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# Hydrogenation of Carbon Monoxide by Tetranuclear Rare Earth Metal Polyhydrido Complexes. Selective Formation of Ethylene and Isolation of Well-Defined Polyoxo Rare Earth Metal Clusters

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The hydrogenation of CO over supported metals to hydrocarbons and oxygenates was discovered by Fischer and Tropsch over 80 years ago.[1] Since then, the Fischer−Tropsch (F−T) reaction has attracted widespread attention because it offers an economically attractive process for the production of low molecular weight commodity chemicals from coal or natural gas, especially in times of limited oil supply.[2] On the other hand, the heterogeneously catalyzed F−T process is inherently nonselective because it produces a Schulz−Flory distribution of hydrocarbons and oxygenates. In attempts to establish more selective catalyst systems and to have a better understanding of the mechanistic aspects, substantial attention has been directed to homogeneous systems. In this endeavor, extensive studies on the reaction of organometallic hydrido complexes with CO have been carried out. Previous studies have shown that the reaction of late transition metal hydrides with CO gives formyl species MC(O)H,[3] while early transition metal (including lanthanide and actinide) hydrides can afford further reaction products such as oxymethylene species $MOCH_2M$[4] and endiolates MOCH═CHOM.[5] Very recently, deoxygenative coupling between CO and a benzylidene/dihydrido binuclear zirconium complex was reported to give phenylallene and the corresponding dioxo zirconium complex.[6] We recently found that rare earth metal polyhydrido complexes can show unique reactivity toward a variety of unsaturated substrates including $CO_2$, isocyanates, and nitriles.[7] Here, we wish to report the reaction of CO with the tetranuclear yttrium and lutetium polyhydrido complexes, $\{Cp'Ln(\mu\text{-}H)_2\}_4(THF)$ ($Cp' = C_5Me_4SiMe_3$, Ln = Y (**1a**), Lu (**1b**)), which leads to selective formation of ethylene and structurally characterizable polyoxo and oxo/hydrido rare earth metal clusters. Oxymethylene and enolate species have been confirmed to be key intermediates in these reactions. The selective formation of ethylene by reduction of CO is rare. Previously reported examples are limited to alane ($AlH_3$) reduction of coordinated CO in $M(CO)_n$[8] and hydrogenation of CO on the surface of $ZrO_2/Al_2O_3$.[9] The ethylene formation mechanisms in these systems remained yet to be clarified.

The reaction of the tetranuclear yttrium octahydrido complex **1a** with CO (1 atm) in toluene at −10 °C occurred rapidly to give the hexahydrido/oxymethylene complex **2a** in 64% isolated yield within 3 min (Scheme 1 and Figure 1). When **2a** was stirred at −10 °C in the presence of CO for a few minutes and then at room temperature in the absence of CO for 1 h, the dioxo/tetrahydrido complex $(Cp'Y)_4(\mu_3\text{-}O)_2(\mu\text{-}H)_4(THF)$ (**4**) was obtained in 60% isolated yield. Simultaneous formation of ethylene was confirmed by NMR ($^1H$, $^{13}C$) and GC analyses.[10] Complex **4** could also be isolated directly from the reaction of **1a** with CO without isolation of **2a** (Scheme 1).

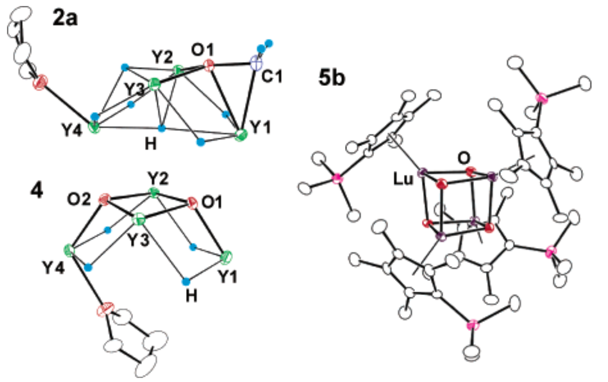
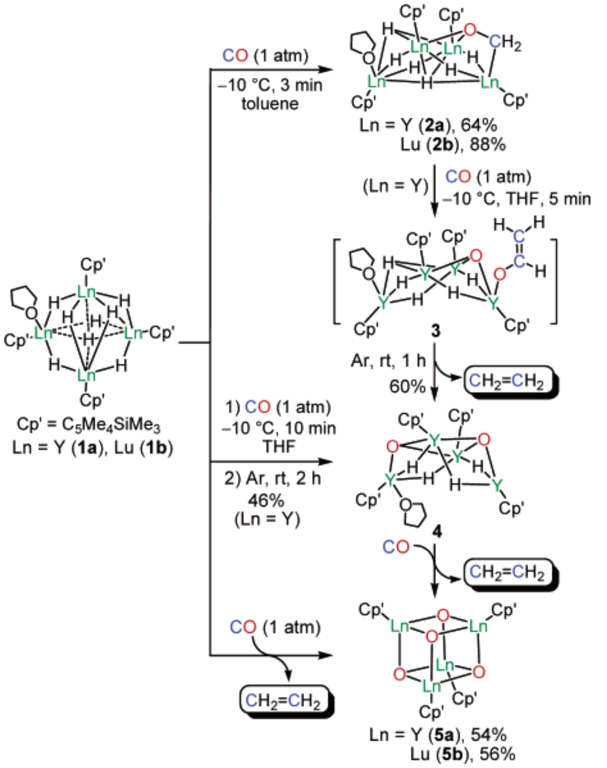


***Figure 1.*** ORTEP drawing of **2a**, **4**, and **5b**. The Cp′ ligands in **2a** and **4** have been omitted for clarity. Selected bond lengths (Å): (**2a**) C1−O1, 1.484(4); Y1−C1, 2.311(4); Y1−O1, 2.377(2); Y2−O1, 2.248(2); Y3−O1, 2.239(2). (**4**) Y−O (avg), 2.161. (**5b**) Lu−O (avg), 2.146.

***Scheme 1.*** Reactions of Yttrium and Lutetium Polyhydrido Complexes **1a**,**b** with Carbon Monoxide



A careful $^1H$ NMR monitoring of the reaction of **2a** with CO in THF-$d_8$ at low temperatures revealed formation of an enolate intermediate such as $(Cp'Y)_4(OCH{=}CH_2)(\mu\text{-}O)(\mu\text{-}H)_5(THF)$ (**3**; Scheme 1), as evidenced by the signals at $\delta$ 7.01 (dd, $J$ = 14.0, 5.4 Hz), 4.42 (d, $J$ = 14.0 Hz), and 4.03 (d, $J$ = 5.4 Hz).[11] These data are comparable with those reported for the enolate protons in

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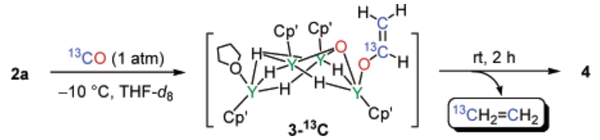
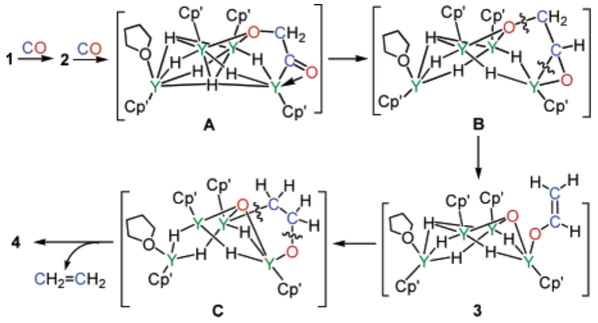
***Scheme 2.*** Reaction of the Hydrido/Oxymethylene Complex **2a** with $^{13}$C-Enriched Carbon Monoxide



***Scheme 3.*** Possible Mechanism for Ethylene Formation



[$(C_5H_5)_2Y(OCH^a{=}CH^b_2)$] ($\delta_a = 6.80$, $\delta_b = 4.16$, 4.03, and $J_{ab} = 12.5$, 5.4 Hz).[12] When the mixture was warmed to room temperature, clean formation of **4** and ethylene was observed together with the disappearance of the enolate species.

The $^{13}$C NMR monitoring of the reaction of **2a** with $^{13}$CO in THF-$d_8$ indicates the formation of the $Y(O^{13}CH{=}CH_2)$ species ($\delta$ 152.8, s) (**3**-$^{13}$C),[11] which on warming to room temperature yielded **4** and $^{13}CH_2{=}CH_2$ (Scheme 2). The reaction of **1a** with $^{13}$CO afforded $^{13}CH_2{=}^{13}CH_2$ and **4**, with the enolate species $Y(O^{13}CH{=}^{13}CH_2)$ being observed at $\delta$ 152.5 (d, $J(^{13}C-^{13}C) = 75.5$ Hz) and 92.7 (d, $J(^{13}C-^{13}C) = 75.5$ Hz).[13] No evidence for formation of an enediolate species such as Y(OCH═CHO)Y was observed.[5]

The reaction of the lutetium polyhydrido complex **1b** with CO (1 atm) in toluene at −10 °C afforded analogously the lutetium hexahydrido/oxymethylene complex **2b** in 88% isolated yield (Scheme 1). The reaction of **2b** with CO was, however, much slower than that of the yttrium analogue **2a**, which after 2 days at room temperature yielded the tetraoxo lutetium cubane complex **5b** with release of ethylene (Scheme 1 and Figure 1). $^1$H NMR monitoring of this reaction did not offer informative evidence for the identification of a possible reaction intermediate. The reaction of the yttrium tetrahydrido/dioxo complex **4** with CO took place rapidly at room or low temperature, which gave cleanly the corresponding tetraoxo complex **5a** and ethylene (Scheme 1).

On the basis of the above observations, a possible reaction mechanism could be proposed, as shown in Scheme 3. Addition of two Y−H bonds in **1** across the C−O triple bond of one molecule of carbon monoxide could give the oxymethylene complex **2** (see also Scheme 1). Subsequent insertion of another molecule of CO into the Y−CH$_2$ bond in **2** would afford an α-oxyacetyl species such as **A** (or its carbenoid isomer). Y−H bond addition across the acyl C−O double bond in **A** could yield the oxametallacyclopropane species **B**, which would produce the enolate species **3** through breaking a C−O bond and the C−Y bond. Addition of another Y−H bond across the C−C double bond of the enolate unit might give the $\beta$-oxyethylene species **C**, which after cleavage of the C−Y bond and the C−O bond yields the dioxo complex **4** with release of ethylene.[14] The formation of the tetraoxo complex **5a** and ethylene from the reaction of **4** with CO could follow an analogous process, although intermediate species analogous to the oxymethylene **2a** or an enolate species **3** were not observed.

In summary, the hydrogenation of carbon monoxide by the tetranuclear rare earth metal polyhydrido complexes **1a** and **1b** resulted in unprecedented selective formation of ethylene under mild conditions. This reaction also afforded a new series of well-defined novel polymetallic rare earth metal complexes, such as the hexahydrido/oxymethylene complex **2a**, the tetrahydrido/dioxo complex **4**, and the tetraoxo cubane complex **5b**, and might shed new light on the mechanistic aspects of the Fischer−Tropsch process.

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**Supporting Information Available:** Experimental details, ORTEP drawings, tables of crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles for **2a**, **4**, and **5b** (pdf, cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) When the reaction mixture containing **4** and ethylene was left at room temperature overnight, formation of the Y ethyl species was observed together with the disappearance of **4** and ethylene. Exposure of this reaction mixture to $H_2$ (1 atm) at room temperature resulted in the quantitative formation of ethane and **4**.
(11) An isomer of **3** might also be present. See Supporting Information for more details. Assignment was confirmed by $^1$H−$^1$H COSY.
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(13) This J(C−C) coupling constant is comparable with those reported for the monosubstituted ethylenes $CH_2{=}CHOR$, and is typical for a C−C double bond. See: Kamieñska-Trela, K. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1995; Vol. 30, p 148.
(14) An intermolecular process might also be possible.

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