Communication

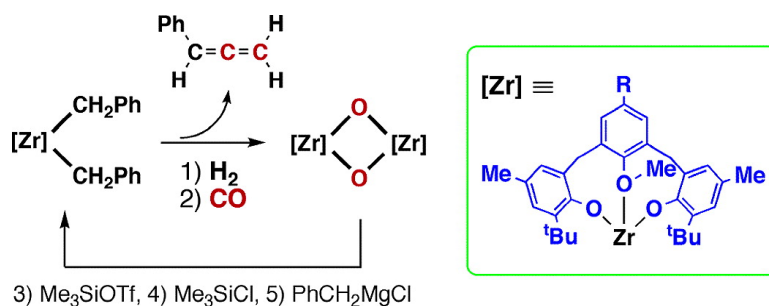# A Synthetic Cycle for H/CO Activation and Allene Synthesis Using Recyclable Zirconium Complexes

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A Synthetic Cycle for H₂/CO Activation and Allene Synthesis Using Recyclable Zirconium Complexes

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Fischer–Tropsch (F-T) synthesis is an important chemical reaction to convert H_2 and CO to hydrocarbons along with water, thereby giving access to organic chemistry on the basis of simple inorganic molecules.[1] The impressive F-T chemical transformation has elicited extensive synthetic efforts to reach chemical understanding of the heterogeneous F-T reaction and to produce soluble metal complexes that can react with H_2 and CO to form hydrocarbons with high product selectivity. Although many soluble metal compounds and reactions relevant to surface species in the heterogeneous F-T process are known,[2-4] well-characterized synthetic systems capable of converting H_2/CO into hydrocarbons have been limited. To explore the transformation of H_2 and CO with metal complexes, we have sought to use zirconium complexes supported by 2,6-bis(3-*tert*-butyl-5-methyl-2-oxybenzyl)-4-R-anisole ligands ([L^R]^{2-}; Scheme 1). Here we report that the [L^R]^{2-} complex of zirconium serves as an easily recycled auxiliary for converting H_2 and CO into allene and $(Me_3Si)_2O$ under mild conditions.

Treatment of the benzyl complex [L^R]Zr(CH₂Ph)₂ (1) with H_2 (1 atm) in toluene at room-temperature resulted in formation of the dinuclear complex {[L^R]Zr}₂(μ-H)(μ-CHPh) (2) in quantitative yield (Scheme 2). The X-ray crystal structure of 2a confirms that the two metal centers are bridged by one benzylidne ligand and two hydrides. This structural feature, coupled with the postulated involvement of alkylidene and hydride surface species in the heterogeneous F-T process,[1,5] led us to study carbonylation of 2 with CO.

Exposure of 2 to CO (1 atm) at room temperature led to clean formation of a bis(μ-oxo) complex {[L^R]Zr}₂(μ-O)₂ (3) and phenylallene. Complete conversion took 15.5 h according to NMR spectroscopy. Phenylallene was characterized by the NMR and GC–MS data. This reaction involves C–C bond formation, hydrogenation, and C–O bond cleavage. The pronounced oxophilicity of the zirconium center manifests itself in formation of 3 in quantitative yield.

To elucidate the reaction mechanism, we performed the reaction of 2a with isotopically enriched ¹³CO in C_6D_6. Monitoring the reaction by ¹³C{¹H} NMR spectroscopy revealed the presence of two detectable intermediates that gradually transform into the final product 3a along with formation of PhHC=¹³C=¹³CH₂ at room temperature (Figure 1). In the ¹³C{¹H} NMR spectrum of PhHC=¹³C=¹³CH₂, the ¹³C-labeled carbon appeared at δ 210.1 and 78.6 as two doublets with $^1J(^{13}C-^{13}C) = 98.7$ Hz. This unambiguously confirms that two carbon units of phenylallene originate from carbon monoxide. On the basis of NMR spectroscopy, the intermediates in the 2a/¹³CO reaction are tentatively characterized as two isomers of ketene–dihydride complexes {[L^R]Zr}₂(μ-H)₂(μ-PhCH=C=O) (A in Scheme 3), which differ by the orientation of the ketene fragment. In the ¹³C{¹H} NMR spectrum, the ¹³C-labeled ketene carbon of the two isomeric intermediates are observed as two singlets of approximately the same intensity at δ 205.6 and 198.0.
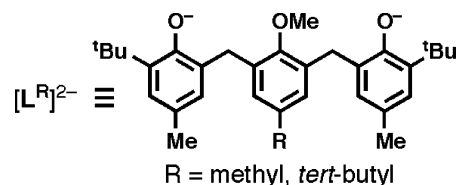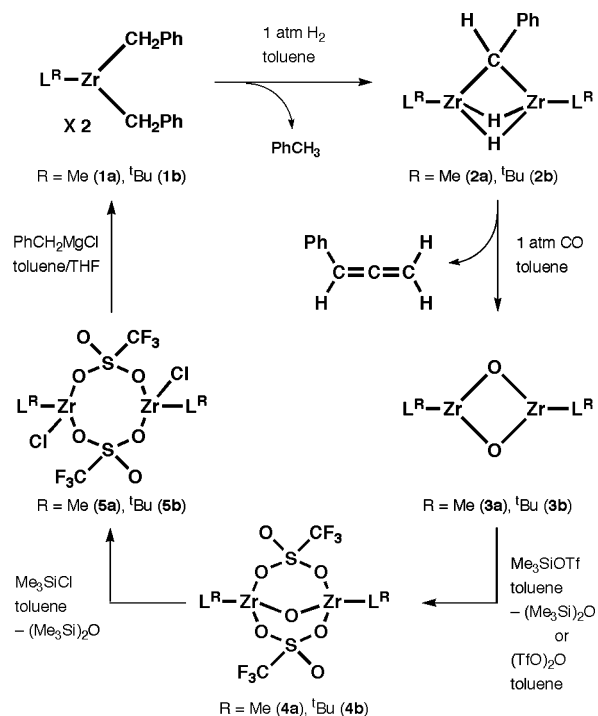
Additionally, in the absence of proton decoupling, each resonance splits into a doublet due to coupling to the vinylic proton of the ketene moiety with $^2J(CH) =$ ca. 13 Hz. The proposed mechanism shown in Scheme 3 is thus based on the observations described above and by the analogy with known reactions of CO with metal complexes.[2,6,7]

The first step is the insertion of CO into the benzylidene unit to give the metal-bound ketene in A,[6,8] as evidenced by NMR studies. A successive step is thought to be a second insertion of CO into one of the Zr–H bonds to give a ketene–formyl complex {[L^R]-Zr}₂(μ-H)(μ-PhCH=C=O)(μ-CHO) (B). The carbenoid character of the formyl ligand leads us to consider facile intramolecular coupling of formyl and ketene units,[4,7] followed by hydride transfer and concomitant deoxygenation leading to the oxo-bridged complex 3 and phenylallene. Obviously, other mechanisms can be considered,[9] including the reaction of the ketene complexes (A) with the second equivalent of CO to form transient {[L^R]Zr}₂(μ-PhCH=
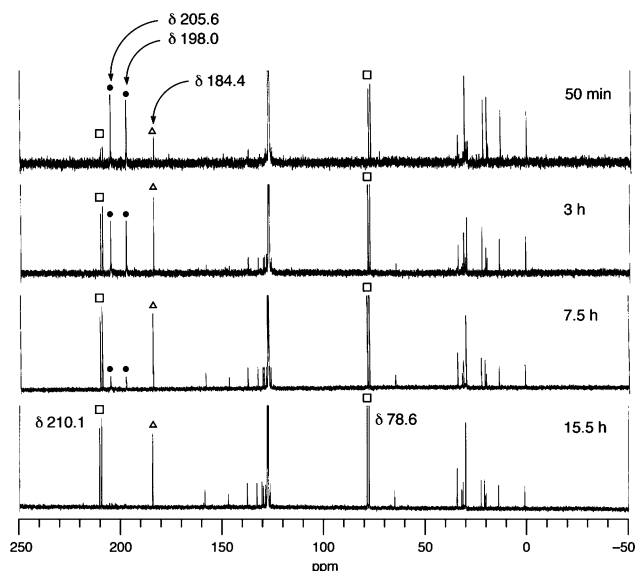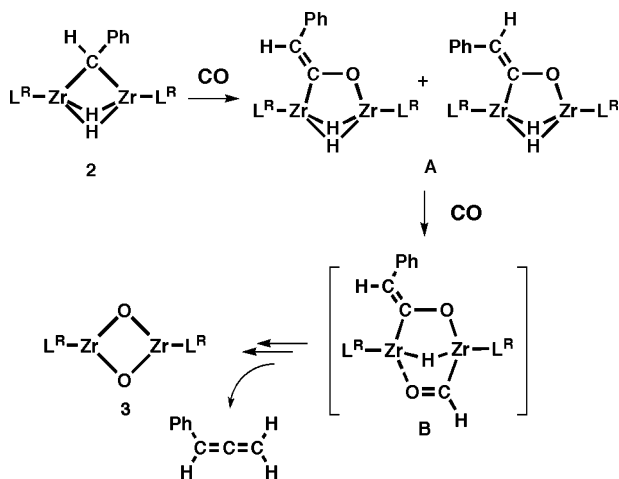
Figure 1. $^{13}C\{^{1}H\}$ NMR monitoring of the reaction of **2a** with ^{13}CO in C_6D_6 at room temperature; ketene intermediates (●), phenylallene (□), and free ^{13}CO (△).

Scheme 3. Proposed Mechanism for the Carbonylation of **2**

$C=O)(\mu\text{-}CH_2O)$ via double migration of two hydride groups followed by formaldehyde−ketene coupling and deoxygenation.

Following a recent protocol of Figueroa and Cummins,[10] treatment of **3** with trifluoromethanesulfonic anhydride (Tf$_2$O) in C$_6$D$_6$ led to clean conversion to $\{[L^R]Zr(OTf)\}_2(\mu\text{-}O)$ (**4**). Complex **4** did not react with excess Tf$_2$O due to the reduced nucleophilicity of the remaining oxo ligand in **4**. Next we examined the reactions of **3** with trimethylsilylated reagents, because the use of the trimethylsilyl moiety in the deoxygenation of oxo complexes could allow for favorable thermodynamic release of (Me$_3$Si)$_2$O. The reaction of **3** with 2 equiv of trimethylsilyltrifluoromethanesulfonate (Me$_3$SiOTf) in C$_6$D$_6$ quantitatively gave the oxo-OTf complex **4** along with (Me$_3$Si)$_2$O according to NMR spectroscopy, while increasing the amount of Me$_3$SiOTf resulted in a complicated mixture of products. When Me$_3$SiCl was used as a mild silylating reagent instead of Me$_3$SiOTf, we found that **4** could be slowly transformed into $\{[L^R]ZrCl\}_2(\mu\text{-}OTf)_2$ (**5**) upon treatment with

excess Me$_3$SiCl in toluene at room temperature for several weeks. On a preparative scale, **5** was isolated as colorless crystals in good yield. Finally, addition of 4 equiv of PhCH$_2$MgCl to **5** gave the corresponding dibenzyl complex **1**, which could be readily separated.

This study demonstrates a synthetic cycle having relevance to F-T chemistry, wherein zirconium alkyl complexes of the [L^R] ligands serve to transform H$_2$ and CO into corresponding allenes via alkylidene intermediates. This transformation involves the activation of H$_2$, formation of C−C, C−H bonds, C−O bond cleavage, and deoxygenative recycling of the oxo-bridging zirconium complexes. All of the preceding reactions are spectroscopically quantitative under mild conditions. Thus, there is much potential for yield optimization, including the combination of consecutive steps.

Supporting Information Available: Experimental procedures and the CIF file for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0567079