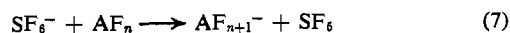


Figure 1. Electron capture ionization efficiency curves ($P(\text{SF}_6)$ 0.62 μ , $P(\text{PF}_5)$ 0.38 μ): \circ , PF_6^- (ion current $\times 100$); \bullet , SF_6^- (ion current $\times 33$); ∇ , SF_5^- .

PF_4^-) can only be detected at electron energies where the primary ion is formed, a comparison of the electron capture ionization efficiency curves for PF_6^- (or PF_4^-) with the curves for SF_6^- and SF_5^- should permit selecting reaction 4 or 5. Typical capture curves for SF_6^- , SF_5^- , and PF_6^- are shown in Figure 1. From this it is clear that reaction 4 is the process leading to the formation of PF_6^- in the ion source. Similar results were obtained for PF_4^- . Thus the general reaction



indicates the fluoride ion transfer process occurring with SF_6^- .

This study was carried out using an Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer⁹ which has been modified for studying ion-molecule reactions. Pressure in the ionization chamber was measured with an MKS Baratron Model 144 capacitance manometer which is attached directly to the ionization chamber by 1 ft of a stainless steel-glass tubing connection apparatus.

Acknowledgment. The support of the Research Corporation is gratefully acknowledged. We thank the National Science Foundation for providing funds to aid in purchasing the mass spectrometer.

(9) J. G. Dillard, *Inorg. Chem.*, **8**, 2148 (1969).

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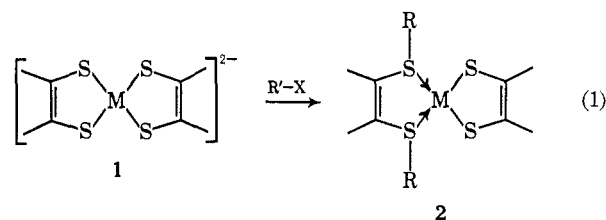
Methyl Derivatives of Tris(*cis*-stilbenedithiolates) of Tungsten and Rhenium¹

Sir:

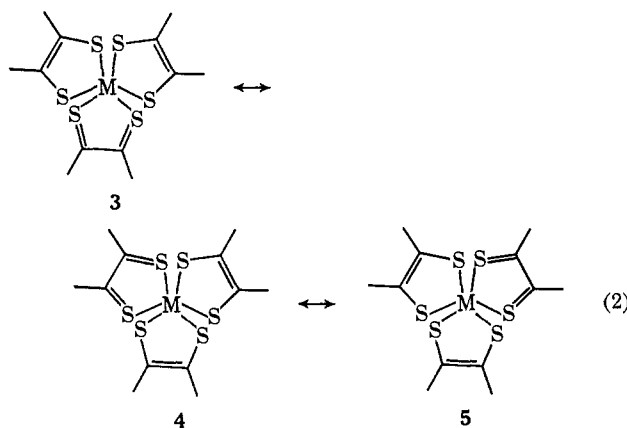
The sulfur atoms in the planar d^8 metal bisdithiienes^{2,3} $\text{MS}_4\text{C}_4\text{R}_4$ with R, e.g., aryl or alkyl, but not with induc-

(1) This work was supported by Grant No. 3486-A3 of the Petroleum Research Fund, administered by the American Chemical Society.

tively electron-attracting substituents such as CF_3 or CN, become sufficiently nucleophilic on reduction to the dianions $\text{MS}_4\text{C}_4\text{R}_4^{2-}$ to react with alkylating agents according to eq 1.⁴ A theoretical analysis of the bond-

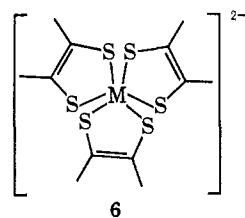


ing situation in the neutral group VI metal trisdithiienes $\text{MS}_6\text{C}_6\text{R}_6$ revealed the ground-state electronic configuration to be fundamentally related to that of the neutral d^8 metal dithiienes, leading to the group theoretically derived set of canonical structures 3-5⁵ mainly contribut-



ing to the ground state.

On reduction to the dianions the neutral group VI metal trisdithiienes could therefore be expected to become "trisdithiolates" 6. However, the bonding in the



anionic derivatives $\text{MS}_6\text{C}_6\text{R}_6^{2-}$ is more complicated than in the planar species $\text{MS}_4\text{C}_4\text{R}_4^{2-}$. Depending on the metal and the dithiene substituents the electrons could initially occupy either of the energetically close-lying orbitals $5e'$ or $2a'_2$. The former is delocalized over the whole molecule of complex but has significant metal character. The latter is a pure ligand π MO. In addition to this ambiguity, a change in the coordination geometry from trigonal prismatic to octahedral or distorted octahedral is likely to occur as a result of the reduction to the dianion. Although the available evi-

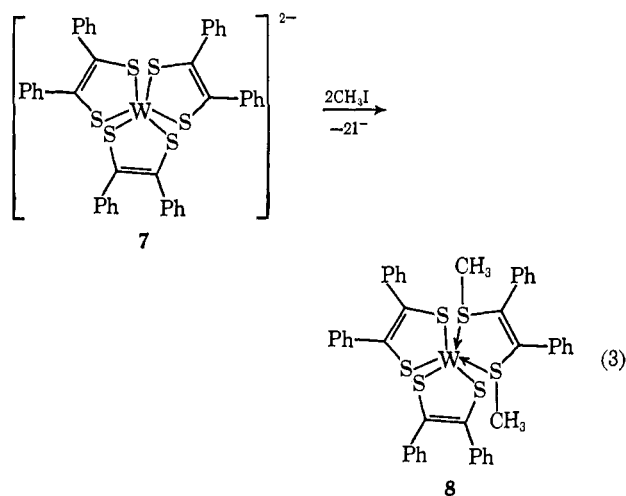
(2) "Dithiienes" are coordination compounds of metals and ligands in a state intermediate between 1,2-dithiodiketones and *cis*-1,2-ethylenedithiolates as, for example, $\text{NiS}_2\text{C}_2\text{Ph}_4$. This nomenclature^{3a} is preferred to the indiscriminate naming of all of the chelates as "dithiolenes."^{3b}

(3) (a) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969); (b) *Transition Metal Chem.*, **4**, 299 (1968), and references cited therein; (c) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(4) G. N. Schrauzer and H. N. Rabinowitz, *J. Am. Chem. Soc.*, **90**, 4297 (1968).

(5) G. N. Schrauzer and V. P. Mayweg, *ibid.*, **88**, 3235 (1966).

dence indicates that the ligands in the reduced species **6** are indeed more nearly dithiolato dianions than in the neutral trisdithienes, it appeared to be of interest to demonstrate the nucleophilicity of the sulfur atoms through alkylation experiments. Previous attempts to methylate the anions $MS_6C_6Ph_6^{2-}$ with $M = Cr, Mo,$ or V ($Ph = phenyl$) failed to yield stable complexes. However, bis(*cis*-methylthiostilbene) was formed, suggesting that the methylation took place but that the desired alkyltrisdithiolato complexes were unstable under the reducing conditions employed. By reducing $WS_6C_6Ph_6$ in tetrahydrofuran with a slight excess of anhydrous hydrazine the hydrazonium salt of $WS_6C_6Ph_6^{2-}$ dissolves in the lower layer of the reaction mixture. Upon the addition of excess methyl iodide reaction occurred according to eq 3. The olive green crystals of dimethyl-



tris(*cis*-stilbenedithiolato)tungsten (**8**) were recrystallized from $CH_2Cl_2-CH_3OH$, mp 211° dec. *Anal.* Calcd for $C_{44}H_{36}S_6W$: C, 56.16; H, 3.86; S, 20.44; W, 19.54. Found: C, 56.32; H, 3.90; S, 20.45; W, 19.80.

Complex **8** reacts with ethylenebis(diphenylphosphine) in the melt to form bis(*cis*-methylthiostilbene) and the known adduct $WS_4C_4Ph_4Ph_2P(CH_2)_2PPh_2$ (**9**),⁶ thus proving the 1,4-S-methylated structure. The infrared spectrum is similar to that of dimethyl(*cis*-stilbenedithiolato)nickel⁴ and typical of a compound containing ethylenedithiolato and bis(*cis*-methylthiostilbene) ligands. The three characteristic infrared "dithiene bands" are

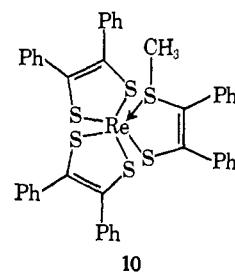
Table I. Absorption Maxima (in CCl_4H Solution) in the Optical Spectra of Methyl Derivatives of Trisdithiolates of W and Re and of Related Complexes

Compound	Obsd, cm^{-1} (log ϵ)
$WS_6C_6Ph_6$	15,150 (4.44); 18,520 (3.48); 23,980 (4.07); 33,330 (4.25)
$WS_4C_4Ph_4 \cdot Ph_2P(CH_2)_2PPh_2$	11,765 (sh) (2.301); 14,815 (2.425); 18,349 (3.209)
$W(CH_3)_2S_6C_6Ph_6$	16,103 (3.611); 20,366 (3.867); 27,624 (4.072)
$ReS_6C_6Ph_6$	8,312 (2.89); 14,184 (4.32); 19,920 (3.65); 23,474 (4.00)
$Re(CH_3)_2S_6C_6Ph_6$	10,163 (3.31); 14,306 (3.93); 19,417 (4.068); 25,840 (sh) (4.193); 32,258 (4.525); 35,587 (4.777)

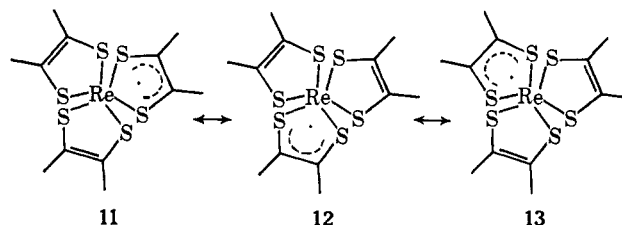
(6) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **88**, 5174 (1966).

absent, indicating a "classical" dithiolato structure rather than an intermediate delocalized binding situation. This is consistent with the optical absorption spectrum (Table I) which lacks the intense low-energy transitions of the prismatic trisdithienes. The nmr spectrum in CS_2 shows a single peak of methyl group protons at 3.25 ppm. The phenyl protons appear as two signals at 7.07 and 7.15 ppm; the intensity ratio of the methyl and phenyl signals is 6:10:20, as expected. Attempts to methylate **8** further were unsuccessful. We have also been unable to obtain methyl derivatives of chromium, molybdenum, or vanadium tris(*cis*-stilbenedithiolates) by the hydrazine reduction method. These complexes, if they exist, are apparently less stable, decomposing as they are formed as also follows from the isolation of bis(*cis*-methylthiostilbene) out of these reaction mixtures. The anions of $WS_6C_6(CF_3)_6$ and $MoS_6C_6(CF_3)_6$ could not be methylated.

However, the methylation of $ReS_6C_6Ph_6^-$ under similar conditions afforded a purple monomethyl derivative, $ReCH_3S_6S_6Ph_6$ (**10**), mp $\sim 350^\circ$ dec (recrystallized from $CCl_2H_2-CH_3OH$). *Anal.* Calcd for $C_{43}H_{33}S_6Re$: C, 55.63; H, 3.58; S, 20.72; Re, 20.06. Found: C, 55.86; H, 3.60; S, 20.43; Re, 20.11. The 1H nmr spectrum of **10** in CS_2 shows a single methyl proton signal at 2.53 ppm and the phenyl protons as three peaks at 7.15, 7.08, and 7.05 ppm in the over-all intensity ratio of 3:20:5:5, in accord with the nonequivalence of the methylated and nonmethylated ligands present. The



infrared spectrum is similar to that of **8** and indicative of a "dithiolato" rather than "dithiene" structure. This also follows from the optical absorption spectrum (Table I, Figure 1) which is similar to that of **8** and atypical for a dithiene. The existence of **8** demonstrates that the ligands in the neutral group VI metal trisdithienes are intrinsically electron deficient and two electrons short of the trisdithiolato structure, thus confirming the ground-state representations **3-5** as well as the MO description. The prismatic neutral trisdithienes of rhenium must contain one electron in an antibonding ligand MO, presumably $2a'_2$, a situation consistent with the lack of asymmetry of the g tensor observed in, e.g., $ReS_6C_6H_6$ or $ReS_6C_6Ph_6$,⁵ and plausibly represented by the set of limiting structures **11-13**.



Since the ions $ReS_6C_6Ph_6^-$ and $WS_6C_6Ph_6^{2-}$ are iso-electronic, complexes **8**, **9**, and **10** thus are derivatives

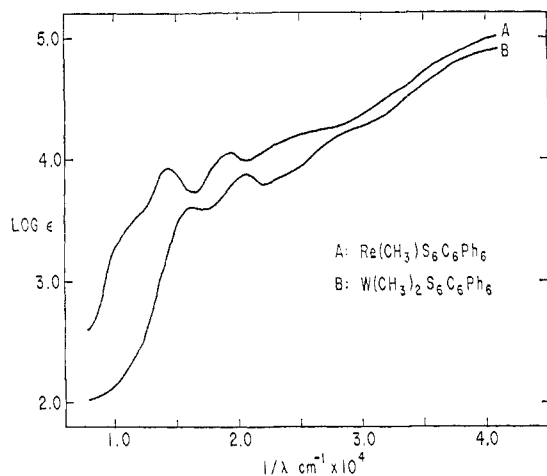


Figure 1. Absorption spectra of complexes 8 and 10 in CH_2Cl_2 .

of W(IV) and Re(V). Their coordination geometry could be trigonal prismatic, but we predict them to be octahedral or distorted octahedral since the prismatic coordination appears to be energetically favored only in the delocalized trisdithienes and not in trisdithiolates. We finally point out that the electronic structure of anions $\text{MS}_6\text{C}_6\text{R}_6^{z-}$ ($z = 1, 2$) may depend on the nature of R as well as M. The unpaired electrons in the anions of first- and second-row transition metal derivatives occupy MO's with appreciable metal character.^{5,7} If these ions are trigonal prismatic this would suggest that the $5e'$ orbital rather than $2a'_2$ is occupied in these cases.

(7) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965).

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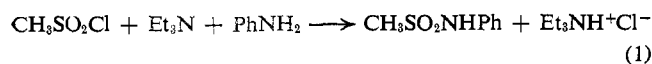
Received August 29, 1969

The Mechanism of Formation of Sulfenes by Dehydrohalogenation of Alkanesulfonyl Chlorides

Sir:

It has been concluded from product analysis studies that sulfenes are produced as unstable intermediates by the action of base on alkanesulfonyl halides possessing at least one α -hydrogen atom.¹ We now report the results of a kinetic investigation which corroborates this hypothesis and permits a relatively detailed description of the mechanism of the formation of sulfenes in this reaction.

We have found that the rate of the reaction of methanesulfonyl chloride with triethylamine and aniline at -25° in 1,2-dimethoxyethane can be measured by isolation of the sulfonanilide, or, more efficiently, by titration of the chloride ion produced, the rate constants obtained either way being the same within experimental error.



(1) For leading references see G. Opitz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967).

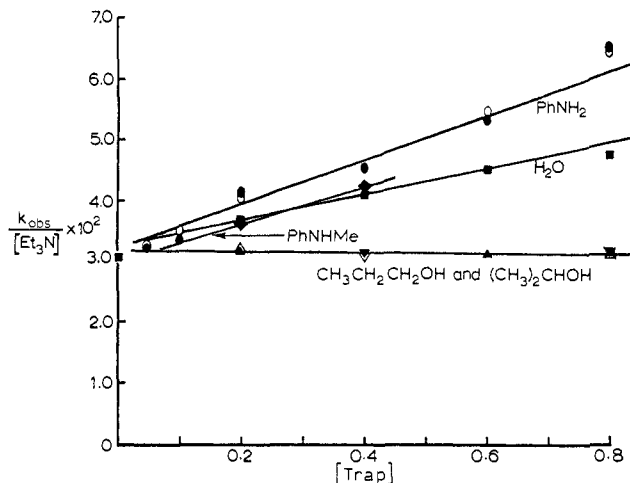


Figure 1. Plot of the pseudo-first-order rate constant divided by the triethylamine concentration (M) of the "sulfene trapping agent" for the reaction of methanesulfonyl chloride (initial concentration $2.0 \times 10^{-3} M$) in 1,2-dimethoxyethane at $-25.0 \pm 0.2^\circ$. "Trapping agents" are indicated above except for 2-propanol and 1-propanol which are given by the triangles (Δ) and inverted triangles (∇), respectively. Closed ellipses, triangles, etc., refer to runs in which $[\text{Et}_3\text{N}] = 4.0 \times 10^{-2} M$; open ellipses, etc., $[\text{Et}_3\text{N}] = 2.0 \times 10^{-2} M$.

The data for this and some related experiments are summarized in Figure 1; analogous results were obtained with phenylmethanesulfonyl chloride and pyridine at 25° . With propyl or isopropyl alcohol as the "sulfene trap" the reaction was found to be strictly second order: first order in both sulfonyl chloride and tertiary amine and zero order in the alcohol. As is evident from Figure 1, with the other "sulfene trapping agents" there is a linear dependence of k_{obs} , the pseudo-first-order rate constant, on the concentration of the "sulfene trap," and each of these straight lines extrapolates to the same intercept within experimental uncertainty. These observations are in accord with eq 2,²

$$\text{rate} = k_2[\text{RSO}_2\text{Cl}][\text{base}] + k_3[\text{RSO}_2\text{Cl}][\text{base}][\text{trap}] \quad (2)$$

in which [base] and [trap] refer to the concentrations of, respectively, the tertiary amine and the "sulfene trapping agent," *i.e.*, aniline, water, etc., as indicated in Figure 1.³ The observation that at least part of the reaction is zero order in a stoichiometric component of the reaction requires the formulation of an intermediate which reacts with that component in a step having no detectable influence on the rate. Taken with previous work these results are reasonably interpreted only in terms of the intermediacy of a sulfene and constitute the first kinetic evidence for such a species.

Three mechanisms for the title reaction which are compatible with the above and previously known data warrant further discussion:⁴ (a) direct one-step elim-

(2) Control experiments showed that reaction of the sulfonyl chloride with the "trapping agents" in the absence of the tertiary amine was negligible under the conditions of the kinetic measurements.

(3) The origin of the third-order component has not been fully investigated, but among the more plausible mechanistic possibilities are (a) hydrogen bonding of the leaving chloride ion in the transition state by the "sulfene trap" and (b) attack of the α hydrogen by a "sulfene trap"-tertiary amine hydrogen-bonded complex. That the third-order term also leads to sulfene formation is shown by the almost exclusive formation of $\text{CH}_2\text{DSO}_2\text{NHPh}$ (after work-up) from the reaction of methanesulfonyl chloride, triethylamine, and aniline- d_2 under conditions in which the third-order term contributes about half of the product.