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Preliminary communication

LIGAND PROMOTED REDUCTIVE ELIMINATION FROM Zr(IV). THE PREPARATION OF ZIRCONACYCLES FROM ALKYLZIRCONIUM(IV) HYDRIDES AND ALKYNES

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SUMMARY

Alkynes induce reductive elimination of alkane from $Cp_2Zr(H)(R)$; zirconacyclopentadienes are formed as well.

In the course of our investigation of the chemistry of alkylzirconium(IV) hydride complexes[1] $Cp_2Zr(R)(H)$ (1), we found that their reaction with alkynes took an unexpected course: rather than reaction by hydride insertion[2] to give (alkyl)(alkenyl)zirconium complexes, elimination of RH occurred and zirconacyclopentadienes were formed.

Preparation of metallacycles (2) can be accomplished rapidly as follows: methylzirconium(IV) complex 1a was prepared as described.[3] A suspension of 295 mg (1.25 mmole) 1a in 10 ml benzene** was stirred with 8.8 mmole 3-hexyne

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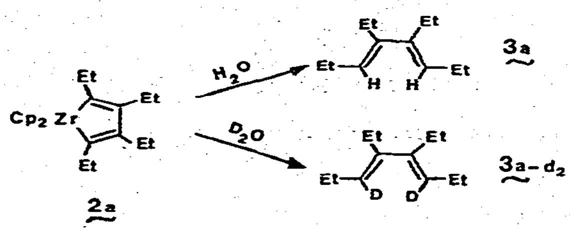
** All solvents were distilled under argon from sodium benzophenone ketyl. All reactions were performed under an atmosphere or dry argon.

at 70° overnight. The resulting red solution was filtered through Celite and the filtrate was evaporated to dryness. Deep red crystalline zirconacycle 2a (R' = Et) was thus isolated in 90% yield and was identified by NMR** and mass spectral† analysis. Hydrolysis of 2a gave 3a and deuterolysis gave 3a-d_2 in nearly quantitative yield as the only volatile products obtained.‡ Structures for these dienes were determined by NMR§ and mass spectral analysis.

[SCHEME 1]



Reaction of 1a with 4-methyl-2-pentyne gave a mixture of deep red metallacycles 2b and 2c (4:1) in 76% total yield.∇ Hydrolysis of the metallacycle mixture gave dienes 3b and 3c which were separated by preparative gas chromatography.# Structures for these dienes were determined by NMR∞ and mass spectral analysis. As expected, these dienes were formed in a 4:1 ratio, thus confirming NMR assignments∇ made for 2b and 2c.

** NMR for 2a (60 MHz in C_6D_6): δ 6.07 (s, 10H), 2.40 (q, 4, J = 7 Hz), 2.27 (q, 4, J = 7 Hz), 1.05 (t, 6, J = 7 Hz), 0.96 (t, 6, J = 7 Hz).

† Molecular ion corresponds to that calculated for $C_{22}H_{30}Zr$.

‡ The zirconium-containing hydrolysis product was not identified.

§ NMR for 3a vinylic proton: δ 5.45 (2H, t, J = 7 Hz), missing for 3a-d_2.

∇ NMR for 2b: δ 6.05 (10H, s), 2.86 (2H, septet, J = 7 Hz), 1.82 (6H, s), 1.07 (6H, d, J = 7 Hz);

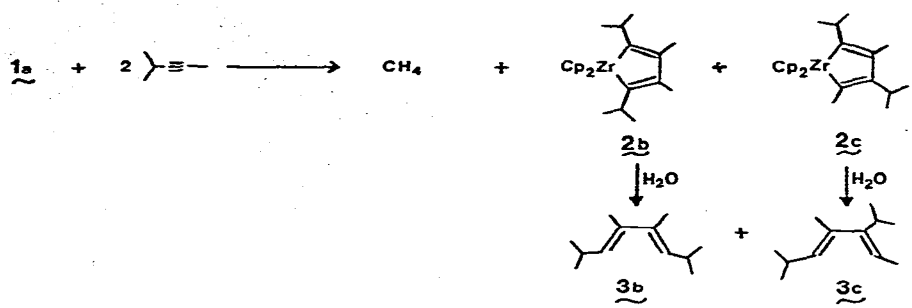
for 2c: δ 6.00 (10H, s), 3.2-2.6 (m, 2H), 1.89 (3H, s), 1.78 (3H, s), 1.31 (6H, d, J = 7 Hz), 0.95 (6H, d, J = 7 Hz).

Separated on 8' x 1/4" 10% Carbowax 20 M.

∞ NMR for 3b, vinylic protons, δ5.22 (2H, d, J = 8 Hz);

for 3c, vinylic protons, δ5.08 (1H, q, J = 8 Hz), 4.93 (1H, d, J = 8 Hz).

[SCHEME 2]



Reaction of 3-hexyne with labeled compound 1c (in benzene solution, room temp, overnight) gave the expected product of reductive elimination, 1,2-dideuteriomethylcyclohexane (80%).[a] In the absence of the alkyne, some alkane was formed under these conditions (ca. 10%). However, this alkane was a complex mixture[a] of methylcyclohexane-d_0, -d_1, and -d_2, indicating that, here, it was not formed by a simple reductive elimination process. These observations suggest that metallacycle formation in the presence of alkyne occurs as shown in Scheme 3.

We believe that the alkyne induces reductive elimination of alkane from $Cp_2Zr(H)(R)$. This can be explained through consideration of the coordination requirements of the metal: direct elimination of RH from "16-electron" complex 1 would involve formation of a "14-electron" intermediate; alkane elimination from "18-electron" species 4 would give a less highly unsaturated complex intermediate (5). This interpretation suggests that any potentially ligating species for Zr(IV) should foster reductive elimination from $Cp_2Zr(H)(R)$. Accordingly, studies involving such ligands (other than alkynes) are currently in progress.

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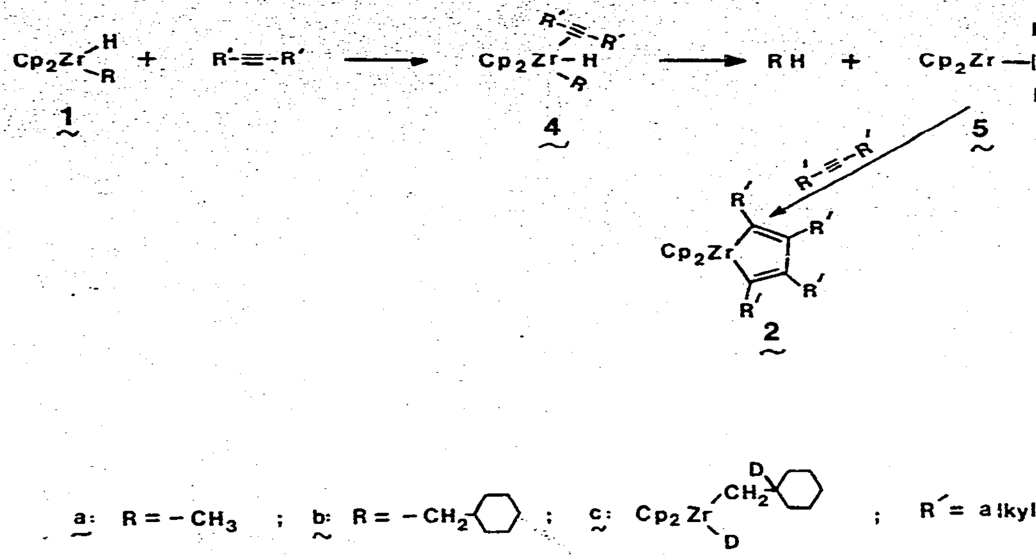
a Determined by gc-mass spectral analysis.

[SCHEME 3]



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