

Cis Addition of Hydrogen Chloride to an Amphiphilic Carbene Complex

Charles P. Casey,* Curtis J. Czerwinski,
Douglas R. Powell, and Randy K. Hayashi

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received February 3, 1997

$\text{Cp}(\text{CO})_2\text{Re}=\text{CHCH}_2\text{CH}_2\text{CMe}_3$ (**1**) displays very unusual amphiphilic reactivity at the carbene carbon atom.¹ The carbene carbon atom of **1** was attacked by the nucleophile PMe_3 to give the zwitterionic complex $\text{Cp}(\text{CO})_2\text{ReCH}(\text{PMe}_3)\text{CH}_2\text{CH}_2\text{CMe}_3$ (**2**), but was also protonated by HCl to give the chloroalkylrhenium complex *cis*- $\text{Cp}(\text{CO})_2\text{ClReCH}_2\text{CH}_2\text{CH}_2\text{CMe}_3$ (**3**). While the addition of phosphines and other nucleophiles to the carbene carbon of **1** is similar to reactions of other d^6 carbene complexes, the protonation of the carbene carbon of **1** is highly unusual.^{2,3} The addition of HCl to $\text{Cp}(\text{CO})_2\text{Re}=\text{CDCH}_2\text{CH}_2\text{CMe}_3$ (**1-d**) at -53°C occurred stereospecifically to give a single diastereomer of *cis*- $\text{Cp}(\text{CO})_2\text{ClReCHDCH}_2\text{CH}_2\text{CMe}_3$ (**3-d**). Upon warming the reaction above -13°C , isomerization occurred to give a 1:1 mixture of the two possible diastereomers of **3-d** without loss of deuterium label.

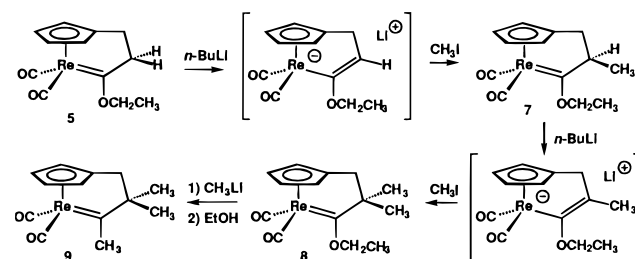
The stereochemistry of the HCl addition was undetermined, since we had not established the absolute stereochemistry of the product and, more importantly, we did not know whether the reactive conformation of **3-d** was the *syn* or *anti* rotamer. Rotation about the $\text{Re}=\text{C}$ bond is expected to be fast,⁴ and the ^1H NMR at -90°C shows only a single, possibly averaged, set of resonances for **1**. To determine the stereochemistry of the addition of HCl to amphiphilic carbene complexes, we synthesized a rotationally restricted analog of **1**, in which a tether between the cyclopentadienyl ring and the carbene carbon precludes rotation about the $\text{Re}=\text{C}$ bond. Here, we report X-ray crystallographic data showing that HCl adds across the $\text{Re}=\text{C}$ bond with *cis* stereochemistry.

We recently reported the synthesis of tethered methoxy- and ethoxycarbene complexes $(\text{CO})_2\text{Re}=\text{C}(\text{OCH}_3)\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ (**4**)⁵ and $(\text{CO})_2\text{Re}=\text{C}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ (**5**).^{6,7} Our initial plan for the synthesis of a tethered analog of **1** involved addition of a methyl nucleophile to either **4** or **5**, with subsequent loss of alkoxide. While related additions of nucleophiles to carbene complexes in this manner are well-known,⁸ we were unable to obtain the desired tethered dialkyl carbene complex by addition of a methyl nucleophile to **4** or **5** due to

competing deprotonation of acidic α -protons of the alkoxy-carbene complexes.⁹

To prevent deprotonation by the attacking nucleophile, the α -protons of **5** were replaced with methyl groups (Scheme 1). Reaction of **5** with *n*-BuLi in THF gave an ethoxycarbene anion that was immediately alkylated with CH_3I to give the mono-methylated complex $(\text{CO})_2\text{Re}=\text{C}(\text{OCH}_2\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ (**7**) as a yellow solid in 78% yield.¹⁰ The dimethylated complex $(\text{CO})_2\text{Re}=\text{C}(\text{OCH}_2\text{CH}_3)\text{C}(\text{CH}_3)_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ (**8**)¹⁰ was obtained as a bright yellow solid in 75% yield by reaction of **7** with *n*-BuLi in THF followed by alkylation with CH_3I .

Scheme 1



Neither ethoxycarbene complex **5** nor dimethylated ethoxycarbene complex **8** reacted with HCl. The alkoxy substituents greatly stabilize carbene complexes by electron donation to the carbene carbon and are probably responsible for the failure of **5** and **8** to react with HCl. While **8** did not react with PMe_3 , it did react with the much more nucleophilic CH_3Li . When a slight excess of CH_3Li (1.3 equiv) was added to a THF solution of **8** at -78°C and the solution was warmed to 25°C , a color change from bright yellow to dark red occurred over 3 h. After quenching the reaction with ethanol, the desired tethered methylcarbene complex $(\text{CO})_2\text{Re}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ (**9**) was isolated by thin-layer chromatography as an orange solid in 28% yield.¹⁰ Key features in the ^1H NMR spectrum of **9** include a singlet at δ 2.05 assigned to the methyl group on the carbene carbon atom and a singlet at δ 1.16 assigned to the α -methyl groups. A characteristic high-frequency ^{13}C NMR resonance at δ 328.1 provided evidence for the presence of a carbene carbon atom.¹¹

The dialkyl carbene complex **9** was much more reactive than the alkoxy-carbene complex **8**. When excess PMe_3 was added to a solution of **9** in CH_2Cl_2 at -78°C , an immediate reaction occurred to give the PMe_3 adduct $(\text{CO})_2\text{ReC}(\text{CH}_3)\text{P}(\text{CH}_3)_3\text{-C}(\text{CH}_3)_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ (**10**), which was isolated as a white solid

(1) Casey, C. P.; Vosejka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713.

(2) Previously, the only other carbene complex shown to have amphiphilic reactivity was Roper's $(\text{CO})_2(\text{Ph}_3\text{P})_2\text{Ru}=\text{CF}_2$. Clark, G. R.; Hoskins, S. V.; Jones, T. C.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1983**, 719.

(3) Other late transition metal carbene complexes have been shown to undergo protonation at the carbene carbon atom, but these complexes do not react with nucleophiles at the carbene carbon atom. (a) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079. (b) Hill, A. F.; Roper, W. R.; Waters, J. M.; Wright, A. H. *J. Am. Chem. Soc.* **1983**, *105*, 5939. (c) Clark, G. R.; Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1984**, *273*, C17.

(4) (a) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (c) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (d) Nakatsuji, H.; Ushio, J.; Han, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1983**, *105*, 426.

(5) Casey, C. P.; Czerwinski, C. J.; Hayashi, R. K. *J. Am. Chem. Soc.* **1995**, *117*, 4189.

(6) Casey, C. P.; Czerwinski, C. J.; Fusie, K. A.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 3971.

(7) The ethoxycarbene complex **5** was used in these studies, since **9** was readily separable by thin-layer chromatography from its ethoxycarbene precursor **8** but not from the related methoxycarbene complex.

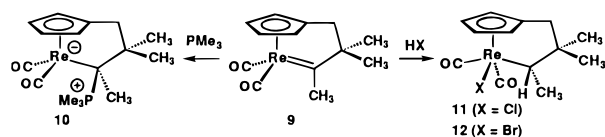
(8) (a) Klabunde, U.; Fischer, E. O. *J. Am. Chem. Soc.* **1967**, *89*, 7141. (b) Kreissl, F. R.; Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 643. (c) Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 563. (d) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5833. (e) Fischer, E. O.; Held, W. *J. Organomet. Chem.* **1976**, *112*, C59. (f) Fischer, E. O.; Held, W.; Kreissl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 656. (g) Fischer, E. O.; Held, W.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 3842. (h) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164. (i) Kim, H. P.; Angelici, R. J. *Organometallics* **1986**, *5*, 2489.

(9) For example, reaction of **4** with CH_3Li followed by quenching with CF_3COOH gave 84% yield of $(\text{CO})_2\text{Re}=\text{C}(\text{OCH}_3)\text{CHDCH}_2(\eta^5\text{-C}_5\text{H}_4)$ (**4-d**) with no recovery of undeuterated **4** and no observation of a methylcarbene complex. Reaction of **4** with $(\text{CH}_3)_2\text{CuLi}$ derived from CuI gave the unexpected product *trans*- $(\text{CO})_2\text{IrReC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ (**6**),¹⁰ possibly through rapid reaction of the undetected methyl carbene complex $(\text{CO})_2\text{Re}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)$ with $(\text{CH}_3)_2\text{CuLi}$, followed by quenching with iodine cation or radical.

(10) See the Supporting Information for experimental details and full characterization.

(11) (a) Kreiter, C. G.; Formacek, V. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 141. (b) Casey, C. P.; Sakaba, H.; Underiner, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 6673. (c) Casey, C. P.; Nagashima, H. *J. Am. Chem. Soc.* **1989**, *111*, 2352. (d) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. C.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852. (e) Darst, K. P.; Lenhart, P. G.; Lukehart, C. M.; Warfield, L. T. *J. Organomet. Chem.* **1980**, *195*, 317.

Scheme 2



in 50% yield (Scheme 2).¹⁰ The addition of PMe_3 breaks the symmetry of the dialkyl carbene complex, and the ^{13}C NMR spectrum of **10** exhibits two diastereotopic CO resonances at δ 211.4 and 209.9 along with five resonances for the inequivalent cyclopentadienyl carbons. Phosphine addition to the carbene carbon atom of **10** is supported by the observation of a ^{13}C NMR doublet ($J_{\text{PC}} = 11.8$ Hz) at δ 13.3 assigned to the alkyl carbon bound to rhenium and of a ^1H NMR doublet ($J_{\text{PH}} = 23.9$ Hz) at δ 2.02 assigned to the adjacent methyl group. Two IR bands of equal intensity at 1863 and 1786 cm^{-1} are consistent with an anionic Re(I) dicarbonyl center.

The reaction of **9** with HCl was examined at low temperature by ^1H NMR spectroscopy. A slight excess of anhydrous HCl was condensed into an NMR tube containing a frozen sample of **9** in CD_2Cl_2 at 77 K. The tube was placed in a precooled NMR probe at -80 °C, and quantitative formation of a single new compound, the HCl adduct *cis*-(CO)₂ClReCH(CH₃)C(CH₃)₂CH₂(η^5 -C₅H₄) (**11**),¹⁰ was observed. The ^1H NMR spectrum showed four cyclopentadienyl multiplets at δ 5.87, 5.75, 5.42, and 5.08, a quartet at δ 3.92 for the proton that had added to the carbene carbon atom, and a doublet at δ 1.60 for the methyl group bound to the original carbene carbon atom. In the ^{13}C NMR spectrum of **11**, two carbonyl resonances were observed at δ 207.9 and 202.5. The IR spectrum showed bands at 2027 and 1928 cm^{-1} in a 1.2:1.0 intensity ratio consistent with a *cis*-(CO)₂Re(III) species.¹² Evaporation of the solvent led to the isolation of **11** as a yellow solid in quantitative yield.

When the reaction was slowly warmed to 25 °C, the ^1H NMR spectrum remained unchanged, indicating that **11** was the kinetic HCl addition product. Even after the reaction stood at room temperature for several days, the spectrum of **11** remained unchanged and no isomerization was seen.

Slow evaporation of a saturated CH_2Cl_2 /pentane solution of **11** gave single crystals suitable for X-ray diffraction.¹³ The crystal structure of **11** shows that the Cl and the H on C3 are on the same side of the Re–C3 bond (Figure 1). This establishes the *cis* stereochemistry of the addition of HCl across the Re=C bond of **9**. *Cis* addition is consistent with concerted addition of HCl across the Re=C bond. While protonation at Re,¹⁴ followed by hydride migration to carbon, cannot be rigorously excluded, it seems unlikely that such a process would lead to stereospecific addition.

(12) (a) Hill, R. H.; Palmer, B. J. *Organometallics* **1989**, *8*, 1651. (b) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. *Organometallics* **1986**, *5*, 53.

(13) See Supporting Information for full details of X-ray structure determination.

(14) (a) Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783. (b) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500. (c) Allen, D. L.; Green, M. L. H.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 541. (d) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Organometallics* **1992**, *11*, 237. (e) Casey, C. P.; Tanke, R. S.; Hazin, P. N.; Kemnitz, C. R.; McMahon, R. J. *Inorg. Chem.* **1992**, *31*, 5474. (f) Gusev, D. G.; Nietlispach, D.; Eremenko, I. L.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3628. (g) Low-temperature protonation at Re has been observed for $\text{Cp}^*(\text{CO})_2\text{Re}(\text{H}_2\text{C}=\text{CH}_2)$ and $\text{Cp}^*(\text{CO})_2\text{Re}(\text{MeC}\equiv\text{CMe})$: Casey, C. P.; Yi, C. S.; Brady, J. T. Unpublished results.

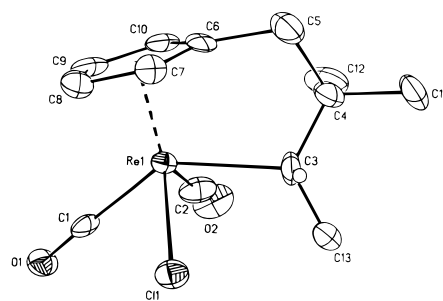


Figure 1. Structure of *cis*-(CO)₂ClReCH(CH₃)C(CH₃)₂CH₂(η^5 -C₅H₄) (**11**). Bond lengths (Å): Re(1)–C(3), 2.329(12); Re(1)–Cl(1), 2.489(3). Bond angles (deg): C(3)–Re(1)–Cl(1), 77.5(4); C(3)–Re(1)–C(2), 79.9(6); C(3)–Re(1)–C(1), 139.6(5); C(1)–Re(1)–C(2), 79.3(2); Cp(cent)–Re(1)–C(3), 103.6°; Cp(cent)–C(6)–C(5), 174.2°.

The related HBr addition product *cis*-(CO)₂BrReCH(CH₃)C(CH₃)₂CH₂(η^5 -C₅H₄) (**12**)¹⁰ was obtained in quantitative yield from addition of anhydrous HBr to a CD_2Cl_2 solution of **9**. The proton that had added to the carbene carbon atom appeared at higher frequency for **12** (δ 4.25) than that for HCl adduct **11** (δ 3.92). When HCl adduct **11** was treated with excess HBr at -80 °C, no formation of **12** was observed, and the spectrum of **11** remained unchanged even upon warming to 25 °C. Similarly, when HBr adduct **12** was treated with excess HCl at -80 °C, no formation of **11** was observed, and the spectrum of **12** remained unchanged upon warming to 25 °C. These results indicate that halide dissociation does not readily occur from either **11** or **12**. The acyclic HCl adduct **3** also failed to interconvert with its related HBr adduct.¹⁵

The tethered HCl and HBr addition products **11** and **12** are remarkably less reactive than their acyclic analogs. While the stereospecifically formed acyclic adduct **3-d** isomerized to a 1:1 mixture of the two possible diastereomers of **3-d** at -13 °C,¹ no evidence for isomerization of the tethered adduct **11** was seen even after long time periods at 25 °C. While acyclic adduct **3** lost HCl at 17 °C to form alkene complex $\text{Cp}(\text{CO})_2\text{Re}(\text{H}_2\text{C}=\text{CHCH}_2\text{CMe}_3)$,¹ the tethered adducts **11** and **12** were stable at 25 °C. While the acyclic HCl adduct **3** added a second equivalent of HCl at low temperature to generate the chain-extended hydroxycarbene complex *cis*-Cp(CO)₂Re=C(OH)CH₂CH₂CH₂CMe₃,¹⁵ no evidence for addition of HCl or HBr to tethered adducts **11** or **12** to produce related hydroxycarbene complexes was seen.¹⁶ The precise way in which the tether destabilizes the transition states for rearrangement of adducts **11** and **12** is not understood.

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

Supporting Information Available: Synthesis and characterization of compounds **6–12** and X-ray crystallographic data for **11** (12 pages). See any current masthead page for ordering and Internet access instructions.

JA970354Z

(15) Casey, C. P.; Sakaba, H.; Underiner, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 6673.

(16) Previous studies show that the longer tether length required for formation of a chain-extended hydroxycarbene complex is easily achieved.⁶ Perhaps, the restricted geometry of the tethered complexes is not optimal for intramolecular hydrogen bonding between the hydroxyl group and Cl.