Inorg. Chem. **1983**, *22*, 3361–3363

Contribution from The Procter & Gamble Company,
Miami Valley Laboratories, Cincinnati, Ohio 45247

Synthesis and Crystal Structure of a Novel Rhodium(I) Complex of an Inside-Out Hexathia Crown Ether

Dennis P. Riley* and Joel D. Oliver

Received March 8, 1983

During the course of an investigation dealing with the use of thioether donor ligands to afford new and interesting chemistry when coordinated to second-row transition metals, we became interested in the potential coordination properties of polydentate macrocyclic thioether ligands. In particular, the potentially hexadentate macrocyclic thioether ligands intrigued us not only because they are similar to the well-known crown ether ligands[1,2] but also because it should be possible to incorporate more than one second-row metal atom onto the ligand. For such complexes containing two or more metal atoms, the metal centers could reside on the same side of the ligand in close proximity to each other with the ligand in a "crownlike" conformation or they could coordinate on opposite sides of the ligand in a trans geometry. Such complexes could exhibit unusual chemistry owing to the proximity of the neighboring metal centers. To define the coordination properties of one member of this class of ligands, we have synthesized the new crown thioether ligand 1,4,7,11,14,17-hexathiacycloeicosane ([20]aneS_6) and have determined the crystal structure of a dinuclear Rh(I) complex with this ligand.

Experimental Section

Reagents. The 1,4,7-trithiaheptane and 1,3-dibromopropane were obtained from Aldrich Chemical Co. and used as supplied. The rhodium dimer complex bis(1,5-cyclooctadiene)bis(μ-chloro)dirhodium, $Rh_2(COD)_2Cl_2$, was purchased from Strem Chemical Co.

Preparation of 1,4,7,11,14,17-Hexathiacycloeicosane (1). One-tenth mole (15.4 g) of 1,4,7-Trithiaheptane was dissolved in 1.5 L of absolute ethanol. To this solution under nitrogen was added 0.2 mol (4.60 g) of sodium metal with stirring. After all the sodium metal reacted, this solution was then heated to reflux and 0.1 mol (20.2 g) of 1,3-dibromopropane was added in a dropwise fashion over a 1-h period. After the addition was complete, the solvent was removed and the solid mass was extracted with chloroform. The chloroform solution was filtered, and activated charcoal was added to this filtrate. This solution was then filtered through a sintered-glass filter funnel covered with filter aid. The volume of the clear chloroform solution was then reduced to a few milliliters. At this point 75 mL of boiling ethanol was added with stirring. This solution was then filtered while hot and allowed to stand undisturbed in a freezer overnight. White crystals resulted and were collected by filtration, washed with diethyl ether, and dried in vacuo for 24 h. The yield was 30% based on the starting dithiol; mp 120–122 °C. Anal. Calcd for $C_{14}H_{28}S_6$: C, 43.26; H, 7.21; S, 49.53. Found: C, 43.72; H, 7.48; S, 49.51.

Preparation of $[Rh_2([20]aneS_6)(COD)_2](PF_6)_2$ (2). To a 50-mL acetone solution (under N_2) containing 1.0 g (2.0 mmol) of the dimeric complex ($[Rh(COD)Cl]_2$) was added 1.02 g (4.0 mmol) of $AgPF_6$.[3,4] The AgCl precipitate was removed by filtration, and 0.80 g (2 mmol) of the ligand [20]aneS_6 was added slowly to the warm solution with vigorous stirring. The acetone was removed via vacuum, and hot MeOH was added until all the red solid dissolved. This solution was filtered, cooled, and allowed to sit undisturbed for 1 day. Deep red crystals formed and were collected via filtration, washed with cold EtOH, followed by Et_2O, and dried in vacuo. A yield of 1.4 g (64% based on Rh) was obtained. Anal. Calcd for $C_{30}H_{52}F_{12}P_2Rh_2S_6$: C, 32.73; H, 4.76; S, 17.47. Found: C, 32.49; H, 4.61; S, 17.71.

Molecular Weight Determinations. The solution molecular weight measurements were made with a Knauer vapor pressure osmometer. Osmometry with chloroform as solvent gave a molecular weight of 390 ± 8 for the free ligand (calcd M_r = 388). Mass spectral analyses of the ligand [20]aneS_6 were carried out in the ammonia chemical ionization mode on a Hewlett-Packard Model 5985B GC-mass spectrometer: parent ion at m/e 406 (where 406 − 18 = 388).

Table I. Summary of Crystal Data and Details of Data Collection

formula	$C_{30}H_{52}F_{12}P_2S_6Rh_2$
fw	1100.87
a, Å	8.895 (3)[a]
b, Å	10.736 (3)
c, Å	21.186 (7)
β, deg	92.32 (3)
Z	2
vol, Å^3	2021.5
space group	$P2_1/n$ (alternative setting of No. 14)
systematic absences	$0k0$ for k odd $h0l$ for $h + l$ odd
d(calcd), g cm^{-3}	1.81
$F(000)$	1112
Data Collection	
cryst dimens, mm	0.45 × 0.40 × 0.30
λ(Mo $K\bar{\alpha}$), Å	0.71073
μ, cm^{-1}	12.58
limiting sphere, deg	$2 \leq 2\theta \leq 50$
scan mode	θ–2θ
scan rate, deg/min	variable 4–29.3
Miller index range	$h,k,\pm l$
reflcns measd	4022
unique reflcns measd	3764
unique reflcns used ($\lvert F_o\rvert \geq 3\sigma(\lvert F_o\rvert)$)	3070
check reflcns[b]	060, 400, 004, 22$\bar{5}$
abs cor	empirical
max (min) trans factor	0.53 (0.48)

[a] Cell constants were obtained from least-squares refinement of 17 general, locally intense reflections. [b] Analysis of these intensities revealed only random variations less than 3% from their mean values.

Crystallographic Study of 2. The structural analysis of **2** was performed at room temperature (~17 °C) on a Syntex P2$_1$ autodiffractometer equipped with a graphite monochromator and a molybdenum target X-ray tube. The crystal data and the details of data collection are given in Table I. All structural calculations were made by using the SHELXTL[5] package with a Data General Eclipse computer. Scattering factors for all atoms and the real and imaginary corrections for anomalous scattering were taken from ref 6. The structure was solved by direct methods and was refined by least-squares procedures to R = 0.044 and R_w = 0.059. The parameters refined in the final least-squares cycles were an overall scale factor, the positional and anisotropic thermal parameters of the non-hydrogen atoms, and the positional and isotropic thermal parameters of the H atoms of the [20]aneS_6 ligand. The H atoms of the COD ligand were included at their fixed idealized positions (d(C–H) = 0.96 Å and ∠H–C–H = 109.5°) with isotropic thermal parameters fixed at 1.2 times the equivalent isotropic thermal parameter of the C atom to which they are attached. The weighting function used was $w = (\sigma^2(\lvert F_o\rvert) + g\lvert F_o\rvert^2)^{-1}$, where $\sigma(\lvert F_o\rvert)$ is the standard deviation of the structure factor based solely on counting statistics and g is an ignorance factor (5.9 × 10^{-4}). A final difference electron density map revealed a featureless background below 0.34 e Å^{-3}, except for peaks ≤1.1 e Å^{-3} in the vicinities of the Rh, S, and F atoms.

Results and Discussion

The synthesis of the ligand [20]aneS_6 (**1**) described here affords a high yield (~30%) of this 20-membered ring.[7] Elemental analysis as well as mass spectral data and, most especially, solution molecular weight measurements confirm

---

(1) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16.

(2) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351.

(3) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

(4) Halpern, J.; Riley, D. P.; Chan, A. S. C.; Pluth, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 8055.

(5) Sheldrick, G. M. "SHELXTL: A Minicomputer Package for Crystal Structure Determination"; Nicolet XRD Division: Fremont, CA, 1981.

(6) Ibers, J. A.; Hamilton, W. C. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(7) Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079.

0020-1669/83/1322-3361$01.50/0

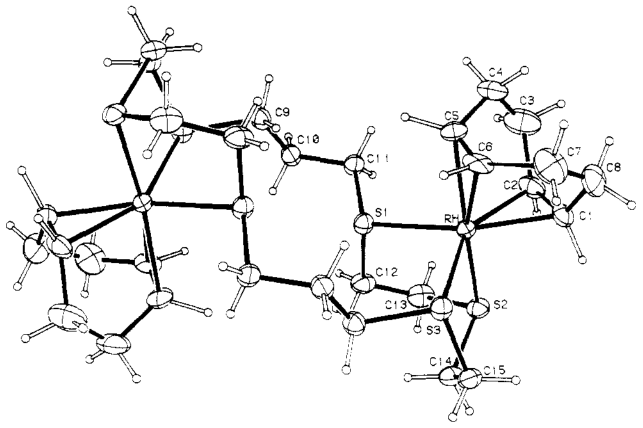

Figure 1. Perspective drawing of the dication illustrating 50% probability ellipsoids and indicating the atom-labeling scheme. The H atoms are drawn artificially small.

that this is indeed the 20-membered ring and not a higher molecular weight oligomer or the 10-membered ring. Attempts to synthesize a number of second-row metal (e.g., Ru and Mo) complexes were made, but to date only the Rh(I) complex described here has been well characterized. This is probably due to the diverse chelating possibilities (e.g., conformational variations and the number and identities of coordinated sulfur atoms) of the ligand, which produces a variety of isomers that are difficult to separate. The synthesis of the Rh(I) complex gave in high yield a complex that was shown by elemental analysis to contain two Rh atoms per [20]aneS_6 ligand.

This new complex is surprisingly stable. Contrary to our expectations, the 1,5-COD units could not be removed by hydrogenating the diene ligand to a paraffin[3,4] even at high temperatures (100 °C) and elevated pressures (100 psig H_2). Additionally, the complex was inert to substitution by a number of very good ligands. For example, triphenylphosphine does not react with this complex. This unusually high stability prompted us to initiate an X-ray crystallographic investigation of this complex in order to determine its stereochemistry.

Crystals suitable for X-ray analysis were obtained as described in the Experimental Section. A perspective drawing of the dication is shown in Figure 1. Atomic coordinates and bond lengths and bond angles are presented in Tables II and III. The complex indeed contains two rhodium centers per [20]aneS_6 ligand related by a crystallographic center of symmetry at the center of the [20]aneS_6 ligand. The [20]aneS_6 ligand thus bridges the two Rh atoms. The crystal structure shows that this is a large, cylindrically shaped cationic complex (~8 × 16 Å) with two of the sulfur atoms pointed toward the center of the [20]aneS_6 ligand ($d(S \cdots S) = 3.607$ (3) Å). Except for two sulfur atoms at each end of the complex, the surface of the cylinder is defined by the hydrocarbon moieties of the complex. Each Rh(I) ion is five-coordinate and consequently possesses a complete 18-e configuration. This fact accounts for the high stability of the complex toward substitution and hydrogenation.

Each Rh(I) center is bound to the three sulfur atoms interrupted by the ethylene linkages and not the trimethylene. In effect, each Rh(I) is bound to a linear tridentate ligand analogous to a $(RS(CH_2)_2)_2S$ moiety. Also, the presence of the olefinic bond between C(5) and C(6) trans to S(2) produces a pronounced trans influence[8] involving the bonds to the Rh atom. The atoms S(1) and S(3) are not trans to an olefin and do not exhibit a trans influence. The Rh–S(2) bond length, 2.320 (1) Å, is much shorter than the other Rh–S bond lengths, 2.462 (1) and 2.482 (1) Å. The Rh–C bond lengths are also affected. The Rh–C bond lengths trans to S(2), 2.216 (6) and 2.197 (5) Å, are significantly longer than the other two Rh–C bond lengths, 2.098 (5) and 2.099 (6) Å. One possible explanation for this bond length anomaly is the transfer of part of the σ-donated electron density from the olefin trans to S(2) via the Rh atom to the empty 3d shell of S(2), thereby strengthening and shortening the Rh–S(2) bond while weakening and lengthening the trans-related Rh–C bonds. The electron density in the antibonding π* orbital of the olefinic bond trans to S(2) does not appear to be affected, since the two C=C bond lengths, 1.392 (8) and 1.383 (9) Å, are very similar.

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

atom	*x*	*y*	*z*	U^a
Rh	4777 (1)	8073 (1)	1335 (1)	31 (1)
S(1)	3855 (1)	8739 (1)	276 (1)	37 (1)
S(2)	2281 (1)	8164 (1)	1610 (1)	41 (1)
S(3)	5027 (1)	10210 (1)	1773 (1)	38 (1)
P	778 (2)	13415 (2)	1009 (1)	54 (1)
F(1)	1828 (4)	13120 (4)	1622 (2)	84 (1)
F(2)	−300 (5)	13670 (4)	419 (2)	100 (2)
F(3)	295 (11)	12029 (5)	1014 (5)	208 (4)
F(4)	2021 (8)	13059 (11)	603 (3)	245 (6)
F(5)	1140 (8)	14781 (5)	1058 (4)	182 (4)
F(6)	−547 (7)	13679 (8)	1460 (3)	162 (3)
C(1)	5164 (6)	6781 (5)	2067 (3)	49 (2)
C(2)	4639 (7)	6159 (5)	1526 (3)	57 (2)
C(3)	5592 (10)	5377 (7)	1106 (4)	93 (3)
C(4)	6934 (9)	6030 (7)	872 (4)	84 (3)
C(5)	6835 (6)	7414 (7)	883 (3)	62 (2)
C(6)	7247 (6)	8130 (6)	1405 (3)	59 (2)
C(7)	7752 (7)	7662 (8)	2064 (4)	80 (3)
C(8)	6778 (8)	6713 (7)	2322 (3)	79 (3)
C(9)	5253 (6)	8595 (5)	−1176 (3)	41 (2)
C(10)	3742 (6)	8098 (5)	−974 (3)	41 (2)
C(11)	3864 (6)	7521 (5)	−322 (2)	40 (2)
C(12)	1826 (6)	8932 (6)	362 (3)	51 (2)
C(13)	1228 (6)	8076 (5)	857 (3)	54 (2)
C(14)	1962 (7)	9779 (5)	1841 (3)	49 (2)
C(15)	3292 (6)	10295 (5)	2198 (2)	46 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The ligand in complex **2** is not in a "crown" conformation but is twisted "inside-out" and serves as a tridentate bridging ligand between the $[Rh^I(COD)]^+$ moieties on opposite sides of the macrocyclic ring. A crystal structure of the related free ligand 1,3,7,10,13,16-hexathiacyclooctadecane, [18]aneS_6, shows that this molecule also can exhibit a twisted, "noncrown", inside-out conformation.[9] While it is possible that different conformers of the hexathia free ligands exist in solution, these two X-ray studies suggest that the "inside-out" conformers are particularly favorable, low-energy states. As a consequence, the coordination chemistry of these large thioether macrocyclic rings is expected to be particularly rich and diverse. It is also significant that an "inside-out" complex has been characterized with the [14]ane S_4 ligand and the second-row metal niobium.[10] In this case the ligand also bridges two Nb centers but as a monodentate ligand. Similarly, the same [14]ane S_4 ligand acts as a bridging bidentate ligand in a Ni(II) complex.[11]

The conformation of this [20]aneS_6 ligand can be characterized by the endocyclic torsion angles. Starting with the C(9)–C(10) bond and proceeding sequentially around the

---

(8) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(9) Hartman, J. A. R.; Wolf, R. E.; Foxman, B. M.; Cooper, S. R. "Abstracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982; American Chemical Society: Washington, DC, 1982; INOR 25.

(10) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 942.

(11) Rosen, W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 262.

Table III. Bond Lengths (Å) and Bond Angles (deg)

Rh-S(1)	2.462 (1)	Rh-S(2)	2.320 (1)
Rh-S(3)	2.482 (1)	Rh-C(1)	2.099 (6)
Rh-C(2)	2.098 (5)	Rh-C(5)	2.216 (6)
Rh-C(6)	2.197 (5)	S(1)-C(11)	1.822 (5)
S(1)-C(12)	1.834 (6)	S(2)-C(13)	1.819 (6)
S(2)-C(14)	1.828 (6)	S(3)-C(15)	1.821 (6)
S(3)-C(9a)	1.812 (5)	C(1)-C(2)	1.392 (8)
C(1)-C(8)	1.514 (9)	C(2)-C(3)	1.509 (11)
C(3)-C(4)	1.486 (11)	C(4)-C(5)	1.489 (11)
C(5)-C(6)	1.383 (9)	C(6)-C(7)	1.534 (10)
C(7)-C(8)	1.458 (11)	C(9)-C(10)	1.524 (8)
C(9)-S(3a)	1.811 (5)	C(10)-C(11)	1.512 (7)
C(12)-C(13)	1.507 (9)	C(14)-C(15)	1.485 (8)

S(1)-Rh-S(2)	86.0	S(1)-Rh-S(3)	95.3
S(2)-Rh-S(3)	86.5	S(1)-Rh-C(1)	154.7 (2)
S(2)-Rh-C(1)	88.4 (2)	S(3)-Rh-C(1)	109.0 (2)
S(1)-Rh-C(2)	116.1 (2)	S(2)-Rh-C(2)	85.9 (2)
S(3)-Rh-C(2)	147.0 (2)	S(2)-Rh-C(5)	159.7 (2)
S(1)-Rh-C(5)	87.1 (2)	C(1)-Rh-C(5)	89.7 (2)
S(3)-Rh-C(5)	113.2 (2)	S(1)-Rh-C(6)	110.4 (2)
C(2)-Rh-C(5)	80.0 (3)	S(3)-Rh-C(6)	82.8 (2)
S(2)-Rh-C(6)	161.2 (2)	Rh-S(1)-C(11)	114.5 (2)
Rh-S(1)-C(12)	103.6 (2)	C(11)-S(1)-C(12)	100.5 (3)
Rh-S(2)-C(13)	104.0 (2)	Rh-S(2)-C(14)	105.5 (2)
C(13)-S(2)-C(14)	101.8 (3)	Rh-S(3)-C(15)	99.6 (2)
Rh-S(3)-C(9a)	112.7 (2)	C(15)-S(3)-C(9a)	102.4 (2)
C(1)-C(2)-C(3)	125.1 (6)	C(2)-C(1)-C(8)	123.6 (5)
C(3)-C(4)-C(5)	114.6 (6)	C(2)-C(3)-C(4)	114.4 (6)
C(5)-C(6)-C(7)	127.1 (6)	C(4)-C(5)-C(6)	123.6 (6)
C(1)-C(8)-C(7)	113.7 (6)	C(6)-C(7)-C(8)	114.4 (6)
C(9)-C(10)-C(11)	111.6 (4)	C(10)-C(9)-S(3a)	110.3 (4)
S(1)-C(12)-C(13)	112.1 (4)	S(1)-C(11)-C(10)	109.8 (4)
S(2)-C(14)-C(15)	111.2 (4)	S(2)-C(13)-C(12)	113.3 (4)
		S(3)-C(15)-C(14)	113.7 (4)

labeled atoms of the ring, the pertinent values are −157, 80, 89, 52, 63, −147, 57, 73, and 154°. The torsion angles observed in the structure of the [18]aneS_6 free ligand[9] are different from these values, but both hexathia crown ethers are "inside out". Allowing for the flexibility of the [18]aneS_6 molecule, its coordination properties as a ligand should be similar to those of the [20]aneS_6 ligand. Such "noncrown", "inside-out" complexes may well be the rule for these large thioether macrocycles. As a consequence, these ligands may prefer to serve as bridging ligands between metal atoms rather than participating in the classical, encapsulating, "crownlike" bonding.

Acknowledgment is made to L. C. Strickland (of these laboratories) for his assistance with the crystal structure investigation. We also thank Dr. Steve Cooper for sending the atomic coordinates of the [18]aneS_6 molecule prior to publication of that structure.

Registry No. **1**, 87156-15-8; **2**, 87156-17-0; [Rh(COD)Cl]$_2$, 12092-47-6; 1,4,7-trithiaheptane, 3570-55-6; 1,3-dibromopropane, 109-64-8.

Supplementary Material Available: Tables of structure factor amplitudes, hydrogen atom parameters, anisotropic thermal parameters, and bond lengths and bond angles (21 pages). Ordering information is given on any current masthead page.

Contribution from the Corporate Research Department,
Dow Corning Corporation, Midland, Michigan 48640

Exchange of Halogens between Tetrahalosilanes and Aryl Halides

Patricia M. Scaduto* and John L. Speier

Received February 14, 1983

Recently, we were studying reactions of bromobenzene with trichlorosilane in the vapor phase above 300 °C in small sealed Pyrex glass tubes and were surprised to find chlorobenzene among the products. The most likely source of chlorobenzene required an unknown exchange process, e.g.

$$\mathrm{SiCl + PhBr = SiBr + PhCl}$$

No example like this was found in published works. Exchanges of halogens between triethyliodosilane and alkyl halides[1] and between trimethyliodosilane and alkyl, benzyl, and allyl halides[2] were reported.

Results and Discussion

Mixtures of $SiCl_4$ and PhBr in a mole ratio of 1/1 underwent reversible exchange, which approached equilibrium at 310 °C in about 115 h. A constant value of about 0.07 was approached when the GLC area ratio of PhCl/PhBr was multiplied by the ratio of the Si–Br bonds/Si–Cl bonds. This latter ratio was calculated as the sum of the area percents of individual halosilanes multiplied by the number of Br or Cl atoms in each halosilane. Thus, in terms of individual bonds, not molecules

$$K = \frac{[\mathrm{C{-}Cl}]}{[\mathrm{C{-}Br}]}\,\frac{[\mathrm{Si{-}Br}]}{[\mathrm{Si{-}Cl}]} = 0.07 \qquad (1)$$

Various molar combinations of $SiCl_4$ and C_6Br_6 produced complex mixtures of compounds corresponding to the equation

$$n\mathrm{SiCl_4} + \mathrm{C_6Br_6} = n\mathrm{SiCl}_{4-m}\mathrm{Br}_m + \mathrm{C_6Br}_{6-nm}\mathrm{Cl}_{nm} \qquad (2)$$

$$m = 0, 1, 2, 3, 4$$

Equilibrium was approached in these systems in about 69 h at 310 °C and in about 1.5 h at 350 °C. The value of K calculated for this system by eq 1 was about 0.1.

To avoid the difficult task of quantitatively separating and identifying the compounds of the formula $C_6Br_{6-nm}Cl_{nm}$ when $nm = 0, 1, 2, 3, 4, 5$, and 6, values for m were approximated as the sum of the area percent of each halosilane multiplied by the number of Si–Br bonds each possessed. The identity of the halosilanes was established by GLC–mass spectrometry. Then $[\mathrm{Si{-}Br}] = nm$, $[\mathrm{Si{-}Cl}] = n(4 - m)$, $[\mathrm{C{-}Cl}] = nm$, and $[\mathrm{C{-}Br}] = 6 - nm$. $SiBr_4$ and C_6Cl_6 produced mixtures of products nearly identical with those from $SiCl_4$ and C_6Br_6, and equilibrium was reached in about the same time at the same temperatures. Values for K calculated by eq 1 ranged from 0.1 to 0.2.

A 1/1 molar mixture of $SiCl_4$ and EtBr was heated at 300 °C. Exchange occurred and approached equilibrium in about 17 h with the following area percents: EtCl, 11; $SiCl_4$, 41; EtBr, 30; $BrSiCl_3$, 15. These values in eq 1 give $K = 0.03$.

These few examples show that reversible exchange occurred in these systems. Equilibrium concentrations of Si-halogen/C–Halogen bonds were approached which were affected very little by the structure of the halosilane or of the organic halide.

Experimental Section

$SiCl_4$ was Dow Corning semiconductor grade. $SiBr_4$ was prepared by passing Br_2 over semiconductor grade silicon at 400 °C (98% pure $SiBr_4$ was produced, as determined by GLC). The organic halides were purchased reagent grade chemicals. All experiments were carried out in sealed 8-mm-o.d., 4-mm-i.d. Pyrex tubes about 17 cm long. Reagents were added to the tubes in a dry ice bath and sealed in

---

(1) Nagai, Y.; Maramatsu, H.; Ohtsuki, M.; Matsumoto, H. *J. Organomet. Chem.* **1969**, *17*, 819.

(2) (a) Friedrich, E. C.; Abma, C. B.; Vartanian, P. F. *J. Organomet. Chem.* **1980**, *187*, 203. (b) Friedrich, E. C.; DeLucca, G. *Ibid.* **1982**, *226*, 143.

0020-1669/83/1322-3363$01.50/0