Ring Strain Perturbation of the Equilibria between Hydroxycarbene Complexes and Metal Acyl Hydride Complexes

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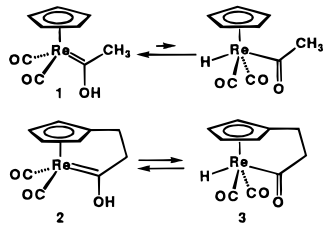
Abstract: The acyl anion complex $[(CO)_2ReC(=O)CH_2CH_2(\eta^5\text{-}C_5H_4)]^-Li^+$ (**7**) in which a two-carbon tether links the cyclopentadienyl ring to the acyl carbon was synthesized by attachment of a 2-lithioethyl side chain to the cyclopentadiene ring of $CpRe(CO)_3$ followed by intramolecular attack of the lithium reagent on a carbonyl group. Alkylation of **7** with $(CH_3)_3O^+BF_4^-$ occurred at oxygen to give the methoxycarbene complex $(CO)_2Re{=}C(OCH_3)CH_2\text{-}CH_2(\eta^5\text{-}C_5H_4)$ (**9**), which was shown by X-ray crystallography to have significant strain associated with the tethered ring. Protonation of **7** gave a mixture of hydroxycarbene complex $(CO)_2Re{=}C(OH)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**2**) and the metal acyl hydride complex *trans*-$(CO)_2HReC(=O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**3**). The unusual observation of the metal acyl hydride is attributed to the two-carbon tether introducing strain into the three-legged piano stool geometry of **2** but leaving the four-legged piano stool geometry of **3** relatively unstrained. In agreement with this hypothesis, no strain was apparent in the X-ray structure of the three-carbon-tethered methoxycarbene complex $(CO)_2Re{=}C\text{-}(OCH_3)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**17**) and only the hydroxycarbene tautomer $(CO)_2Re{=}C(OH)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**18**) was observed at equilibrium. A two-carbon tether did not introduce sufficient strain into the aminocarbene complex $(CO)_2Re{=}C[NH(CH_3)]CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**19**) to allow observation of its iminoacyl hydride tautomer.

Introduction

Metal acyl hydride complexes are important in organometallic chemistry as key proposed intermediates in hydroformylation and aldehyde decarbonylation.[1] A number of stable acyl hydride complexes have been isolated.[2] Hydroxycarbene complexes are important as proposed intermediates in CO reduction processes, including the Fischer−Tropsch process.[3] In 1968, Fischer isolated the first transition metal hydroxycarbene complex, $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OH)CH_3$ (**1**), by protonation of a rhenium acyl anion.[4] Since Fischer's report, other hydroxycarbene complexes have been synthesized by protonation of acyl anions, by addition of HX to metal alkyl complexes, and by other methods.[5] Although metal acyl hydrides and hydroxycarbene complexes are tautomers, no one has previously reported an equilibrium between the two isomers. For example, Fischer saw no metal acyl hydride in equilibrium with **1**.

We have found that introduction of a two-carbon tether between the carbene carbon and the cyclopentadienyl ring of Fischer's compound perturbs the equilibrium between hydroxycarbene complexes and metal acyl hydrides to such a large extent that both isomers are readily observed in equilibrium. We have hypothesized that the tether introduces ring strain into the three-legged piano stool geometry of the hydroxycarbene complex $(CO)_2Re{=}C(OH)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**2**) but leaves the four-legged piano stool geometry of the metal acyl hydride complex *trans*-$(CO)_2HReC(=O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**3**) relatively



unstrained.[6] Here we report the full details of this first observation of an equilibrium between a hydroxycarbene

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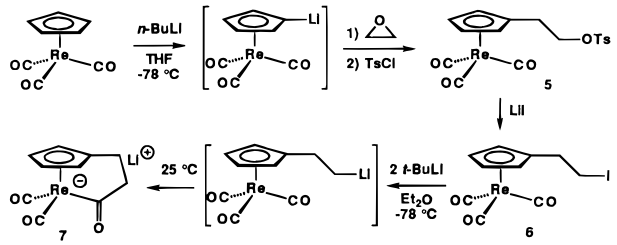
Scheme 1



complex and its isomeric metal acyl hydride. Support for the ring strain hypothesis was obtained from the observation that an unstrained longer chain tethered compound behaves like Fischer's hydroxycarbene complex **1** in that only the carbene tautomer is observed.

Results and Discussion

The rhenium carbene complex $Cp(CO)_2Re{=}CHCH_2CH_2CMe_3$ (**4**) displays highly unusual amphiphilic behavior: both nucleophiles and electrophiles added to the carbene carbon of **4**.[7] While the addition of nucleophiles such as PMe_3 to the carbene carbon of **4** to give $Cp(CO)_2ReCH(PMe_3)CH_2CH_2CMe_3$ is the expected reactivity of a d^6 carbene complex such as **4**, the addition of the electrophile H^+ to the carbene carbon of **4** in its reaction with HCl is very unusual and was investigated in detail. The addition of HCl to the deuterium-labeled carbene complex $Cp(CO)_2Re{=}CDCH_2CH_2CMe_3$ (**4-*d***) occurred stereospecifically to give a single diastereomer of *cis*-$Cp(CO)_2ClReCHDCH_2CH_2CMe_3$.[7] However, the absolute stereochemistry of this process could not be determined because of the expected rapid rotation about the Re=C bond which interconverts syn and anti rotamers about the Re=C bond.[8] To determine the absolute stereochemistry of the addition of HCl across the Re=C bond, we set out to construct complexes in which rotation about the Re=C bond was prevented by the incorporation of a two-carbon tether between the cyclopentadienyl ring and the carbene carbon atom.[9]

Synthesis of an Acyl Rhenium Anion with a Two-Carbon Tether. Our synthetic 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). Reaction of $CpRe(CO)_3$ with *n*-BuLi in THF at −78 °C generated the known ring-metalated complex $(\eta^5\text{-}C_5H_4Li)Re(CO)_3$[10] which reacted with ethylene oxide and then tosyl chloride to give the tosylate $(\eta^5\text{-}C_5H_4CH_2CH_2OTs)Re(CO)_3$ (**5**) as a white solid in 89% isolated yield.

Tosylate **5** was characterized spectroscopically and by X-ray crystallography (Figure 1). As expected for an unstrained $CpML_3$ three-legged piano stool complex, the angles between the carbonyl ligands are near 90° (87.5, 88.7, and 92.0) and the Cp centroid−Re−CO angles are 126°. The alkyl side chain is bent slightly away from Re (182.7° Cp centroid−C(8)−C(9) angle). These angles in the unstrained complex **5** are important for comparison with strain in the tethered hydroxycarbene complex **2** as detailed later.

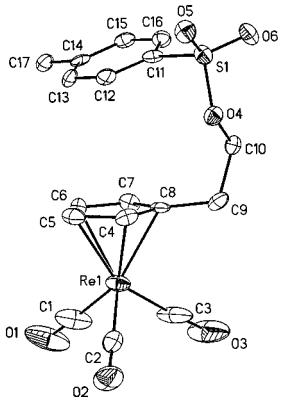
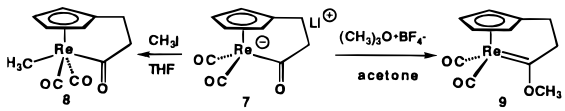


Figure 1. X-ray crystal structure of $(CO)_3Re(\eta^5\text{-}C_5H_4CH_2CH_2OTs)$ (**5**).

Reaction of **5** with LiI gave the iodide $(\eta^5\text{-}C_5H_4CH_2CH_2I)Re(CO)_3$ (**6**) in 85% isolated yield.[11] When a solution of iodide **6** in Et_2O at −78 °C was treated with 2 equiv of *t*-BuLi and then warmed to room temperature, lithium−halogen exchange followed by intramolecular attack on a carbonyl ligand gave the desired acyl anion complex $[(CO)_2ReC(=O)CH_2CH_2(\eta^5\text{-}C_5H_4)]^-Li^+$ (**7**) which was isolated as an air sensitive yellow powder in 59% yield.[12] The ^1H NMR spectrum of **7** in THF-d_8 exhibited two AA′BB′ pseudotriplets at δ 5.20 and 5.11 assigned to the two sets of cyclopentadienyl protons and two triplets at δ 2.83 and 1.98 assigned to the two methylene groups of the alkyl side chain. The observation of two bands of equal intensity at 1898 and 1819 cm^{-1} in the IR spectrum (THF) is consistent with the formulation of **7** as an anionic dicarbonyl complex.

Alkylation of Rhenium Acyl Anion 7 at Oxygen and at Re. By changing reagents, we were able to regioselectively methylate **7** at either rhenium or oxygen. Reaction of **7** with CH_3I gave exclusive Re methylation on the basis of ^1H NMR spectroscopy of the crude reaction mixtures. Reaction of **7** with CH_3I in THF gave the methyl acyl complex $(CO)_2(CH_3)ReC(=O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**8**) as a yellow oil in 45% yield. Regioselective methylation of **7** at oxygen to give **9** was



best accomplished using $(CH_3)_3O^+BF_4^-$ in acetone.[13] ^1H NMR spectroscopy of the reaction mixture showed exclusive formation of methoxycarbene complex $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**9**), which was isolated as a yellow crystalline solid in 75% yield. Similarly, reaction of **7** with $(CH_3CH_2)_3O^+BF_4^-$ gave the ethoxycarbene complex $(CO)_2Re{=}C(OCH_2CH_3)CH_2$-

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(11) The bromide $(\eta^5\text{-}C_5H_4CH_2CH_2Br)Re(CO)_3$ was made similarly. See the Supporting Information for full experimental details and characterization.

(12) Reaction of the bromide $(\eta^5\text{-}C_5H_4CH_2CH_2Br)Re(CO)_3$ with *n*-BuLi gave the elimination product $(\eta^5\text{-}C_5H_4CH{=}CH_2)Re(CO)_3$. Reaction of the bromide with *t*-BuLi gave a 67:33 mixture of elimination and metal−halogen exchange products. Reaction of the iodide with *n*-BuLi gave a 38:62 mixture of elimination and metal−halogen exchange products. See the Supporting Information for full experimental details and characterization.

(13) Methylations of **7** with $(CH_3)_3O^+BF_4^-$, CH_3I, and $CF_3SO_3CH_3$ in acetone, THF, and CH_2Cl_2 were analyzed by ^1H NMR spectroscopy. For $(CH_3)_3O^+BF_4^-$, in acetone, **8**:**9** = 0:100 (72% yield), in THF, **8**:**9** = 33:67 (88% yield), and in CH_2Cl_2, **8**:**9** = 33:67 (55% yield). For CH_3I, in acetone, **8**:**9** = 100:0 (75% yield), in THF, **8**:**9** = 100:0 (43% yield), and in CH_2Cl_2, **8**:**9** = 100:0 (55% yield). For $CF_3SO_3CH_3$, in acetone, **8**:**9** = 20:80 (39% yield), in THF, **8**:**9** = 25:75 (20% yield), and in CH_2Cl_2, **8**:**9** = 20:80 (48% yield).

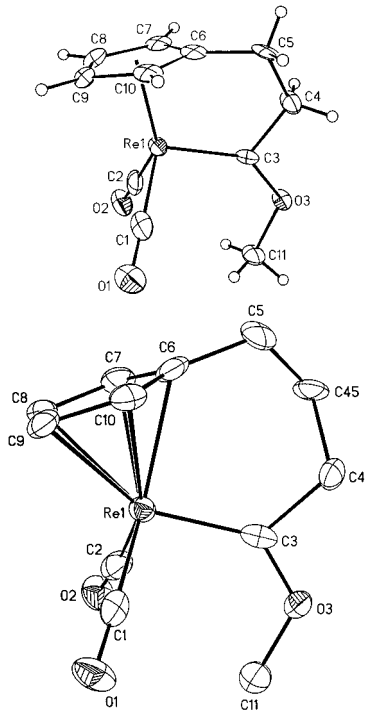


Figure 2. Top: X-ray structure of $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**9**). Bottom: X-ray structure of $(CO)_2Re{=}C(OCH_3)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**17**).

$CH_2(\eta^5\text{-}C_5H_4)$. Bergman and Goldberg observed similar dependence of regioselectivity on the nature of the alkylating agent in studies of the acyl anion $[(\eta^5\text{-}C_5H_5)Re(CO)_2COCH_3]^-Li^+$.[14]

The X-ray crystal structure of tethered methoxycarbene complex **9** (Figure 2, top) shows that ring closure produces a moderately strained $CpReL_3$ system in comparison with untethered carbene complexes such as $(C_5H_5)(CO)_2Re{=}C(OH)CH_3$ (**1**). The alkyl tether of the cyclopentadienyl ring of **9** is bent down 9° toward Re [Cp(cent)−C(5)−C(6) = 171°], while in untethered systems the alkyl groups bend up away from the metal center.[15] Ring strain also narrows the angle between the Cp centroid, rhenium, and the carbene carbon atom to 112° from the 126° ideal angle for a three-legged piano stool $CpReL_3$ system. The C(6)−C(5)−C(4)−C(3) torsion angle of only 30° is indicative of substantial torsional strain in the tether.

Equilibrium between Hydroxycarbene Complex 2 and Metal Acyl Hydride Complex 3. Protonation of an aqueous solution of acyl rhenium anion **7** with HCl followed by extraction into CH_2Cl_2 led to the isolation of a mixture of the expected hydroxycarbene complex $(CO)_2Re{=}C(OH)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**2**) and the unanticipated metal acyl hydride complex *trans*-$(CO)_2HReC(=O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**3**) as a yellow oil in 50% isolated yield. Treatment of this mixture with *n*-BuLi in Et_2O at −78 °C regenerated acyl anion **7**.

The ^{1}H NMR spectrum in CD_2Cl_2 indicated the presence of a 25:75 mixture of **2**/**3**. Each tautomer had its own well-separated AA′BB′ patterns for cyclopentadienyl protons and two triplets for the two-carbon tether. The minor species **2** had a resonance at δ 11.00 assigned to a hydroxycarbene proton, while the major species **3** had a resonance at δ −8.69 characteristic of a metal hydride. Upon treatment with D_2O, both the hydroxyl and hydride resonances of **2** and **3** disappeared immediately.

In the ^{13}C NMR spectrum of the 25:75 mixture of **2**/**3** in CD_2Cl_2, a resonance at δ 292.5 is assigned to the carbene carbon of **2** and a more intense resonance at δ 234.3 is assigned to the acyl carbon of **3**. In the coupled ^{13}C NMR spectrum, the resonance at δ 292.5 appears as a singlet, excluding the possibility that the minor species is the aldehyde formed from reductive elimination from **3**. An aldehyde carbon would appear near δ 200 as a doublet with J_{CH} = 100−150 Hz.

The IR spectrum of the 25:75 mixture of **2**/**3** in CH_2Cl_2 has carbonyl stretching bands at 1954 and 1870 cm^{-1} assigned to **2** and more intense bands at 2023 and 1925 cm^{-1} assigned to **3**. In addition, a weaker band at 1615 cm^{-1} is assigned to the acyl group of **3**.

The ratio of hydroxycarbene complex **2** to metal acyl hydride **3** showed a strong solvent dependence. In CD_3OD and THF-d_8, hydroxycarbene complex **2** was the only species observed by ^{1}H NMR, in acetone-d_6, a 91:9 mixture of **2**/**3** was seen, and in C_6D_6, a 50:50 mixture of **2**/**3** was seen. The ^{1}H NMR spectra of mixtures of **2** and **3** in 10:1, 5:1, 2:1, and 1:1 mixtures of CD_2Cl_2−acetone-d_6 showed a smooth change in the **2**:**3** ratio from 25:75 in pure CD_2Cl_2 to the 91:9 ratio observed in acetone-d_6.[16] While there is no correlation of the equilibrium constant with solvent polarity, more of the hydroxycarbene is seen in the better hydrogen-bonding solvents methanol, THF, and acetone.

The equilibrium between **2** and **3** is temperature dependent, and shifts toward the hydroxycarbene isomer at low temperature. Equilibrium constants (K_{eq} = [**3**]/[**2**]) measured by ^{1}H NMR spectroscopy in a 9:1 mixture of CD_2Cl_2−acetone-d_6 changed from 0.46 at −60 °C to 0.77 at 24 °C (Table 1 and Figure 1 in the Supporting Information). The derived thermodynamic parameters were $\Delta G = 0.14 \pm 0.06$ kcal mol^{-1}, $\Delta H = 0.82 \pm 0.03$ kcal mol^{-1}, and $\Delta S = 2.3 \pm 0.1$ cal K^{-1} mol^{-1} at 297 K.

The interconversion of **2** and **3** is rapid at low temperature. When acetone-d_6 was condensed into a CD_2Cl_2 solution of **2** and **3** at −78 °C, the conversion from a 25:75 ratio of **2**/**3** to an 80:20 equilibrium mixture was monitored by ^{1}H NMR spectroscopy at −50 °C. Within 6 min, half of excess **3** was converted to **2** (62:38 ratio of **2**/**3**). After 45 min, an 80:20 equilibrium ratio of **2**:**3** was observed.

Aldehyde Formation in the Decomposition of 2 and 3. The mixture of hydroxycarbene complex **2** and metal acyl hydride **3** decomposed to a number of unidentifiable products when it was heated above 40 °C in C_6D_6. When the thermolysis of the mixture of **2** and **3** was carried out in the presence of excess PPh_3 in benzene at 80 °C, clean formation of a single new compound, the untethered aldehyde $(\eta^5\text{-}C_5H_4CH_2CH_2CHO)Re(CO)_2PPh_3$ (**10**), occurred in 80% isolated yield. A singlet ($\omega_{1/2}$ = 2 Hz) at δ 9.7 in the ^{1}H NMR spectrum of **10** in CD_2Cl_2 was assigned to the aldehyde proton. In the $^{13}C\{^1H\}$ NMR spectrum, the aldehyde carbonyl resonance appeared at δ 200.7. The IR spectrum in CH_2Cl_2 exhibited two strong bands of equal intensity at 1920 and 1856 cm^{-1}, consistent with a $CpM(CO)_2L$ unit, and a less intense band at 1703 cm^{-1} assigned to the aldehyde carbonyl.

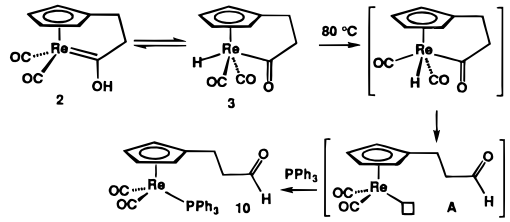
We suggest that aldehyde formation results from reductive elimination from an unseen *cis* metal acyl hydride isomer that generates reactive intermediate **A** in which a tethered aldehyde is connected to a coordinatively unsaturated rhenium dicarbonyl fragment (Scheme 2). Decomposition of **A** in the absence of added ligand produces a mixture of unidentified products, but **A** is efficiently trapped by PPh_3 to give **10**. Fischer reported that thermal decomposition of the untethered hydroxycarbene complex $(C_5H_5)(CO)_2Re{=}C(OH)CH_3$ (**1**) gave $CpRe(CO)_3$ and acetaldehyde.[3] Fischer proposed that cleavage of the Re=C bond produced free methylhydroxycarbene that rearranged to

(14) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 1285.

(15) For example, in $(C_5H_4COCH_3)Re(CO)_3$, the acyl carbon is bent 1.7° away from Re. Khotsyanova, T. L.; Kuznetsov, S. I.; Bryukhova, E. V.; Makarov, Yu. V. *J. Organomet. Chem.* **1975**, *88*, 351.

(16) In 10:1 CD_2Cl_2−acetone-d_6, **2**:**3** = 53:47. In 5:1 CD_2Cl_2−acetone-d_6, **2**:**3** = 66:33. In 2:1 CD_2Cl_2−acetone-d_6, **2**:**3** = 77:23. In 1:1 CD_2Cl_2−acetone-d_6, **2**:**3** = 83:17.

Scheme 2



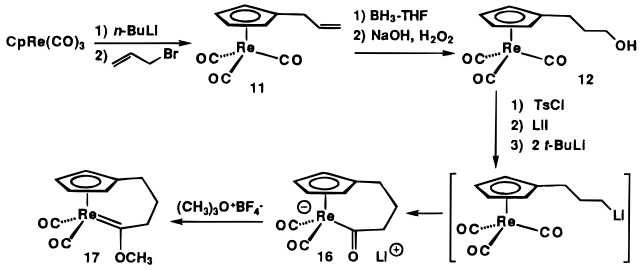
acetaldehyde. We suggest that decomposition of **1** may also occur via reductive elimination from an unseen metal acyl hydride intermediate in equilibrium with **1**.

Reexamination of Fischer's Acyclic Hydroxycarbene Complex 1. Our observation of an acyl hydride complex in equilibrium with a hydroxycarbene complex contrasts with Fischer's report that only a hydroxycarbene isomer was observed for $(C_5H_5)(CO)_2Re{=}C(OH)CH_3$ (**1**). We have repeated Fischer's synthesis of **1** and looked for spectroscopic evidence for an acyl hydride species in solvents that favor this isomer. Close examination of the hydride region of the ^1H NMR spectra of **1** in either C_6D_6 (25 °C) or CD_2Cl_2 (−80 °C) showed no signals (3% would have been readily detected) 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 **1** and no evidence for an acyl hydride isomer. This implies that, in an untethered system such as **1**, the hydroxycarbene form is >2 kcal mol^{-1} more stable than the acyl hydride.

Ring Strain Hypothesis for Selective Destabilization of Tethered Hydroxycarbene Complex 2. The observation that no metal acyl hydride can be detected in equilibrium with **1** demonstrates that the $Cp(CO)_2Re$ system has a strong preference for the hydroxycarbene tautomer. The observation that the tethered metal acyl hydride **3** is of comparable stability to its tethered hydroxycarbene tautomer **2** requires a significant perturbation of the normal equilibrium by the tether. The possibility that the hydroxycarbene complex is destabilized by having an enforced arrangement of the hydroxycarbene ligand in a plane perpendicular to the Cp ring and with the oxygen anti to the ring can be excluded by the observation that this geometry is seen in the X-ray crystal structures of $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OCH_2C(CH_3)_2CH_2Cl)C_6H_4CH_3$,[17] $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OCH_2CH_3)C_6H_5$,[18] and $\eta^5\text{-}C_5H_5(CO)_2Re{=}C(OCH_3)[\eta^5\text{-}C_5H_4Re(CO)_3]$.[19]

We suggest that the tether introduces significant strain that destabilizes hydroxycarbene tautomer **2**, but leaves the tethered metal acyl hydride tautomer **3** unstrained. The X-ray crystal structure of the tethered methoxycarbene complex **9** showed strain in the distortion of the expected three-legged piano stool geometry: the alkyl substituent on the Cp ring was pulled down 9° toward rhenium and the $Cp_{centroid}$−Re−carbene carbon angle was contracted from the normal 126° to the observed 112° angle. The two-carbon tether does not significantly strain the four-legged piano stool geometry of the rhenium acyl hydride tautomer **3**. 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. For example, *trans*-$Cp(CO)_2Re(COCH_3)CH_3$[14] has a 112° Cp(centroid)−Re−acyl carbon angle, which is similar to the angle in the tethered carbene complex **9**. Overall, tethering the side chain destabilizes **2** relative to **3** and provides a rationale for the observation of acyl metal hydrides only in the tethered system.

Scheme 3



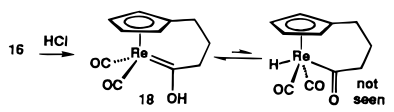
A Longer Chain Tether To Test the Ring Strain Hypothesis. To test the role of strain on the equilibrium between **2** and **3**, we prepared an unstrained hydroxycarbene with a three-carbon tether connecting the cyclopentadienyl ligand and the carbene carbon. Our strain hypothesis predicted that only the hydroxycarbene tautomer should be seen for the unstrained three-carbon tether system.

Our synthetic approach involved attaching an allyl substituent to the cyclopentadienyl ligand and converting it to a primary iodide. A lithium−halogen exchange reaction would generate the three-carbon-chain alkyllithium species that would react to form the intramolecular three-carbon-tethered acyl anion (Scheme 3).

Treatment of $CpRe(CO)_3$ with *n*-BuLi in THF at −78 °C gave the ring-metalated anion which reacted with allyl bromide to give the allyl-substituted $(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)Re(CO)_3$ (**11**) in 85% yield. Hydroboration−oxidation gave a mixture of the desired primary alcohol $(\eta^5\text{-}C_5H_4CH_2CH_2CH_2OH)Re(CO)_3$ (**12**) and the secondary alcohol $[\eta^5\text{-}C_5H_4CH_2CH(OH)CH_3]Re(CO)_3$ (**13**) in a 4:1 ratio. The alcohols could not be separated, but when the mixture was treated with tosyl chloride in pyridine, only the primary alcohol **12** reacted to give the tosylate $(\eta^5\text{-}C_5H_4CH_2CH_2CH_2OTs)Re(CO)_3$ (**14**), which was isolated by thin-layer chromatography. Reaction of **14** with LiI gave the iodide $(\eta^5\text{-}C_5H_4CH_2CH_2CH_2I)Re(CO)_3$ (**15**) in 90% yield. Treatment of **15** with 2 equiv of *t*-BuLi gave the three-carbon-tethered acyl anion $[(CO)_2ReC(=O)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)]^-Li^+$ (**16**) as an air sensitive yellow powder in 48% yield. Methylation of **16** with $(CH_3)_3O^+BF_4^-$ in acetone gave methoxycarbene complex $(CO)_2Re{=}C(OCH_3)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**17**) as a yellow solid in 95% isolated yield.

X-ray crystallography of **17** (Table 1 and Figure 2, bottom) revealed little strain in this three-legged piano stool complex compared with the two-carbon-tethered carbene complex **9**. Its structure is similar to that of unstrained $CpReL_3$ complexes. The first carbon of the tether of **17** is nearly in the plane of the cyclopentadienyl ring [$Cp_{(cent)}$−C(6)−C(5) = 179.2°], as expected for an unstrained complex. The $Cp_{(cent)}$−Re−C(3) angle of 123.1° is close to the ideal 126° angle of unstrained three-legged piano stool complexes. The nearly staggered torsion angles of the tether [C(4)−C(45)−C(5)−C(6), −65°; C(3)−C(4)−C(45)−C(5), 72°] are indicative of a relaxed geometry.

Reaction of an aqueous suspension of acyl anion **16** with aqueous HCl followed by extraction into CH_2Cl_2 led to the isolation of the three-carbon-tethered hydroxycarbene complex $(CO)_2Re{=}C(OH)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**18**) in 57% isolated



yield. Only the hydroxycarbene species was seen by NMR and IR spectroscopy; no evidence for an acyl metal hydride in

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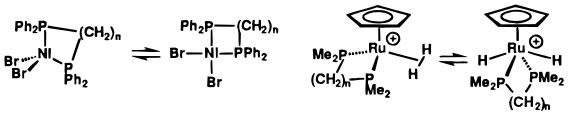
Table 1. Selected Bond Lengths (Å) and Angles (deg) for $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**9**) and $(CO)_2Re{=}C(OCH_3)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**17**)

	9	**17**		**9**	**17**
Re1−C1	1.894(14)	1.884(10)	C3−O3	1.329(12)	1.342(11)
Re1−C2	1.882(14)	1.908(12)	O3−C11	1.483(12)	1.436(11)
Re1−C3	1.982(10)	1.989(10)	Re−C3−C4	118.6(7)	124.8(6)
C1−Re1−C2	87.2(5)	87.2(4)	O3−C3−C4	105.1(8)	101.5(7)
C1−Re1−C3	97.7(4)	94.8(4)	C3−C4−C5	111.8(9)	
C2−Re1−C3	96.5(4)	92.3(4)	C3−C4−C45		115.8(7)
$Cp_{(cent\ 1)}$−Re−C1	126.8	126.0	C4−C45−C5		114.3(8)
$Cp_{(cent\ 1)}$−Re−C2	129.3(9)	126.0	C4−C5−C6	111.5(8)	
$Cp_{(cent\ 1)}$−Re−C3	111.8(9)	123.1	C45−C5−C6		114.5(8)
Re−C3−O3	136.2(7)	136.2(7)	$Cp_{(cent\ 1)}$−C6−C5	170.7	179.2
C3−O3−C11	119.4(8)	120.8(7)			

equilibrium with **18** was found. Even in CH_2Cl_2, the solvent which favored the acyl hydride species in the mixture of **2** and **3**, only hydroxycarbene **18** was observed. The ^{1}H NMR spectrum of **18** in CD_2Cl_2 exhibited a sharp singlet at δ 9.15 assigned to the hydroxyl proton, and only one set of AA′BB′ pseudotriplets in the Cp region, at δ 5.35 and 5.25. Close examination of the hydride region of the spectrum revealed no metal hydride resonances between δ 0 and δ −20. ^{13}C NMR spectroscopy of **18** also provided evidence for only one isomer. The carbene carbon resonance appeared at characteristically high frequency (δ 296.0), and no acyl carbon resonances were seen between δ 260 and δ 210. The IR spectrum of **18** in CH_2Cl_2 had only two carbonyl bands of equal intensity at 1945 and 1864 cm^{-1}, as expected for a $Cp(CO)_2ReX$ complex.

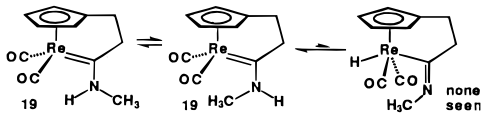
The observation that only the hydroxycarbene tautomer is seen for the unconstrained hydroxycarbene complex (η^5-C_5H_5)$(CO)_2Re{=}C(OH)CH_3$ (**1**) and for the unstrained three-carbon-tethered hydroxycarbene complex **18** supports our ring strain hypothesis. Only the two-carbon-tethered hydroxycarbene complex **2** is so destabilized by ring strain that its energy is increased to that of the unstrained four-legged piano stool metal acyl hydride tautomer **3**.

The effect of ring strain on equilibria has been observed previously. For example, variation in ring size affects the equilibria between cyclic hemiacetals and acyclic hydroxy aldehydes[20] and the equilibria between ω-hydroxy acids and lactones.[21] In organometallic chemistry, the diphosphine chelate ring size often influences equilibria. For example, the equilibria between tetrahedral and square planar forms of $Br_2Ni[Ph_2P(CH_2)_n$-$PPh_2)_2$ depends strongly on the chelate ring size.[22] Recently, Angelici reported that the equilibrium constants for protonation at the metal atom of iron−diphosphine complexes are affected by the chelate ring size.[23] Heinekey reported that the equilibrium between Ru(η^2-H_2)(diphosphine) and $Ru(H)_2$(diphosphine) complexes depends upon the ring size of chelating diphosphine.[24]



Relative Stability of Tethered Aminocarbene Complexes and Metal Iminoacyl Hydride Complexes. Although iminoacyl hydride complexes are tautomers of aminocarbene complexes, none have been reported. We investigated the possibility that a two-carbon tether between a cyclopentadienyl ring and an aminocarbene carbon might introduce sufficient strain to allow observation of an iminoacyl hydride complex.

Reaction of the two-carbon-tethered methoxycarbene complex **9** with a 10-fold excess of methylamine in THF produced the (methylamino)carbene complex $(CO)_2Re{=}C[NH(CH_3)]CH_2$-$CH_2(\eta^5\text{-}C_5H_4)$ (**19**) in quantitative yield. No evidence for a metal iminoacyl hydride was obtained even in CD_2Cl_2, which favored the metal acyl hydride in the mixture of **2** and **3**. A 5:1 ratio of two isomers about the *N*-carbene carbon partial double bond of **19** was observed. The ^{1}H NMR spectrum of



19 in CD_2Cl_2 shows a resonance for the amine proton of the major isomer as a broad singlet at δ 9.00, and for the minor isomer at δ 9.15. A doublet at δ 3.20 is assigned to the amine methyl group of the major isomer, and a doublet at δ 3.17 is assigned to the amine methyl group of the minor isomer. The ^{13}C NMR shows a resonance for the carbene carbon of the major isomer of **19** at δ 247.5 and for the minor isomer at δ 247.0. No resonances attributable to a metal iminoacyl hydride complex were observed.[25]

Experimental Section

(η^5-$C_5H_4CH_2CH_2OTs$)$Re(CO)_3$ (5). *n*-BuLi (4.0 mL, 1.5 M pentane solution, 6.0 mmol) was added to a solution of $CpRe(CO)_3$ (2.00 g, 5.97 mmol) in THF (50 mL) at −78 °C. After the solution was stirred for 3 h at −78 °C, ethylene oxide[26] (12.29 mmol) was condensed into it under vacuum. After 2 h the bright yellow solution was warmed to 0 °C, and tosyl chloride (1.15 g, 6.00 mmol) in THF (5 mL) was added. After 30 min at 25 °C, THF was evaporated under vacuum, and the resulting brown paste was extracted with CH_2Cl_2 (2 × 20 mL). The CH_2Cl_2 solution was filtered through Celite to remove LiCl, and solvent was evaporated. The resulting brown oil was purified by column chromatography (silica gel, CH_2Cl_2) to give **5** as an orange oil (2.83 g, 89%). Crystalline **5** was obtained by slow cooling of a CH_2-Cl_2−hexane solution, mp 82−83 °C. ^{1}H NMR (acetone-d_6, 200 MHz): δ 7.75 (d, J = 8 Hz, 2H, aryl), 7.45 (d, J = 8 Hz, 2H, aryl),

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(21) Carter, S. R.; Haworth, W. N.; Robinson, R. A. *J. Chem. Soc.* **1930**, 2125.
(22) Van Hecke, G. R.; Horrocks, W. DeW., Jr. *Inorg. Chem.* **1966**, *5*, 1968.
(23) Sowa, J. R., Jr.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 160.
(24) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675.
(25) Similarly, no evidence for a metal iminoacyl hydride species in equilibrium with the analogous three-carbon aminocarbene complex $(CO)_2Re{=}C[NH(CH_3)]CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ or with the acyclic aminocarbene complex (η^5-C_5H_4)$(CO)_2Re{=}C[NH(CH_3)]CH_3$ was observed. See the Supporting Information for details.
(26) Ethylene oxide as obtained from MG Industries was contaminated with approximately 10% CO_2 (gas phase IR spectroscopy). Use of the contaminated ethylene oxide followed by protonation gave the known acid (η^5-$C_5H_4CO_2H$)$Re(CO)_3$[10a] rather than the expected alcohol (η^5-$C_5H_4CH_2$-CH_2OH)$Re(CO)_3$. Ethylene oxide from a lecture bottle was purified by condensation into a flask at −23 °C and 400 mmHg. Carbon dioxide did not condense under these conditions. Pure ethylene oxide was distilled from the collection flask as needed.

5.47 (m, C_5H_4), 4.18 (t, $J = 7.4$ Hz, CH_2O), 2.80 (t, $J = 7.4$ Hz, CH_2CH_2O), 2.45 (s, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 194.5 (CO); 145.6 (CSO_2); 132.9 (CCH_3); 130.3, 128.1 (aryl CH); 104.6 (Cp CCH_2); 85.1, 84.5 (Cp CH); 71.1 (CH_2O); 28.2 (CH_2CH_2O); 21.7 (CH_3). IR (THF): 2020 (s), 1928 (vs) cm^{-1}. HRMS: *m/z* calcd for $C_{17}H_{15}ReO_6S$ 534.0148, found 534.0147. Anal. Calcd for $C_{17}H_{15}ReO_6S$: C, 38.27; H, 2.83. Found: C, 38.60; H, 2.82.

(η^5-$C_5H_4CH_2CH_2I$)Re(CO)$_3$ (6). A solution of **5** (1.79 g, 3.36 mmol) and LiI (0.500 g, 3.73 mmol) in acetone (40 mL) was refluxed overnight. Solvent was evaporated, and the brown residue was extracted with CH_2Cl_2, filtered through Celite to remove lithium tosylate, and purified by column chromatography (silica gel, CH_2Cl_2) to give **6** as a yellow oil (1.40 g, 85%). ^1H NMR (acetone-d_6, 200 MHz): δ 5.70 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 5.53 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 3.37 (t, $J = 7.4$ Hz, CH_2I), 3.00 (t, $J = 7.4$ Hz, CH_2CH_2I). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 194.6 (CO); 104.5 (Cp CCH_2); 85.0, 84.3 (Cp CH); 32.7 (CH_2CH_2I); 5.3 (CH_2I). IR (THF): 2019 (m), 1923 (s) cm^{-1}. HRMS: *m/z* calcd for $C_{10}H_8ReO_3I$ 489.9073, found 489.9046.

Li$^+$[(CO)$_2$ReC(=O)CH$_2$CH$_2$(η^5-C$_5$H$_4$)]$^-$ (7). *t*-BuLi (0.75 mL, 1.7 M pentane solution, 1.3 mmol) was added to a solution of **6** (0.310 g, 0.634 mmol) in Et_2O at −78 °C. Upon warming to room temperature, a fine yellow precipitate formed and was collected on a frit, washed with cold pentane, and dried under vacuum to give **7** (0.146 g, 0.377 mmol, 59%), which was shown to contain ∼0.25 mol of Et_2O/mol of **7** by ^1H NMR. ^1H NMR (THF-d_8, 200 MHz): δ 5.20 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 5.11 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 2.83 (t, $J = 7.7$ Hz, $C_5H_4CH_2$), 1.98 (t, $J = 7.7$ Hz, $C_5H_4CH_2CH_2$). IR (THF): 1898 (s), 1819 (s), 1515 (w) cm^{-1}.

(CO)$_2$Re=C(OH)CH$_2$CH$_2$(η^5-C$_5$H$_4$) (2) and (CO)$_2$(H)ReC(=O)-CH$_2$CH$_2$(η^5-C$_5$H$_4$) (3). Aqueous HCl (0.5 M, 4 mL) was added via syringe to a mixture of 10 mL of CH_2Cl_2 and 10 mL of a yellow aqueous solution of **7** (0.600 g, 1.55 mmol). After 15 min of vigorous stirring, the CH_2Cl_2 layer was decanted, washed with H_2O, dried ($MgSO_4$), and concentrated to give a mixture of **2** and **3** as a dark yellow oil (0.284 g, 0.78 mmol, 50%). HRMS: *m/z* calcd for $C_{10}H_9ReO_3$ 364.0111, found 364.0119.

^1H NMR (THF-d_8, 200 MHz) (only **2** observed): δ 13.17 (br s, OH), 5.59 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 5.45 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 3.02 (t, $J = 7.7$ Hz, $C_5H_4CH_2CH_2$), 2.33 (t, $J = 7.7$ Hz, $C_5H_4CH_2$). ^1H NMR (acetone-d_6, 200 MHz) (**2**:**3** = 91:9): (for **2**) δ 13.11 (br s, OH), 5.67 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 5.47 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H,C_5H_4), 3.07 (t, $J = 7.7$ Hz, $C_5H_4CH_2CH_2$), 2.39 (t, $J = 7.7$ Hz, $C_5H_4CH_2$); (for **3**) δ 5.79 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 5.31 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 3.36 (t, $J = 7.7$ Hz, $C_5H_4CH_2CH_2$), 2.28 (t, $J = 7.7$ Hz, $C_5H_4CH_2$), −8.91 (s, ReH). ^1H NMR (CD_2Cl_2, 200 MHz) (**2**:**3** = 25:75): (for **2**) δ 11.0 (br s, OH), 5.60 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 5.48 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 3.05 (t, $J = 7.7$ Hz, $C_5H_4CH_2CH_2$), 2.41 (t, $J = 7.7$ Hz, $C_5H_4CH_2$); (for **3**) δ 5.76 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 5.16 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 3.38 (t, $J = 7.7$ Hz, $C_5H_4CH_2CH_2$), 2.34 (t, $J = 7.7$ Hz, $C_5H_4CH_2$), −8.69 (s, ReH). ^1H NMR (C_6D_6, 200 MHz) (**2**:**3** = 50:50): (for **2**) δ 10.75 (br s, OH), 4.90 (s, 4H, C_5H_4), 3.08 (t, $J = 7.7$ Hz, $C_5H_4CH_2CH_2$), 1.30 (t, $J = 7.7$ Hz, $C_5H_4CH_2$); (for **3**) δ 4.68 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 4.17 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 2.59 (t, $J = 7.7$ Hz, $C_5H_4CH_2CH_2$), 1.58 (t, $J = 7.7$ Hz, $C_5H_4CH_2$), −8.65 (s, ReH).

The ratio of **2**:**3** in CD_2Cl_2−acetone-d_6 solvent mixtures was measured by ^1H NMR spectroscopy. Complete equilibration occurred prior to the first measurement. The equilibrium constant varied as a function of the molar ratio of solvents: In 10:1 CD_2Cl_2−acetone-d_6, **2**:**3** = 47:53. In 5:1 CD_2Cl_2−acetone-d_6, **2**:**3** = 66:33. In 2:1 CD_2Cl_2−acetone-d_6, **2**:**3** = 77:23. In 1:1 CD_2Cl_2−acetone-d_6, **2**:**3** = 83:17.

$^{13}C\{^1H\}$ NMR (THF-d_8, 125 MHz) (only **2** observed): δ 292.5 (Re=C); 204.0 (CO); 84.7 (Cp CCH_2); 84.3, 79.7 (Cp CH); 30.1 ($C_5H_4CH_2CH_2$); 29.5 ($C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz) (**2**:**3** = 25:75): (for **2**) δ 292.4 (Re=C); 204.0 (CO); 84.3 (Cp CCH_2); 84.1, 79.2 (Cp CH); 27.9 ($C_5H_4CH_2CH_2$); 26.5 ($C_5H_4CH_2$); (for **3**) δ 234.3 (ReC=O); 203.5 (CO); 85.0 (Cp CCH_2); 82.3, 76.1 (Cp CH); 30.6 ($C_5H_4CH_2CH_2$); 29.9 ($C_5H_4CH_2$).

The ratio of **2** to **3** was also estimated by IR spectroscopy. **2** has ν_{sym} at 1945 cm^{-1} and ν_{asym} at 1870 cm^{-1} of approximately equal intensity; **3** has ν_{sym} at 2020 cm^{-1} and ν_{asym} at 1925 cm^{-1} overlapping with the 1945 cm^{-1} band of **2**. Comparison of the relative integrated intensities of ν_{asym} of **2** at 1870 cm^{-1} and ν_{sym} of **3** at 2020 cm^{-1} (after making corrections for relative absorbances as outlined below) were used to approximate the ratio of **2** to **3**. A 1:1 ratio of $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**9**)/$(CO)_2(CH_3)ReC(=O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**8**) (as determined by ^1H NMR spectroscopy) had relative integrated absorbances for ν_{asym} for **9** at 1864 cm^{-1} and ν_{sym} for **8** at 2019 cm^{-1} of 1.2:1. Similar intensity differences were assumed for **2** and **3**, and an appropriate correction was applied.

IR ν (relative integrated absorbance, assignment): (solid (Nujol mull)) 2026 (0.07, ν_{sym}(**3**)), 1954 (0.42, ν_{sym}(**2**)), 1935 (0.09, ν_{asym}(**3**)), 1882 (0.42, ν_{asym}(**2**)) cm^{-1}; (**2**:**3** = 6:1) (in CH_2Cl_2) 2023 (0.10, ν_{sym}(**3**)), 1954 and 1925 (0.18, ν_{sym}(**2** and ν_{asym}(**3**)), 1870 (0.04, ν_{asym}(**2**)), 1615 (0.04, **3**) cm^{-1}; (**2**:**3** = 1:3) (in acetone) (**2**) 1946 (0.17), 1869 (0.14); (**3**) 2019 (0.10), 1924 (0.17) cm^{-1}; (C_6H_6) (**2**) 1949 (0.12), 1872 (0.08); (**3**) 2021 (0.13), 1927 (0.22) cm^{-1}; (THF) (**2**) 1944 (0.19), 1869 (0.17); (**3**) 2019 (0.10), 1924 (0.21) cm^{-1}.

Thermolysis of 2 and 3 in the Presence of PPh$_3$. Formation of (η^5-C$_5$H$_4$CH$_2$CH$_2$CHO)Re(CO)$_2$PPh$_3$ (10). A solution of **2** and **3** (30 mg, 0.08 mmol) in C_6H_6 was combined with PPh_3 (50 mg, 0.19 mmol) and heated for 12 h at 80 °C in a sealed tube. Solvent was evaporated, and thin layer chromatography gave **10** as a white solid (30 mg, 60%). ^1H NMR (acetone-d_6, 300 MHz): δ 9.74 (s, $\omega_{1/2} = 2.0$ Hz, CHO), 7.70−7.40 (m, PPh_3), 5.05 (three-line pattern, AA′BB′, 4.0 Hz separation of outer lines, 2H, C_5H_4), 4.78 (three-line pattern, AA′BB′, 5.5 Hz separation of outer lines, 2H, C_5H_4), 2.65 (m, $C_5H_4CH_2CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 202.8 (ReC=O); 200.7 (CHO), 137.8 (d, $J_{PC} = 50$ Hz, ipso phenyl), 133.0 (d, $J_{PC} = 10.9$ Hz, ortho phenyl), 129.6 (s, para phenyl), 128.0 (d, $J_{PC} = 10.9$, meta phenyl), 105.3 (Cp CCH_2), 84.4 (Cp CH), 82.3 (Cp CH), 45.4 ($C_5H_4CH_2CH_2$), 29.6 ($C_5H_4CH_2$). ^{31}P NMR (CD_2Cl_2, 121 MHz): δ 38.6. IR (CH_2Cl_2): 1920 (s), 1856 (s), 1703 (m) cm^{-1}. HRMS: *m/z* calcd for $C_{28}H_{24}O_3PRe$ 626.1021, found 626.1017.

(C$_5$H$_5$)(CO)$_2$Re=C(OH)CH$_3$ (1) was prepared as described by Fischer[9] and more fully characterized spectroscopically. MeLi (1.4 mL, 1.4 M Et_2O solution, 2.0 mmol) was added to a solution of $CpRe(CO)_3$ (620 mg, 1.85 mmol) in Et_2O (50 mL) at −78 °C. The solution was warmed to 25 °C, and a yellow precipitate formed which was collected on a frit and washed with Et_2O to give $Li^+[(C_5H_5)(CO)_2Re{=}C(O)CH_3]^-$ as a yellow powder (270 mg, 79%). Aqueous H_2SO_4 (1 mL, 2 N) was added to a suspension of the acyl anion in Et_2O at −78 °C. Upon being warmed to 25 °C, the solution turned clear orange. The solution was dried ($MgSO_4$), filtered, and concentrated to leave an orange residue. Preparative thin layer chromatography (silica gel, 1:1 hexane−toluene) gave a yellow band ($R_f = 0.1$) from which **1** was obtained as a yellow solid. ^1H NMR: (C_6D_6, 300 MHz) δ 4.71 (s, C_5H_5), 4.34 (s, OH), 1.85 (s, CH_3); (CD_2Cl_2, 500 MHz, 25 °C) δ 5.54 (s, C_5H_5), 9.32 (s, OH), 2.31 (s, CH_3); (CD_2Cl_2, 500 MHz, −80 °C) δ 5.54 (s, C_5H_5), 9.92 (s, OH), 2.23 (s, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 286.7 (Re=C), 205.0 (CO), 90.0 (C_5H_5), 30.6 (CH_3). IR (KBr): 1944 (s), 1845 (s) cm^{-1}. HRMS: *m/z* calcd for $C_9H_9ReO_3$ 352.0111, found 352.0129.

(CO)$_2$(CH$_3$)ReC(=O)CH$_2$CH$_2$(η^5-C$_5$H$_4$) (8). A solution of **7** (100 mg, 0.26 mmol) and CH_3I (0.31 mmol) in THF was stirred at room temperature for 1 h. THF was evaporated under vacuum. The yellow residue was extracted with CH_2Cl_2 and filtered through Celite. Preparative TLC (silica gel, 1:1 hexane−Et_2O) gave a pale yellow band ($R_f = 0.30$) from which **8** was isolated as a yellow oil (43.8 mg, 0.116 mmol, 45%). ^1H NMR (THF-d_8, 300 MHz): δ 5.96 (three-line pattern, AA′BB′, 7.1 Hz separation of outer lines, 2H, C_5H_4), 4.94 (three-line pattern, AA′BB′, 6.7 Hz separation of outer lines, 2H, C_5H_4), 3.23 (t, $J = 7.4$ Hz, $C_5H_4CH_2CH_2$), 2.23 (t, $J = 7.4$ Hz, $C_5H_4CH_2$), 0.65 (s, $ReCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 230.9 (ReC=O); 195.7

(CO); 90.4 (Cp *C*CH_2); 86.9, 86.1 (Cp CH); 28.7 ($C_5H_4CH_2CH_2$); 14.6 ($C_5H_4CH_2$); −37.3 (CH_3). IR (CH_2Cl_2): 2020 (s), 1948 (vs), 1616 (w) cm^{-1}. HRMS: *m/z* calcd for $C_{11}H_{11}ReO_3$ 378.0267, found 378.0232.

$(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (9). A solution of **7** (222 mg, 0.57 mmol) and $(CH_3)_3O^+BF_4^-$ (90 mg, 0.61 mmol) in acetone was stirred for 24 h at 25 °C. Solvent was evaporated under vacuum, and the resulting yellow residue was extracted with CH_2Cl_2 and filtered through Celite. Preparative TLC (silica gel, 1:1 hexane−Et_2O) gave a bright yellow band ($R_f = 0.70$) from which **9** was isolated as a yellow solid. Recrystallization by slow cooling of a CH_2Cl_2−hexane solution gave pure **9** (162 mg, 0.429 mmol, 75%). ^1H NMR (CD_2Cl_2, 200 MHz): δ 5.56 (three-line pattern, AA′BB′, 4.2 Hz separation of outer lines, 2H, C_5H_4), 5.45 (three-line pattern, AA′BB′, 4.0 Hz separation of outer lines, 2H, C_5H_4), 4.16 (s, OCH_3), 3.12 (t, $J = 7.4$ Hz, C_5H_4-CH_2CH_2), 2.33 (t, $J = 7.4$ Hz, $C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 296.2 (Re═C); 201.2 (CO); 99.6 (Cp *C*CH_2); 86.1, 85.1 (Cp CH); 67.1 (OCH_3); 29.6 ($C_5H_4CH_2CH_2$); 29.2 ($C_5H_4CH_2$). IR (CH_2Cl_2): 1945 (s), 1865 (s) cm^{-1}. HRMS: *m/z* calcd for $C_{11}H_{11}O_3$-Re 378.0267, found 378.0269. Anal. Calcd for $C_{11}H_{11}O_3Re$: C, 35.01; H, 2.94. Found: C, 34.77; H, 2.78.

$(CO)_2Re{=}C(OCH_2CH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$. A solution of **7** (3.1 g, 8.0 mmol) and $(CH_3CH_2)_3O^+$ BF_4^- (2.3 g, 12.0 mmol) in acetone was stirred for 24 h at 25 °C. Solvent was evaporated, and the resulting yellow residue was extracted with CH_2Cl_2 and filtered through Celite. Column chromatography (silica gel, 1:1 hexane−Et_2O) gave a bright yellow band ($R_f = 0.80$) from which $(CO)_2Re{=}C(OCH_2CH_3)CH_2CH_2$-($\eta^5$-$C_5H_4$) was isolated as a yellow solid, mp 103−106 °C (2.2 g, 5.6 mmol, 70%). ^1H NMR (acetone-d_6, 300 MHz): δ 5.71 (three-line pattern, AA′BB′, 4.1 Hz separation of outer lines, C_5H_4), 5.52 (three-line pattern, AA′BB′, 4.4 Hz separation of outer lines, C_5H_4), 4.44 (q, $J = 7.4$ Hz, OCH_2), 3.15 (t, $J = 7.4$ Hz, CH_3), 2.35 (t, $J = 7.4$ Hz, $C_5H_4CH_2CH_2$), 1.44 (t, $J = 7.4$ Hz, $C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 292.5 (Re═C), 205.0 (CO), 124.1 (Cp *C*CH_2), 85.9 (Cp CH), 85.2 (Cp CH), 84.8 (OCH_2), 77.3 (CH_3), 25.0 ($C_5H_4CH_2$), 14.8 ($C_5H_4CH_2CH_2$). IR (hexane): 1959 (s), 1887 (s) cm^{-1}. HRMS: *m/z* calcd for $C_{12}H_{13}O_3Re$ 392.0424, found 392.0427. Anal. Calcd for $C_{12}H_{13}O_3Re$: C, 36.82; H, 3.35. Found: C, 36.92; H, 3.37.

(η^5-$C_5H_4CH_2CH{=}CH_2$)$Re(CO)_3$ (11). *n*-BuLi (4.0 mL, 1.5 M pentane solution, 6.0 mmol) was added to a solution of $CpRe(CO)_3$ (2.00 g, 5.97 mmol) in THF (50 mL) at −78 °C. After the solution was stirred for 3 h at −78 °C, allyl bromide (13.2 mmol) was condensed into it under vacuum. After 2 h the bright yellow solution was warmed to room temperature. THF was evaporated under vacuum, and the resulting yellow oil was purified by column chromatography (silica gel, CH_2Cl_2) to give **11** as a yellow oil (1.90 g, 85%). ^1H NMR (acetone-d_6, 300 MHz) δ 5.84 (ddt, $J = 17$, 10, 6.9 Hz, 1H, C*H*═CH_2), 5.50 (s, 4H, C_5H_4), 5.14 (ddt, $J = 17$, 2.0, 1.7 Hz, 1 H, CH═CH*H*), 5.08 (ddt, $J = 10$, 2.0, 1.0 Hz, CH═C*H*H), 3.23 (ddd, $J = 6.9$, 1.7, 1.0 Hz, $C_5H_4CH_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 194.9 (CO); 136.0 (*C*H═CH_2); 117.7 (CH═*C*H_2); 109.5 (Cp *C*CH_2); 84.2, 83.9 (Cp CH); 32.5 ($C_5H_4CH_2$). IR (CH_2Cl_2): 2020 (s), 1925 (vs) cm^{-1}. HRMS: *m/z* calcd for $C_{11}H_9ReO_3$ 376.0082, found 376.0098.

(η^5-$C_5H_4CH_2CH_2CH_2OH$)$Re(CO)_3$ (12) and (η^5-$C_5H_4CH_2CH$-$(OH)CH_3$)$Re(CO)_3$ (13). A THF solution of BH_3·THF (4.4 mL, 1.0 M) was added to a solution of **11** (1.64 g, 4.4 mmol) in THF at −78 °C. After 2 h at room temperature, H_2O (5 mL), NaOH (5 mL, 15% aqueous solution), and H_2O_2 (5 mL, 30% aqueous solution) were added. After 1 h, solid K_2CO_3 (2 g, 14.5 mmol) was added. The organic layer was removed, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and chromatographed to give a 4:1 mixture of **12**/**13** (1.06 g, 61%) as a clear oil used without further purification. The spectroscopic data for **12** are the following. ^1H NMR (CD_2Cl_2, 300 MHz): δ 5.29 (m, C_5H_4), 3.62 (t, $J = 6.3$ Hz, $C_5H_4CH_2$), 2.49 (dd, $J = 8.1$, 7.7 Hz, CH_2-OH), 1.96 (br s, OH) 1.71 (ddt, $J = 8.1$, 7.7, 6.3 Hz, $C_5H_4CH_2CH_2$). ^1H NMR (acetone-d_6, 300 MHz): δ 5.50 (three-line pattern, AA′BB′, 4.1 Hz separation of outer lines, 2H, C_5H_4), 5.45 (three-line pattern, AA′BB′, 4.0 Hz separation of outer lines, 2H, C_5H_4), 3.60 (m, $C_5H_4CH_2$), 2.51 (m, CH_2OH), 1.74 (m, $C_5H_4CH_2CH_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 195.0 (CO), 111.1 (Cp *C*CH_2), 84.6, (Cp CH), 83.8 (Cp CH), 61.5 (COH), 34.6 ($C_5H_4CH_2$), 24.5 ($CH_2CH_2CH_2$). IR (for mixture of **12** and **13**) (CH_2Cl_2): 3416 (w, br), 2020 (s), 1925 (vs) cm^{-1}. HRMS (for mixture of **12** and **13**): *m/z* calcd for $C_{11}H_{11}ReO_4$ 394.0217, found 394.0181. The spectroscopic data for **13** are the following. ^1H NMR (CD_2Cl_2, 300 MHz): δ 5.39 (three-line pattern, AA′BB′, 4.3 Hz separation of outer lines, 2H, C_5H_4), 5.34 (three-line pattern, AA′BB′, 4.1 Hz separation of outer lines, 2H, C_5H_4), 3.60 (d, $J = 7.7$ Hz, $C_5H_4CH_2$), 2.45 (m, C*H*OH), 2.05 (br s, OH), 1.18 (d, $J = 7.7$ Hz, CH_3). ^1H NMR (acetone-d_6, 300 MHz): δ 5.55 (m, C_5H_4), 3.82 (d, $J = 7.7$ Hz, $C_5H_4CH_2$), 2.50 (m, CH_2OH), 1.15 (d, $J = 7.7$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 194.3 (CO), 107.3 (Cp *C*CH_2), 84.6, (Cp CH), 83.3 (Cp CH), 65.8 (COH), 37.7 ($C_5H_4CH_2$), 29.9 (CH_3).

(η^5-$C_5H_4CH_2CH_2CH_2OTs$)$Re(CO)_3$ (14). A solution of **12** and **13** (1.06 g, 2.7 mmol) was combined with tosyl chloride in pyridine at −78 °C. After 24 h at −20 °C, the solution was poured into aqueous HCl at 0 °C. The aqueous solution was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. Excess tosyl chloride and residual $CpRe(CO)_3$ were removed by sublimation at 50 °C, and the remaining material was chromatographed (SiO_2, 1:1 hexane−Et_2O) to give **14** as a white solid (0.737 g, 50%). ^1H NMR (acetone-d_6, 300 MHz): δ 7.81 (d, $J = 8$ Hz, 2H, aryl), 7.49 (d, $J = 8$ Hz, 2H, aryl), 5.50 (three-line pattern, AA′BB′, 4.3 Hz separation of outer lines, 2H, C_5H_4), 5.47 (three-line pattern, AA′BB′, 4.1 Hz separation of outer lines, 2H, C_5H_4), 4.10 (t, $J = 6.2$ Hz, $C_5H_4CH_2$), 2.48 (dd, $J = 7.5$, 6.0 Hz, CH_2O), 2.45 (s, CH_3), 1.86 (ddt, $J = 7.5$, 6.2, 6.0 Hz, CH_2CH_2O). $^{13}C\{^1H\}$ NMR (CD_2-Cl_2, 125 MHz): δ 194.3 (CO); 144.9 (CSO_2); 132.7 (*C*CH_3); 129.8, 127.6 (aryl CH); 109.1 (Cp *C*CH_2); 83.8, 83.3 (Cp CH); 69.2 (CH_2O); 30.7 ($C_5H_4CH_2$); 23.9 (CH_2CH_2O); 21.3 (CH_3). IR (CH_2Cl_2): 2021 (s), 1924 (vs) cm^{-1}. HRMS: *m/z* calcd for $C_{18}H_{17}ReO_6S$ 548.0305, found 548.0311. Anal. Calcd for $C_{18}H_{17}ReO_6S$: C, 39.48; H, 3.13. Found: C, 39.28; H, 2.82.

(η^5-$C_5H_4CH_2CH_2CH_2I$)$Re(CO)_3$ (15). A solution of **14** (0.700 g, 1.4 mmol) and LiI (0.380 g, 2.8 mmol) in acetone (40 mL) was refluxed overnight. Solvent was evaporated, and the brown residue was extracted with CH_2Cl_2, filtered through Celite to remove lithium tosylate, and purified by column chromatography (silica gel, CH_2Cl_2) to give **15** as a yellow oil (0.634 g, 90%). ^1H NMR (acetone-d_6, 200 MHz): δ 5.22 (m, 4H, C_5H_4), 3.13 (t, $J = 6.7$ Hz, $C_5H_4CH_2$), 2.45 (dd, $J = 7.7$, 7.5 Hz, CH_2I), 1.91 (ddt, $J = 7.7$, 7.5, 6.7 Hz, CH_2CH_2I). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 194.4 (CO); 109.2 (Cp *C*CH_2); 84.0, 83.5 (Cp CH); 31.5 ($C_5H_4CH_2$); 20.2 (CH_2CH_2I); 5.3 (CH_2I). IR (THF): 2022 (m), 1926 (s) cm^{-1}. HRMS: *m/z* calcd for $C_{10}H_{10}ReO_2I$ ($M - CO^+$) 475.9280, found 475.9307 (molecular ion $C_{11}H_{10}ReO_3I$, 503.9230, overlapped with an instrument reference peak).

$Li^+[(CO)_2ReC(=O)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)]^-$ (16). *t*-BuLi (1.5 mL, 1.7 M pentane solution, 2.55 mmol) was added to a solution of **15** (0.600 g, 1.19 mmol) in Et_2O at −78 °C. Upon warming to room temperature, a fine yellow precipitate formed and was collected on a frit, washed with cold Et_2O, and dried under vacuum to give **16** (0.268 g, 0.64 mmol, 48%), which was shown to contain ∼0.5 mol of Et_2O/mol of **16** by ^1H NMR. ^1H NMR (THF-d_8, 200 MHz): δ 5.51 (three-line pattern, AA′BB′, 4.3 Hz separation of outer lines, 2H, C_5H_4); 5.43 (three-line pattern, AA′BB′, 4.3 Hz separation of outer lines, 2H, C_5H_4); 3.26 (t, $J = 6.9$ Hz, $C_5H_4CH_2$), 2.55 (m, $C_5H_4CH_2CH_2CH_2$), 2.02 (m, $C_5H_4CH_2CH_2$). IR (THF): 1902 (s), 1822 (s), 1505 (w) cm^{-1}.

$(CO)_2Re{=}C(OCH_3)CH_2CH_2CH_2(\eta^5\text{-}C_5H_4)$ (17). A solution of **16** (0.300 g, 0.72 mmol) and $(CH_3)_3O^+BF_4^-$ (0.120 g, 0.8 mmol) in acetone was stirred for 24 h at 25 °C. Solvent was evaporated, and the resulting yellow residue was extracted with CH_2Cl_2 and filtered through Celite. Preparative TLC (silica gel, 1:1 hexane−Et_2O) gave a yellow band ($R_f = 0.80$) from which **17** was isolated as a yellow solid (0.270 g, 0.69 mmol, 95%). ^1H NMR (acetone-d_6, 200 MHz) δ 5.46 (three-line pattern, AA′BB′, 4.0 Hz separation of outer lines, C_5H_4), 5.38 (three-line pattern, AA′BB′, 4.0 Hz separation of outer lines, C_5H_4), 4.20 (s, OCH_3), 2.44 (m, $C_5H_4CH_2$), 1.88 (m, $C_5H_4CH_2CH_2CH_2$), 1.68 (m, C_5H_4-CH_2CH_2). ^1H NMR (CD_2Cl_2, 200 MHz): δ 5.31 (s, C_5H_4), 4.21 (s, OCH_3), 2.40 (m, $C_5H_4CH_2$), 1.88 (m, $C_5H_4CH_2CH_2CH_2$), 1.67 (m, C_5H_4-CH_2CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 297.7 (Re═C); 204.6 (CO); 110.3 (Cp *C*CH_2); 86.6 (Cp CH); 84.3 (Cp CH); 64.4 (OCH_3), 51.2 ($C_5H_4CH_2$); 29.8 ($C_5H_4CH_2CH_2$); 25.6 ($C_5H_4CH_2CH_2CH_2$). IR (hexane): 1958 (vs), 1886 (vs) cm^{-1}. HRMS: *m/z* calcd for $C_{12}H_{13}O_3$-Re 392.0424, found 392.0423. Anal. Calcd for $C_{12}H_{13}O_3Re$: C, 36.82; H, 3.35. Found: C, 37.12; H, 3.46.

Table 2. Crystal Structure Data for (η^5-$C_5H_4CH_2CH_2OTs$)$Re(CO)_3$ (**5**), $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5$-$C_5H_4)$ (**9**), $(CO)_2Re{=}C(OCH_3)CH_2CH_2CH_2(\eta^5$-$C_5H_4)$ (**17**)

compound	**5**	**9**	**17**
empirical formula	$C_{17}H_{15}ReO_6S$	$C_{11}H_{11}ReO_3$	$C_{12}H_{13}ReO_3$
color; habit	white; block	yellow; needle	yellow; prism
crystal size, mm	0.5 × 0.2 × 0.2	0.5 × 0.1 × 0.1	0.5 × 0.4 × 0.3
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
unit cell dimens			
a, Å	10.969(3)	7.965(2)	8.3767(5)
b, Å	8.128(2)	8.624(2)	8.0042(4)
c, Å	20.227(3)	9.224(2)	17.1995
α, deg	90	116.48(2)	90
β, deg	104.152(9)	90.53(2)	95.170(2)
γ, deg	90	109.43(2)	90
vol, Å^3	1748.5(7)	525.4(2)	1148.51(11)
no. of peaks to determine cell	48	51	5120
θ range of cell peaks	1.94−22.49	1.50−22.50	3−25.5
temperature, K	116(2)	113(2)	133(2)
Z	4	2	4
formula wt	533.55	377.40	391.42
density (calcd), Mg m^{-3}	2.027	2.386	2.264
abs coeff, mm^{-1}	7.099	11.546	10.568
F(000)	1024	352	736
*R*1, %	3.60	4.06	3.46
*wR*2, %	8.36	10.66	9.70
S, gof	1.038	1.101	1.121

$(CO)_2Re{=}C(OH)CH_2CH_2CH_2(\eta^5$-$C_5H_4)$ (18). Aqueous HCl (0.5 M, 4 mL) was added to a mixture of 10 mL of CH_2Cl_2 and 10 mL of a yellow aqueous solution of **16** (0.268 g, 0.64 mmol). After 15 min of vigorous stirring, the CH_2Cl_2 layer was decanted, washed with H_2O, dried ($MgSO_4$), and concentrated to give **18** (0.137 g, 0.36 mmol, 57%) as a dark yellow oil. ^{1}H NMR (acetone-d_6, 200 MHz): δ 12.30 (s, OH), 5.35 (s, C_5H_4), 2.40 (m, $C_5H_4CH_2$), 1.75 (m, $Re{=}CCH_2$), 1.70 (m, $C_5H_4CH_2CH_2$). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 9.15 (s, OH), 5.35 (three-line pattern, AA′BB′, 4.4 Hz separation of outer lines, C_5H_4), 5.25 (three-line pattern, AA′BB′, 4.0 Hz separation of outer lines, C_5H_4), 2.38 (m, $C_5H_4CH_2$), 1.77 (m, $Re{=}CCH_2$), 1.68 (m, $C_5H_4CH_2CH_2$). ^{1}H NMR (C_6D_6, 200 MHz): δ 8.70 (s, OH), 4.75 (three-line pattern, AA′BB′, 4.4 Hz separation of outer lines, C_5H_4), 4.50 (three-line pattern, AA′BB′, 4.0 Hz separation of outer lines, C_5H_4), 1.60 (m, $C_5H_4CH_2$), 1.20 (m, $Re{=}CCH_2$), 1.05 (m, $C_5H_4CH_2CH_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 296.0 (Re=C); 205.0 (CO); 110.1 (Cp CCH_2); 86.0 (Cp CH); 85.1 (Cp CH); 50.6 ($C_5H_4CH_2$); 30.1 ($C_5H_4CH_2CH_2$); 25.0 ($C_5H_4CH_2CH_2CH_2$). IR (THF): 1945 (s), 1864 (s) cm^{-1}. HRMS: *m/z* calcd for $C_{11}H_{11}ReO_3$ 378.0267, found 378.0282.

$(CO)_2Re{=}C(HNCH_3)CH_2CH_2(\eta^5$-$C_5H_4)$ (19). Methylamine (9 mmol) was condensed into a solution of **9** (400 mg, 1.06 mmol) in THF (10 mL). After 12 h solvent was evaporated to give **19** as a yellow solid (366 mg, 92%). ^{1}H NMR (CD_2Cl_2, 200 MHz) (two isomers, 5:1 major/minor): (major isomer) δ 9.00 (br s, NH), 5.40 (three-line pattern, AA′BB′, 4.1 Hz separation of outer lines, C_5H_4), 5.27 (three-line pattern, AA′BB′, 4.1 Hz separation of outer lines, C_5H_4), 3.36 (t, J = 7.3 Hz, $C_5H_4CH_2$), 3.20 (d, J = 4.7 Hz, CH_3), 2.26 (t, J = 7.3 Hz, $C_5H_4CH_2CH_2$); (minor isomer) δ 9.15 (br s, NH), 5.70 (three-line pattern, AA′BB′, 4.1 Hz separation of outer lines, C_5H_4), 5.55 (three-line pattern, AA′BB′, 4.1 Hz separation of outer lines, C_5H_4), 3.71 (t, J = 7.3 Hz, $C_5H_4CH_2$), 3.17 (d, J = 4.7 Hz, CH_3), 2.85 (t, J = 7.3 Hz, $C_5H_4CH_2CH_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): (major isomer) δ 247.5 (Re=C); 206.1 (CO); 120.0 (Cp CCH_2); 83.2 (Cp CH); 82.5 (Cp CH); 69.9 (CH_3); 41.2 ($C_5H_4CH_2$); 23.3 ($C_5H_4CH_2CH_2$); (minor isomer) δ 247.0 (Re=C); 205.0 (CO); 117.9 (Cp CCH_2); 80.1 (Cp CH); 79.8 (Cp CH); 65.0 (CH_3); 41.5 ($C_5H_4CH_2$); 23.6 ($C_5H_4CH_2CH_2$). IR (CH_2Cl_2): 1916 (s), 1837 (s) cm^{-1}. HRMS: *m/z* calcd for $C_{11}H_{12}NO_2Re$ 377.0428, found 377.0431.

X-ray Crystallographic Determination and Refinement. Slow cooling of a saturated CH_2Cl_2−hexane solution of **5** gave white crystals suitable for X-ray analysis. Slow cooling of a saturated CH_2Cl_2−hexane solution of **9** gave yellow crystals suitable for X-ray analysis. Slow diffusion of hexane into a saturated solution of **17** in Et_2O in an inert atmosphere glovebox gave yellow crystals suitable for X-ray analysis. Intensity data were obtained with graphite-monochromated Mo Kα radiation on a Siemens P4 diffractometer at −125 °C. Crystallographic computations were carried out with SHELXTL and SHELXL−93.[27] A semi-empirical absorption correction was applied. The initial positions of the Re atoms were obtained by automatic Patterson interpretation. Other non-hydrogen atoms were obtained from successive Fourier difference maps coupled with isotropic least-squares refinement. All non-hydrogen atoms were refined anisotropically. Idealized positions were used for the hydrogen atoms. Crystallographic data are presented in Table 2. Atomic coordinates and equivalent isotropic displacement parameters and a complete list of bond lengths and angles are presented in the Supporting Information.

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Supporting Information Available: Tables listing X-ray crystallographic data for **5**, **9**, and **17** and bond angles and distances and text describing general experimental methods and experimental details and charcterization for (η^5-$C_5H_4CH_2CH_2$-Br)$Re(CO)_3$, (η^5-$C_5H_4CH{=}CH_2$)$Re(CO)_3$, $(CO)_2Re{=}C[NH(CH_3)]CH_2CH_2CH_2(\eta^5$-$C_5H_4)$, and ($\eta^5$-$C_5H_4$)$(CO)_2Re{=}C[NH(CH_3)]CH_3$ (28 pages). See any current masthead page for ordering and Internet access instructions.

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(27) Sheldrick, G. M. *SHELXTL Version 5 Reference Manual*; Siemens Analytical X-ray Instruments, Inc., 1994.