Journal of Organometallic Chemistry, 136 (1977) C19—C22

Preliminary communication

MIXED-METAL HYDRIDE COMPLEXES CONTAINING Zr—H—Al BRIDGES. SYNTHESIS AND RELATION TO TRANSITION-METAL-CATALYZED REACTIONS OF ALUMINUM HYDRIDES

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(Received May 9th, 1977)

Summary

Dialkylaluminum hydrides and Cp_2ZrX_2 ($Cp = \pi^5\text{-}C_5H_5$; X = Cl, H, alkyl) were found to react by aggregation to give mixed Zr—Al trihydride complexes containing Zr—H—Al bridges. Reactions of these mixed-metal hydrides are discussed and structural parallels between them and known aluminum hydride complexes are drawn.

Reactivity patterns of main group metal hydrides can be altered by interaction with certain transition metal salts; for example, several titanium(IV) or zirconium(IV) salts catalyze the terminal hydroalumination of acyclic internal olefins [1,2] or the addition of $LiAlH_4$ to alkynes and alkenes [3,4]. These processes could be envisioned (reaction 1) to occur by initial formation of a discrete transition metal hydride by simple H— for X—ligand exchange followed by addition of the transition metal hydride to the unsaturated organic unit. Ligand transfer of the resulting alkyl or alkenyl unit from Zr (or Ti) to Al in exchange for H would then give the observed organoaluminum product and regenerate the zirconium (or titanium) hydride. To begin to elucidate mechanistic patterns for reactions of aluminum hydrides and zirconium (or titanium) salts, we have studied tractable model systems which involve the interaction of dialkylaluminum hydrides with several organozirconium complexes, Cp_2ZrX_2 ($Cp = \eta^5\text{-}C_5H_5$; X = H, Cl, alkyl). We find, in contrast to reaction 1, that reaction of dialkylaluminum hydride with Cp_2ZrX_2 proceeds not by simple ligand exchange but rather by aggregation to yield structurally related, mixed Al—Zr trihydrido complexes containing Al—H—Zr bridges.

Mixed-metal species containing Zr—H—Al linkages can be prepared as follows. Cp_2ZrH_2 [5] (approx. 0.7 g; 3 mmol) is added slowly to a stirred solution of

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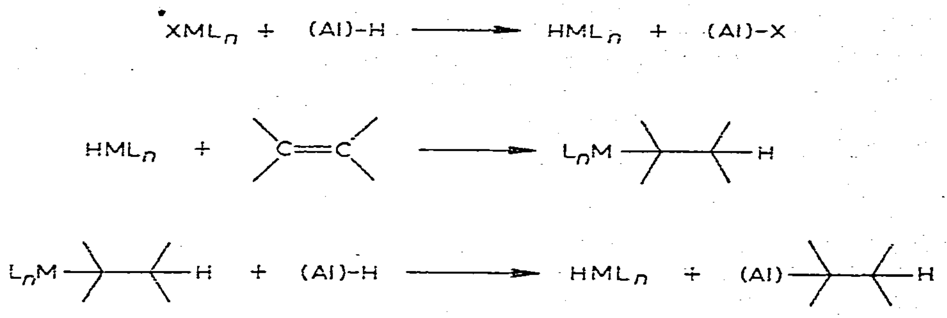

(1)

M = Zr^{IV} or Ti^{IV}
L$_n$ = non-transferred ligands
X = transferred ligand

0.40 g (2.81 mmol) of diisobutylaluminum hydride (DIBAH) in 10 ml benzene at room temperature*. After approx. 15 min, the solution becomes deep blue and is filtered to remove excess Cp_2ZrH_2. The deep blue, oily complex (I) which is isolated is thermally unstable and decomposes at room temperature. Its structure is assigned on the basis of its ^{1}H NMR spectrum (Table 1). Treatment of I with one equivalent of i-Bu_2AlCl immediately produces the thermally stable (at room temperature) pale violet, oily complex II, whose formulation is consistent with its cryoscopic molecular weight determination in benzene (mol. wt. calcd. 542, found 499)**. The ^{1}H NMR spectrum of II (Table 1) bears striking resemblance to the AB_2 patterns reported for Cp_2NbH_3 [6] and Cp_2TaH_3 [7]. For such trihydrides coordination of Et_3Al (as a Lewis acid) to the central hydride ligand results in an upfield shift of this ligand in the ^{1}H NMR spectrum of the resulting complex III. Coordination of Al to the central hydride ligand in I and to the external hydride ligands in II is postulated by comparison with NMR spectra reported [8] for III. Bonding for the bridging hydride units is different in III from that in I or II. In III, the aluminum spe-

TABLE 1[a]

^{1}H NMR SPECTRA OF COMPOUNDS I, II, IV AND IV'

Complex[b]	δ(Cp)	δ(Zr—H)	δ(Zr—H—Al)
I	5.57(10)	—	−0.28(2), −2.03(1) (br)
II	5.67(10)	−0.90(t, 1)	−2.03(d,2, J 7 Hz)
IV	5.62(10)	−1.20(t, 1)	−2.06(d,2, J 7 Hz)
IV'	5.65(10)	−1.10(t, 1)	−1.99(d,2, J 7 Hz)

[a] Note that all resonances show some concentration dependence. [b] Spectra recorded in C_6D_6.

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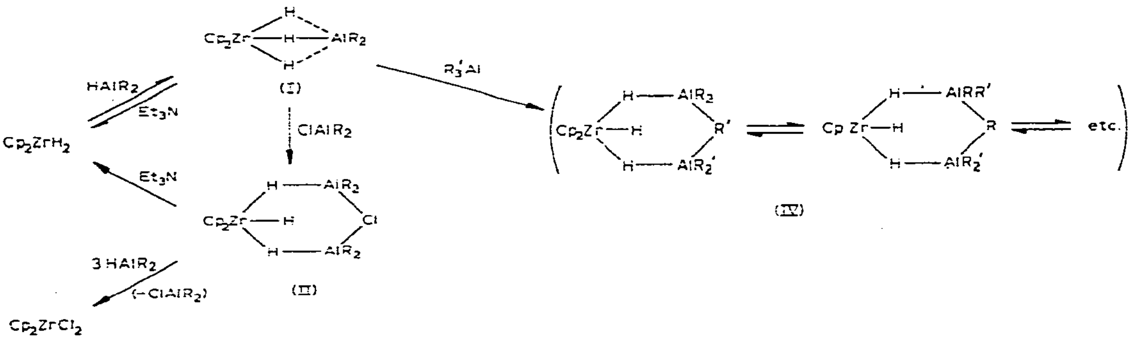
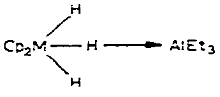
* All reactions were performed under argon in solvents distilled from sodium benzophenone ketyl or in a nitrogen atmosphere dry box.

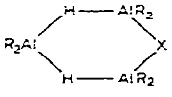
** Molecular weight determinations were complicated by difficulties associated with quantitative manipulations of these viscous materials.

cies simply acts as a Lewis acid toward the saturated metal trihydride complex. In I and II, however, dialkylaluminum hydride acts both as an acceptor and a donor ligand toward the coordinatively unsaturated transition metal hydride species. Reaction of Cp_2ZrCl_2 with 3 equivalents of DIBAH also gives II (plus 1 equivalent $i\text{-}Bu_2AlCl$). Treatment of either I or II with Et_3N precipitates Cp_2ZrH_2 (identified by its quantitative reaction with acetone to give $Cp_2Zr(O\text{-}i\text{-}Pr)_2$). Treating I with 1 equivalent of $(CH_3)_3Al$ also produces an oily complex displaying a high field AB_2 pattern in its ^1H NMR spectrum (Table 1). The structure of this complex (IV) is assigned on the basis of these data and on cryoscopic molecular weight determination in benzene (mol. wt. calcd. 438, found 406). Interestingly, these new Zr—H—Al complexes (II, IV) are mixed-metal analogues of organoaluminum aggregates (V) [9,10] in which an H—Al—H unit is formally replaced by H—Zr(H)—H.





(III) (M = Mo,Tc)



(V)

R = i-butyl, R′ = CH_3 ; X = Cl [11] , i-butyl [12]

Transmetalation of alkyl groups from Zr to Al in exchange for H is a necessary step to regenerate mixed-metal hydride complexes in catalytic sequences such as that one suggested in reaction 1*,**. It is, therefore, significant that Cp_2ZrR_2'' (R″ = neo-hexyl)*** reacts with excess DIBAH to give Zr—H—Al complexes and alkylaluminum (reaction 3). The course of this transmetalation reaction is worthy of note. To a solution of Cp_2ZrR'' in benzene was added two equivalents of DIBAH. ^1H NMR analysis of the resulting product showed two triplets (δ −1.18 ppm and δ −2.85 ppm, J 4.5 Hz), suggesting the formation of a complex (VI) analogous to the one previously prepared [13]

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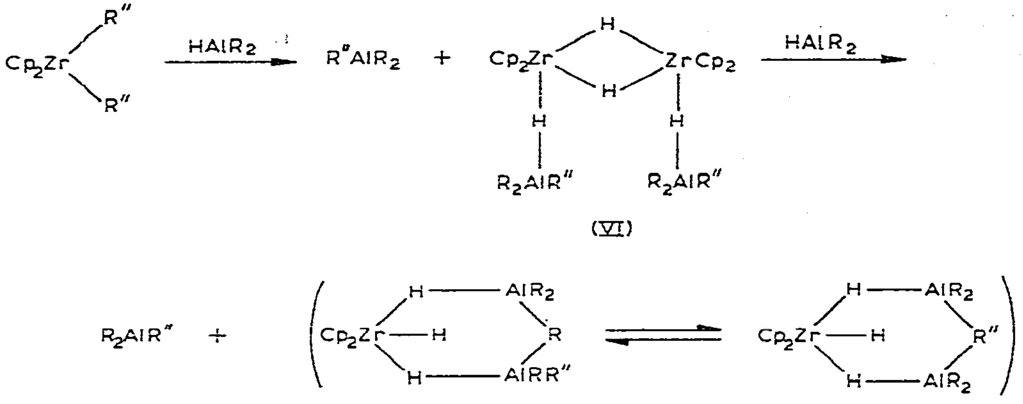
* For sequences such as those shown in reaction 1, a zirconium complex has been shown to react with acetylenes or olefins to yield alkenyl-zirconium or (terminal) alkylzirconium compounds [11].

** Transmetalation of organic ligands from Zr to Al in exchange for Cl has been noted [12].

*** Prepared from Cp_2ZrH_2 and neo-hexene (in C_6D_6, δ(Cp) 5.75; δ(Zr—CH_2) 0.27).

from Cp_2ZrH_2 and $(CH_3)_3Al$*. Further addition of DIBAH gives trihydrido complex IV′ as the sole Zr-containing material. neo-Hexyl group transfer from Zr to Al was demonstrated by oxygenation, hydrolysis and positive GLC analysis for (i-butanol and) neo-hexanol (75%). In similar fashion, $Cp_2Zr(Cl)R''$ with DIBAH gave II and R_2AlR''.



(VI)

(IV′)

(3)

(R″ = neo-hexyl ; R = i-butyl)

The model studies described above clearly demonstrate that Zr-promoted reactions of aluminum hydrides might not proceed by simple ligand exchange processes but rather could involve complex mixed-metal hydride species. The study of catalytically active systems is, therefore now in progress.

Acknowledgements

The authors acknowledge generous support for this work given by the National Science Foundation (CHE 76-02130).

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*Here, as in III, the trialkulaluminum species acts simply as a Lewis acid toward a saturated metal hydride (dimeric) complex.