and tin homologues have also been synthesized.[5,6] Here we report what we believe is the most direct and efficient synthesis of **1** to date.

The silanamine (**1**) and related sulfinylamines have proven useful as synthetic precursors to selected heterocycles,[4,8] symmetric disulfides,[5] and additional sulfinylamines.[5–7,9–12] Preliminary experiments also indicate that **1** has fluorescent properties associated with its ultraviolet absorption bands characterized below, which suggests that the reaction described in this communication may be of considerable interest for trace sulfur dioxide analysis by fluorescent methods.

This reaction was first observed during experiments designed to stabilize by silylation reactive sulfur-containing molecules produced photochemically from SO$_2$ and hydrocarbons. The results indicated that residual SO$_2$ in the mixture reacted readily with the silylating reagent to form a new product which was separated by gas chromatography. Verification with anhydrous sulfur dioxide showed that HMDS reacts directly whereas trimethylchlorosilane (TMCS) is unreactive under ambient conditions.

Although **1** can be formed by bubbling SO$_2$ through pure HMDS or a dilute HMDS pentane solution, a more efficient and preferred procedure was developed. A measured amount (1:1 or 1:3 HMDS:SO$_2$) of SO$_2$ was transferred via a mercury-diffusion-pumped high-vacuum line into a liquid-nitrogen-cooled reaction vessel containing degassed HMDS. The reaction was then carried out by closing the Teflon stopcock to the vessel and letting the mixture warm to room temperature. Almost immediately upon melting of the mixture the reaction proceeds to completion forming a finely divided solid. The mixture of products can be removed as a pentane slurry from which the precipitate is filtered. The filtrate can then be collected and the pentane removed by evaporation in a stream of dry nitrogen. Alternately the liquid can be separated from the solid by vacuum distillation. Since the solid readily sublimes at room temperature, distillation either at reduced temperature or via a multiple trap procedure is necessary to ensure separation.

Purification of the product (**1**) was carried out gas chromatographically at 67 °C by using 5% SE-30 silicone oil on 45/60 mesh, acid-washed, DMCS-treated Chromosorb P in a 25 ft × $^1/_4$ in. aluminum column. The product was eluted with a retention volume of 570 mL at a helium carrier flow rate of 60 mL/min and was separated from hexamethyldisiloxane which is invariably present by a difference in retention volume of +120 mL. The pure product was collected at liquid-nitrogen temperature in a 1-mL glass trap fitted with a drying tube at the exit. Collection and storage in a dry atmosphere were included in the procedure because **1** reacts slowly with moisture in the air, leaving a solid white residue on the walls of the container.

It should be noted that the overall reaction is readily reproducible and proceeds in high yield. Although the detailed stoichiometry of the reaction products has not yet been determined with certainty, the amount of **1** produced represents some 22% of the total mass of reactants used. Thus from 60 g of SO$_2$ and HMDS in a 1:1 mole ratio, 13 g of the silanamine (**1**) is recovered. A further comment on the reaction conditions is also warranted. Whereas the initial studies were carried out under high vacuum to ensure reactant purity, it is clear that such stringent conditions are not required as long as moisture is carefully excluded. In fact this reaction has even been run in the air by simply blowing SO$_2$ gas through HMDS liquid although a nitrogen atmosphere or modest vacuum conditions at low temperature are preferred.

The pure (>99%) compound **1** has the following physical and spectral characteristics (IR and NMR have been reported previously and compare well). IR: 1302 cm^{-1} (strong) and 1132 cm^{-1} (medium) corresponding to the NSO asymmetric and symmetric vibrations, 570 cm^{-1} (medium) from NSO bending, and 1258 cm^{-1} (strong), 858 cm^{-1} (strong), and 770 cm^{-1} (medium) associated with the Si–CH$_3$ group. 60-MHz ^{1}H NMR: one singlet at δ(CCl$_4$) 0.35 (external Me$_4$Si). Mass spectroscopy: m/e (M − 15) = 120 (100%), no parent ion observed which is normal for trimethylsilyl compounds,[13] m/e = 73 (5%) from Si(CH$_3$)$_3^+$, m/e = 90 (8%) from HO—Si(CH$_3$)$_3^+$, and m/e = 75 (17%) from HO═Si(CH$_3$)$_2^+$, two products expected in the rearrangement of the trimethylsilyl group from nitrogen to oxygen via a four-membered ionic intermediate, and m/e = 46 (40%), probably corresponding to the NS$^+$ residual fragment following the rearrangement. UV: 237 and 295 nm in an absorbance ratio ~10:1, respectively, which are expected for sulfinylsilanamines.[9,14] Anal. Calcd: C, 26.6; H, 6.7; N, 10.4; Si, 20.8; S, 23.7; O, 11.8. Found: C, 26.20; H, 6.95; N, 10.21; Si, 20.46; S, 23.05; O, 12.04.

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Registry No. **1**, 7522-26-1; SO$_2$, 7446-09-5; HMDS, 32713-31-8.

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Synthesis of Methylhydrazine in Nonaqueous Solvents

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Interest in the syntheses of hydrazine, methylhydrazine, and 1,1-dimethylhydrazine has developed because of their use as rocket fuels. The synthetic processes reported in the literature for the preparation of these substituted hydrazines in most instances are cumbersome requiring multiple step separations of these hydrazines from dilute aqueous solutions[1–4] and, therefore, are expensive. Apart from cost, some of the processes are known to involve intermediates that are hazardous and carcinogenic.[5] Alternate procedures for synthesizing the substituted hydrazines are, therefore, needed. One of the reactions[6–9] which has been investigated as the basis for an

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alternate process in recent years is the chloramination reaction reported by Sisler and co-workers.[10-14] The formation of hydrazine or alkyl-substituted hydrazines by the reaction of gaseous chloramine with liquid ammonia or liquid amines has been demonstrated.[11,12] However, a large ratio of amine to chloramine (of the order of 400:1) is required to obtain an acceptable yield of hydrazines. Also, only scanty information is available in the open literature on the synthesis of methylhydrazine.[3,8,11] From the recovery point of view, the synthesis of methylhydrazine in nonaqueous solvents is desirable. In this paper, attempts to synthesize methylhydrazine in nonaqueous solvents by the chloramination of methylamine are reported.

Experimental Section

Materials and Analysis. All solvents used were reagent grade. Methylhydrazine obtained from Aldrich Chemicals was refluxed over KOH pellets in an atmosphere of nitrogen. The fraction boiling at 87.5 °C was collected and used for these studies. Methylamine was supplied by the Matheson Co. Chloramine was produced by the gas-phase reaction of ammonia and chlorine by using a generator similar to that described by Sisler et al.[10] Ammonia-free chloramine solutions were prepared by passing the effluent gases from the chloramine generator through a solvent and removing the dissolved ammonia by passing the resulting solution through a column of anhydrous copper sulfate. The concentrations of chloramine in these solutions were determined iodometrically. The concentrations of hydrazines were determined by the iodate method.[3] Symmetrical hexahydro-1,4-dimethyltetrazine was prepared[15] by reacting formaldehyde with methylhydrazine. Its purity was established by comparing its melting point, elemental analysis and mass spectral data with those which are reported in the literature.[15] The proton magnetic resonance spectra were recorded on a Varian Associates A-60-A spectrometer. The gas chromatographic data were obtained on a Varian Model 3700 gas chromatograph equipped with a CDS-111 data analyzer and Soltic Model 252 integrater recorder. A 6-ft Carbowax column having the composition 10% Carbowax 20M + 5% KOH on Chrom WAW, 80/100 mesh, was used. Unless otherwise stated, the chromatograms were obtained by using the following parameters: injector temperature, 170 °C; column temperature, 80 °C; helium flow rate, 20 mL/min; thermal conductivity detector temperature, 160 °C; thermal conductivity current, 150 mA; filament temperature, 180 °C. The various reaction products were identified by comparing their NMR spectra and retention times with the NMR spectra and the retention times of the known substances. A Nester/Faust spinning-band column was used for fractional distillation.

Reaction of the Chloramine–Ammonia Mixture with Methylamine in the Presence of Potassium Hydroxide. A cylindrical reaction vessel of 1.5-L capacity was charged with a 325-mL methanol solution containing 0.53 mol of KOH and 1.22 mol of methylamine. The inlet of the reaction vessel was connected to the chloramine generator, and the outlet of the reaction vessel was connected to a vent through a dry ice–acetone cold finger. Approximately 0.17 mol of NH_2Cl (along with the reactor gases) was bubbled through the amine–potassium hydroxide solution over a period of 105 min. A white solid precipitated, and the solution turned yellow. The reaction mixture was kept at room temperature for 2 h to allow the volatile gases to escape. The total hydrazine content (total N–N bonded material) of the reaction mixture was estimated by titrating a sample of the reaction mixture in acidic medium with KIO_3 solution and was found to be 0.15 mol or 84% of theoretical hydrazine on the basis of the amount of chloramine used. The total hydrazine content dropped to 0.11 mol when the solution was examined after a 16–17-h storage in a dry nitrogen atmosphere. The solid was then separated from the solution by decantation. The weight of the dry solid was 7.6 g and was identified as KCl by its flame color and chloride analysis. Anal. Calcd: Cl, 47.55. Found: Cl, 47.64.

Table I

fraction	distillation range, °C	vol, mL	% CH_3-OH^a	% CH_3-$NHNH_2$^{a}	% H_2O-NH_2NH_2^{a}	remarks
1	83–86	1	61.1	34.3		
2	86–87.5	4	38.0	60.2		6 other unidentified products
3	87.5–106	1	36.0	61.0		
4	106	3	11.0	9.0	77	
5	106–113	4			95	

[a] Percents are based on the data obtained on the CDS-11 data system.

Table II

total hydrazine content in fraction 5	0.014 mol
mp of sulfate derivative (obsd)	258–260 °C
mp of sulfate derivative (lit.[16])	254 °C
mp of benzaldehyde derivative (obsd)	89–90 °C
mp of benzaldehyde derivative (lit.[16])	93 °C
% N estimated by iodate method	21.53
% N calcd for $NH_2NH_4SO_4$	21.65

Table III

fraction	distillation range, °C	products	%	source of identification
1	up to 80	CH_3OH, CH_3NH_2, N_2		GC
2	80–112	CH_3OH	21.8	GC, NMR
		CH_3NHNH_2	38	GC, NMR, mp of sulfate deriv
		$CH_3NHN{=}CH_2$	5.7	GC, NMR
		$(CH_3NNHCH_2)_2$		GC, NMR
		NH_2NH_2	28.3	GC, mp of sulfate deriv
		H_2O		GC
		others	6	GC

The yellow solution obtained after the removal of the solid was fractionated on a spinning-band column. The fraction recovered below 65 °C was mainly methanol having a trace amount of N–N bond containing material. The gas chromatographic analysis did not show the presence of methylhydrazine in this material. After most of the methanol was distilled out, 3 g of solid KOH was added to the remaining solution (approximately 30 mL), and the spinning-band column was replaced by a Vigreux column. The compositions of the various fractions collected are summarized in Table I.

The proton NMR spectrum of the second fraction showed three peaks at δ 2.50, 3.08 and 3.98 downfield from internal tetramethylsilane. From comparison with the proton NMR of methanol and methylhydrazine mixture, the peak at δ 2.50 was assigned to $N-CH_3$ protons of methylhydrazine, the peak at δ 3.08 to the methyl protons of methanol, and the peak at δ 3.98 to both N–H and OH protons.

The presence of water and hydrazine in fraction no. 5 was indicated by gas chromatographic and proton NMR spectrum analyses. The other information regarding fraction 5 is summarized in Table II. One of the components in fraction 5, therefore, was hydrazine.

The pot residue had reducing properties toward KIO_3 in the acidic solution and showed the presence of both hydrazine and methylhydrazine by other tests.

Reaction of the Chloramine–Ammonia Mixture with Methylamine in the Presence of Sodium Methoxide. Chloramine (0.20 mol) from the chloramine generator was passed into a 300-mL methanol solution containing 18 g (0.33 mol) of sodium methoxide and 1.0 mol of

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methylamine over a 2-h period as described above. A white solid formed, and the solution became yellow. After the solution stood for 2 h at room temperature, 15 g (0.26 mol) of NaCl was separated.[25] The total hydrazine content estimated in the solution was 0.166 mol or 83% of theory on the basis of the NH_2Cl used.

The solution was distilled first on the spinning-band column. When the volume of the solution was reduced to 50 mL, the spinning-band column was replaced by a Vigreux column. Two main fractions were collected. The results are summarized in Table III. It is apparent that hydrazine was formed along with methylhydrazine in this experiment also.

Reaction of Chloramine with Methylamine in Nonaqueous Solvents in the Absence of a Fixed Base. In a typical reaction, methylamine (0.375 mol) was transferred under an oxygen-free nitrogen atmosphere to a flask containing 50 mL of anhydrous ether at −78 °C, fitted with a condenser and a pressure-equalizing funnel. Ammonia-free chloramine solution in ether (500 mL, 75 mmol chloramine) was added rapidly from the funnel to the amine solution which was stirred with a magnetic stirrer. No apparent reaction took place in the initial stage. After complete addition of the chloramine solution, the solution was brought to room temperature. A small amount of solid was separated. The solution was kept overnight. A test sample of the solution showed the presence of NH_2Cl with only a very slight change (0.134 to 0.110 M) in NH_2Cl concentration. The solution gave a negative test for N–N bonded compounds when tested with KIO_3. The mixture was then refluxed for several hours. It still gave a negative test for N–N bonded compounds. The solids formed were found to be a mixture of methylammonium chloride with a trace of ammonium chloride.

The reaction was repeated in the presence of ammonia by passing the effluent gases of the chloramine generator into the amine solution in the absence of a fixed base. No evidence of a reaction between chloramine and methylamine was observed.

This experiment was carried out with and without ammonia by using xylene, methanol, diglyme, a mixture of diglyme and ether, and a mixture of methanol and diglyme as solvents in the absence of a fixed base. In none of these cases was any evidence for the formation of N–N bonded compounds found as shown by the KIO_3 test.

Reaction of Chloramine with Methylhydrazine. The reactions were carried out under different experimental conditions to determine (a) the products of reaction and (b) the relative reactivity of chloramine toward methylamine, methylhydrazine, and KOH.

(1) Reaction in the Presence of Ammonia. Chloramine (about 0.1 mol) from the chloramine generator was passed into 0.10 mol of CH_3NHNH_2 in 75 mL of dry ethanol over a 60-min period. An exothermic reaction yielded a small amount of white solid in a yellow solution which then turned colorless on standing. The solid and the solution examined after 2 h showed no reducing properties toward acidic KIO_3 solution. The gas chromatographic and proton NMR analyses of the solution showed 99.97% methanol and a trace of NH_3. The solid was identified as NH_4Cl by its infrared spectrum.

(2) Reaction with Ammonia-Free Chloramine. To a solution of methylhydrazine (0.054 mol) in anhydrous diethyl ether (10 mL) was added slowly 0.027 mol of NH_2Cl in 50 mL of ether while maintaining the temperature at 0 °C. The reaction was immediate and exothermic with the formation of a white solid. The reaction mixture was stirred for 1 h after the addition of the chloramine solution and then filtered. The filtrate was mostly ether and had no reducing properties toward acidic iodate solution. The solid after recrystallization from acetone and drying melted at 123.5 °C. Anal. Calcd for $[(CH_3)_2C{=}NNH_2CH_3]Cl$: C, 39.21; H, 8.98; N, 22.85; Cl, 28.98. Found: C, 39.08; H, 9.06; N, 22.77; Cl, 28.97. The proton NMR had three peaks at δ 2.10, 2.22, and 2.28 downfield from internal tetramethylsilane with another broad peak at δ 9.82. These data and the melting point are in accord with reported data for acetone methylhydrazone hydrochloride.[17]

(3) Reaction of Chloramine with a Mixture of Methylamine and Methylhydrazine. A 80-mL methanol solution containing 0.05 mol of methylamine and 0.08 mol of methylhydrazine was treated with the effluent from the chloramine generator for 1 h (approximately 0.1 mol of NH_2Cl). A clear solution with no reducing property toward acid KIO_3 was obtained at the end of the chloramine addition. The gas chromatographic analysis of the solution showed the presence of methylamine but not of methylhydrazine, thus showing that chloramine reacts preferentially with methylhydrazine in the CH_3NH_2–CH_3NHNH_2 mixture.

(4) Reaction of Ammonia-Free Chloramine with Methylhydrazine in the Presence of KOH. A 25-mL methanol solution containing 0.05 mol of KOH and 0.05 mol of methylhydrazine was treated with a 250-mL ether ammonia-free solution of 0.05 mol of NH_2Cl. Immediate reaction occurred, yielding a solid and a yellow solution. After the solid was filtered out, the solution was concentrated in vacuo. No methylhydrazine was detected by gas chromatographic analysis, although the solution had reducing properties. There were several other products observed by gas chromatographic analysis of this solution, but only water and *sym*-hexahydro-1,4-dimethyltetrazine were identified.

Discussion

The results of this study show conclusively that in the nonaqueous solvents tried (ether, xylene, methanol, and diglyme) chloramine does not react with methylamine to form methylhydrazine at ordinary temperatures in the absence of fixed base such as potassium hydroxide or sodium methoxide. These results parallel the results obtained in anhydrous ether by Audrieth and Diamond[1] and Wiberg and Schmidt.[19] The results, however, are in strong contrast to those obtained in the chloramination of ammonia,[13] dimethylamine,[18] and methylhydrazine.

The fact that methylhydrazine can be recovered from the reaction between chloramine and methylamine in the presence of a fixed base suggests that chloramine reacts preferentially with the fixed base, resulting in the formation of an intermediate, which then reacts with methylamine, forming methylhydrazine. It appears that methylhydrazine does not react with chloramine as long as both the fixed base and the amine are present.

Three different mechanisms for the formation of hydrazines from the reaction of chloramine with ammonia or amines have been proposed. Anbar and Yagil[20] proposed the formation of hydroxylamine by the displacement of Cl^- by OH^- from chloramine. According to this mechanism, hydroxylamine then reacts with ammonia (or an amine), forming the hydrazine. This mechanism appears to be improbable for two reasons: (1) There is no report in the literature of obtaining methylhydrazine by an NH_2OH–CH_3NH_2 reaction. (2) We have found that no methylhydrazine formation occurs when hydroxylammonium sulfate reacts in basic solution with methylamine.[24]

The bimolecular displacement of Cl^- from chloramine by the amine (or ammonia) bases proposed by Cahn and Powell,[21] namely $NH_2Cl + {:}B \rightarrow B{:}NH_2^+ + Cl^-$ (where B is an electron donor), clearly does not apply to our data for the reaction does not occur when fixed base is absent. It appears that whereas the Cahn and Powell displacement mechanism operates in the ammonia and dimethylamine chloraminations, a third mechanism proposed by Audrieth and co-workers[22] may be operative in the methylamine chloramination. In this mechanism, the intermediate formation of the imide radical in the presence of strong base is postulated:

$$NH_2Cl + OH^- \rightarrow NHCl^- + H_2O$$

$$NHCl^- \rightarrow NH + Cl^-$$

The imide radical then reacts with methylamine to yield the hydrazine:

$$CH_3NH_2 + NH \rightarrow CH_3NHNH_2$$

Drago and Sisler[23] have previously shown that this mechanism

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is *not* operative in the chloramination of ammonia in alkali hydroxide solutions. The factors which determine which mechanism operates in the various instances are not evident at this time.

The results reported here indicate no unexpected products except the formation of *sym*-hexahydro-1,4-dimethyltetrazine and water when the reaction was carried out in the presence of sodium methoxide. These products and the drop in the concentration of total N–N bonded material on storing the reaction solutions over a period of time are attributed to the aerial oxidation[24] of methylhydrazine or other N–N bonded compounds during filtration, distillation, and handling, although care was taken to minimize contact of these products with the atmosphere.

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Registry No. CH_3NH_2, 74-89-5; NH_2Cl, 10599-90-3; $[(CH_3)_2C{=}NNH_2CH_3]Cl$, 73531-89-2; CH_3NHNH_2, 60-34-4; NH_2NH_2, 302-01-2; $CH_3NHN{=}CH_2$, 36214-48-9; $(CH_3NNHCH_2)_2$, 695-20-5.

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(25) Although glass wool filters are used in the chloramine generator to check the flow of NH_4Cl from the chloramine generator to the reaction vessel, this does not completely prevent NH_4Cl from going to the reaction vessel. This NH_4Cl then reacts with CH_3ONa to form NaCl, NH_3, and CH_3OH. The observed amount of NaCl, therefore, was more than the calculated amount.

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Synthesis and Molecular Geometry of *fac*-$Cr(CO)_3(PEt_3)_3$

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Structural studies on octahedral phosphine-substituted metal carbonyl complexes such as $Cr(CO)_5(PPh_3)$,[1] $W(CO)_5[P(t\text{-}Bu)_3]$,[2] $\{cis\text{-}Mn(CO)_2[P(OMe)_2Ph]_4\}\{PF_6\}$,[3] fac-$Cr(CO)_3(PH_3)_3$,[4] and *cis*-$Cr(CO)_2(PH_3)_4$[5] have revealed only very minor geometric irregularities attributable to steric interaction between the phosphine ligands and the $M(CO)_x$ fragment. The role of ligand size in the *reactions* of these octahedral complexes is, nonetheless, clear-cut.[6–8] Thus, Reimann and Singleton[6] have shown that the smaller phosphine and phosphite ligands react with $M(CO)_5Br$ (M = Mn, Re) replacing *four* carbonyl ligands, whereas larger ligands replace no more than *two* ligands. Studies on the group 6 metal carbonyls also provide evidence for steric interactions both in reactions and in product distribution.[8,9] Thus, with $Cr(CO)_6$, the most highly substituted complex obtainable with PPh_3 is *trans*-$Cr(CO)_4(PPh_3)_2$, whereas smaller ligands (such as PH_3) yield species of stoichiometry $Cr(CO)_2L_4$.[5,9]

Table I. Experimental Data for the X-ray Diffraction Study of *fac*-$Cr(CO)_3(PEt_3)_3$

A. Crystal Parameters[a] at 26 °C

cryst system: monoclinic	$\beta = 105.094\ (17)°$
space group: $P2_1$	$V = 1338.1$ Å^3
$a = 8.4198\ (12)$ Å	$Z = 2$
$b = 16.2973\ (35)$ Å	mol wt 490.1
$c = 10.1002\ (19)$ Å	ρ(calcd) = 1.217 g/cm^3

B. Measurement of Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda} = 0.710\ 730$ Å)
monochromator: highly oriented graphite, equatorial
reflctns measd: $+h$, $+k$, $\pm l$
2θ range: 4.5–45.0°
scan type: θ(crystal)–2θ(counter)
scan range: $[2\theta(\text{Mo K}\alpha_1) - 1.0]° \rightarrow [2\theta(\text{Mo K}\alpha_2) + 1.0]°$
reflctns collected: 1972 total, 1830 independent
stds: 3 every 47 reflections, no significant decay
abs coeff: $\mu = 6.11$ cm^{-1}; no correction necessary
ignorance factor: $p = 0.015$

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ component of the 24 reflections of the forms $\{\bar{1}81\}$, $\{511\}$, $\{125\}$, $\{163\}$, $\{\bar{5}52\}$, and $\{\bar{5}25\}$, all with $2\theta = 20.0$–$29.0°$.

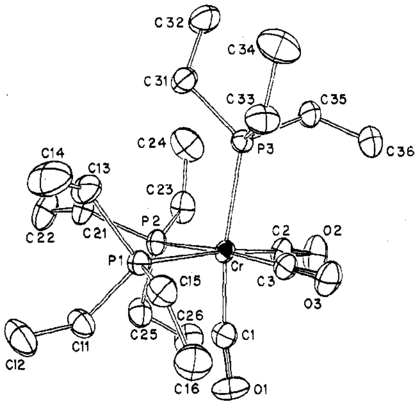

Figure 1. Labeling diagram for *fac*-$Cr(CO)_3(PEt_3)_3$ (ORTEP-II diagram; 50% ellipsoids; hydrogen atoms omitted).

The cis and trans isomers of $Mo(CO)_4L_2$ have been prepared, and steric interactions have been invoked to interpret the reactions of the cis complexes.[8] The most common method of measuring steric interactions involves the "cone angle" of the ligand, as determined from molecular models.[7] This has been correlated with reaction rates, although it should be noted that (in some cases) the crystallographically determined cone angle differs from that obtained from models.[10]

In order to obtain further information on steric interactions in "crowded" phosphine-substituted $M(CO)_6$ derivatives, we have undertaken a single-crystal X-ray diffraction study of *fac*-$Cr(CO)_3(PEt_3)_3$, which was prepared as described below. (Note that the direct reaction of $Cr(CO)_6$ with PEt_3 yields only cis and trans isomers of $Cr(CO)_4(PEt_3)_2$.[11])

Experimental Section

Preparation of ***fac*****-$Cr(CO)_3(PEt_3)_3$.** A sample of 0.5 g of $CrCl_2$ was suspended in toluene (30 mL). PEt_3 (1.0 mL) was added to the suspension and stirred vigorously for 30 min, during which time the solution changed from green to very intense blue. $Na^+[Mn(CO)_5^-]$(0.8 g) was added and stirred for 1 h during which the solution became

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