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Supplementary Material Available: Listings of observed and calculated structure factors, positional parameters, anisotropic thermal parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

Stepwise Reduction of Carbon Disulfide in the Coordination Sphere of Tungsten. A Transition-Metal-Mediated Synthesis of Dithioacetals[1]

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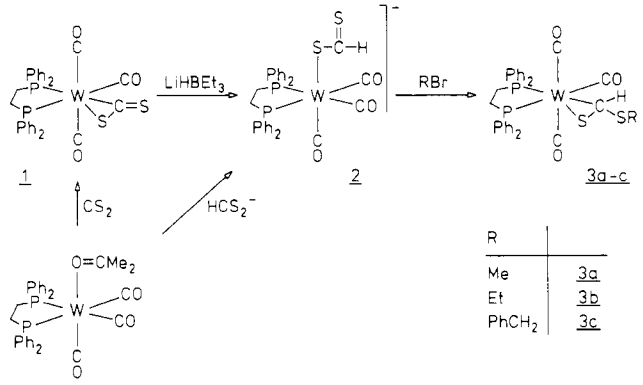
Summary: Reduction of *mer*-$W(CO)_3(dppe)(\eta^2\text{-}CS_2)$ (**1**) with $LiHBEt_3$ yields the dithioformate complex *fac*-$Et_4N[W(CO)_3(dppe)(\eta^1\text{-}SCHS)]$ (**2**) which may also be obtained by a simple ligand exchange reaction. Compound **2** reacts with alkyl halides in two steps via dithio ester complexes *mer*-$W(CO)_3(dppe)(\eta^2\text{-}SCHSR)$ (**3**) to dithiocarbenium ion derivatives *mer*-$[W(CO)_3(dppe)(\eta^2\text{-}R'SCHSR)]X$ (**4**). $LiHBEt_3$ reduces **4** to dithioacetal complexes *mer*-$W(CO)_3(dppe)(\eta^1\text{-}R'SCH_2SR)$ (**5**) which isomerize photochemically to the corresponding *fac* compounds **6**. Lewis bases readily displace the dithioacetal from **6** but not from **5**.

Transition-metal complexes of carbon disulfide are often seen as models for analogous but less readily available complexes of carbon dioxide. Studies of their reactivity may ultimately help in the development of transition-metal-mediated conversions of CO_2 into organic products.

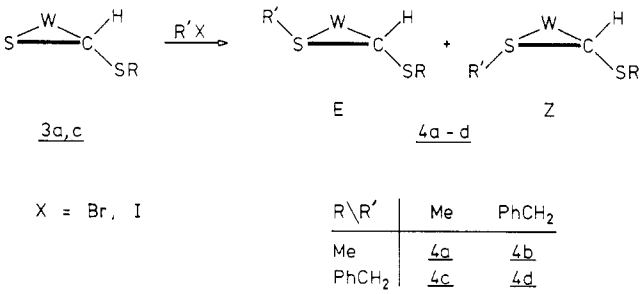
The number of known CS_2 complexes is vast,[2] and their reactions include electrophilic attack at sulfur,[2] sulfur abstraction,[2] cycloaddition with alkynes,[3] coupling with CS_2,[4] and oxidation to thiocarbonato species.[5]

After we had found that trialkylphosphines add at the CS_2 carbon atom of *mer*-$W(CO)_3(dppe)(\eta^2\text{-}CS_2)$ (**1**),[3f] we looked for reactions of other simple nucleophiles with **1**. Indeed, **1** reacts smoothly with $Li[HBEt_3]$ to give *fac*-$[W(CO)_3(dppe)(\eta^1\text{-}SCHS)]^-$ (**2**) which is isolated as Et_4N^+ salt.[6] Dithioformate complexes have mostly been obtained by insertion of CS_2 into metal–hydrogen bonds.[7] **2** and a number of other dithioformate complexes can also be prepared simply by ligand exchange reactions[8,9] (Scheme I).

Scheme I



Scheme II



2 reacts readily with mild alkylating agents such as alkyl or benzyl halides. Thus reaction with a stoichiometric amount of methyl bromide gives the methyl dithioformate complex **3a**.[10] Similarly the ethyl and benzyl derivatives

(1) Presented in part at the 29th IUPAC Congress, Köln, 1983; Abstracts of Papers, p 56.

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(6) A solution of **1** (0.26 g, 0.35 mmol) in THF (30 mL) is treated with a slight excess of $LiHBEt_3$ (0.5 M in THF). After addition of Et_4NBr (0.3 g, 1.4 mmol, dissolved in 10 mL of CH_2Cl_2) the solution is taken to dryness and the residue recrystallized twice from CH_2Cl_2/ethanol to remove LiBr and some dark decomposition products. **2** is isolated as dark orange microcrystalline powder in 46% yield.

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(8) To a solution of $W(CO)_3(dppe)$(acetone), freshly prepared by photolyzing $W(CO)_4(dppe)$ (5.52 g, 7.95 mmol) in acetone,[3f] is added $Et_4N[HCS_2]$ (2.07 g, 10.0 mmol). After evaporation to dryness, the residue is dissolved in 200 mL of CH_2Cl_2, some violet byproduct is filtered off, and ethanol (50 mL) is added. Upon slow evaporation in vacuo an orange powder separates. Recrystallization from CH_2Cl_2/ethanol yields 5.0 g (72%) of **2**: IR ν(CO) (CH_2Cl_2) 1910 (s), 1815 (s), 1790 (s) cm^{-1}; ^1H NMR (CH_2Cl_2, 60 MHz) HCS_2, 11.4 ppm. Anal. Calcd for $C_{38}H_{45}NO_3P_2S_2W$: C, 52.24; H, 5.19; N, 1.60. Found: C, 52.39; H, 5.22; N, 1.57.

(9) Buchner, W.; Schenk, W. A. *Inorg. Chem.*, in press. Schenk, W. A.; Rüb, D., unpublished results.

(10) A solution of **2** (0.87 g, 1.0 mmol) in THF (50 mL) is treated with a stoichiometric amount of methyl bromide. After 1.5 h the solution is filtered through Celite and evaporated to 20 mL. Addition of 10 mL of ethanol and further evaporation give **3a** (0.50 g, 66%) as orange powder: ^1H NMR ($CDCl_3$, 60 MHz) HCS_2, 5.30, SCH_3, 2.57 ppm. Anal. Calcd for $C_{31}H_{28}O_3P_2S_2W$: C, 49.09; H, 3.72. Found: C, 49.18; H, 3.83. **3b** and **3c** were prepared similarly. **3b**: yield 55%; ^1H NMR ($CDCl_3$, 60 MHz) HCS_2, 5.23, SCH_2, 2.85, CH_3, 1.33 ppm (^3J(H–H) = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) HCS_2, 47.63 (^1J(C–H) = 179 Hz), SCH_2, 37.27 (^1J(C–H) = 137 Hz), CH_3, 14.20 (^1J(C–H) = 126 Hz), CO(eq), 211.8, CO(ax), 198.8, 197.6 ppm; ^{31}P NMR ($CDCl_3$, 36.44 MHz) 41.7 (^1J(W–P) = 209 Hz), 42.6 ppm (^1J(W–P) = 219 Hz, ^2J(P–P) = 15 Hz). Anal. Calcd for $C_{32}H_{30}O_3P_2S_2W$: C, 49.75; H, 3.91; S, 8.30. Found: C, 49.98; H, 3.87; S, 8.38. **3c**: yield 77%; ^1H NMR ($CDCl_3$, 60 MHz) HCS_2, 5.15; SCH_2, 4.10 ppm. Anal. Calcd for $C_{37}H_{32}O_3P_2S_2W$: C, 53.25; H, 3.86; S, 7.68. Found: C, 53.42; H, 4.09; S, 7.86.

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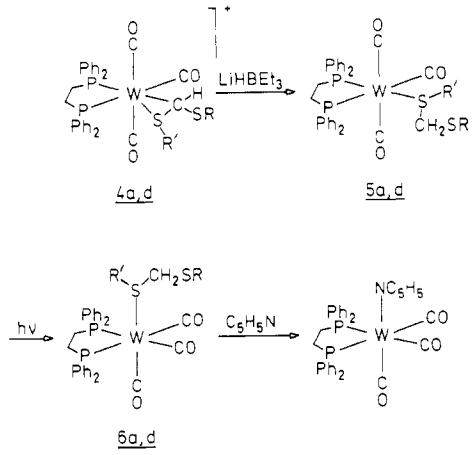
Scheme III



3b and **3c** are obtained (Scheme I). The ^1H and ^{13}C resonances of η^1-coordinated dithioformate ion typically appear at low field (e.g., 11.7 and 240 ppm, respectively, in $[W(CO)_5SC(S)H]^-$[9]). The high-field resonances found for the HCS_2 moiety in **3b** clearly indicate η^2-coordination of the C=S group. The complexes **3** are thus analogous to the recently discovered η^2-thioformaldehyde complexes of Os, Re, Mn, and Rh.[11] In this bonding mode the C=S group appears to be a very good π acceptor as judged from the high CO stretching frequencies of **3a–c** (2008 (w), 1940 (m), 1892 (s) cm^{-1} (CS_2), virtually identical for the three compounds). η^1-Coordination of the C=S group was found in various $M(CO)_5$ derivatives of thioketones, esters, and amides.[12] Apparently the higher electron density at the $W(CO)_3$(dppe) fragment favors the side-on bonding mode.

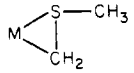
The dithio ester complexes **3** react with further alkyl halide according to Scheme II. The products **4** may be seen as composed of either a dithiocarbenium ion

$$R\bar{S}\text{–}C^+(H) - \bar{S}R \leftrightarrow RS^+{=}C(H) - \bar{S}R'$$

as a two-electron donor and a tungsten(0) unit or a dithiocarbanion

$$R\bar{S}\text{–}C^-(H)\text{–}\bar{S}R'$$

as a four-electron donor and a tungsten(II) unit. Analogous alkylations have been reported for η^2-thioformaldehyde complexes;[11a,be] however, compounds with the structural unit



have been obtained much earlier by a different route.[13]

If R′ = Me, a 7:3 mixture of *E* and *Z* isomers is formed in the second alkylation step as seen from the ^1H and ^{31}P NMR spectra.[14] Benzyl bromide appears to react more selectively giving only one compound, probably the sterically less encumbered *E* isomer. On this basis we tentatively assign the minor peaks in the NMR spectra of **4a** and **4c** to the *Z* isomers. Interestingly, reaction of **3a** with benzyl bromide gives **4b**, whereas reaction of **3c** with methyl bromide gives **4c** (as *E*/*Z* mixture) which is an isomer of **4b**. No interconversion occurs at room temperature, even over a period of several days.

The cations **4** again add hydride at carbon forming meridional dithioacetal complexes **5**[15] (Scheme III). The *mer* isomers **5** are stable in the dark; exposure to ambient light, however, causes quantitative rearrangement to the facial complexes **6**.[16] The dithioacetal is readily displaced from **6** under fairly mild conditions.[17] By contrast, **5** reacts with $P(OPh)_3$ only slowly at 60 °C to give a mixture of *fac*- and *mer*-$W(CO)_3$(dppe) [$P(OPh)_3$]. Probably the rate-determining step for the thermal substitution of the dithioacetal from **5** is the intramolecular isomerization **5** → **6**. A similar situation has been encountered for the substitution of maleic ester from *mer*-$Mo(CO)_3$(dppe)(di-

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(14) **4a** and **4d** may be synthesized directly from **2**. **4a**: A solution of **2** (1.75 g, 2.0 mmol) in THF (60 mL) is treated with methyl iodide (1 mL) at ambient temperature for 1 h. After filtration the product is precipitated by adding toluene (35 mL). NMR reveals the presence of *E* and *Z* isomers. *E*: ^1H NMR ($CDCl_3$, 60 MHz) SCH_3, 2.78, $WSCH_3$, 1.97, WCH, 5.28 ppm; ^{31}P NMR ($CDCl_3$, 36.44 MHz) 35.0 (J(W–P) = 211 Hz), 34.6 ppm (J(W–P) = 188 Hz, J(P–P) = 15 Hz). *Z*: ^1H NMR ($CDCl_3$, 60 MHz) SCH_3, 2.47, $WSCH_3$, 1.80, WCH, 4.97 ppm; ^{31}P NMR ($CDCl_3$, 36.44 MHz) 35.5 ppm (J(W–P) = 194 Hz), 34.6 (J(W–P) = 207 Hz, J(P–P) = 16 Hz). After recrystallization from CH_2Cl_2/toluene 1.20 g (60%) of (*E*)-**4a** is obtained as iodide with 1 mol of toluene of crystallization: yellow crystalline powder; IR ν(CO) (CH_2Cl_2) 2043 (m), 1985 (m), 1920 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{31}IO_3P_2S_2W{\cdot}C_7H_8$: C, 47.19; H, 3.96; S, 6.46. Found: C, 46.47; H, 3.86; S, 6.70. **4d**: A solution of **2** (1.75 g, 2.0 mmol) in nitromethane (10 ml) is treated with benzyl bromide (1 mL) at 40 °C for 1 h. Upon evaporation to 3 mL **4d** precipitates as yellow crystals which are collected by filtration and washed with ethanol and ether: yield 1.55 g (77%) of pure *E* isomer; ^1H NMR ($CDCl_3$, 60 MHz) SCH_2, 3.68, $WSCH_2$, 2.70 (unresolved AB systems), WCH, 4.87 ppm. Anal. Calcd for $C_{44}H_{39}BrO_3P_2S_2W$: C, 52.55; H, 3.91; S, 6.38. Found: C, 52.04; H, 3.76; S, 6.21. **4b**: To a solution of **3a** (0.41 g, 0.54 mmol) in CH_2Cl_2 (2 mL) is added 0.3 mL of benzyl bromide. After 15 min **4b** is precipitated with 3 mL of ether, collected on a frit, washed with ether, and dried in vacuo: yield 0.50 g (91%); ^1H NMR ($CDCl_3$, 60 MHz) SCH_3, 2.17, $WSCH_2$, 2.80 (unresolved AB system), WCH, 5.23 ppm. Anal. Calcd for $C_{38}H_{35}BrO_3P_2S_2W{\cdot}CH_2Cl_2$: C, 46.18; H, 3.68; S, 6.32. Found: C, 46.88; H, 3.80; S, 6.25. **4c**: To a solution of **3c** (0.70 g, 0.84 mmol) in nitromethane (10 mL) is added 0.5 mL of methyl bromide. After 30 min the mixture is evaporated in vacuo to 3 mL and 10 mL of ether is added. The resulting yellow oil is treated with NH_4PF_6 (0.16 g, 1.0 mmol) in CH_2Cl_2 (10 mL). Filtration through Celite and precipitation with ethanol gives **4c** as the hexafluoro phosphate salt: ^1H NMR ($CDCl_3$, 60 MHz) *E*, SCH_2, 4.25, $WSCH_3$, 1.60, WCH, 4.87 ppm, *Z*, SCH_2, 4.00, $WSCH_3$, 1.17, WCH, 4.93 ppm. Anal. Calcd for $C_{38}H_{35}F_6O_3P_3S_2W$: C, 45.89; H, 3.55; S, 6.45. Found: C, 45.96; H, 3.69; S, 6.18.

(15) **4d** (1.0 g, 1.0 mmol) is treated with 3 mL of Li[$HBEt_3$] (0.5 M in THF) at 0 °C. After filtration 2 mL of ethanol and 10 mL of water are added, the yellow crystalline **5d** is collected on a frit, washed with water and ethanol, and dried in vacuo: yield 0.76 g (82%); IR ν(CO) (benzene) 1955 (w), 1855 (vs) cm^{-1}; ^{31}P NMR ($CDCl_3$, 36.44 MHz) 49.3 (J(W–P) = 320 Hz), 36.2 (J(W–P) = 222 Hz, J(P–P) = 15 Hz). Anal. Calcd for $C_{44}H_{40}O_3P_2S_2W$: C, 57.03; H, 4.35; S, 6.92. Found: C, 57.21; H, 4.19; S, 7.03.

(16) A solution of **5d** (0.20 g, 0.22 mmol) in benzene (2.5 mL) is stirred under ambient light. After complete conversion (IR, 10 min under direct sunlight) the product is precipitated with hexane. A nearly quantitative yield of yellow crystalline **6d** is obtained: IR ν(CO) (benzene) 1934 (s), 1835 (s) cm^{-1}. Anal. Calcd for $C_{44}H_{40}O_3P_2S_2W$: C, 57.03; H, 4.35. Found: C, 56.62; H, 4.43.

(17) **6d** (0.45 g, 0.49 mmol) is treated overnight with 0.25 mL of pyridine in 3 mL of THF. After removal of the solvent the dry residue is extracted with 3 mL of hexane. Filtration, addition of 1 mL of ethanol, and evaporation to 0.5 mL gave colorless crystalline $(PhCH_2S)_2CH_2$. Recrystallization from ethanol and sublimation at 110 °C (0.1 torr) yielded about 30 mg (24%) of product which still had a low melting point (47–48 °C (lit.[18] 54–55 °C)) but gave the expected ^1H NMR [($CDCl_3$, 60 MHz) SCH_2S, 3.35(2), SCH_2Ph, 3.82 (4), C_6H_5, 7.27 ppm (10)] and mass spectrum [*m/e* 260 (7.5), M^+, 169 (1.5), $M^+ - C_7H_7$, 136 (40), $M^+ - C_7H_8S$, 91 (100), $C_7H_7^+$)]. Alternatively the free dithioacetal may be obtained by irradiating **5d** in THF/pyridine.

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methyl maleate).[19] This is in accord with the cis labilization model[20] and casts some doubt on the recent interpretation of ligand dissociation from compounds *trans*-$Cr(CO)_4(PR)_3(L)$ as occurring *without* initial rearrangement to the cis isomers.[21]

Dithioacetals are important intermediates in organic syntheses.[22] The reaction sequence described in this communication amounts to a transition-metal-mediated synthesis of this class of compounds from either CS_2 or dithioformate. Not only is the organic product readily removed from the complex, but also the metal is recovered in a suitably reactive form to repeat the cycle. Work is in progress to extend this synthesis to different dithiocarboxylates as well as to nucleophiles other than hydride.

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Significance of the Temperature Dependence of the Deuterium KIE Associated with the Protic Cleavage of Dialkylmercurials[1]

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Summary: The temperature dependence of the kinetic isotope effect associated with the protic cleavage of di-*n*-octylmercury by several carboxylic acids and hydrogen chloride is reported. The results reveal that reaction is accompanied by proton tunneling which is not influenced by electronic factors but is increased by steric factors. calculations suggest a barrier width of 1.2–1.4Å. A mineral acid (anhydrous hydrogen chloride) exhibits a behavior significantly different from that of carboxylic acids. The influence of solvent and added halide on transition-state parameters is also reported.

The protic cleavage of carbon–metal σ bonds ranks among the simplest of all electrophilic substitution processes.[2] For a variety of reasons,[3] the most definitive (kinetic and stereochemical) studies of protonolyses have focused on the protic cleavage of organomercurials. In an effort to extend our understanding of the nature of such processes, we have determined the temperature dependence of the deuterium kinetic isotope effect (KIE) associated with the cleavage of a representative organomercurial by various protic acids.

$$RHgR \xrightarrow{HA\text{-}DA} RH(D) + RHgA$$

The resulting data are seen in Tables I and II and reveal several heretofore unknown aspects about the nature of such protonolyses. First, they indicate that in dioxane, protic cleavage with carboxylic acids is accompanied by appreciable proton tunneling.[4,5] Second, they show that within an homologous series, the extent of tunneling is not significantly influenced by the strength of the carboxylic acid (electronic factors) but is notably affected by steric considerations. Third, calculations based on the Bell theory[5a] of protein tunneling suggest a barrier width, a, of ca. 1.2–1.4 Å and a classical transition state which remains essentially *symmetrical* as the steric bulk of the acid increases.

Fourth, as judged by the comparatively similar rate constants, k_H, the change from polar (dioxane) to nonpolar (nonane) solvent results in only a minor (ca. a factor of 4) influence on the rate of protic cleavage of dialkylmercurials by carboxylic acids (cf. entries 1 vs. 8 and 5 vs. 9). Nevertheless, the KIE parameters for the same entries reveal that the mechanism of protonolysis is moderately influenced by the nature of the solvent. In fact, the situation in nonane is complicated by the fact that carboxylic acids are associated (dimeric) in hydrocarbon solvent but unassociated (monomeric) in dioxane at varitually all concentrations.[8,15a] Thus, the unusual solvent effect, i.e., $k_{nonane} > k_{dioxane}$, and the rate accelerating salt effect observed in dioxane (vide infra), are both consistent with the likelihood that the protic demercuration of dialkylmercurials by carboxylic acids in dioxane and nonane proceeds by different mechanisms.

Fifth, the behavior of hydrogen chloride stands in distinct contrast to that of carboxylic acids (cf. entries 1–5 and 10): the tunneling apparent with carboxylic acids is experimentally unobserved with anhydrous hydrogen chloride.

Sixth, although the calculated tunnel corrections (Table

(1) Supported by the NSF, Grant CHE 80-17045, and the DOE, Contract No. DE-ASO5-80Er10661.

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(3) Organomercurials are readily prepared in high purity, can be manipulated with facility, and are monomeric in solution.
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