Rare-Earth Complexes

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Reduction of Transition-Metal-Coordinated Carbon Monoxide by a Rare-Earth Hydride Cluster: Isolation of Well-Defined Heteromultimetallic Oxycarbene, Oxymethyl, Carbene, and Methyl Complexes**

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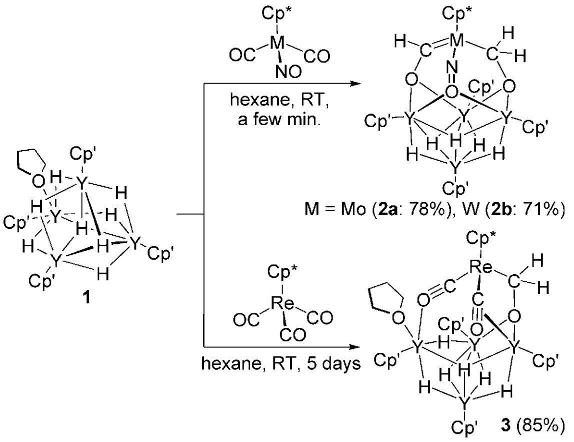
The reduction of coordinated carbon monoxide (CO) in transition-metal carbonyl complexes by metal hydrides[1–3] is of critical importance, not only for mechanistic aspects of the Fischer–Tropsch synthesis,[4] which involves the hydrogenation of CO in the presence of transition-metal catalysts, but also because of its potential applications in the development of homogeneous catalytic systems for the selective formation of hydrocarbons and oxygenates. To date, extensive studies have been carried out on the hydrogenation of coordinated CO by main-group-metal hydride reagents (e.g., $LiAlH_4$ and $NaBH_4$) or transition-metal hydride complexes, for example $[Cp^*_2ZrHX]$ ($Cp^* = C_5Me_5$; X = H, halide).[2,3] The formation of various products (or intermediates) such as formyl (M−CHO), oxycarbene (M=CHOM), enediolate (MOCH=CHOM), oxymethyl (MCH_2OM), and methyl (M−Me or M-CH_2-M) species has been observed, but only a limited number of these compounds has been structurally characterized. In contrast, the reduction of coordinated CO by rare-earth (Group 3 and lanthanide) metal hydrides has hardly been studied. The only precedent was the reaction of scandocene hydride complex $[Cp^*_2ScH(thf)]$ with $[CpCo(CO)_2]$ ($Cp = C_5H_5$), which yielded the scandoxycarbene species $[CpCo(CO)C(H)OScCp^*_2]$.[3f]

We recently found that rare-earth-metal polyhydride complexes bearing cyclopentadienyl ligands such as $[\{Cp'Y(\mu\text{-}H)_2\}_4(thf)]$ (**1**; $Cp' = \eta^5\text{-}C_5Me_4SiMe_3$) can show unique reactivity toward various unsaturated substrates, including gaseous CO and CO_2.[5–7] Herein, we report the reactions of the yttrium hydride cluster **1** with coordinated CO ligands in Group 6, 7, and 9 metal complexes, which afforded a new series of structurally well-defined heterometallic oxycarbene, oxymethyl, carbene oxo, and methyl oxo complexes. The reaction pattern depends on the nature of the transition-metal carbonyl complexes. Mechanistic aspects of these reactions are also described.

We first investigated the reaction of **1** with one equivalent of the Group 6 carbonyl complexes $[Cp^*M(CO)_2(NO)]$ (M = Mo, W; Scheme 1).[8] The mixture in hexane was kept at room temperature for several minutes, and the reaction yielded the mixed oxymethyl oxycarbene complexes **2a** and **2b**, respectively, as a result of the reduction of two C≡O bonds of carbonyl ligands by addition of the three Y−H bonds in **1**. No intermediates were observed by ^1H NMR spectroscopy. In the ^1H NMR spectrum of **2a**, the hydrogen atom attached to the oxycarbene carbon atom appeared far downfield at $\delta_H = 12.35$ ppm (1 H), whereas the oxymethyl hydrogen atoms were observed at $\delta_H = 4.53$ (1 H) and 4.58 ppm (1 H). The ^{13}C NMR spectrum of **2a** had resonances at $\delta_C = 307.1$ ppm for the oxycarbene carbon atom and $\delta_C = 66.9$ ppm for the oxymethyl carbon atom. The structures of **2a** and **2b** were confirmed by X-ray diffraction studies (Figure 1 a).[9] The X-ray structure analysis established the structural identity as an oxymethyl oxycarbene complex in which two carbonyl ligands were reduced by nucleophilic hydride ligands. Each oxygen atom forms a bridge between two yttrium atoms. The W1=C2 bond (1.889(11) Å) in **2b** is shorter than the corresponding bonds in $[Cp_2W{=}CHO{-}Zr(H)Cp^*_2]$ (2.005(13) Å)[3b] and $[(CO)_5W{=}CPh_2]$ (2.14(2) Å),[10] whereas the C2−O2 bond (1.374(11) Å) is comparable to that in $[Cp_2W{=}CHO{-}Zr(H)Cp^*_2]$ (1.35(2) Å).



Scheme 1. Reactions of **1** with $[Cp^*M(NO)(CO)_2]$ (M = Mo, W) or $[Cp^*Re(CO)_3]$.

Next, we examined the reaction of complex **1** with one equivalent of the Group 7 carbonyl complex

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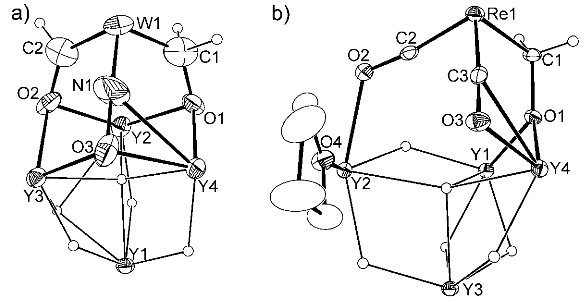
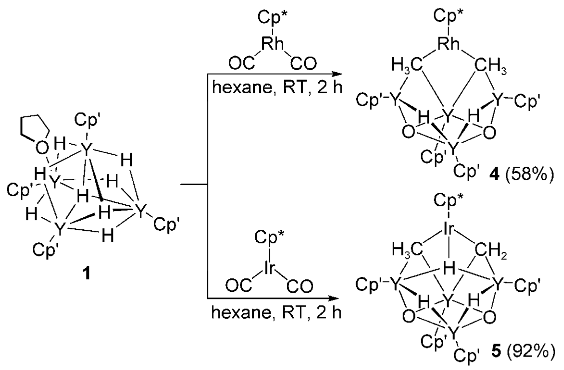


Figure 1. ORTEP diagrams of a) **2b** and b) **3** with 30% thermal ellipsoids. The Cp′ and Cp* ligands and the lattice solvent have been omitted for clarity. Selected bond lengths [Å]: **2b**: W1–C1 1.915(12), W1–C2 1.889(11), W1–N1 1.837(9), C1–O1 1.400(11), C2–O2 1.374(11), N1–O3 1.287(9), Y2–O1 2.301(5), Y4–O1 2.284(5), Y2–O2 2.265(6), Y3–O2 2.271(6), Y3–O3 2.286(6), Y4–N1 2.721(12), Y4–O3 2.318(6). **3**: Re1–C1 2.194(5), Re1–C2 1.824(6), Re1–C3 1.840(6), C1–O1 1.449(6), C2–O2 1.203(6), C3–O3 1.220(6), Y1–O1 2.188(4), Y4–O1 2.228(3), Y2–O2 2.344(4), Y4–C3 2.594(5), Y4–O3 2.473(4).



Scheme 2. Reactions of **1** with [Cp*M(CO)$_2$] (M = Rh, Ir).

[Cp*Re(CO)$_3$],[11] which gave oxymethyl dicarbonyl complex **3** as yellow crystals in 85% yield (Scheme 1). In this reaction, one C≡O bond of the carbonyl ligand in the rhenium tricarbonyl complex was reduced to an O–CH$_2$ single bond by addition of the two Y–H bonds in **1**. In the ^{1}H NMR spectrum, signals for the OCH$_2$ group were observed at δ_H = 4.46 (1H) and 4.64 ppm (1H) as two doublets (J_{HH} = 8.3 Hz), which are comparable to those in **2a**. The existence of two CO ligands in **3** was confirmed by its ^{13}C NMR spectrum (δ_C = 226.9 and 227.2 ppm); the IR spectrum also showed bands for a μ-η^1,η^2-CO ligand at 1674 cm^{-1} and a μ-η^1,η^1-CO ligand at 1767 cm^{-1}. An X-ray structure analysis showed that **3** contains one OCH$_2$ group, one μ-η^1,η^2-CO moiety, and one μ-η^1,η^1-CO moiety (Figure 1b). The C1–O1 bond (1.449(6) Å) is significantly longer than those of the carbonyl ligands (C2–O2 1.203(6) and C3–O3 1.220(6) Å) and comparable to that in **2b** (C1–O1 1.400(11) Å), so the bond can be viewed as a C–O single bond. Whereas O2 is obviously bonded to the Y2 atom (Y2–O2 2.344(4) Å), C2 is beyond a reasonable bonding distance (Y2–C2 3.184 Å), consistent with the μ-η^1,η^1 coordination mode of the CO ligand. By contrast, bonding interactions of Y4 with both C3 and O3 were observed for the μ-η^1,η^2-CO ligand (Y4–C3 2.594(5) and Y4–O3 2.473(4) Å).

These results show that the degree of reduction of the C≡O bonds of carbonyl complexes by **1** depends on the nature of the transition metal. Moreover, it also appears that C≡O bonds may be more reduced when the carbonyl complex has fewer CO ligands. We therefore examined the reduction of the C≡O bonds in the Group 9 carbonyl complexes [Cp*M(CO)$_2$] (M = Rh, Ir).[12] The reaction of complex **1** with one equivalent of the rhodium dicarbonyl complex [Cp*Rh(CO)$_2$] in hexane at room temperature for 2 h gave the dimethyl dioxo complex **4** in 58% yield (Scheme 2). In this reaction, two C≡O bonds of the carbonyl ligands in [Cp*Rh(CO)$_2$] were completely hydrogenated and cleaved by addition of six Y–H bonds of **1**. A similar C≡O bond cleavage of carbonyl ligands was observed in the reaction of **1** with the iridium carbonyl complex [Cp*Ir(CO)$_2$] (Scheme 2). The addition of five Y–H bonds in **1** to the two carbonyl ligands and one Y–H bond to the iridium metal center give the mixed methyl carbene dioxo hydride complex **5** in 92% yield.

In the ^{1}H NMR spectrum of **4**, the two μ-CH$_3$ ligands attached to the rhodium center were equivalent, giving a single signal at δ_H = −0.88 ppm (6H). The ^{13}C NMR spectrum showed a resonance for the μ-CH$_3$ carbon atom at δ_C = −8.4 ppm as a doublet of triplets (J_{CRh} = 35.7 Hz, J_{CY} = 8.1 Hz) as a result of coupling with one rhodium and two yttrium atoms. To identify the origin of the μ-CH$_3$ carbon atoms in **4**, we also performed the reaction of **1** with [Cp*Rh(^{13}CO)$_2$]. The ^{13}C NMR spectrum revealed the presence of a strong ^{13}C-labeled methyl carbon (Rh-^{13}CH$_3$-Y) signal at δ_C = −8.2 ppm (dt, J_{CRh} = 35.4 Hz, J_{CY} = 7.8 Hz; see Figure S1 in the Supporting Information). The ORTEP diagram of **4** clearly shows that there are no bonding interactions between C1(C2) and O1(O2) (Figure 2a). The bond lengths for Rh1–C1 (2.183(4) Å) and Rh1–C2 (2.192(4) Å) are slightly greater than those reported for [{Cp*Rh(CH$_3$)(μ-CH$_2$)}$_2$] (Rh–CH$_3$ 2.102(16) and 2.135(16) Å),[13] but within the range for a Rh–C σ bond. The bridging methyl carbon atoms C1 and C2 are not symmetrically located between the two yttrium centers that they bridge, with pairs of distances of 2.816(4)/2.699(4) and 2.811(5)/2.698(5) Å, respectively.

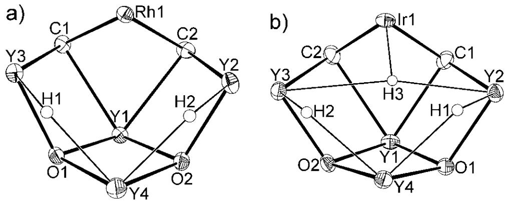
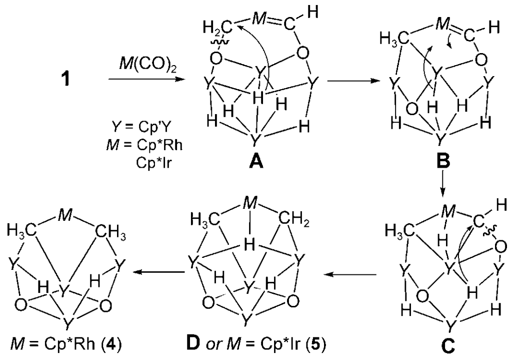


Figure 2. ORTEP diagrams of a) **4** and b) **5** with 30% thermal ellipsoids. The Cp′ and Cp* ligands and the lattice solvent have been omitted for clarity. Selected bond lengths [Å]: **4**: Rh1–C1 2.183(4), Rh1–C2 2.192(4), Y1–C1 2.699(4), Y1–C2 2.698(5), Y3–C1 2.816(4), Y2–C2 2.811(5), Y–O (av) 2.170; **5**: Ir1–C1 2.1776(13), Ir1–C2 2.1892(13), Y1–C1 2.5673(13), Y1–C2 2.7756(15), Y2–C1 2.5206(13), Y3–C2 2.7195(14), Y–O (av) 2.169.

The overall structure of **5** is similar to that of **4** (Figure 2b). However, the bonds Y1–C1 (2.5673(13) Å) and Y2–C1 (2.5206(13) Å) in **5** are much shorter than Y3–C2

(2.7195(14) Å) and Y1−C2 (2.7756(15) Å). The latter are comparable to those for the Y−CH_3 bonds in **4**. These results might suggest that **5** could contain one methyl carbon atom (C2) and one carbene carbon atom (C1). The ^1H and ^{13}C NMR spectrum of **5** showed that its structure in solution may be fluxional to some extent. The ^1H NMR spectrum had a singlet at $\delta_H = -0.77$ ppm assignable to the μ-CH_3 group. However, the ^{13}C NMR spectrum had a doublet at $\delta_C = -28.5$ ppm ($J_{CY} = 4.0$ Hz) for the methyl carbon, suggesting that this carbon atom has a significant bonding interaction with only one yttrium atom in solution, which is different from its solid-state structure. The μ-CH_2 carbene unit appeared in the ^{13}C NMR spectrum as a doublet of doublets at $\delta_C = 37.4$ ppm ($J_{CY} = 28.1$, 32.1 Hz), indicating that the carbene carbon atom has bonding interactions with two yttrium atoms, which is consistent with the solid-state structure. However, the ^1H NMR spectrum of the μ-CH_2 carbene unit had two doublets of doublets at $\delta_H = 0.12$ and -0.33 ppm ($J_{HY} = 11.1$, $J_{HH} = 15.6$ Hz), suggesting that the carbene protons only couple with one yttrium atom.

In an effort to obtain information pertaining to the mechanism of this C≡O bond cleavage, we monitored the reaction of **1** with [Cp*Rh(CO)$_2$] in [D$_8$]toluene by low-temperature ^1H NMR spectroscopy (Scheme 3, see also the Supporting Information, Figure S2). When the reaction was monitored at −20 °C for 20 min, an oxycarbene oxymethyl species **A** and a methyl carbene dioxo hydride species **D** were observed (**A**/**D** = 60:40). When the temperature was increased to 0 °C, **A** was gradually converted into **D** and a trace of complex **4** as the reaction proceeded. Finally, when the temperature was increased to room temperature, **D** was converted into **4** (about 60 %) together with by-products (about 40 %) and a small amount of ethene ($\delta_H = 5.25$ ppm).[14] Although intermediates **A** and **D** could be observed by ^1H NMR spectroscopy, they could not be isolated.



Scheme 3. Plausible reaction mechanism for the formation of **4** and **5**.

On the basis of these observations, we propose the following reaction mechanism for the formation of **4** and **5** (Scheme 3). Addition of three Y−H bonds in **1** across the two C≡O bonds in [Cp*M(CO)$_2$] (M = Rh, Ir) gives the oxycarbene oxymethyl complex **A**, which has a similar structure to **2a** and **2b**. Subsequently, nucleophilic substitution of the C−O bond by an Y−H bond in **A** affords the oxycarbene methyl oxo complex **B**, which has been detected as an intermediate from the reaction of **1** with [Cp*Ir(CO)$_2$] at −10 °C.[15] Addition of an Y−H bond across the M=C unit in **B** then gives the oxycarbene methyl oxo hydride complex **C**, which after substitution of the C−O bond by an Y−H bond in **C** yields the carbene methyl dioxo hydride complex **D** or **5**. Finally, formal reductive elimination of the CH_2 and the H groups from M (Rh) gives the dimethyl dioxo complex **4**. The formation of the Y_4Ir analogue of **4** from complex **5** was not observed, probably because reductive elimination from Ir has a higher energy barrier than from Rh.[16]

In summary, we have demonstrated the stepwise reduction of the C≡O bonds of carbonyl ligands in transition-metal complexes by a yttrium hydride cluster **1** to give novel heterometallic oxycarbene, oxymethyl, carbene oxo, and methyl oxo complexes. These reactions not only afford a new series of heterometallic complexes bearing a robust tetranuclear yttrium skeleton,[17] but they could also provide clues for the design of the homogeneous catalysts for selective reduction of CO to give hydrocarbons. Further studies on the reactivity of these complexes are now in progress.[18]

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