Characterization and Evidence for Alkylation of $CpRe(CO)_2H^-$ in the Conversion of $CpRe(CO)_2H_2$ to $CpRe(CO)_2R_2$. Synthesis of a Rhenacyclopentane and Its Thermolysis to Methylcyclopropane

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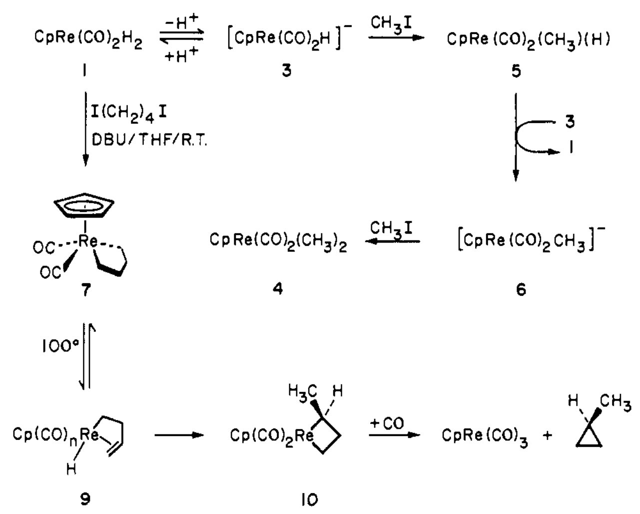
Treatment of $CpRe(CO)_2H_2$ (**1**: Cp = η^5-C_5H_5) with KOH in ethanol recently was reported[1] to give $CpRe(CO)_2^{2-}$ (**2**). Subsequent treatment of the product of this reaction with electrophiles led to several complexes having the formula $CpRe(CO)_2R_2$. We found this system to be interesting because of the surprisingly low apparent first and second pK_a's of the dihydride and because of the possible extension of the dialkylation reaction to the synthesis of metallacycles by using 1,*n*-dihaloalkanes.[2] In this communication we confirm the dialkylation reaction and report its successful application to the synthesis of a rhenacyclopentane. However, we have obtained evidence that **2** should be reformulated as $CpRe(CO)_2H^-$ (**3**), double alkylation occurring by sequential alkylation/deprotonation/alkylation steps. We also report preliminary results of the thermolysis of the rhenacyclopentane, which undergoes a novel ring contraction and reductive elimination sequence leading to methylcyclopropane.

In an attempt to prepare dianion **2**, we treated dihydride **1**[3] with an ethanolic solution of either KOH or KOEt. Upon addition of the solid dihydride to the basic solution a precipitate (K^+**3**) immediately appeared. Recrystallization of this material from THF yielded K^+**3** as slightly yellow crystals. Cation exchange of K^+**3** with tetraethylammonium bromide in THF followed by recrystallization from THF yielded yellow crystals of Et_4N^+**3**. Both salts were characterized by ^1H NMR and solution IR spectroscopy and elemental analysis.[4] The IR spectrum of Et_4N^+**3** is identical with the spectrum reported for Et_4N^+**2**, while the spectrum of K^+**3** differs only in the existence of a small shoulder which may be attributed to a weak ion pair formation. However, ^1H NMR exhibits a clear hydride resonance and a single Cp resonance in 1:5 intensity ratio as well as (for Et_4N^+**3**) a correct integration for 1 cation per Cp ring. On the basis of these data and the elemental analysis, we propose that the product of the reaction of dihydride **1** with base is $CpRe(CO)_2H^-$.

As reported earlier,[1] reaction of **3** with 1 equiv of MeI at low concentration (9.45 mM) leads to formation of $CpRe(CO)_2(Me)_2$ (**4**). However, we observe formation of an equal amount of dihydride **1** in this reaction. In contrast, when hydrido anion **3** is treated with an *excess* of MeI at high concentration (1.4 M) the exclusive product is the thermally sensitive hydrido methyl complex $CpRe(CO)_2(H)(Me)$ (**5**).[5] These results suggested to us the mechanism illustrated in Scheme I, involving sequential single deprotonation and alkylation steps for the alkylation of dihydride[6,7] **1**. At low MeI concentrations the initially formed hydrido methyl complex **5** is deprotonated by another equivalent of hydrido anion **3**, forming $CpRe(CO)_2Me^-$; this is subsequently alkylated to give the dimethyl complex **4**. At high concentrations of MeI all of the hydrido anion **3** is consumed before the second deprotonation step can occur, stopping the reaction at $CpRe(CO)_2(Me)(H)$.

Scheme I



The ability to convert dihydride **1** to the corresponding dialkyl complex **4** suggested the possibility of preparing metallacycles from 1,*n*-dihaloalkanes. However, in the dialkylation reaction half of the available rhenium is consumed as a simple base, yielding 1 equiv of the dihydride **1**. In an attempt both to use the rhenium more efficiently and to prepare a metallacycle, we examined the reaction of 1,4-diiodobutane and dihydride **1** in THF in the presence of the amine base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Under these conditions two new IR absorptions appeared at 1990 and 1910 cm^{-1} as the absorptions of the dihydride vanished. Chromatography (silica, hexane) and crystallization from hexane yielded metallacycle **7** as yellow air-stable crystals in 53% yield based on rhenium. Rhenacyclopentane **7** has been characterized by ^1H and ^{13}C NMR, IR, elemental analysis, solution molecular weight determination, and mass spectrometry.[8] The mass spectrum exhibits molecular ions at 362 and 364 in the correct intensity ratio for the two naturally occurring isotopes of rhenium. The molecular weight determined by the Signer isothermal distillation method[9] (363, calcd 363) is consistent with a mononuclear structure. The ^1H NMR exhibits a single Cp resonance and an $A_2B_2C_2D_2$ pattern in the alkyl region. This is consistent with a cis geometry of the metallacycle ring about the rhenium center making the faces exo and endo to the Cp ring inequivalent.

Thermolysis of metallacycle **7** in benzene-d_6 in a sealed tube proceeds rapidly at 100 °C and gives methylcyclopropane[10] in approximately 40% yield. Traces of 1-butene are also observed. $CpRe(CO)_3$[11] is produced in 50% yield along with another un-

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(1) Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783–787.

(2) Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, *1*, 1571–1579.

(3) Dihydride **1** was prepared in 72% yield by a modified route involving Zn/HOAc reduction of $CpRe(CO)_2Br_2$ (see ref 11b). This preparation will be described in detail in a later publication. For examples of the use of this reduction method in related systems, see: (a) Graham, W. A. G.; Moss, J. R. *Inorg. Chem.* **1977**, *16*, 75–79. (b) Shapley, J. R.; Adair, P. C.; Lawson, R. J.; Pierpont, C. G. *Ibid.* **1982**, *21*, 1702.

(4) $[Et_4N][CpRe(CO)_2H]$: ^1H NMR (200 MHz, CD_3CN) 4.86 (s, 5 H), 3.16 (q, J = 7.3, 8 H), 1.20 (d of t, J = 14, 6.1, 12 H, −12.35 (s, 1 H); IR (THF) 1846 (s), 1770 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_2NRe$: C, 41.08; H, 5.98; N, 3.19. Found: C, 41.41; H, 6.08; N, 3.31. Mp (under N_2) 118.5–120.5 °C. $KCpRe(CO)_2H$: ^1H NMR (CD_3CN) 4.87 (s, 5 H), −12.38 (s, 1 H); IR (THF) 1859 (s), 1775 (s), 1760 (sh) cm^{-1}. Anal. Calcd for $C_7H_6O_2ReK$: C, 24.20; H, 1.74; K, 11.3. Found: C, 24.42; H, 1.74; K, 11.3.

(5) Complex **5**: isolated yield 54% based on **3**; ^1H NMR ($CDCl_3$) 5.16 (s, 5 H), 0.68 (d, 3 H, J = 6.5), −10.12 (q, 1 H, J = 6.5); IR (hexane) 2014 (s), 1953 (vs); MS (70 eV) 322/324 M^+ ($^{185}Re/^{187}Re$). Anal. Calcd for $C_8H_9O_2Re$: C, 29.71; H, 2.81. Found: C, 29.59; H, 2.81.

(6) A referee has pointed out that a similar explanation was suggested for the formation of $Me_2Os(CO)_4$ from $Na[HOs(CO)_4]$ and CH_3I, cf.: (a) L'Eplattenier, F. *Inorg. Chem.* **1969**, *8*, 965. See also: (b) Carter, W. J.; Kelland, J. W.; Okrasinski, S. J.; Warner, K. E.; Norton, J. R. *Ibid.* **1982**, *21*, 3955.

(7) So far attempts to deprotonate $[CpRe(CO)_2H]^-$ have been unsuccessful; no reaction occurs when **3** is treated with $Li[N(i\text{-}Pr)_2]$ in acetonitrile or glyme. Apparently the difference between pK_1 and pK_2 for **1** is much larger than for polycarbonyl dihydrides such as $H_2Fe(CO)_4$ and $H_2Os(CO)_4$.[6b]

(8) **7**: ^1H NMR ($CDCl_3$) 5.32 (s, 5 H), 2.70 (m, 2 H), 2.20 (m, 2 H), 1.75 (m, 2 H), 1.60 (m, 2 H); (benzene-d_6) 4.34 (s, 5 H), 2.51 (m, 2 H), 2.38 (m, 2 H), 1.82 (m, 4 H); ^{13}C NMR ($CDCl_3$) 209.3 (s, 90.3 (d, J = 181), 36.6 (t, J = 126), 6.7 (t, J = 135); IR (THF) 1990 (s), 1910 (s) cm^{-1}. MS (70-eV electron impact), 362/364 M^+ ($^{185}Re/^{187}Re$). Anal. Calcd for $C_{11}H_{13}O_2Re$: C, 36.35; H, 3.61. Found: C, 36.02; H, 3.53.

(9) (a) Signer, R. *Justus Liebigs Ann. Chem.* **1930**, *478*, 246. (b) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

(10) Identified by comparison of its ^1H NMR spectrum and gas chromatographic retention time with those of an authentic sample.

identified rhenium fragment. We propose that formation of methylcyclopropane occurs by the mechanism outlined in Scheme I. Loss of CO or $\eta^5 \rightleftharpoons \eta^3$ isomerization of the cyclopentadienyl ring first generates a coordinatively unsaturated rhenium center. Next β-elimination gives rhenium butenyl hydride **9**, which may then reinsert the olefinic fragment in either of two ways: to regenerate the five-membered metallacycle **7** or to give rhenacyclobutane **10**. The rhenacyclobutane then rapidly reductively eliminates methylcyclopropane.[12] This is the first known example of a metallacyclopentane to metallacyclobutane ring contraction that leads to cyclopropane. It is interesting to contrast this reaction with one reported by Schrock et al.[13] in the tantalum series, where a similar ring contraction leads to olefins via β-elimination followed by reductive elimination.

Further studies involving attempts to isolate the rhenacyclobutane intermediates, characterize the second organometallic thermolysis product, and prepare larger ring systems are in progress.

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Registry No. 1, 78809-05-9; **2**, 80926-01-8; **3**, 87145-47-9; K^+**3**, 87145-51-5; Et_4N^+**3**, 87145-52-6; **4**, 55839-81-1; **5**, 87145-48-0; **6**, 87145-49-1; **7**, 87145-50-4; $CpRe(CO)_3$, 12079-73-1; methylcyclopropane, 594-11-6.

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(11) (a) Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1958**, 4314–4317. (b) King, R. B.; Reimann, R. H. *Inorg. Chem.* **1976**, *15*, 179–183.

(12) In agreement with this hypothesis, attempts to prepare the parent complex $CpRe(CO)_2CH_2CH_2CH_2$ from 1,3-diiodopropane and 1,3-propaneditosylate have yielded only cyclopropane.

(13) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451–5453.

Correlation between Thiophene Hydrodesulfurization Activity and the Number of First Sulfur Neighbors As Determined by EXAFS in Sulfided CoMo/γ-Al_2O_3 Samples

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Several attempts have been made to correlate the hydrodesulfurization (HDS) activity with chemical or physical parameters in CoMo HDS catalysts. For example, both O_2 chemisorption[1,2] and ESR signal intensity[3] have been found to correlate with the HDS activity in MoS_2 and sulfided Mo/γ-Al_2O_3. Similarly, for a given CoMo/γ-Al_2O_3 sample that was of modified activity following its use, Tauster and Riley[4] found that O_2 chemisorption correlated with HDS activity. On the other hand, Chung and Massoth[5] and Lôpez Agudo et al.[6] found that adding Co to Mo/γ-Al_2O_3 only slightly increases O_2 chemisorption, while the HDS activity increases at least by one order of magnitude. Similar results were obtained in our laboratory for the CoMo/γ-Al_2O_3 samples described below.[7] Thus O_2 chemisorption does not generally correlate with activity.

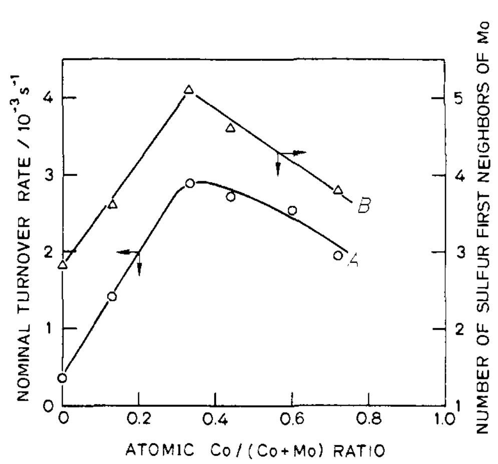

Figure 1. Dependence of NTR (curve A) and N_S (curve B) on the atomic Co/(Co + Mo) ratio of CoMo/γ-Al_2O_3 samples prepared by incipient wetness impregnation.

Here we present a correlation between the thiophene HDS activity and a structural parameter determined by X-ray absorption spectroscopy (XAS). To our knowledge, this is the first time this correlation has been noted.

Two series of samples were prepared. The first series involved incipient wetness impregnation of γ-Al_2O_3 powder with ammonium heptamolybdate solution, resulting in 7.7% Mo loading when dried and heated in air at 773 K for 2 h. Subsequent impregnations with $Co(NO_3)_2$ solutions of different concentrations produced a series with varying Co but approximately constant Mo loading. The second series was prepared by bulk impregnation of γ-Al_2O_3 pellets, using the same order of impregnation as above. The samples were reduced 0.5 h at 503 K in H_2 and then sulfided in 2% H_2S/H_2 for 0.5 h at 503 K, 0.5 h at 553 K, and 1.5 h at 613 K.

After sulfidation, the catalysts were tested for thiophene HDS in a fixed bed reactor at 573 K and atmospheric pressure. A nominal turnover rate (NTR, number of molecules of thiophene reacting per second per Mo atom) at 5% conversion of thiophene was used to compare the HDS activity of these samples. Curve A in Figure 1 shows the value of NTR vs. the atomic ratio α = Co/(Co + Mo). The nominal turnover rate increased with Co addition up to α = 0.33, and further Co addition decreased the thiophene HDS activity. This "volcano" curve has been widely reported in the literature[8,9] for unsupported and supported CoMo HDS catalysts.

The XAS measurements of the sulfided CoMo/γ-Al_2O_3 samples were carried out in a controlled-atmosphere cell at room temperature. After sulfidation, the samples were cooled to room temperature in the gas mixture used in the sulfidation and were kept under this mixture. Spectra were taken near the K edges of Co and Mo.

The radial distribution function (RDF) of the Co EXAFS in the samples up to α = 0.44 showed that no discrete Co phase was present. Only one single main peak at approximately 175 pm was observed in these samples. The sample with α = 0.72 showed both RDF of the Co EXAFS and near-edge structure very similar to Co_9S_8.

The RDF of the Mo EXAFS of MoS_2 and the sulfided CoMo/γ-Al_2O_3 samples were very similar. They showed two main peaks at approximately 192 and 280 pm. These peaks correspond to backscattering from sulfur and molybdenum, respectively. The number of S and Mo neighbors (N_S and N_{Mo}, respectively) of Mo in the sulfided samples was estimated from the height and position

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(5) Chung, K. S.; Massoth, F. E. *J. Catal.* **1980**, *64*, 332.

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