J. Am. Chem. Soc. 1995, 117, 4189−4190

Equilibrium between a Hydroxycarbene Complex and a Metal Acyl Hydride Complex

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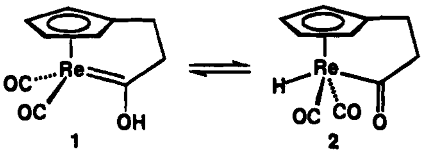
Received December 27, 1994

The amphiphilic rhenium carbene complex $Cp(CO)_2Re{=}CDCH_2CH_2CMe_3$ undergoes stereospecific addition of HCl to produce a single diastereomer of *cis*-$Cp(CO)_2ClReCHDCH_2CH_2CMe_3$,[1] but the absolute stereochemistry of the process could not be determined in part because rotation about the Re=C bond is expected to be fast.[2] In the course of synthesizing a rotationally restricted rhenium carbene complex having a two-carbon link between the cyclopentadienyl ligand and the carbene carbon atom, we discovered an equilibrium between the hydroxycarbene complex $(CO)_2Re{=}C(OH)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**1**) and the isomeric metal acyl hydride complex *trans*-$(CO)_2HReC({=}O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**2**).



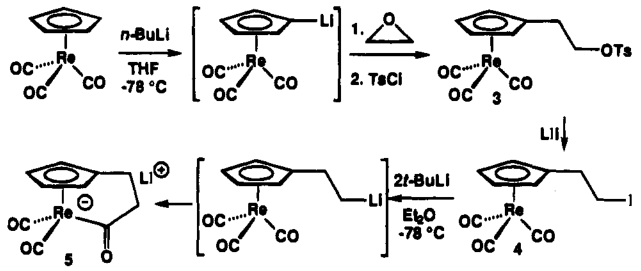
1 **2**

The first isolated transition metal hydroxycarbene complex was synthesized by Fischer in 1968 by protonation of a metal acyl anion.[3,4] Metal acyl hydrides have been synthesized[5] as models for key proposed intermediates in both hydroformylation[6] and aldehyde decarbonylation.[7] The equilibration of **1** and **2** reported here constitutes the first observation of the interconversion of a hydroxycarbene complex and its isomeric metal acyl hydride.

Our approach to a rotationally restricted rhenium carbene complex involved initial attachment of a 2-lithioethyl side chain to the cyclopentadiene ring of $CpRe(CO)_3$ followed by intramolecular attack of the lithium reagent on a carbonyl group (Scheme 1). Metalation of the cyclopentadienyl ring of $CpRe(CO)_3$[8] followed by reaction with ethylene oxide and then tosyl chloride gave the crystalline tosylate $(\eta^5\text{-}C_5H_4CH_2CH_2OTs)Re(CO)_3$ (**3**)[9] (89% yield), which was converted to the corresponding iodide $(\eta^5\text{-}C_5H_4CH_2CH_2I)Re(CO)_3$ (**4**) (85% yield)[9] by treatment with LiI in acetone.

Treatment of a solution of **4** in Et_2O at −78 °C with 2 equiv of *t*-BuLi gave the anionic acyl metal complex $Li^+[(CO)_2ReC({=}O)CH_2CH_2(\eta^5\text{-}C_5H_4)]^-$ (**5**)[9] as an air sensitive yellow powder in 48% overall yield from $CpRe(CO)_3$. The IR spectrum (THF) of **5** had two bands of equal intensity at 1898 and 1819 cm^{-1}, consistent with an anionic dicarbonyl complex.

Scheme 1



Protonation of an aqueous solution of **5** with HCl followed by extraction into CH_2Cl_2 led to the isolation of a mixture of the expected hydroxycarbene complex $(CO)_2Re{=}C(OH)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**1**) and the metal acyl hydride complex *trans*-$(CO)_2HReC({=}O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**2**) as a yellow oil. Treatment of this mixture of **1** and **2** with *n*-BuLi at −78 °C regenerated **5**. The ^1H NMR spectrum of the isolated oil in CD_2Cl_2 showed the presence of a 75:25 ratio of complexes, each with its own well-separated AA′ patterns for cyclopentadienyl protons and two triplets for the two-carbon tether.[9] The minor species (**1**) had a resonance at δ 11.00 assigned to a hydroxycarbene proton, while the major species (**2**) had a resonance at δ −8.69 characteristic of a metal hydride. Upon treatment with D_2O both the hydride and hydroxyl proton resonances disappeared immediately.

In the ^{13}C NMR spectrum of the mixture of **1** and **2** in CD_2Cl_2, a resonance at δ 292.5 was assigned to the carbene carbon of **1** and a more intense resonance at δ 234.3 was assigned to the acyl carbon of **2**. In the IR spectrum in CH_2Cl_2, carbonyl stretching bands at 1954 and 1870 cm^{-1} are attributed to **1** and bands at 2023 and 1925 cm^{-1} are attributed to **2**, as is a weak acyl band at 1615 cm^{-1}. In THF, an OH stretch for **1** was observed at 3643 cm^{-1}.

The ratio of hydroxycarbene complex **1** to metal acyl hydride **2** showed a strong solvent dependence. In THF-d_8, hydroxycarbene complex **1** was the only species observed by ^1H NMR; in acetone-d_6, a 91:9 **1**:**2** mixture was seen; and in C_6D_6, a 50:50 **1**:**2** mixture was seen. While there is no correlation of the equilibrium constant with solvent polarity, more of the hydroxycarbene is seen in the better hydrogen bonding solvents THF and acetone.

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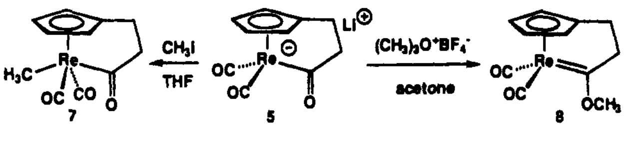
The interconversion of **1** and **2** is rapid at low temperature. When acetone-d_6 was condensed into a CD_2Cl_2 solution of **1** and **2** at −78 °C, the conversion from a 25:75 ratio of **1**:**2** to an 80:20 equilibrium mixture was monitored by ^1H NMR spectroscopy at −50 °C. Within 6 min, half of the excess **2** was converted to **1** and a 62:38 ratio of **1** : **2** was reached. After 45 min, an 80:20 equilibrium ratio of **1**:**2** was observed.

Our observation of an acyl hydride complex in equilibrium with a hydroxycarbene complex differs from Fischer's report of $(C_5H_5)(CO)_2Re{=}C(OH)CH_3$ (**6**)[3] for which only a hydroxycarbene isomer was observed. We repeated Fischer's synthesis of **6** and looked for evidence of an acyl hydride species. Close examination of the hydride region of the ^1H NMR spectra of **6** in either C_6D_6 (25 °C) or CD_2Cl_2 (−80 °C) showed no signals attributable to an acyl hydride. Similarly, the ^{13}C NMR spectrum in C_6D_6 showed a resonance at δ 286.7 for the carbene carbon of **6** and no evidence for an acyl hydride isomer. This implies that, in an untethered system such as **6**, the hydroxycarbene form is appreciably more stable than the acyl hydride. We propose that tethering the carbene carbon to the cyclopentadienyl ligand in **1** introduces significant strain which destabilizes the hydroxycarbene isomer and makes it comparable in energy to the acyl hydride isomer. As a result, both **1** and **2** can be observed in solution.

Evidence for strain in **1** relative to **2** came from studies of the regioselective methylation products of acyl anion **5**. Reaction of **5** with CH_3I in *THF* gave exclusive Re methylation, and the methyl acyl complex $(CO)_2(CH_3)ReC({=}O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**7**)[9] was isolated as a yellow oil in 43% yield. Regioselective methylation of **5** at oxygen was accomplished using $(CH_3)_3OBF_4$ in acetone. ^1H NMR spectroscopy of the reaction mixture showed exclusive formation of methoxycarbene complex $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**8**),[9] which was isolated as a yellow solid in 72% yield.



The X-ray crystal structure of tethered methoxycarbene complex **8** shows that ring closure produces a moderately strained $CpReL_3$ system in comparison with untethered carbene complexes such as $(C_5H_5)(CO)_2Re{=}C(OH)CH_3$ (**6**) (Figure 1). The alkyl tether of the cyclopentadienyl ring of **8** is bent down 9° toward Re [Cp(centroid)−C(6)−C(5) = 171°], while in untethered systems the alkyl groups bend up away from the metal center.[10] Ring strain also narrows the angle between the Cp centroid, rhenium, and the carbene carbon atom to 111.8° from the 126° ideal angle for a three-legged piano stool $CpReL_3$ system. This angle is close to the 112.2° Cp(centroid)−Re−acyl carbon angle seen in the four-legged piano stool complex *trans*-$Cp(CO)_2Re(COCH_3)CH_3$.[11] In general, four-legged piano stool complexes $CpML_4$ have substantially wider L−M−L angles and narrower Cp(centroid)−M−L angles than related three-legged piano stool compounds. Thus, tethering of the alkyl side chain introduces strain into the three-legged piano stool geometry of hydroxycarbene complex **1** but leaves the four-legged piano stool geometry of the metal acyl hydride complex **2** unstrained. Overall, tethering the side chain stabilizes **2** relative to **1** and provides a rationale for the observation of acyl metal hydrides only in tethered systems.

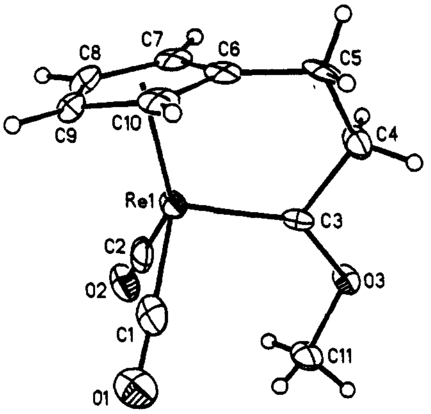


Figure 1. Structure of $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**8**). Selected bond lengths (Å) and angles (deg): Re−C(3), 1.982(10); C(3)−O(3), 1.329(12); O(3)−C(11), 1.483(12); Re−C(3)−C(4), 118.6(7); Re−C(3)−O(3), 136.2(7); C(3)−C(4)−C(5), 111.8(9); C(4)−C(5)−C(6), 111.5(8).

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Synthesis and characterization of compounds **1**−**8** and X-ray crystallographic data for **8** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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