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Preliminary communication

COMPETITIVE PATHWAYS FOR THE CARBONYLATION OF ZIRCONOCENE ALKYL HYDRIDES

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SUMMARY

Competitive pathways for carbonylation of zirconocene alkyl hydrides give products of reductive elimination and multiple reduction of CO.

We recently suggested[1] that alkyl zirconium(IV) hydrido complexes $Cp_2Zr(H)R$ (R = alkyl) are models for conceivable intermediates in the Zr(IV)-catalyzed reductive polymerization of CO by aluminum hydrides.[2] To elucidate homologation steps in such Fischer-Tropsch type processes we have studied the reaction between $Cp_2Zr(H)R$ and CO. This procedure gives rise to condensation products formed by zirconium hydride reduction of zirconium acyls. Reductive elimination of R(H) from $Cp_2Zr(H)R$ is also observed; elimination is induced by the presence of CO.

A series of complexes, $Cp_2Zr(H)R$, were prepared[1] and were treated with CO. Reaction products were analyzed for organic products before and after hydrolysis. For example, **1a** (192 mg, 0.6 mmole) dissolved

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in 10 ml toluene reacted with CO (0.9 equiv) at 0° over 15 min giving methylcyclohexane (50%) as the major volatile product. Hydrolysis of the resulting mixture gave cyclohexylethanol (20%), cyclohexylacetaldehyde (5%), 3-cyclohexyl-2-oxopropanol (ca. 1%) and several trace unidentified oxygen-containing products.

Results of deuterium labelling studies suggest the sequence shown in Reaction 1.[*] Zirconium complex **1** becomes saturated by coordination of CO. The resulting 18 valence electron species (**2**) then partitions between reductive elimination of alkane and CO "insertion." For **1b**, the alkane formed is methylcyclohexane-d_1 (>95% d_1),[**] confirming that it is formed by straightforward reductive elimination.[3] [***] Alkyl group migration to coordinated CO is competitive with alkane elimination and should give rise to an acyl zirconium hydrido complex (**3**). This unobserved intermediate can then be reduced by another equivalent of **1** to give **4**. Consistent with this is the observation that hydrolysis of the reaction mixture with D_2O gives the alcohol **5**; as well, **1b**, on reaction with CO and protonolysis, also gives **5**.[†]

The postulated intermediate **4** can further insert CO to give a compound which yields an acyloin on hydrolysis (Reaction 2). As anticipated, the relative yield of this CO homologation product increases with increasing CO

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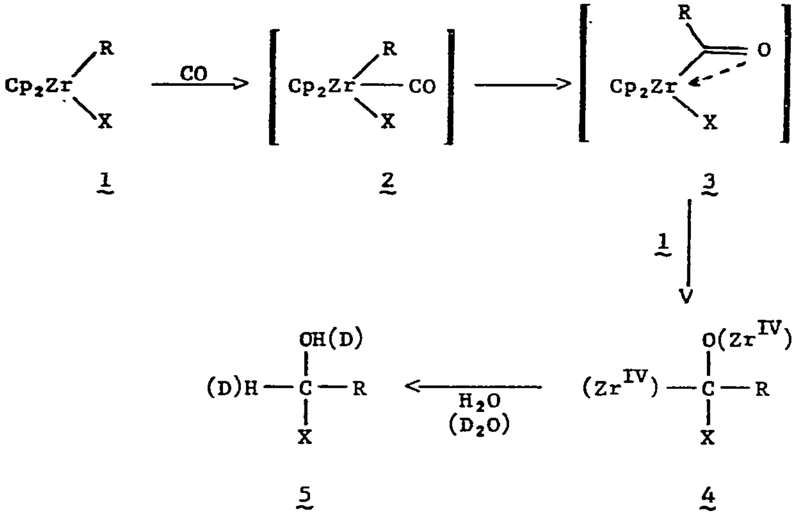
[*] **1** is dimeric in solution; we postulate that reaction with CO proceeds through a reactive monomer.[1]

[**] Methylcyclohexane-d_1 is almost exclusively labeled in the methyl group. Reductive elimination induced by CO is hence faster than scrambling of the hydride label between the β-position of the alkyl group and the metal.[1]

[***] $Cp_2Zr(CO)_2$ (approx. 25%) is also isolated. We note that $Cp_2Zr(CO)_2$ can react with **1** to give alkane as the only observed organic product prior to or on hydrolysis.

[†] A small yield of the corresponding aldehyde is produced on hydrolysis. The acyl carbon atom is derived from CO (proved by ^{13}CO labeling experiment and GC/MS). However, deuterium labeling experiments (**1b**, with H_2O workup) suggest that the aldehyde is not formed by a simple elimination from **3**.



1a: $Cp_2Zr(H)(cyclohexylmethyl)$

b: $Cp_2Zr(D)(cyclohexylmethyl)$

c: $Cp_2Zr(H)(CH_3)$

d: $Cp_2Zr(H)(cyclohexyl)$

pressure. Carbonylation (100 atm) of **1c** at room temperature for 4.5 hr gave, after hydrolysis, 2-oxopropanol as the major insertion product. Formation of the acyloin precursor by sequential insertion of CO was demonstrated as follows: Treatment of **1a** with ^{13}CO (1 atm) gave **6** (1%) (identified by GC/MS and ^{13}C NMR) which demonstrated that both of the added carbons are derived from CO. Treatment of **1a** with ^{13}CO (1 atm) followed by ^{12}CO (100 atm) gave **7** (5%) on hydrolysis. The structure of the acyloin precursor has not yet been established; ^{13}C NMR analysis of zirconium-containing materials prior to hydrolysis suggests that this precursor is not a simple acyl zirconium species.[‡]

The multiple reduction (Reaction 1) of CO by **1** has been modeled by

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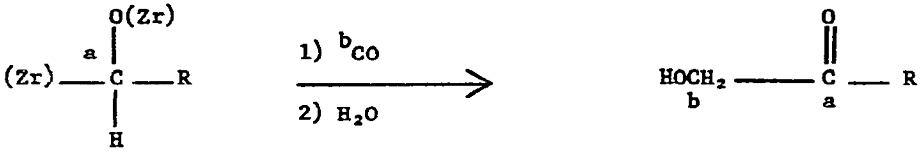
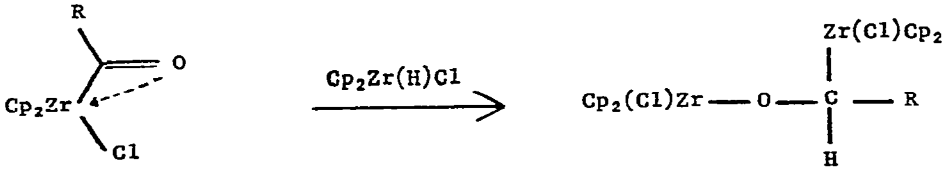
[‡] The structure of this acyloin has been verified by comparison with independently synthesized material.



6: $C_a = C_b = {}^{13}C$
7: $C_a = {}^{13}C$, $C_b = {}^{12}C$

examining the reaction between acylzirconium compound 8 and $Cp_2Zr(H)Cl$ (Reaction 3). The product obtained, 9, is analogous to the one reported for reduction of CO by $Cp_2Zr(H)Cl$.[4]



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R = (cyclohexylmethyl)

In the reaction between $Cp_2Zr(Cl)R$ with CO (to give isolable acyl complexes), the qualitative relative rates for acyl formation (with varying R) are cycloalkyl > n-alkyl.[5] It is noteworthy therefore that relative yields of reductive elimination versus insertion products for the reaction between 1 and CO depend on R: for R = cyclohexyl, 70% insertion and 5% elimination; for R = n-alkyl, 30% insertion and 50% elimination.

Our results using the C_5H_5 ligand are markedly different from those reported for permethyl zirconocene compounds. The reaction between $(C_5Me_5)_2Zr(H)R$ and CO[6] gives an enolate as the major zirconium-containing product and aldehyde as the only organic product observed on hydrolysis. In this case, bimolecular reduction of the acyl group of the zirconium acyl hydride complex may not be feasible for steric reasons, and reductive elimination of RCHO and rearrangement to the enolate could predominate. The observation of CO-induced elimination of RH from $(C_5H_5)_2Zr(H)R$ but not from $(C_5Me_5)_2Zr(H)R$ may be due simply to different relative alkyl "insertion" and reductive elimination rates from $(C_5X_5)_2Zr(H)(R)(CO)$, the reasons for which remain to be determined.

We had noted[3] that dialkylacetylenes cleanly induced reductive elimination from zirconocene alkyl hydrides to give metalacycles. CO-induced elimination from 1 enables the (low yield) synthesis of $Cp_2Zr(CO)_2$. These observations suggest that ligand-induced reductive elimination from 1 is a general route to reactive zirconium(II) complexes. Our results in this area will be reported shortly.

ACKNOWLEDGMENTS

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REFERENCES

1. K. I. Gell and J. Schwartz, J. Am. Chem. Soc., 100 (1978) 3246.
2. L. I. Shoer and J. Schwartz, J. Am. Chem. Soc., 99 (1977) 5831.
3. M. Yoshifuji, K. I. Gell, and J. Schwartz, J. Organometal. Chem., 153 (1978) C15.
4. G. Fachinetti, C. Floriani, A. Roselli, and S. Pucci, J. Chem. Soc., Chem. Commun. (1978) 269.
5. C. A. Bertelo and J. Schwartz, J. Am. Chem. Soc., 97 (1975) 228.
6. J. M. Manriquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, J. Am. Chem. Soc., 100 (1978) 2716.