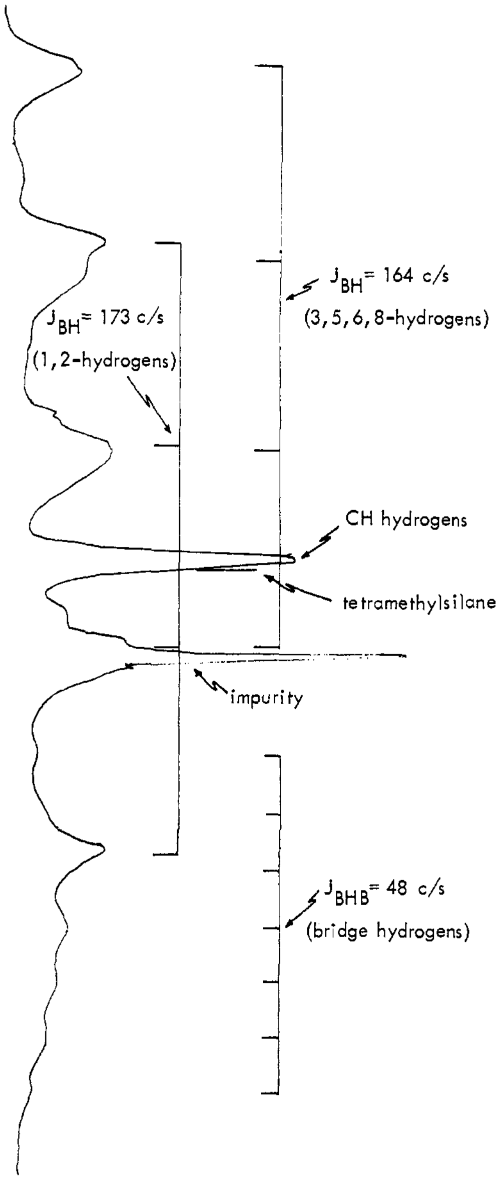

Figure 3. The 60-MHz ^{1}H nmr spectrum of 4,7-$C_2B_6H_{10}$.

though it is a *nido*-borane according to its empirical formula,[6] and/or equivalent electron counting scheme,[8,9] has an open arachno structure.

A tentative reaction mechanism which may account for the production of $C_2B_6H_{10}$ and its by-products follows. In the thermal decomposition of diborane one of the transient products is generally conceded to be $[B_3H_7]$, present in pseudoequilibrium with B_2H_6,[10] and since diborane is thermally less stable than $C_2B_3H_5$, a plausible mechanism for formation of $C_2B_6H_{10}$ is the reaction

$$C_2B_3H_5 + [B_3H_7] \longrightarrow C_2B_6H_{10} + H_2 \qquad (2)$$

$C_2B_6H_8$ is produced as a by-product, and at slightly higher reaction temperatures the ratio of $C_2B_6H_8$ to $C_2B_6H_{10}$ increases proportionately with the temperature increase, suggesting that $C_2B_6H_8$ evolves from $C_2B_6H_{10}$ by simple loss of hydrogen, *i.e.*

$$C_2B_6H_{10} \longrightarrow C_2B_6H_8 + H_2 \qquad (3)$$

$C_2B_5H_7$ and $CH_3CB_5H_8$, other major by-products in the diborane–$C_2B_3H_5$ reaction, are possibly formed by direct assimilation of B_2H_6 by $C_2B_3H_5$, *i.e.*

$$C_2B_3H_5 + B_2H_6 \longrightarrow CH_3CB_5H_8 \qquad (4)$$

$$C_2B_3H_5 + B_2H_6 \longrightarrow C_2B_5H_7 + 2H_2 \qquad (5)$$

Alternatively, $C_2B_5H_7$ might arise by loss of BH_3 from $C_2B_6H_{10}$.

$$C_2B_6H_{10} \longrightarrow C_2B_5H_7 + BH_3 \qquad (6)$$

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Chemistry of Thiocarbonyl Complexes of Chromium, Molybdenum, and Tungsten

Sir:

Several metal thiocarbonyl complexes have previously been prepared,[1-3] but little is known about the chemistry of the thiocarbonyl ligand. We now report the preparation of the first group VI metal thiocarbonyl complexes and some novel reactions of these compounds.

Anions of Cr, Mo, and W were prepared by stirring the hexacarbonyls, $M(CO)_6$, with excess sodium amalgam in refluxing tetrahydrofuran for 12 hr. Studies of Hayter[4] and Kaska[5] indicate that $M_2(CO)_{10}{}^{2-}$ and possibly some $M(CO)_5{}^{2-}$ are produced in these reductions. These solutions were cooled to room temperature and added rapidly to a tetrahydrofuran solution of thiophosgene (Cl_2CS). After stirring the mixture several minutes, it was evaporated to dryness under reduced pressure. Sublimation of the residue at 50–60° under high vacuum yielded a mixture of $M(CO)_6$ and $M(CO)_5(CS)$. The $M(CO)_6$ complexes were removed from the mixtures by repeated crystallization at −20° from pentane or hexane solutions, in which the thiocarbonyl complexes were appreciably more soluble. Chromatography of the thiocarbonyl-containing solutions on Florisil with pentane followed by sublimation yielded the pure air- and moisture-stable yellow $M(CO)_5(CS)$ complexes.[6]

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[6] Analytical data for $Cr(CO)_5(CS)$. Calcd: C, 30.51; H, 0.00; S, 13.56. Found: C, 30.14; H, <0.01; S, 13.59. $W(CO)_5(CS)$. Calcd: C, 19.55; H, 0.00; S, 8.70. Found: C, 18.93; H, <0.01; S, 8.36. Satisfactory elemental analyses have also been performed on all other new compounds reported here except $Mo(CO)_5(CS)$.

Table I. Spectroscopic Data

Compound	Infrared data[a]	Proton nmr data[b]	M+[c] (mol wt)
$Cr(CO)_5(CS)$	ν(CO) 2091 w, 2023 m, 1997 vs		236
	ν(CS) 1253 vs[d]		(236)
$Mo(CO)_5(CS)$	ν(CO) 2096 w, 2020 m, 1995 vs		280
	ν(CS) 1247 vs[d]		(280)
$W(CO)_5(CS)$	ν(CO) 2096 w, 2007 m, 1989 vs		368
	ν(CS) 1258 vs[d]		(368)
$Cr(CO)_5CNCH$[e]	ν(CO) 2068 w, 1958 vs		
	ν(CN) 2173 vw		
$Mo(CO)_5CNCH_3$[f]	ν(CO) 2071 w, 1960 vs		
	ν(CN) 2173 vw		
$W(CO)_5CNCH_3$	ν(CO) 2069 w, 1956 vs	6.55 s	365
	ν(CN) 2177 vw		(365)
$W(CO)_5CNCH_2COOCH_3$	ν(CO) 2063 w, 1957 vs	5.60 (2) s, 6.20 (3) s	423
	ν(CN) 2159 vw		(423)
trans-$Cr(CO)_4(CS)(PPh_3)$	ν(CO) 2044 w, 1992 vw, 1960 vs	2.70 m	470
	ν(CS) 1230 vs[d]		(470)
trans-$W(CO)_4(CS)(PPh_3)$	ν(CO) 2052 w, 1981 vw, 1956 vs	2.75 m	602
	ν(CS) 1247 vs[d]		(602)
trans-$W(CO)_4(CS)(NC_5H_5)$	ν(CO) 2062 vw, 1950 vs	1.5 (2) m, 2.3 (1) m,	419
	ν(CS) 1224 vs[d]	2.7 (2) m	(419)
trans-$W(CO)_4(PPh_3)CNCH_3$	ν(CO) 2018 w, 1932 w, 1913 vs	2.70 (15) m,	599
	ν(CN) 2148 vw	7.10 (3) d, $^5J_{P-H} = 1.5$ Hz	(599)
$W(CO)_5C(SH)N(CH_2)_5$	ν(CO) 2070 w, 1974 vw,	1.1 (1) s, 6.15 (2) m,	453
	1937 s, 1929 s, 1915 m	6.40 (2) m, 6.28 (6) s	(453)
$W(CO)_5C(SH)N(CH_3)_2$	ν(CO) 2071 w, 1975 vw,	1.05 (1) s, 6.60 (3) s,	413
	1938 s, 1932 s, 1916 m	6.72 (3) s	(413)

[a] Measured in *n*-hexane solution. [b] Measured in chloroform-d_1 solution with tetramethylsilane as internal standard, τ values given. [c] Molecular ion found by mass spectrometry. [d] Measured in carbon disulfide solution. [e] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1246 (1972). [f] M. Bigorgne, *J. Organometal. Chem.*, **1**, 101 (1963).

Overall yields were determined from the reaction mixtures by glc for the Cr and W complexes.[7] The Cr complex was obtained in 3–5% yield and the W analog in 12–15% total yield. The molybdenum complex did not appear to be sufficiently stable to be detected under the gas chromatographic conditions used, but the yields were estimated to be in the range of 2–4% in small preparations. Attempts to repeat the molybdenum reactions on a large scale gave substantially decreased yields. This fact and the apparent lower stability of $Mo(CO)_5(CS)$ relative to the Cr and W derivatives hampered the characterization of this compound; it was not isolated in pure form. However, its spectroscopic and chemical properties strongly support its formulation as $Mo(CO)_5(CS)$.

The ν(CO) bands of the $M(CO)_5(CS)$ complexes appear at significantly higher frequencies than for most other $LM(CO)_5$ complexes (*cf.* $M(CO)_5CNCH_3$ in Table I). These bands occur at positions quite close to those of the $M(CO)_5PF_3$ complexes.[8] Since PF_3 is known to be one of the best π-acceptor ligands, it appears that the thiocarbonyl group is also effective at removing electron density from the central metal.

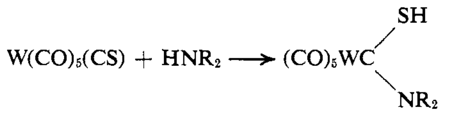
The Cr and W thiocarbonyl complexes were found to readily undergo substitution reactions.

$$M(CO)_5(CS) + L \longrightarrow trans\text{-}M(CO)_4(CS)(L) \qquad (1)$$

Refluxing $W(CO)_5(CS)$ in xylene with equimolar triphenylphosphine for 20 min gave *trans*-$W(CO)_4(CS)(PPh_3)$. Likewise, reaction under the same conditions with pyridine produced *trans*-$W(CO)_4(CS)(NC_5H_5)$. In the presence of equimolar triphenylphosphine in refluxing toluene, $Cr(CO)_5(CS)$ was converted to *trans*-$Cr(CO)_4(CS)(PPh_3)$ within 15 min.

The trans geometry of these products was assigned on the basis of the three observed ν(CO) bands, which may be assigned[9] to the A_1 (weak), the B_1 (very weak), and the E (very strong) modes in these C_{4v} symmetry complexes. As expected, the ν(CS) frequency in the *trans*-$M(CO)_4(CS)(L)$ derivatives is lower than in the parent $M(CO)_5(CS)$ complexes. It should be noted that the $M(CO)_5(CS)$ complexes undergo substitution under milder conditions than those required for substitution in the parent $M(CO)_6$ complexes.[10] This observation and the trans geometry of the products suggest a labilization of the carbonyl groups by the CS ligand in $M(CO)_5(CS)$.

The thiocarbonyl ligand itself has been found to be considerably more reactive than coordinated carbon monoxide. For example, $W(CO)_5(CS)$ reacts with piperidine and dimethylamine in hexane at room temperature to produce aminothiocarbene complexes in approximately 30% yield.



$$W(CO)_5(CS) + HNR_2 \longrightarrow (CO)_5WC{\begin{smallmatrix} SH \\ NR_2 \end{smallmatrix}} \qquad (2)$$

Both products exhibit unusual infrared spectra (Table I) in that the low symmetry of the ligand causes splitting of the intense E carbonyl mode and appearance of the forbidden B_1 fundamental.[9] Their proton nmr spectra (Table I) show the nitrogen substituent R groups to be nonequivalent, presumably because rotation about the carbon–nitrogen bond is restricted by multiple bonding. Restricted rotation has been previously

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(7) Excellent separations were achieved using a 0.25 in. × 5 ft 2% SE-30 column at temperatures of 60–150° and a helium flow rate of 25 cm³/min.

(8) For $W(CO)_5PF_3$, ν(CO) 2103 w, 2007 m, 1983 vs cm^{-1}. The values for the Cr and Mo complexes are within 10 cm^{-1} of these: R. L. Keiter and J. G. Verkade, *Inorg. Chem.*, **8**, 2115 (1969); R. J. Clark, private communication.

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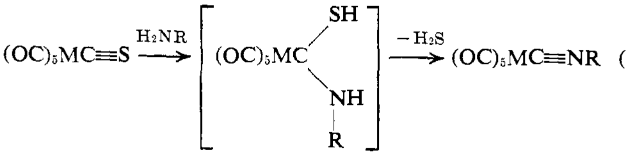
noted in thiocarbamoyl,[11] amidinium,[12] and aminocarbene[13] complexes. Surprisingly the -SH proton occurs at low field and does not exchange with D_2O in acetone at 35° over a 20-min period.

Primary amines also react with the $M(CO)_5(CS)$ complexes. These reactions may proceed through a complex similar to those isolated from the secondary amine reactions. Hydrogen sulfide is rapidly lost with formation of isocyanide complexes.



$$(OC)_5MC{\equiv}S \xrightarrow{H_2NR} \left[(OC)_5MC(SH)(NHR)\right] \xrightarrow{-H_2S} (OC)_5MC{\equiv}NR \qquad (3)$$

Methyl isocyanide complexes were produced in essentially quantitative yield within 10 min when the $M(CO)_5(CS)$ compounds were allowed to react with methylamine in pentane solution at room temperature. The substituted complex *trans*-$W(CO)_4(CS)(PPh_3)$ reacted more slowly, yielding the expected trans isocyanide compound after several hours. This lower reactivity probably results from a slower rate of amine attack on the thiocarbonyl carbon atom, which has a higher electron density than in the $W(CO)_5(CS)$ derivative.

An unusual isocyanide complex, $W(CO)_5CNCH_2COOCH_3$, was produced when $W(CO)_5(CS)$ in methanol was treated with glycine methyl ester. Aniline, hydrazine, and ammonia do not react with $W(CO)_5(CS)$ at room temperature. The complex $C_5H_5Fe(CO)_2(CS)^+$ was previously reported to react with methylamine, giving a thiocarbamoyl complex[14] rather than a coordinated isocyanide.

The amine reactions reported here clearly indicate that the CS ligand is much more susceptible to nucleophilic amine attack than is CO. Milder nucleophiles such as alchols and water did not react with $W(CO)_5(CS)$. Likewise, attempts to alkylate the S atom with $Et_3O^+BF_4^-$ gave no reaction.

Acknowledgment. We are grateful for support of this research through a National Defense Education Act (Title IV) Fellowship to B. D. D.

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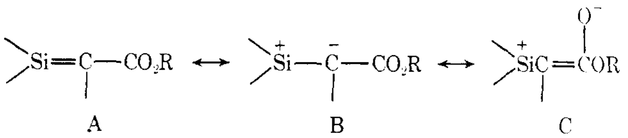
Formation of an Unstable Silicon–Carbon Double Bond in the Photodecomposition of Trimethylsilyldiazoacetate

Sir:

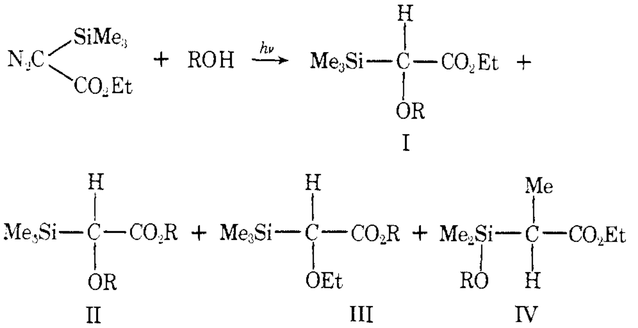
Recently, reports were published on the photochemical reactions of disilane[1] and silacyclobutane.[2] It was shown that an unstable intermediate with a silicon–carbon double bond is important in these reactions and that it reacts with alcohol to form an alkoxysilane.

We have initiated an investigation of the photochemical decomposition of ethyl trimethylsilyldiazoacetate[3] in alcohols, and we have established the formation of intermediate A which may be resonance stabilized by the contribution of structures B and C.



A B C

When ethyl trimethylsilyldiazoacetate is photolyzed with a high-pressure mercury lamp in alcohols, four products, I–IV, are obtained in approximately 60–90% yield. All four products were structurally characterized by ir, nmr, and elemental analyses. Product I may be rationalized in terms of a trimethylsilyl(carbethoxy)carbene reaction, and product III has been explained by a Wolff rearrangement, probably not involving carbene intermediate.[4,5] Product II may be derived *via* both carbene and ion pair[4,5] paths. The formation of IV, with a methyl migration, is quite interesting and is the main concern of the present communication. This reaction is quite general since rearranged products were formed in each system studied. The efficiency of migration varies with respect to solvent alcohol in the order *t*-BuOH > *i*-PrOH > EtOH > MeOH, in contrast with O–H insertion products (I and II) (Table I).



I II III IV

Table I. Photolysis of Ethyl Trimethylsilyldiazoacetate in Alcohols

Alcohol	Relative product yields, %			
	I	II	III	IV
MeOH	64	14	12	10
EtOH[a]	87			13
i-PrOH[b]	35	22	22	21
t-BuOH	40	17	8	35

[a] Products I, II, and III are all identical in ethanol. [b] Relative yields of I and II are obtained by nmr.

This implies that when the carbene does not show sufficient reactivity toward an oxygen atom (formation of products I and II *via* oxygen ylide), probably owing to steric hindrance of a neighboring bulky group,[6] then

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