for Ph_2Hg, K_2 is large for all three at −105 °C.[15]

We have carried out a quantitative measurement of K_2 for PhI. Between −75 and −20 °C, all species [$(PhLi)_2$, $(PhLi)_1$, PhI, $Ph_2I^-Li^+$] are in rapid equilibrium (above coalescence). We have measured values for ΔH° and ΔS° for the phenyllithium monomer–dimer equilibrium,[16] so the population of the other species (PhI, $Ph_2I^-Li^+$) can be calculated from the average chemical shift of the ortho carbon in the ^{13}C NMR spectrum. We obtained $\Delta H^\circ = -9.9 \pm 0.6$ kcal/mol and $\Delta S^\circ = -44 \pm 9$ eu for eq 2.[17] Thus K_2 is 0.02 M^{-1} at 0 °C (a solution 0.1 M in PhLi and PhI is 0.1% associated), 30 M^{-1} at −78 °C (44% associated), and 1780 M^{-1} at −105 °C (92% associated). The corresponding association constant K_2 for Ph_2Te is almost the same as for PhI, as shown by an experiment in which 1 equiv of PhI was added to a solution of $Ph_3Te^-Li^+$ in THF at −105 °C.[20] Half of the $Ph_3Te^-Li^+$ was converted to $Ph_2I^-Li^+$.

Summary. Iodine, tellurium, and mercury ate complexes have been characterized as intermediates in the $PhLi/Ph_nM$ (M = I, Te, Hg) exchange reaction in THF solution at low temperatures. Monomeric phenyllithium is the reactive species in the Li/I and Li/Te exchanges. The formation constant for $Ph_2I^-Li^+$ is strongly temperature dependent, consistent with the powerful solvent-ordering capacity of a solvent-separated ion pair.[18]

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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[15] No PhLi or Ph_2Te could be detected in the ^{13}C NMR spectrum of 1:1 $PhLi/Ph_2Te$ solution at −105 °C (5–10% would have been seen).

[16] For $2(PhLi)_1 \rightleftharpoons (PhLi)_2$, $\Delta H^{\ddagger} = -7.4 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -2.5 \pm 1$ eu, $\Delta H^\circ = 0.5 \pm 0.7$ kcal/mol, and $\Delta S^\circ = 10 \pm 6$ eu. Green, D. P. Ph.D. Thesis, University of Wisconsin, 1989.

[17] For the equilibration of lithium fluorenide contact and separated ion pairs in THF: $\Delta H^\circ = -7.5$ kcal/mol and $\Delta S^\circ = -22$ eu.[18] Rate studies for the PhLi/ArBr exchange in ether ($\Delta H^{\ddagger} = 14$ kcal/mol, $\Delta S^{\ddagger} = -24$ eu)[7b] and THF (223 °K, $\Delta H^{\ddagger} = 9.5$ kcal/mol, $\Delta S^{\ddagger} = -30$ eu)[19] show negative entropies of activation.

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[20] Kinetic experiments such as depicted in Figure 1 of ref 1a show that K_2's for Te and I are also identical within experimental error at −78 °C.

Desulfurization of Thiophene and Thiophenol by a Sulfido–Cobalt–Molybdenum Cluster: Toward a Homogeneous Hydrodesulfurization Catalyst

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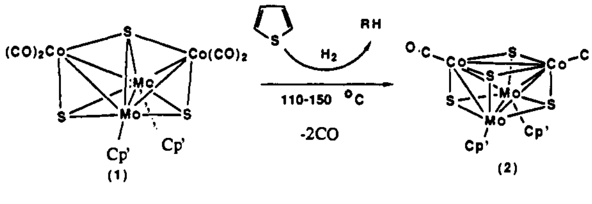
Received June 25, 1990
Revised Manuscript Received December 13, 1990

Conventional hydrodesulfurization (HDS)[1] catalysts are prepared by the coimpregnation of Mo (or W) and Co (or Ni) salts on an alumina support, followed by sulfidation with H_2S/H_2. The active site is thought to consist of small crystallites of MoS_2 with Co atoms coordinated to sulfur at the edges of the basal planes.[2] The mechanism of HDS has been studied through the aid of surface science and organometallic modeling studies,[3] but as yet there is no clear consensus on the detailed structure of the active site or on the mechanistic details of the HDS reaction itself.[4]

We have prepared sulfided bimetallic clusters[5] which mimic the metal composition of commerical HDS catalysts and have shown that one such cluster, $Cp'_2Mo_2Co_2(CO)_4S_3$ ($Cp' = CH_3C_5H_4$) (**1**), when supported on alumina and sulfided, produces the same active site as found in commercial Mo/Co/S catalysts.[6] We have begun an investigation of the solution chemistry of cluster **1** to see if a homogeneous analogue of the surface-bound HDS catalyst may be constructed.

Cluster **1** reacts under N_2 with thiophene[7] at temperatures ranging from 110 to 150 °C to give a >90% isolated yield of $Cp'_2Mo_2Co_2(CO)_2S_4$[9] (**2**), with the production of some black, insoluble material. If **1** is heated to 150 °C in toluene under N_2, no conversion to **2** takes place and **1** can be recovered unchanged. This indicates that **2** is not a decomposition product of **1**. The high yields (quantitative by NMR) of **2** obtained also indicate that **1** does not decompose to **2**. If the reaction is conducted under 200 psi (ca. 15 atm) of H_2, cluster **2** is again produced in high yields, the black solid is not formed, and analysis of the gases revealed the presence of ethane, propane, and butanes along with significant amounts of ethene, propene, and butene (eq 1). Compared to the hydrocarbon product slate from heterogeneous HDS catalysis, cracking and hydrogenation are more prevalent in the homogeneous reaction.



(1)

Reactions of thiophene with mononuclear organometallics result in the formation of either π-complexes or S-bound thiophene complexes, but the desulfurization of these complexes has not been reported.[11] There is only one other example of the reaction of thiophene with a transition-metal cluster: the reaction of $Fe_3(CO)_{12}$ with thiophene gives FeS and low yields of the dimetallic species $Fe_2(CO)_6(C_4H_4)$.[12] Thus, eq 1 represents the first desulfurization of thiophene accompanied by a clean, high-yield organometallic conversion.[13]

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[7] The reaction was carried out in a glass-lined Parr stainless steel reactor with thiophene as the solvent. Thiophene was purified according to the procedure outlined by Angelici (see ref 8) and was found to be stable when heated in the reactor to 150 °C in the presence of H_2. In a typical reaction, 100--200 mg of **1**, 30–40 mL of thiophene, and 200 psig of H_2 were used.

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[9] Complete conversion of **1** to **2** was obtained within 2 h at 150 °C and 6 h at 110 °C. Cluster **2** was isolated by decanting the reaction mixture from the reactor (inside a N_2-filled glovebag) into a Schlenk flask, followed by removal of the thiophene under vacuum. The solid residue was extracted with dichloromethane and filtered. Evaporation of the dichloromethane under vacuum resulted in pure **2** (as evidenced by ^1H NMR). The Cp analogue of **2** has been synthesized previously (see ref 10), and **2** could be identified on the basis of IR, ^1H NMR, MS, and elemental analysis. For **2**: IR (KBr) 1960, 1935 cm^{-1} (ν_{CO}); ^1H NMR (C_6D_6) δ 5.08 (m, 4 H), 4.86 (m, 4 H), 1.64 (s, 6 H); MS (EI) 652 (P^+), 624 ($P^+ - CO$), 596 ($P^+ - 2CO$); Anal. Calcd for $C_{14}H_{14}Mo_2Co_2O_2S_4$: C, 25.68; H, 1.93. Found: C, 25.78; H, 2.16.

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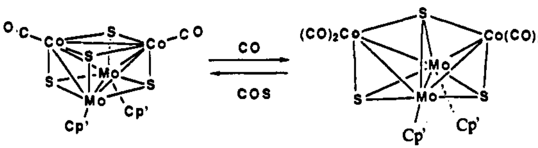
0002-7863/91/1513-1416$02.50/0

The reactions of **1** mimic desulfurization of thiophene over metal surfaces. Thiophene has been shown to readily undergo stoichiometric desulfurization on single-crystal surfaces such as Mo(100)[14] and Mo(110).[15] The products of these reactions are gaseous dihydrogen, surface carbon, and surface sulfur with no evidence for the formation of hydrocarbons. The deposition of sulfur on the metal surface is analogous to the formation of **2** from **1**. The reaction of **1** with thiophene in the absence of hydrogen also produces a black insoluble material which is presumed to be the carbon-containing residue from the desulfurization of thiophene. It is interesting to note that this residue is not produced when the desulfurization is conducted under H_2.

Conversion of **2** back to **1** would complete the cycle necessary for homogeneous, HDS catalysis. Thus, **2** gave a 20% conversion to **1** after 12 h when heated to 150 °C in toluene under 1000 psi of CO (eq 2), COS was identified via GC–MS as the only gaseous product. Independent experiments have shown that **1** abstracts sulfur from COS to form **2**. Thus, a higher CO pressure would give a higher conversion of **2** to **1**, Neither cluster **1** nor **2** reacts with H_2 (500 psi, 150 °C).



(2)

The reactions depicted in eqs 1 and 2 form the basis for a homogeneous catalytic cycle for the desulfurization of thiophene. However, under actual catalytic conditions (1000 psi of CO, 200 psi of H_2, thiophene), the forward reaction was inhibited by the presence of excess CO and no conversion of **1** to **2** was obtained.

In refluxing toluene, **1** (250 mg) reacted with thiophenol (1.0 mL in 100 mL of toluene) to give an 80% isolated yield of **2** after 7 h. Benzene was identified by GC–MS as the organic product. This reaction is the homogeneous analogue of the reaction of thiophenol on Mo(110)[16] surfaces, which produces adsorbed sulfur and benzene, Cleavage of aryl C–S bonds by transition-metal clusters has been reported,[17] but a mixture of organometallic products results. Under catalytic conditions (1000 psi of CO, 150 °C), PhSH (18 mmol) reacts with **1** (0.16 mmol) in 50 mL of xylene to afford only 0.01 mmol of PhH, 0.06 mmol of PhCHO, 0.04 mmol of PhCOSPh (phenyl thiobenzoate), 0.23 mmol of PhSSPh, and two as yet unidentified species with molecular weights of 134 and 204 (GC–MS, ca 0.03 and 0.02 mmol, respectively).[18] The sum of the yields of desulfurized compounds is approximately equal to the amount of **1** reacted; therefore, the desulfurization does not appear to be catalytic, but the formation of PhSSPh does. This reaction is under further investigation.

tert-Butyl isothiocyanate reacts with **1** in refluxing toluene to give, after 3 h, two products, **3** and **4**, in a 3;2 ratio, that are derived from **2** by substitution of the carbonyl groups by one or two *t*-BuNC ligands, respectively:[19]

$$\underset{\mathbf{1}}{\mathrm{Cp'_2Mo_2Co_2S_3(CO)_4}} + t\text{-BuNCS} \rightarrow \underset{\mathbf{3},\ x=1;\ \mathbf{4},\ x=2}{\mathrm{Cp'_2Mo_2Co_2S_4(CO)_{2-x}(CN\text{-}}t\text{-}\mathrm{Bu)}_x}$$

Sulfur abstraction from isothiocyanates has been observed previously.[20-22]

In summary, it is possible to desulfurize thiophene and thiophenol through the use of a sulfido bimetallic cluster in reactions analogous to those over single-crystal surfaces and in some respects to the Co/Mo/S-catalyzed HDS process. Further studies into the mechanism of these reactions should provide insight into the mechanism of HDS catalysis,

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE-8619864).

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[19] $Cp'_2Mo_2Co_2S_3(CO)_4$ (0.095 g, 0.040 mmol) was dissolved in 40 mL of toluene, and *t*-BuNCS (0.21 mL, 1.66 mmol) was added. The solution was refluxed under N_2 for 8 h. After removal of the solvent, a ^1H NMR spectrum of the brown solid in C_6D_6 showed a 3:2 ratio of $Cp'_2Mo_2Co_2S_4(CO)$(*t*-BuNC)–$Cp'_2Mo_2Co_2S_4$(*t*-BuNC)$_2$. The compounds were identified by comparison of their spectra with those of authentic compounds prepared from the cubane, **2**, and *t*-BuNC. For **3**: ^1H NMR δ 5.31 (m, 2), 5.26 (m, 2), 5.01 (m, 2), 4.98 (m, 2), 1.83 (s, 6), 0.88 (s, 9); IR 2111 m, 1953 s. For **4**: ^1H NMR δ 5.46 (m, 4), 5.11 (m, 4), 2.00 (s, 6), 0.88 (s, 18); IR 2101, 2071 cm^{-1}; MS(FAB), $[P]^+ = 762$.

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Catalytic Asymmetric Arylation of 2,3-Dihydrofuran with Aryl Triflates

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Received October 16, 1990

There has been considerable recent interest in the use of Heck-type arylation and alkenylation of olefins for constructing carbon skeletons of biologically important organic compounds.[1,2] Development of "asymmetric Heck reactions" where the carbon–carbon bond formation proceeds with high enantioselectivity would provide new efficient routes to the optically active compounds. Shibasaki and Overman have recently reported their pioneering works on the asymmetric Heck reactions, where in-

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