%, ^1H NMR vs internal standard).



(3)

3 2a

The reaction of the acyl **3** with an equimolar amount of diisobutylaluminum chloride proceeded in higher yield to give the ketone complex **5** (eq 4).[13] These reactions are

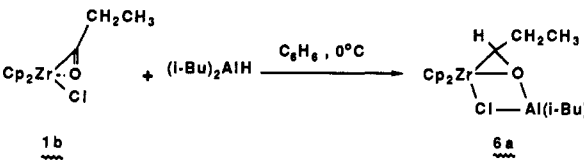


(4)

3 5

rapid; no intermediates could be observed for the formation of **5** when a frozen toluene-d_8 solution of **3** and diisobutylaluminum chloride was allowed to thaw in the NMR probe that had been cooled to –50 °C.

Zirconium aldehyde complexes are prepared by treatment of $Cp_2Zr(Cl)COR$ with diisobutylaluminum hydride. The aldehyde complex **6a** (R = CH_2CH_3) forms rapidly upon addition of $(i\text{-}Bu)_2AlH$ to a C_6D_6 solution of **1b** (80% yield, ^1H NMR, eq 5). The aldehyde complexes were



(5)

1b 6a

isolated as yellow oils and characterized by hydrolysis to the primary alcohols and by spectroscopic comparison with the ketone complexes **2** and related aldehyde complexes reported in the literature.[14] In particular, the ^1H and ^{13}C

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(10) A preliminary account of a portion of this work has appeared: Waymouth, R. M.; Klauser, K. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6385.

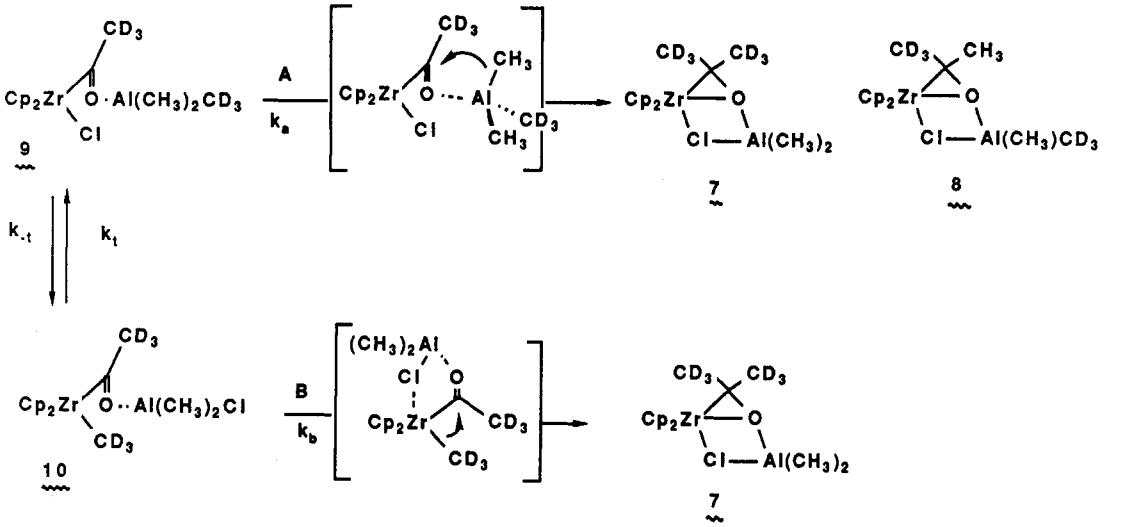
(11) Treatment of the acyl complexes **1** with $AlCl_3$ results in the transmetalation of the acyl ligand from zirconium to aluminum. Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.

(12) Treatment of $Cp_2Zr(Me)COMe$ with 0.5 equiv of R_2AlX leads to the formation of trinuclear zirconium ketone complexes $(Cp_2Zr(\mu\text{-}\eta^2\text{-}OCR))_2(\mu\text{-}X)(\mu\text{-}AlR_2)$. Waymouth, R. M.; Potter, K. S.; Schaefer, W. P.; Grubbs, R. H., manuscript in preparation.

(13) The ^1H NMR spectrum of the diisobutylaluminum adduct **5** displays doublets for the methyl (1.21 ppm) and methylene (0.33 ppm) protons of the isobutyl groups (see Experimental Section). However, these protons are diastereotopic in the static structure represented in eq 4 and 8, suggesting that there is a fluxional process which interconverts the isobutyl groups on the NMR time scale. This process most likely involves rotation around the aluminum–oxygen bond. Further studies are underway to address this point.

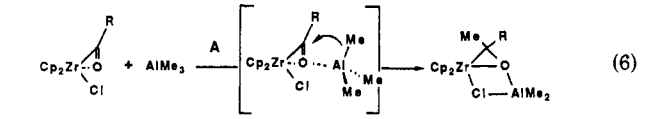
(14) For representative early-transition-metal aldehyde complexes see: (a) Gambarrota, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 1690. (b) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 278. (c) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (d) Erker, G.; Kropp, K. *Chem. Ber.* **1982**, *115*, 2437. (e) Kropp, K.; Skibbe, V.; Erker, G. *J. Am. Chem. Soc.* **1983**, *105*, 3353. (f) Kropp, K.; Skibbe, V.; Erker, G. *Tetrahedron* **1982**, *38*, 1285. (g) Skibbe, V.; Erker, G. *J. Organomet. Chem.* **1983**, *241*, 15. (h) Roddick, D. M. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1984. (i) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846. (j) Marsella, J. A.; Folting, D.; Huffman, J. C.; Caulton, K. G. *J. am. Chem. Soc.* **1981**, *103*, 5596. See also: (k) Fernandez, J. M.; Emerson, K.; Larsen, R. H.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268.

Scheme I

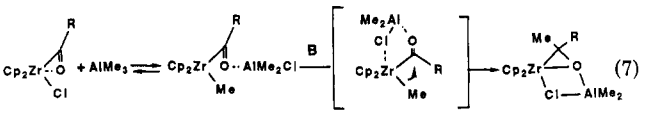


NMR spectra of complex **6a** exhibit characteristic[14] resonances at 3.15 and 82.9 ppm for the aldehydic proton and the carbonyl carbon, respectively. The spectroscopic data and crystallographic data on related compounds[12,14,17] suggest that the bonding in these complexes is best described in terms of metalloxiranes rather than π-complexes.

Mechanism. Two possible reaction pathways for the formation of **2a–e** from the chloro acyl complexes **1** are given in eq 6 and 7. The simplest mechanism (path 1, eq 6) involves the direct reductive alkylation[15] of the acyl ligand by Me_3Al. Similar mechanisms have been proposed for reductions of acyl ligands by boranes,[16] metal hydrides,[14] and zirconium alkyls.[17] Another mechanistic possibility (path B, eq 7) involves a stepwise pathway proceeding by initial transmetalation to give the alkyl acyl complex **3**, followed by a 1,2-migration of the alkyl group to the acyl ligand.



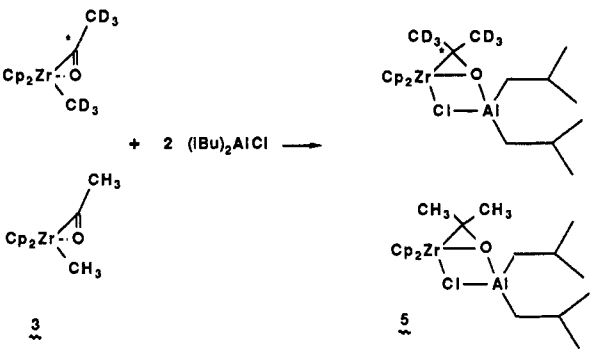
(6)



(7)

The observation that the alkyl acyl complexes **3** react with alkylaluminum chlorides to give ketone complexes establishes the feasibility of the latter mechanism but does not rule out direct alkylation (path A). Before further conclusions could be drawn regarding the mechanism of ketone formation from the chloro acyl complexes, it was necessary to establish in detail the mechanism of the reaction between $Cp_2Zr(Me)COMe$ (**3**) and dialkylaluminum chloride reagents. Isotopic labeling studies were employed to probe the mechanism of these reactions and the role of the aluminum reagent.

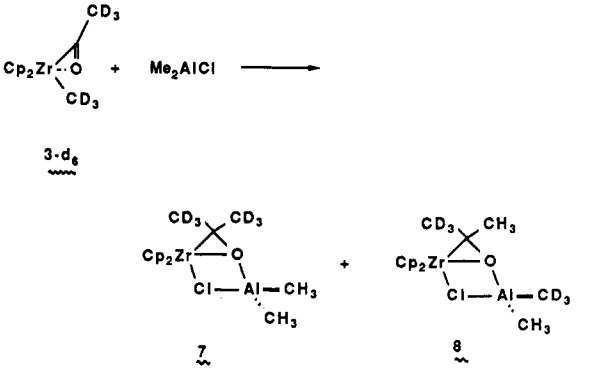
Norton has shown that zirconium ketone complexes can be formed in bimolecular reactions between zirconium acyl complexes and dimethylzirconocene.[17] To rule out that more than one zirconium center is involved in the reaction of **3** with dialkylaluminum chloride reagents, a crossover experiment was carried out. The reaction between a mixture of **3**-d_6-^{13}C and **3** and diisobutylaluminum chloride gives the ketone complexes **5**-d_6-^{13}C and **5** (eq 8). No



(8)

crossover products were detected by ^1H or ^{13}C NMR of the ketone complexes or by GC/mass spectroscopy of the alcohols generated upon hydrolysis of the reaction mixture, a clear indication that the ketone complexes are formed at one zirconium center.

Deuterium labeling studies provided further information on the mechanism of this reaction. Treatment of the **3**-d_6 with Me_2AlCl in toluene-d_8 at 0 °C produced the ketone complexes **7** and **8** in a ratio of 4.8:1 and an overall yield of 60% (eq 9). The observed product ratio clearly es-



(9)

tablishes that the predominant pathway for the reaction

(15) This mechanism is similar to that proposed for the reductive alkylation of organic carbonyl substrates by alkylaluminum reagents. Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 9, p 499.

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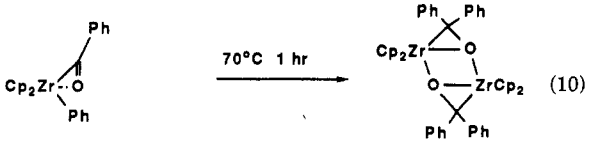
(17) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952.

between **3** and Me_2AlCl (eq 2 and 8) involves the intramolecular migration of the methyl group to the acyl ligand and not transmetalation to the **1** followed by direct alkylation by $Al(CH_3)_2CD_3$. As seen in Scheme I, the acyl intermediates **1** and **3** are related by transmetalation between the chloro acyl Me_3Al adduct **9** and the alkyl acyl Me_2AlCl adduct **10**. Treatment of **3**-d_6 with Me_2AlCl should initially produce **10**. Transmetalation to **9** followed by alkylation by $Al(CH_3)_2CD_3$ would produce **7** and **8** in a statistical ratio[18] of 1:2 due to scrambling of the labeled methyl groups at the aluminum center. The experimentally observed ratio of 4.8:1 (7:8) rules out A as the dominant pathway and implies that the major pathway from the acyl intermediate **10** involves the Lewis acid assisted coupling of the alkyl and acyl ligands (path B).

The observation of a small amount of the d_3 ketone complex **8** indicates that scrambling processes are competitive with coupling of the alkyl and acyl ligands of **10**. The d_3 ketone complex **8** could be formed by transmetalation to **9** followed by either (1) direct alkylation of the acyl ligand of **9** by $Al(CH_3)_2CD_3$ or (2) transmetalation back to **10** (with scrambling of the labeled methyl groups) followed by coupling of the alkyl and acyl ligands. At the present time, we cannot distinguish between these two possibilities since no direct information is available concerning the relative rates of direct alkylation of the acyl ligand vs transmetalation from **9** to **10** (k_a vs k_{-t}, Scheme I). For similar reasons, we cannot rule out A as a pathway for formation of the ketone complexes **2** from the chloro acyl complexes **1** and trialkylaluminum reagents. Given that the relative rates of alkylation vs transmetalation are sensitive[11] to both the nature of the acyl ligand and the aluminum reagent, both pathways must be considered in a mechanism for the formation of ketone and aldehyde complexes from zirconium acyl complexes and alkylaluminum reagents.[19] Further studies will be required to determine the factors that govern the relative rates of alkylation (or hydride addition, path A) vs transmetalation, reductive coupling (path B).

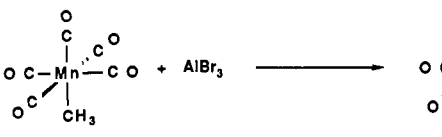
A significant result of the labeling studies is the demonstration that ketone complexes can be formed by an *intramolecular* migration of an alkyl group to a cis acyl ligand and that aluminum reagents induce this coupling reaction. In a related study, Erker has shown[20] that in the absence of dialkylaluminum chlorides, the acyl Cp_2Zr(Ph)COPh isomerizes to the benzophenone complex $[Cp_2ZrOCPh_2]_2$ after one hour at 70 °C (eq 10). In the



(10)

presence of AlR_2Cl, the acyl complex **3** rearranges rapidly at −50 °C to give the ketone complexes (eq 3 and 4). Although these reactions yield different products, it is clear that the aluminum reagent facilitates the coupling of alkyl and acyl ligands at zirconium centers. The role of the aluminum reagent in promoting this coupling reaction is not clear, but it is likely that the aluminum reagent helps to increase the electrophilicity of the acyl carbon by coordinating to the oxygen of the acyl ligand, thereby facilitating migration of the alkyl to the acyl ligand.[21]

Implications: CO Reduction. The role of alkylaluminum reagents in mediating the formation of zirconium ketone complexes and the formation of ketone complexes from acyl precursors have important implications for CO reduction. Molecular Lewis acids[6,7] and aluminum oxides[6c,d] promote the migratory insertion of CO to give acyl complexes (eq 11). Our results imply that Lewis



(11)

acidic centers can also assist in the further reduction of acyl ligands to give ketone complexes. Ketone complexes have been proposed as intermediates to explain branching in hydrocarbons produced over metal oxide CO reduction catalysts;[22] the present results provide a mechanistic rational for the formation of such intermediates on the catalyst surface.

Conclusions

We have demonstrated that aluminum reagents promote the intramolecular coupling of zirconium alkyl and acyl ligands. These results introduce an additional mechanistic pathway for the reduction of transition-metal acyl complexes. Transmetalation, followed by an intramolecular ligand coupling, has been shown to be an important pathway for the formation of zirconium ketone and aldehyde complexes; similar pathways might be important in reactions of other transition-metal acyl complexes.[19] The reactivity of these zirconium ketone and aldehyde complexes,[10,23] as well as the synthesis and structure of related trinuclear Zr_2Al bridging ketone complexes,[12] will be the subjects of forthcoming papers.

Experimental Section

General Procedures. The general experimental techniques and procedures were described previously.[23] The acyl complexes **1a–e**,[11] **4**,[24] and **4**-d_6-^{13}C were prepared by literature procedures. Me_3Al was used neat (Alfa) or as 2 M solutions in toluene (Aldrich). Et_3Al, Me_2AlCl, $(i\text{-}Bu)_2AlCl$, and $(i\text{-}Bu)_2AlH$ were obtained neat from Texas Alkyls and were used without further purification. Mesitylene was dried over calcium hydride, vacuum transferred, and stored in the drybox. NMR solvents were purified as previously described.[23] All NMR chemical shifts are reported in parts per million relative to TMS and were recorded at 25 °C unless otherwise indicated. Mass spectra were obtained at the UC Riverside Mass Spectra facility.

$Cp_2Zr(\mu\text{-}\eta^2\text{-}OCMe_2)(\mu\text{-}Cl)AlMe_2$ (2a). In a typical procedure, 0.563 g of **1a** (1.88 mmol) was suspended in 10 mL of 1/1 benzene/hexane and cooled to 0 °C in an ice bath. This suspension was treated with 1 mL of a 2 M solution of Me_3Al to give a yellow solution. Solvent was removed in vacuo at 0 °C and the pale yellow residue washed with two 5-mL portions of pentane to give **2a** as a pale yellow powder (0.465 g, 1.31 mmol, 79%): ^1H NMR (C_6D_6) 5.57 (s, 10 H), 1.49 (s, 6 H), −0.28 ppm (s, 6 H); ^{13}C NMR (C_6D_6) 109.9, 80.9, 33.5, −6.32 ppm. Anal. Calcd for

(18) This ratio assumes a negligible kinetic isotope effect.
(19) A transmetalation, reductive coupling mechanism (path B) might also be applicable to reductions observed when acyl ligands are treated with hydrido[14] and alkyl[17] zirconium reagents.
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(21) Calculations on the isomerization of $Cp_2Zr(Me)COMe$ to the ketone complex $Cp_2Zr(OCMe_2)$ in the absence of Lewis acids suggest that the electrophilicity of the acyl carbon is important in favoring the 1,2-migration of the alkyl to the acyl ligand. Hofmann, P., manuscript in preparation. We thank Prof. Hofmann for communicating his results prior to publication.
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$C_{15}H_{22}OClZrAl$: C, 48.4; H, 6.0; Cl, 9.5. Found: C, 48.47; H, 5.96; Cl, 9.61.

$Cp_2Zr[\mu\text{-}\eta^2\text{-}OC(Me)CH_2CH_3](\mu\text{-}Cl)AlMe_2$ (2b). The acyl **1b** (0.690 g, 2.204 mmol) was treated with Me_3Al by using the procedure described for **2a** to give **2b** as a pale yellow powder (0.728 g, 1.89 mmol, 86%): ^1H NMR (C_6D_6) 5.61 (s, 5 H), 5.59 (s, 5 H), 1.92 (m, J = 6.3 Hz, 1 H), 1.62 (m, 1 H), 1.43 (s, 3 H), 0.884 (t, J = 7.37 Hz, 3 H), −0.25 ppm (s br, 6 H); ^{13}C NMR (C_6D_6) 110.0, 109.9, 86.6, 38.9, 29.9, 12.4 ppm.

$Cp_2Zr[\mu\text{-}\eta^2\text{-}OC(Me)CH_2CH_2CMe_3](\mu\text{-}Cl)(AlMe_2)$ (2c). The acyl **1c** (0.500 g, 1.36 mmol) was treated with Me_3Al by using the procedure described for **2a** to give **2c** as a yellow powder (0.450 g, 1.02 mmol, 75%): ^1H NMR (C_6D_6) 5.68 (s, 5 H), 5.61 (s, 5 H), 1.97 (m, 2 H), 1.47 (s, 3 H), 1.35 (m, 2 H), 0.94 (s, 9 H), −0.22 (s, 3 H), −0.29 ppm (s, 3 H); ^{13}C NMR (C_6D_6) 110.0, 109.08, 85.5, 41.4, 40.8, 30.9, 30.5, 29.7, 6.13 ppm. Anal. Calcd for $C_{20}H_{32}OClZrAr$: C, 54.31; H, 7.30. Found: C, 54.25; H, 7.26.

$Cp_2Zr[\mu\text{-}\eta^2\text{-}OC(Et)CH_2CH_2CMe_3](\mu\text{-}Cl)AlEt_2$ (2d). Neat Et_3Al (0.395 mL, 2.8 mmol) was dissolved in benzene and cannulated dropwise into a precooled (0 °C) benzene solution of the acyl **1c** (1.043 g, 2.82 mmol). Solvent was removed in vacuo to afford a waxy yellow solid, which was washed with three 5-mL portions of pentane to give **2d** as a light yellow powder (0.880 g, 64%): ^1H NMR (C_6D_6) δ 5.68 (s, 5 H), 5.64 (s, 5 H), 1.94 (m, J = 7.32 Hz, 2 H), 1.68 (m, J = 7.32 Hz, 2 H), 1.39 (m, 3 H), 1.25 (m, 2 H), 0.96 (s, 9 H), 0.90 (m, 3 H), 0.35 ppm (m, 4 H). Anal. Calcd for $C_{23}H_{38}OClZrAl$: C, 57.05; H, 7.91; Cl, 7.32. Found: C, 56.98; H, 7.89; Cl, 7.41.

$Cp_2Zr[\mu\text{-}\eta^2\text{-}OC(Me)CH(CH_2)_5](\mu\text{-}Cl)AlMe_2$ (2e). The acyl **1e** was treated with Me_3Al by using the procedure described for **2a** to give **2e** as a light yellow powder (0.734 g, 1.668 mmol, 91%): ^1H NMR (C_6D_6) 5.63 (s, 5 H), 5.62 (s, 5 H), 1.69 (m, 5 H), 1.47 (m, 1 H), 1.36 (s, 3 H), 1.20 (m, 5 H), −0.29 (s, 3 H), −0.38 ppm (s, 3 H).

$Cp_2Zr(\mu\text{-}\eta^2\text{-}OCMe_2)(AlMe_2Cl)(py)$ (4). The ketone complex **2a** (0.700 g, 1.88 mmol) was dissolved in benzene and treated with excess pyridine via syringe. The resulting pale yellow solution was filtered through a pad of Celite on a fine frit and evacuated to give **4** as a yellow powder (0.556 g, 1.24 mmol, 66%). A sample for analysis was obtained by dissolving **2a** in a minimum of pyridine, layering with Et_2O, and cooling slowly to −50 °C: ^1H NMR (C_6D_6) 8.40 (m, 2 H), 6.80 (m, 1 H), 6.50 (m, 2 H), 5.76 (s, 10 H), 1.73 (s, 6 H), −0.12 ppm (s, 6 H); ^{13}C NMR (C_6D_6) 148.2, 138.9, 124.3, 109.8, 78.1, 35.3. Anal. Calcd for $C_{20}H_{27}OClZrAl$: C, 53.25; H, 6.03; N, 3.11; Cl, 7.86. Found: C, 53.25; H, 6.06; N, 3.21; Cl, 7.93.

Formation of 5 from 3. The acyl **3** (28 mg, 0.10 mmol) was weighed into an NMR tube modified with a 14/20 joint and dissolved in 0.500 mL of toluene-d_8 containing 5 μL of mesitylene as an internal standard. Diisobutylaluminum chloride (0.02 mL) was condensed into the NMR tube at 77 K and the tube sealed with a torch under CO. The solution was allowed to thaw at −50 °C, and the NMR spectra were recorded at −10 °C. Integration of the cyclopentadienyl and mesitylene resonances of the ^1H NMR spectrum indicated an 87% yield of the ketone complex **5**: ^1H NMR (C_7D_8) 5.57 (s, 10 H), 1.50 (s, 6 H), 1.35 (m, 2 H), 1.21 (d, J = 6.6 Hz, 12 H), 0.33 ppm (d, J = 7.08 Hz, 4 H); ^{13}C NMR (C_7D_8): 109.3, 80.3, 33.5, 28.5, 26.5, 21.2 ppm.

$Cp_2Zr[\mu\text{-}\eta^2\text{-}OCH(CH_2CH_3)](\mu\text{-}Cl)(Al(i\text{-}Bu)_2)$ (6a). The acyl **1b** (0.766 g, 2.44 mmol) was suspended in 10 mL of 1/1 benzene/hexane and cooled to 0 °C. Neat $(i\text{-}Bu)_2AlH$ (0.352 g, 2.47 mmol) was dissolved in hexane and cannulated into the acyl suspension to give a yellow solution. This solution was stirred for 15 min and evacuated to give **6a** as a yellow oil, which turned brown upon standing for 2 h at room temperature: ^1H NMR (C_6D_6) 5.59 (s, 5 H), 5.58 (s, 5 H), 3.15 (dd, J = 8.1 Hz, J = 8.3 Hz, 1 H), 2.15 (m, 2 H), 1.80 (m, 1 H), 1.59 (m, 1 H), 1.20 (m (br), 12 H), 1.04 (t, J = 7.32 Hz, 3 H), 0.36 ppm (d, J = 7.32 Hz, 4 H); ^{13}C NMR (C_6D_6) 109.2, 109.1, 82.8, 32.4, 28.95, 28.90, 26.8, 15.9 ppm.

$Cp_2Zr(\mu\text{-}\eta^2\text{-}OC(H)CH_2CH_2)(\mu\text{-}Cl)(Al(i\text{-}Bu)_2)$ (6b) was prepared in a manner similar to that of **6a**: ^1H NMR (C_6D_6) 5.65 (s, 5 H), 5.62 (s, 5 H), 3.17 (m, 1 H), 1.20 (m, 12 H), 0.97 (s, 9 H), 0.39 (s, 2 H), 0.32 ppm (s, 2 H).

Crossover Experiment. The acyl **3** (8 mg, 0.029 mmol) and the doubly labeled acyl **3**-d_6-^{13}C (9 mg, 0.031 mmol) were weighed into an NMR tube modified with a 14/20 joint. A side-arm addition tube was charged with 5 μL of mesitylene, 0.14 mL (0.072 mmol) of neat $(i\text{-}Bu)_2AlCl$, and 0.500 mL of toluene-d_8 and attached to the NMR tube. The contents of the side arm were added to the sample at 77 K, and the NMR tube was sealed under CO. The sample was thawed at −50 °C and placed in a precooled −30 °C NMR probe. **5**, **5**-d_6-^{13}C: ^1H NMR (C_7D_8, −30 °C) 5.57 (s, 20 H), 1.51 (s, 6 H), 1.35 (m, 4 H), 1.21 (d, J = 6.5 Hz, 24 H), 0.38 ppm (d, J = 6.5 Hz, 8 H); ^{13} C NMR (C_7D_8, −30 °C) 79.7 ppm. The NMR tube was then cracked open and the sample hydrolyzed with water to afford the labeled and unlabeled 2-propanols: ^1H NMR (C_7D_8) 3.58 (m, J = 6.1 Hz, 1 H), 0.94 ppm (d, J = 6.1 Hz, 6 H); ^{13}C NMR (C_7D_8) 63.3 ppm (d, J = 140.1 Hz). GC–mass spectroscopy of the hydrolyzed samples yielded peaks at 49 ($CD_3{}^{13}CHOH^+$) and at 45 ($CH_3{}^{12}CHOH^+$) amu, but none at 48 ($CD_3{}^{12}CHOH^+$) or at 46 ($CH_3{}^{13}CHOH^+$) amu.

Labeling Studies. An NMR tube, modified with a 14/20 joint, was charged with 13 mg (0.045 mmol) of the doubly labeled acyl **3**-d_6-^{13}C, fitted with a side-arm addition tube and a gas bulb adaptor. To the side-arm addition tube were added 0.17 mL of a 2.6 M C_6D_6 solution of $AlMe_2Cl$, 0.500 mL of C_7D_8, and 5 μL of mesitylene as an internal standard. The contents of the addition tube were added to the acyl at 77 K, the NMR tube was sealed under CO, and the spectra were recorded at 0 °C. Integration of the cyclopentadienyl vs the mesitylene resonances indicated a 60% yield of **7** and **8**. Integration of the cyclopentadienyl vs the methyl resonance at 1.48 ppm revealed a ratio of 4.8:1 for **7**:**8**: ^1H NMR (C_7D_8) 5.51 (s, 20 H), 1.48 (d, J = 5.37 Hz, 0.63 H), −0.21 ppm (s, 11 H); ^{13}C NMR (C_7D_8) 79.7 ppm; ^2D NMR (C_7D_8) 1.43 ppm.

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Registry No. **1a**, 77001-15-1; **1b**, 83385-24-4; **1c**, 82808-20-6; **1d**, 104114-54-7; **2a**, 114789-53-6; **2b**, 114762-78-6; **2c**, 114762-79-7; **2d**, 114762-80-0; **2e**, 114762-81-1; **3**, 60970-97-0; **3**-d_6-^{13}C, 114762-88-8; **4**, 114762-82-2; **5**, 114762-83-3; **6**-d_6-^{13}C, 114762-85-5; **6a**, 114762-84-4; **7**, 114762-86-6; **8**, 114762-87-7; $AlMe_3$, 75-24-1; $AlEt_3$, 97-93-8; Me_2AlCl, 1184-58-3; $(i\text{-}Bu)_2AlCl$, 1779-25-2; $(i\text{-}Bu)_2AlH$, 1191-15-7.