platinum–nitrogen bonds. Such factors may also affect the binding of platinum(II) ammine complexes with the heterocyclic bases in DNA, as additional work has recently revealed.[29]

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Registry No. $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$, 85370-19-0; ^{195}Pt, 14191-88-9.

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(29) Comess, K.; Lippard, S. J. To be submitted for publication.

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Restudy of the Action of Sulfur Dioxide on Dry Trimethylamine Oxide: Iodine Oxidation and Lewis Acid Chemistry of the Most Reactive Product, $(CH_3)_2(H)NCH_2SO_3$

Anton B. Burg

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Further study of the action of SO_2 on dry $(CH_3)_3NO$ has led to new chemistry of $(CH_3)_2(H)NCH_2SO_3$ ("KS8")—often the major product but sometimes exceeded by $(CH_3)_3NSO_3$, with small yields of $(CH_3)_3NH^+$. X-ray study of a single crystal (monoclinic) of KS8 showed the space group $P2_1/c$, with 12 molecules per unit cell: $V = 1860$ (1) Å^3, $a = 12.069$ (5) Å, $b = 12.434$ (6) Å, $c = 13.413$ (6) Å, and $\beta = 112.50$ (3)°. The nontetrahedral angles are O–S–C = 105.3°, O–S–O = 113.5°, and S–C–N = 112.7°. Aqueous iodine oxidizes KS8 (with first-order kinetics) to give SO_4^{2-}, 2 I^-, 3 H^+, and presumably $(CH_3)_2(H)NCH_2OH^+$. Attempts to stabilize the presumed initial product $(CH_3)_3NOSO_2$ by attaching HCl or BF_3 below −78 °C led only to the Lewis-acid chemistry of KS8. With HCl at 70 °C, KS8 quantitatively liberates SO_2, forming $(CH_3)_2NH_2Cl$, H_2O, the known salt $(CH_3)_2N{=}CH_2^+Cl^-$ ("CDMA"), $xH_2CO{\cdot}HCl$, and yCDMA·HCl. CDMA was identified by X-ray study of a single (orthorhombic) crystal. Its space group is *Pmmn* with two molecules per unit cell: $V = 244.4$ (1) Å^3, $a = 6.198$ (2) Å, $b = 7.034$ (3) Å, $c = 5.607$ (1) Å, and $\alpha = \beta = \gamma = 90°$. Cl^- is coplanar with NC_3 units. CDMA or KS8 with HCl in liquid SO_2 forms polymers and a product conjectured to be $(CH_3)_2NCH_2SO_2Cl$. KS8 with BF_3 at 55 °C quantitatively liberates SO_2; then the ^{13}C NMR spectrum indicates the product to be $(CH_3)_2(H)NCH_2O{\cdot}2BF_3$. Solvent acetone removes the BF_3 from this, forming what seems to be $(CH_3)_2NCH_2OH$. Peripheral aspects seem worthy of further study.

The original study of the action of SO_2 on very well dried $(CH_3)_3NO$ at low temperatures gave a main product believed to be $(CH_3)_3NOSO_2$, with two lines of physical evidence suggesting as much as 20% of the relatively inert isomer $(CH_3)_3NSO_3$,[1] soon confirmed elsewhere.[2] The obvious structure $(CH_3)_3NOSO_2$ was contradicted many years later,[3] but the correct structure $(CH_3)_2(H)NCH_2SO_3$ (now confirmed by X-ray crystallography) was recognized only very recently, by King and Skonieczny,[4] who called it product 8; hence it is called hereafter "KS8". However, ref 3 and 4 do not mention $(CH_3)_3NSO_3$; its ^1H NMR singlet is covered by the doublet for CH_3 in KS8.

The present study has shown that even a very slow addition of SO_2 to $(CH_3)_3NO$ (as the solid or in solution) at temperatures as low as −100 °C gives KS8 with yields of $(CH_3)_3NSO_3$ seldom less than 15%, but sometimes more than 50%, most cleanly determined by the ^{13}C NMR spectrum of the mixture. Such results seem to require reconsideration of the suggested reaction mechanism.[4]

It seems reasonable to suggest that the initial formation of $(CH_3)_3NOSO_2$ provides far more than enough energy to cleave the N–O bond even at −100 °C. Then the side-by-side $(CH_3)_3N$ and SO_3 would directly form $(CH_3)_3NSO_3$ or sulfonation at a C–H bond would give KS8. Some of the protons from this sulfonation would account for minor yields (near 8%) of $(CH_3)_3NH^+$. However, if $(CH_3)_3NOSO_2$ ever could be made by a low-energy process, it might well rearrange in the Polonovski manner;[4] then $(CH_3)_3NSO_3$ might well be absent.

If the presumed initial product $(CH_3)_3NOSO_2$ could go to KS8 only by a Polonovski-like rearrangement,[4] this process might be slow enough at −78 °C or lower to permit stabilization by Lewis acids, forming secondary adducts such as $(CH_3)_3NOSO_2{\cdot}HCl$ and $(CH_3)_3NOSO_2{\cdot}BF_3$—expected because the N–O oxygen would enhance the base action of the S–O oxygen, just as addition of O^{2-} to SO_2 makes the stronger base SO_3^{2-}. However, numerous attempts failed to produce such adducts even at −100 °C. Warmed with HCl or BF_3, the low-temperature product showed only the chemistry of KS8, with $(CH_3)_3NSO_3$ and $(CH_3)_3NH^+$ inert.

This Lewis-acid chemistry includes the action of HCl on solid KS8 to form the interesting salt $(CH_3)_2N{=}CH_2^+Cl^-$ or on the SO_2 solution to form the conjectured $(CH_3)_2NCH_2SO_2Cl$, and the action of BF_3 on solid KS8 to form $(CH_3)_2(H)NCH_2O{\cdot}2BF_3$. Other Lewis acids also could have interesting consequences. Also, the first-order oxidation of KS8 by KI_3 opens the study of KS8 as a reducing agent.

Experimental Methods

Chemical Procedures. All volatile reagents, reactants, solvents, and products were managed in a relatively simple Stock-type high-vacuum system, permitting quantitative work with complete exclusion of moisture. Nonvolatiles were brought to reaction in tubes like those shown in Figure 1, often modified for specific purposes. For example, a tube of type A, with the neck a lengthened to facilitate sealing off and reopening to the vacuum line, was used for the action of HCl (at 5 atm pressure and 70 °C) on KS8 in chamber d. After removal of the volatiles to the vacuum line for separation and measurement, the CDMA was sublimed to chamber ab, next sealed off at b. Solvent SO_2 was brought in and neck a sealed off again; now the SO_2 solution of CDMA was poured into the NMR tube, to be sealed off with the sample at −196 °C. The less volatile sublimate $(CH_3)_2NH_2Cl$ was managed in the same way.

Tubes of type B were used for the action of SO_2 on $(CH_3)_3NO$ dissolved in $HCCl_3$, H_2CCl_2, or HCF_2Cl. The amine oxide was dehydrated by evacuation at 25 °C (16 h) and resublimation until no more water came to the U-trap at −196 °C. Any sublimate that reached the upper bulb could be washed down by refluxing the solvent. After the SO_2 reaction, the suspended precipitate could be pipetted into an NMR tube

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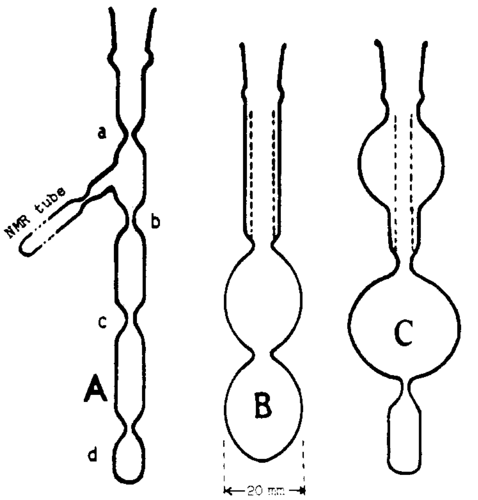

Figure 1. Representative reaction tubes. Each connects to the high-vacuum line through a stopcock with two standard-taper ground joints. Tube A was designed to withstand 6 atm of internal pressure. The internal dotted lines in tubes B and C represent cylindrical inserts serving to receive and remove sublimates.

and the solvent replaced by SO_2, or the solvent could be evaporated from bulb B, so that the solid products could be treated with various reagents. Any sublimable product (such as CDMA) could be captured on the inserted tube (dotted lines) and weighed in dry air.

Type C tubes were used for the action of SO_2 on solid $(CH_3)_3NO$, which was sublimed so as to cover a maximal area of the large bulb. Any of it reaching the top bulb could be removed by means of the insert. Samples could be weighed in either type of bulb.

Standardized NMR Spectra. Recordings of ^1H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were done mostly by the IBM WP270SY-FT instrument, but for quantitative work with ^{13}C, the Bruker AM360-FT spectrometer was preferred. Coupling multiplicity will be shown as $_nJ$, in s^{-1} ("Hz"); thus $_3J$ means a triplet. Half-height widths of peaks will be given by "hw" (s^{-1}). Singlets could be used to identify products only under well-standardized conditions, next described. Each solution or "neat" liquid was in a sealed-off 5-mm NMR tube (usually a Wilmad 507PP or 528PP), immersed in acetone-d_6 in a 10-mm NMR tube; then the chemical shift δ (ppm, downfield from tetramethylsilane for ^1H or ^{13}C or upfield from methyl borate or Cl_3CF for ^{11}B or ^{19}F) usually (but not always) was reliably unique. The ^1H quintet for acetone-d_5 at δ = 2.054 served as a convenient check point and a test for resolution; for ^{13}C, acetone-d_6 at 29.8 ppm had similar utility.

The ^1H spectra of all compounds which might have had some relevance to the present study are displayed as follows:

$(CH_3)_2NH{\cdot}SO_2$?	$\delta = 2.56$ (sharp, no J, CH_3)
	$\delta = 5.10$ (hw = 13, NH or OH?)
$(CH_3)_3NSO_2$	$\delta = 2.59$ (sharp, no J)
$(CH_3)_3NSO_3$	$\delta = 3.37$ (sharp, no J)
$(CH_3)_2(H)NCH_2SO_3$ (KS8)	$\delta = 3.38$ ($_2J = 4.96$, CH_3)
	$\delta = 4.24$ ($_2J = 5.44$, CH_2)
	$\delta = 8.95$ (hw = 20, NH)
HCl	$\delta = 2.85$
H_2O in acetone	$\delta = 2.87$
CH_3NH_3Cl	$\delta = 3.10$ (hw = 11, CH_3)
	$\delta = 7.3$ (hw = 25, NH_3)
$(CH_3)_2NH_2Cl$	$\delta = 3.04$ ($_2J = 5.73$, CH_3)
	$\delta = 7.6$ ($_3J = 45$, hw = 37, NH_2)
$(CH_3)_3NHCl$	$\delta = 3.19$ ($_2J = 5.10$, CH_3)
	$\delta = 9.3$ ($_3J$ = ?, low and broad, NH)
$(CH_3)_3NO{\cdot}HCl$	$\delta = 3.89$ (sharp, no J, CH_3)
	$\delta = 8.8$ (low and broad, OH)
$(CH_3)_2N{=}CH_2Cl$ (CDMA)	$\delta = 4.08$ (hw = 6, CH_3)
	$\delta = 8.18$ (hw = 6, CH_2)
$[(CH_3)_2N]_2CH_2$ (BAM, neat)	$\delta = 1.734$ (sharp, no J, CH_3)
	$\delta = 2.164$ (sharp, no J, CH_2)

All samples except BAM were solutions in liquid SO_2.

An important superposition occurs in the ^1H spectrum of KS8 with $(CH_3)_3NSO_3$. The CH_3 groups may appear as a doublet with the upfield branch raised and broadened by the $(CH_3)_3NSO_3$ singlet superposed on the downfield side of that branch. On the JEOL-90 instrument, the $(CH_3)_3NSO_3$ peak filled the space between the two branches, which then appeared as a slightly crooked singlet, even while the surrounding acetone-d_5 was well resolved. For a quantitative analysis, one uses the integral for the CH_2 group in KS8, multiplied by 3 and subtracted from the CH_3 integral, to give the relative intensity of the nine protons in $(CH_3)_3NSO_3$. The ^{13}C spectrum gives the same result more directly but not so quickly.

In slightly wet acetone-d_6, H-bonding places H_2O very near to free HCl in SO_2. Confusion is avoided either by careful drying or by using a different lock liquid such as C_6D_6.

Pertinent ^{13}C spectra of authentic known compounds are listed as follows, again for SO_2 solutions except for BAM:

KS8	$\delta = 71.2$ ($_3J = 151$, CH_2)
	$\delta = 46.0$ ($_4J = 145.8$, 2 CH_3)
$(CH_3)_3NSO_3$	$\delta = 50.1$ ($_4J = 144.5$)
CDMA	$\delta = 169$ ($_3J = 178$, CH_2)
	$\delta = 50.4$ ($_4J = 147.6$, 2 CH_3)
$(CH_3)_2NH_2Cl$	$\delta = 37.5$ ($_4J = 143$)
$(CH_3)_2NH{\cdot}BF_3$	$\delta = 37.4$ ($_4J = 142$)
BAM (neat)	$\delta = 83.9$ ($_3J = 134$, CH_2)
	$\delta = 43.3$ ($_4J = 133$, 4 CH_3)

KS8 Chemistry

New Synthesis. A novel method for making KS8 was planned according to the equation

$$\underset{\text{"BAM"}}{[(CH_3)_2N]_2CH_2} + H_2O + 2SO_2 \rightarrow \underset{\text{"KS8"}}{(CH_3)_2(H)NCH_2SO_3} + (CH_3)_2NH{\cdot}SO_2 \quad (1)$$

The best experiment began with 14.69 mmol of BAM and 15.47 mmol of water (both determined by weight), mixed into 2 mL of dry ether with 19 mmol of SO_2, in a vertical reaction tube attached to the vacuum line. The initial rapid reaction precipitated an oil, which soon solidified. At this point, a trace of $(CH_3)_2NH$ was isolated in the vacuum line. Now more SO_2 (35 mmol) was added, and the reaction went to completion. The solid mass was triturated in 4.7 g of dry methanol, which then was diluted by 3 volumes of dry ether. The fine crystals were collected, ether-washed on a paper filter, and freed from ether and methanol by heating at 70 °C. A final crop of crystals precipitated from the ether–methanol filtrate at −40 °C. Then evaporation left an oil, empirically formulated as $(CH_3)_2NH{\cdot}SO_2$, but not necessarily having this simple structure. The observed yield of 99% pure KS8 (assayed by KI_3 titration; cf. next section) was 1.66 g, representing 91% of the original BAM. For very high purity, KS8 can be dissolved in liquid SO_2 and reprecipitated by dry methanol and ether.

With more study, this new synthesis might become virtually quantitative, with a bench-top procedure for more convenience. One limitation is uncertain purity of the BAM; another, the manner of action by SO_2. Less efficient experiments showed pitfalls. With the calculated amount of water, but too little access to SO_2, the hydrolysis of BAM can lead to low yields. Or, with too much SO_2, much of the BAM may be precipitated (as a BAM·SO_2 complex?) and so lose reactive contact with the water. However, even the worst results were better than the best yields by prior methods. Since BAM is commercially available, or easily made from $(CH_3)_2NH$ and H_2CO, eq 1 appears to represent the method of choice.

The synthesis of KS8 from $(CH_3)_2NH$ and $HOCH_2SO_3Na$ ("KS9") was attempted in the vacuum line, but the yield (60%) and purity (83%) were discouraging.

Iodine Titration. An interesting first-order reaction occurs when an aqueous solution of KS8 is titrated by iodine. With pure KS8 at a fixed temperature, each increment of standard KI_3 solution gives a starch–iodine color, which fades out after a measurable time interval Δt, determined solely by the quantity Q of KS8 still present and the increment of KI_3. The results determine an equation of the type $\log Q = \log Q_0 - rt$, where Q_0 is the initial quantity of KS8, t is the sum of the Δt values, and r is the rate constant. A typical equation for results at 22 °C was $\log Q = 2.472 - 0.000241t$, for Q and Q_0 in micromoles and t in seconds. Precise measurement of Δt may be difficult near the beginning, and near the end, the very slow fade-out may be poorly judged; but for most of the process, deviations may average as low as 1%.

When such a titration is used for assaying impure KS8, any S(IV) impurity causes an initially steeper line, interfering with the estimate of Q_0. In such a case, Q_0 is the number that linearizes the log Q vs t plot, after the final end point has been determined. This end point is estimated by extrapolation, and then one adds slightly more than the required KI_3. On the next day, the correct end point is found by back-titration with standard thiosulfate. Then with Q_0 determined as the zero-time intercept of the best line, $Q - Q_0$ determines the S(IV) impurity.

A reasonable equation for this titration reaction is

$$(CH_3)_2(H)N^+CH_2SO_3^- + 2H_2O + I_2 \rightarrow (CH_3)_2(H)N^+CH_2OH + 2I^- + SO_4^{2-} + 3H^+ \quad (2)$$

Indeed, titration of weighed samples of KS8, first by KI_3 to virtual completion and then with standard NaOH, showed 3.01 or 3.04 H^+ per KS8, with either methyl orange or phenolphthalein indicator. Thus, it appears that the N–H bond here is about as firm as in $(CH_3)_3NH^+$.

Equation 2 can explain the first-order kinetics if the rate-determining step is hydrolysis to liberate sulfitic material, which iodine oxidizes very rapidly. However, the initial equilibrium concentration of S(IV) material (before any KI_3 is added) must be very slight, for each point falls on the line even if there is a long time interval between any fade-out and the next increment of KI_3. If time permitted an appreciable buildup of S(IV) material, this would not be true.

Reaction 2 was studied further by ^1H NMR, with D_2O as the lock solvent for nearly equimolar KS8 and KI_3. The end product (after 21 h at 25 °C) was virtually free of impurities. There were two sharp peaks: CH_2 at $\delta = 4.30$ and 2 CH_3 at $\delta = 2.52$, credibly assignable to the major product of reaction 2. The DOH peak at $\delta = 4.05$ was much stronger. At the 6-h point, however, the strongly visible peaks were for CH_3 groups in KS8 at $\delta = 2.79$ and its product three times as intense at $\delta = 2.53$ ppm, meaning 75% completion of reaction 2; and with these were three nearly equal minor peaks at $\delta = 2.58$, 2.46, and 2.42 ppm, together amounting to 13% of the significant protons. These must be assigned to reaction intermediates, for they were all gone at the end point.

It seems to be a reasonable conjecture that the rate-determining step of the iodine reaction 2 is composed of at least two stages: hydration and C–S bond cleavage, with ionization to give free HSO_3^-. It is a standard kinetic principle that successive first-order reactions amount to one first-order process. This subject may be worth the attention of kinetic specialists.

Meanwhile, it is not difficult to believe that the dimethylammoniomethanol ion from reaction 2 would be stable in solution. Its conjugate base, $(CH_3)_2NCH_2OH$, reported as formed in aqueous solution from $(CH_3)_2NH$ and H_2CO, with $\Delta G_{298} = -6.53$ kcal,[6] has been used for making useful products, even though its isolation as a pure substance seems difficult.[7] The present study of KS8 with BF_3 led to an interesting adduct, as the SO_2 was displaced. No formaldehyde could be found in the solution from reaction 2, although similar material has evolved formaldehyde under steam distillation.[5]

KS8 Solvation by Sulfur Dioxide. The original study of $(CH_3)_3NO$ with SO_2 showed that the product could hold 1.80–1.90 SO_2, with the deficiency from $(CH_3)_3NO{\cdot}2SO_2$ ascribed to the $(CH_3)_3NSO_3$ impurity.[1] Those observations now seem to apply well enough to KS8. In a direct test, 0.504 mmol of KS8, all dissolved in liquid SO_2 at −78 °C, retained 0.81 SO_2 per KS8 after 90 min under vacuum, with an equilibrium pressure below 1 mm at −78 °C. Complete removal of the added SO_2 required 10 min at 23 °C. It is suggested that the C–SO_3 dative bond in KS8 has enough base-enhancing effect on O for weak attachment of SO_2. The well-known formation of $S_2O_5^{2-}$ from SO_3^{2-} and SO_2 is analogous. Moreover, another experiment employed 0.231 mmol of KS8, 0.570 mmol of SO_2, and 0.490 mmol of HCl for reaction at −78 °C, after which pumping at −78 °C left a residue roughly formuated as $KS8{\cdot}SO_2{\cdot}HCl$.

Reaction of Solid KS8 with HCl. The action of dry HCl on KS8 crystals is like the hydrolysis aspect of reaction 2, liberating SO_2 at rates not much slower. With HCl in great excess in a sealed tube at 25 °C, liquefaction was visible within 3 h. At this point some SO_2 could be found by opening the tube to the vacuum line but for quantitative liberation of SO_2, the process was continued for 16–20 h at 70 °C. The consumption of HCl in eight such experiments ranged from 1.3 to 1.7 units per unit of KS8. The yield of water (determined by weighing the H_2O–HCl azeotrope and titrating the HCl with standard NaOH) varied considerably from an average of 0.5 unit per unit of KS8. The saltlike product $(CH_3)_2N{=}CH_2^+Cl^-$ ("CDMA") was isolated in yields as high as 50% by high-vacuum sublimation at 70 °C. It was identified by X-ray crystallography (vide infra), confirming chemical inferences in the original literature.[5] Its ^1H and ^{13}C NMR spectra also agreed with an authentic sample. It melted sharply at 130 °C. The less volatile product $(CH_3)_2NH_2Cl$ (vacuum sublimable above 110 °C) also was identified by its ^1H and ^{13}C NMR spectra.

The results of such experiments suggest the equations

$$(CH_3)_2(H)NCH_2SO_3 + HCl \rightarrow \underset{\text{CDMA}}{(CH_3)_2N{=}CH_2^+Cl^-} + SO_2 + H_2O \quad (3)$$

$$(CH_3)_2(H)NCH_2SO_3 + H_2O + HCl \rightarrow (CH_3)_2NH_2Cl + HOCH_2SO_3H \quad (4)$$

$$HOCH_2SO_3H \rightarrow H_2O + SO_2 + H_2CO \quad (5)$$

$$xH_2CO + HCl \rightarrow xH_2CO{\cdot}HCl \quad (6)$$

$$y(CH_3)_2N{=}CH_2^+Cl^- + HCl \rightarrow y(CH_3)_2N{=}CH_2Cl{\cdot}HCl \quad (7)$$

The stoichiometry would suggest that x and y here are small, but simplicity is not implied, for a fairly polar open-chain high polymer could occlude an adduct of HCl with H_2CO or CDMA. The following experiments are pertinent.

Direct Action of HCl on CDMA. A 0.591-mmol sample of CDMA was made from BAM + 2HCl[5] (in a tube like that in Figure 1A) and isolated by high-vacuum sublimation. Less volatile material was removed by sealing off the bottom bulb. Action by 0.776 mmol of HCl at 25 °C soon formed a gummy liquid. Removal of excess HCl at −78 °C left the adduct CDMA·1.025HCl. Removal of more HCl at 100 °C changed this formula to CDMA·0.43HCl; thus y in eq 7 would be 2.3.

Formed at −78 °C, the adduct CDMA·HCl was a mobile liquid at 23 °C (rather than a gum), but in liquid SO_2 its ^1H NMR spectrum showed broad peaks at $\delta = 8.18$ (hw = 95; 11%), 6.50 (hw = 86; 9%), and 3.91 (hw = 100; 77%). However, polymer bonding could not have been strong, for 77% of the CDMA could be recovered by vacuum sublimation at 70 °C.

A different product was indicated when CDMA (0.37 mmol) was nearly all precipitated by HCl (0.33 mmol) in liquid SO_2, in an NMR tube at 23 °C. During 16 h almost all of the precipitate was redissolved; after 45 h at 23 °C, the ^1H NMR spectrum showed $\delta = 8.2$ (hw = 140; 12%), 4.0 (hw = 116; 62%), and 3.6 (hw = 65; 21%), best explained as polyionic aggregates of the unit $(CH_3)_2(H)NCH_2Cl^+Cl^-$. There was also a very sharp ^1H spectrum for a substance X, showing $\delta = 4.84$ ($_2J = 4.74$; 1.2%) and 3.13 ($_2J = 5.42$; 3.6%), present at far lower intensity in the earlier CDMA + HCl experiment, but far more important when KS8 reacted with HCl in liquid SO_2. For this X, the structure $(CH_3)_2NCH_2SO_2Cl$ might reasonably be conjectured but lacks confirmation. An alternative—CDMA with SO_2 attached to N and Cl^- to the CH_2^+ group—ought to show the very different NMR spectra of CDMA simply dissolved in liquid SO_2.

NMR Study of the Reaction of KS8 with HCl in Liquid SO_2. A 0.56-mmol sample of pure KS8 with 1.20 mmol of HCl, in liquid SO_2 in a sealed NMR tube, was stored for 16 h at −78 °C and 1 h at 23 °C; then KS8 represented 84% of the ^1H NMR spec-

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trum. A 5% peak at $\delta = 8.0$ (hw = 30) rose to 35% during 23 h but was replaced by $\delta = 7.5$ (hw = 68; 25%) during 6 days, going to $\delta = 7.3$ (hw = 40; 22%) during 12 days). At the start there was a broad peak at $\delta = 3.8$ (hw = 50), which increased steadily to 36% during 12 days. At the 23-h point, KS8 had fallen to 1%, but substance X now accounted for 40% of the protons and persisted at that level. Equally persistent was a 2% broad triplet at $\delta = 8.5$ (${}_3J = 40$).

At no stage of this NMR monitoring was there any evidence for free CDMA or $(CH_3)_2NH_2Cl$; cf. eq 3 and 4. Then if it is assumed that substance X actually is $(CH_3)_2NCH_2SO_2Cl$, it becomes reasonable to write the equation

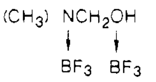
$$(CH_3)_2(H)NCH_2SO_3 + HCl \rightarrow (CH_3)_2NCH_2SO_2Cl + H_2O \quad (8)$$

for a process that is faster than the attack by HCl on solid KS8 but far slower than the action of water and HCl to form aggregates that in liquid SO_2 need not include $(CH_3)_2NH_2Cl$.

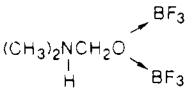
The difference of X from SO_2-solvated CDMA is seen most clearly in the ^{13}C NMR spectrum of the final product of the above 12-day experiment. This does indeed show CDMA material at $\delta = 169$ (${}_3J = 180 \pm 10$) and 50.4 (${}_4J = 135 \pm 10$), but the peaks are broad and shallow, suggesting CDMA trapped in a polymer. For substance X, however, the same chart shows a clear, sharp 5:2:14:2:5 pseudotriplet for CH_2 at $\delta = 80.6$ (pseudo ${}_3J = 160$) and, for 2 CH_3, an equally sharp 4:2:15:3:15:2:4 pseudoquartet at $\delta = 40.8$ (pseudo ${}_4J = 165$).

Action of BF_3 on Solid KS8. The displacement of SO_2 from solid KS8 by BF_3 seemed faster than the analogous HCl reaction: the yield of SO_2 was quantitative after 18 h at 55 °C. Four experiments using BF_3 in excess gave the combining ratio of BF_3 to KS8 as 2.02, 1.99, 2.04, or 2.00, forming a very viscous, pale yellow liquid. Overheating (e.g. 18 h at 115 °C) in an earlier experiment had given a red-brown liquid. Two of the four experiments were done directly in sealed NMR tubes, with volatiles to be removed to the vacuum line through a tube opener.

The empirical formula of the viscous-liquid product could represent either of two isomers, namely



$$(CH_3)\ \underset{BF_3}{\underset{\downarrow}{N}}CH_2\underset{BF_3}{\underset{\downarrow}{O}}H$$



$$(CH_3)_2\underset{H}{\underset{|}{N}}CH_2O\genfrac{}{}{0pt}{}{\nearrow BF_3}{\searrow BF_3}$$

The NMR spectra show that only one of these is present, strongly favoring the isomer with two BF_3 groups on the oxygen atom.

The viscosity-broadened ^1H NMR spectrum of the neat liquid showed CH_2 at $\delta = 6.98$ and 2 CH_3 at $\delta = 2.89$, both with hw = 67. In liquid SO_2, these peaks were far sharper, now at $\delta =$ 7.89 and 3.76. The downfield shift would be due to SO_2 solvation through H—a deshielding effect, not affecting the ^{13}C spectra. For ^{13}C in both samples, CH_2 was at $\delta = 168.2$ (${}_3J = 183$) and 2 CH_3 at $\delta = 49.8$ (${}_4J = 183$). Comparison of these results with the analogous spectra for $(CH_3)_2NCH_2$ in KS8 shows ^1H signals in CH_3 shifted downfield only 0.38 ppm and ^{13}C signals in CH_3 only 3.8 ppm farther downfield, whereas for ^1H signals in CH_2 the downfield shift is 3.65 ppm and for ^{13}C signals in CH_2 it is 97 ppm. With two BF_3 groups on the oxygen atom, strong deshielding of both H and C in CH_2 would be expected, but the effect on the distant CH_3 groups would be far less, as observed. If BF_3 were on O and N, the deshielding for CH_2 and CH_3 would be much more nearly alike.

The odd proton here assigned to N–H was not clearly distinguished from impurities due to incipient destruction of the $(CH_3)_2NCH_2$ unit. In SO_2 there was a sharp peak at $\delta_H = 5.61$ (14%) and a sharp ^{13}C triplet at $\delta = 67$ (${}_3J = 180$; 10%).

Action of Acetone on the 2 BF_3 Complex. When acetone-d_6 was used as the solvent for the adduct $(CH_3)_2(H)NCH_2O{\cdot}2BF_3$, its effect was to remove BF_3; then very slowly, $(CD_3)_2CO{\cdot}BF_3$ decomposed to red material, of unknown character. However, there was time enough to obtain the new ^{13}C NMR spectrum of $(CH_3)_2NCH_2OH$, which probably had lost both BF_3 units. Its CH_2 group now appeared at $\delta = 53.8$ (${}_3J = 146$) and 2 CH_3 at $\delta = 43.8$ (${}_4J = 144$)—actually upfield of the same groups in KS8. A solvating effect of acetone may have affected these results, but not very strongly.

Any ^{13}C spectrum of $(CD_3)_2CO{\cdot}BF_3$ would have been lost by exchange with the far larger amount of free $(CD_3)_2CO$.[8] However, there was an interesting minor feature: a sunburst septet at $\delta = 36.7$ (${}_7J = 19.4$), probably representing some further chemistry of $(CH_3)_2NCH_2OH$, for it was not seen in the blank run of acetone-d_6 with BF_3. The ^1H NMR spectrum of this denuded $(CH_3)_2NCH_2OH$ was confused by the $(CD_3)(CD_2H)CO{\cdot}BF_3$ impurity and also the ^{19}F and ^{11}B spectra lacked information value.

Reaction of KS8 with BF_3 in Liquid SO_2. An exploratory experiment showed that the action of BF_3 on KS8 in liquid SO_2 is a complex process beginning at −78 °C with formation of an adduct roughly formulated as $KS8{\cdot}2SO_2{\cdot}BF_3$. After 19 h at −78 °C with excess BF_3, removal of volatiles brought the rough formula to $KS8{\cdot}SO_2{\cdot}1.35BF_3$. When this residue was warmed to 23, 50, and 100 °C with excess BF_3, there was modest absorption of BF_3 (now 1.54 per KS8) and the total sulfur content was 74% of that in the original KS8. However, KI_3 titration now showed only 12% survival of KS8. The data showed an abnormally low rate constant: $\log Q = 1.762 - 0.000112t$, again for Q in micromoles. There may have been an initial first-order step, such as liberation of KS8 from a BF_3 adduct, having its own effect on the overall rate. Meanwhile, the denatured KS8 had lost character in ways subject to further study, including generation of H_2CO (deposited as a polymer with the volatiles in the vacuum line), possible amine complexes, and sulfur compounds not oxidizable by iodine.

Amine Oxide–SO_2 Experiments

Initial Product. Numerous experiments were planned to form the SO_2 complex of $(CH_3)_3NO$ at temperatures in the range −78 to −100 °C, with or without solvents such as H_2CCl_2 and HCF_2Cl. The products, in liquid SO_2 at 25 °C, were identified by their NMR spectra. Usually, more than 90% of the amine oxide went to form KS8 and $(CH_3)_3NSO_3$ in varying ratios; $(CH_3)_3NH^+$ accounted for the rest. It was assumed that low-temperature NMR would have given no different results, for any structure resistant to the high energy of direct $(CH_3)_2NO–SO_2$ bonding would not have changed further on warming.

Two experiments illustrate the extreme variation of the ratio of $(CH_3)_3NSO_3$ to KS8 with changing experimental conditions. In one of these, the dry solid amine oxide (0.964 mmol), adhering to the walls of a large bulb (Figure 1C, with an attached NMR tube as in Figure 1A), was exposed at −78 °C to SO_2(g) coming from a U-tube in the vacuum line (at −100 to −80 °C), until 3.4 mmol of SO_2 had been absorbed; the excess would have included solvation of the product KS8. Now the total SO_2 was brought up to 10.5 mmol and the solution was delivered to the NMR tube (cf. Experimental Methods). Then the ^{13}C NMR spectrum, with ^1H decoupled and integrals measured, showed 73% KS8, 20% $(CH_3)_3NSO_3$, and 7% $(CH_3)_3NH^+$ ion, all quite consistent with the inferences on page 1634 of ref 1.

In a contrasting experiment, a solution of $(CH_3)_3NO$ (ca. 1 mmol) in H_2CCl_2 received SO_2 for 1 h at −100 to −83 °C. After removal of all excess SO_2 and solvent (vacuum, 50 °C), the ^{13}C spectrum (in SO_2 solution as before) showed only 35% KS8, with 55% $(CH_3)_3NSO_3$ and 7% $(CH_3)_3NH^+$. A 3% impurity appeared at $\delta = 58.5$, with ${}_4J = 144$. Thus, it seemed that the solvent dramatically favored $(CH_3)_3NSO_3$ but had little effect upon the minor yield of $(CH_3)_3NH^+$. The ^1H spectrum confirmed this ion, at $\delta = 3.19$ (${}_2J = 5.09$), and also confirmed the ratio of $(CH_3)_3NSO_3$ to KS8 as 1.6.

After complete removal of the SO_2 from this sample, a KI_3 titration showed only 80% of the expected KS8, for no obvious reason. Also mysterious is the absence of doublets in the ^1H spectrum of the CH_2 and CH_3 groups in KS8, while the doublet for $(CH_3)_3NH^+$ was well resolved.

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Table I. Summary of X-ray Studies of CDMA and KS8

	CDMA	KS8
formula	$(CH_3)_2N{=}CH_2^+Cl^-$	$(CH_3)_2(H)NCH_2SO_3$
mol wt	93.557	139.18
cryst syst	orthorhombic	monoclinic
cryst size, mm	0.45 × 0.35 × 0.45	0.25 × 0.8 × 0.05
cryst formation	vacuum resublimed	slow recryst/EtOH
instrument	Nicolet/Syntex $P2_1$	
radiation	Mo Kα (0.71069 Å)	
temp, °C	25	
$(\sin\theta)/\lambda$ limit, Å^{-1}	0.5385	0.538
method of struct soln	std heavy atoms	direct
no. of reflns measd	406	2903
no. of rflns used	237	1936
refinement program	SHELX-76	
agreement factors	$R(F) = 0.0657$, $R_w(F) = 0.0657$	$R(F) = 0.059$, $R_w(F) = 0.070$
no. of variables	30	217
space group	*Pmmn* (No. 59)	$P2_1/c$ (No. 14)
unit cell		
a, Å	6.198 (2)	12.069 (5)
b, Å	7.034 (3)	12.434 (6)
c, Å	5.607 (1)	13.413 (6)
α, deg	90	
β, deg	90	112.50 (3)
γ, deg	90	
V, Å^3	244.4 (1)	1860 (1)
Z	2	12
D(calcd), g/cm^3	1.276	0.763

The high yield of $(CH_3)_3NSO_3$ from this experiment does not necessarily mean that dilution always will favor this product, for the yields of KS8 from earlier (and less accurate) work with HCF_2Cl as the solvent gave yields of KS8 roughly judged to range between 40 and 70%. In dry methanol at −78 °C, the yield of $(CH_3)_3NSO_3$ was one-sixth as high as for KS8, as might have been predicted from the aqueous experiments in ref 2. A full study of the many variables affecting the yields of KS8 and $(CH_3)_3NSO_3$ would require much time and effort. What is important here is that high yields of $(CH_3)_3NSO_3$ are possible and must be considered in any discussion of reaction mechanisms.

HCl Reaction. Of the two experiments just described, the one converting 73% (0.704 mmol) of the amine oxide to KS8 was chosen for an example of the action of HCl on the mixed product. After removal of the solvent SO_2 under vacuum up to 70 °C, the white solid was treated with 1.363 mmol of dry HCl, toward which the components $(CH_3)_3NSO_3$ and $(CH_3)_3NH^+$ would be inert. After 20 h at 68 °C, the total SO_2 was measured as 0.712 mmol, neatly confirming the estimated yield of KS8. The consumed HCl was 0.94 mmol, and the yield of water was 0.21 mmol; again as with pure KS8, some of the HCl would have been caught in the H_2CO and CDMA polymers. Finally, 0.327 mmol of CDMA and 0.313 mmol of $(CH_3)_2NH_2Cl$ were delivered by high-vacuum sublimation.

Boron Fluoride Experiments. Most of the experiments on the action of BF_3 on the SO_2–$(CH_3)_3NO$ product were done before the KS8 chemistry was known and so could not be planned with such information in mind. However, there was agreement with the 2:1 ratio of BF_3 absorbed to SO_2 displaced. When BF_3 and HCl were employed simultaneously, the BF_3 won the contest: small proportions of HCl were absorbed. The fuller study of the BF_3–KS8 reaction would be peripheral to the present purpose but might be assigned to a broader study of KS8 with strong Lewis acids, such as PF_5, CF_3PF_4, AsF_5, SO_3, etc.

X-ray Crystallography

Essential to the understanding of the KS8–HCl reaction was the identification of CDMA by X-ray study of a single crystal, showing the ionic salt $(CH_3)_2N{=}CH_2^+Cl^-$ as suggested in the prior literature.[5] A similar study of KS8 removed any possible doubt of its molecular structure, for which earlier evidence[4] was strong but circumstantial. Indeed, a contrary opinion might have been based upon the iodine titration and the action of HCl or BF_3 to displace SO_2—all more predictable if the structure were $(CH_3)_2(H)NCH_2OSO_2$ as in ref 3.

Table II. Final Atomic Coordinates for CDMA[a]

atom	*x*	*y*	*z*
Cl	0.000	0.500	0.068 (1)
N1	0.000	0.000	0.473 (1)
C1	0.000	0.175 (1)	0.615 (1)
C2	0.000	0.000	0.248 (1)
H11	0.000	0.301 (2)	0.505 (2)
H21	0.000	−0.098 (2)	0.138 (2)
H12	−0.127 (2)	0.164 (2)	0.739 (2)

[a] Here the first row refers to the $N{=}CH_2$ carbon.

Table III. Average Bond Parameters for KS8

	Bond Lengths (Å)		
S–O	1.450 (5)	N–CH_2	1.513 (8)
S–CH_2	1.822 (6)	N–CH_3	1.531 (8)
	Bond Angles (deg)		
O–S–C	105.3 (3)	H_2C–N–CH_3	110.1 (6)
O–S–O	113.5 (3)	H_3C–N–CH_3	109.7 (6)
S–C–N	112.7 (4)		

Table IV. Final Atomic Coordinates for $(CH_3)_2(H)^+NCH_2SO_3^-$[a]

atom	*x*	*y*	*z*
S1	0.8052 (1)	0.0994 (1)	0.1199 (1)
O1	0.7587 (4)	0.0343 (5)	0.1858 (4)
O2	0.7788 (5)	0.0486 (5)	0.0159 (4)
O3	0.7756 (4)	0.2117 (4)	0.1172 (5)
C1	0.9676 (6)	0.0994 (5)	0.1853 (6)
N1	1.0186 (5)	−0.0131 (4)	0.1953 (4)
C2	1.0123 (7)	−0.0734 (6)	0.2914 (6)
C3	0.1498 (7)	−0.0066 (7)	0.2045 (8)
S2	0.8557 (1)	−0.2359 (1)	0.4878 (1)
O4	0.8758 (5)	−0.2233 (5)	0.3891 (4)
O5	0.8624 (5)	−0.1361 (4)	0.5444 (5)
O6	0.9265 (5)	−0.3204 (5)	0.5559 (6)
C4	0.7005 (6)	−0.2818 (6)	0.4406 (5)
N2	0.6680 (5)	−0.3335 (5)	0.5276 (4)
C5	0.5344 (6)	−0.3656 (7)	0.4760 (7)
C6	0.6876 (8)	−0.2634 (8)	0.6254 (6)
S3	0.4937 (1)	0.0166 (1)	0.6735 (1)
O7	0.5196 (5)	0.0944 (4)	0.6051 (4)
O8	0.5861 (4)	−0.0641 (4)	0.7185 (5)
O9	0.4528 (5)	0.0637 (5)	0.7525 (4)
C7	0.6392 (6)	0.0532 (6)	0.4189 (5)
N3	0.6952 (5)	0.1185 (5)	0.3549 (4)
C8	0.8293 (6)	0.1365 (7)	0.4230 (6)
C9	0.6327 (7)	0.2261 (6)	0.3172 (7)

[a] Here C1, C4, and C7 are the N–C–S carbons in a three-molecule pattern.

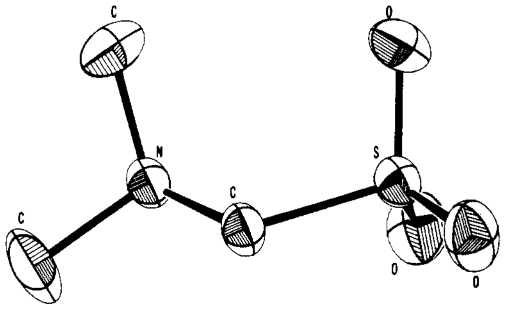

Figure 2. Ortep projection for KS8, without the nine H atoms. In the far simpler pattern for CDMA, the thermal ellipsoids are closely similar to these.

The details of these X-ray studies are as follows.

CDMA. A suitable crystal of $(CH_3)_2N{=}CH_2^+Cl^-$ was obtained by recrystallizing this sublimate (from the KS8–HCl reaction) in a vacuum-sealed tube at 70 °C. For the X-ray scan, it was protected from moisture by enclosure in a thin-walled quartz capillary tube. The data were collected and computer-processed by Kuei-Shang Huang, under the direction of Dr. Robert Bau. The conditions and numerical results are listed in Tables I and

II, in both of which the estimated standard deviations are in parentheses. The equal N—CH_3 distances are 1.464 (6) Å, and the N═CH_2 distance is 1.264 (9) Å. The H_3C—N—CH_3 bond angle is 114.1 (3)°, and the H_3C—N═CH_2 angle is 123.0 (3)°. The Ortep diagram is a simple NC_3 plane with coplanar Cl^-, not quite equidistant from the CH_2 group and one CH_3 group. In the larger picture, each Cl^- is hexagonally surrounded by three NC_3 units, each of which embraces three Cl^- ions.

KS8. Microcrystalline KS8 was recrystallized to suitable size and shape by convective heating at 35 °C in a vertical test tube with ethanol. The data were collected and computer-processed by Kuei-Shang Huang and Raymond C. Stevens. The conditions and numerical results are listed in Tables I, III, and IV. The Ortep projection is shown in Figure 2.

Acknowledgments. I am grateful to Kuei-Shang Huang and Raymond C. Stevens for the two X-ray proofs of structure. Gratitude is due also to the National Science Foundation for aiding our acquisition of the 270-FT and 360-FT NMR instruments, in my use of which Allan Kershaw gave essential assistance.

Registry No. BAM, 51-80-9; CDMA, 30354-18-8; KS8, 68507-34-6; SO_2, 7446-09-5; $(CH_3)_3NO$, 1184-78-7.

Supplementary Material Available: Listings of anisotropic temperature factors for CDMA and for KS8 (1 page); tables of observed and calculated structure factors for CDMA and for KS8 (9 pages). Ordering information is given on any current masthead page.

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Lewis-Base Adducts of Group 11 Metal(I) Compounds. 49. Structural Characterization of Hexameric and Pentameric (Triphenylphosphine)copper(I) Hydrides

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Red and orange 1:1 adducts of copper(I) hydride with triphenylphosphine have been isolated from tetrahydrofuran as hexameric and pentameric cluster species that have been characterized crystallographically. The red hexameric species $[(PPh_3)CuH]_6{\cdot}0.5thf$ crystallizes in the monoclinic space group $P2_1$ with $a = 14.464$ (10) Å, $b = 16.252$ (9) Å, $c = 21.487$ (5) Å, $\beta = 91.38$ (3)°, $Z = 2$, and $R = 0.052$ for 5932 observed ($I \geq 3\sigma(I)$) reflections. Cu–P distances are 2.200 (3)–2.246 (3) Å. Hydrogen atoms have been located by refinement at the centers of six triangular faces equatorial about a quasi-$\bar{6}$ axis of the octahedral copper skelton. A crystalline "hydrolysis" product of this compound, tentatively formulated as $[(PPh_3)_6Cu_6H_4O]{\cdot}thf$, has also been structurally characterized, crystallizing in the orthorhombic space group *Pbca* with $a = 40.19$ (2) Å, $b = 22.78$ (2) Å, $c = 21.72$ (2) Å, $Z = 8$, and $R = 0.071$ for 5041 observed reflections in a lattice isomorphous with the previously recorded $[(PPh_3)CuH]_6{\cdot}dmf$ compound. An orange pentameric species, formulated as $[(PPh_3)CuH]_5{\cdot}thf$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.827$ (6) Å, $b = 12.952$ (8) Å, $c = 54.226$ (14) Å, $\beta = 95.96$ (4)°, $Z = 4$, and $R = 0.095$ for 2393 observed reflections. The copper atoms are disposed in a distorted-trigonal-bipyramidal array with $Cu_{ax}{\cdots}Cu_{eq}$ distances ranging between 2.431 (7) and 2.582 (7) Å and $Cu_{eq}{\cdots}Cu_{eq}$ distances between 2.493 (8) and 2.608 (7) Å. The Cu–P distances range between 2.16 (1) and 2.21 (1) Å. Hydride positions were not found.

Introduction

One of the most intensively studied stoichiometric copper(I) hydride species is the 1:1 adduct with triphenylphosphine, structurally characterized as a hexameric cluster, $[(PPh_3)CuH]_6$, and incorporating a solvate molecule of dimethylformamide (dmf).[2] Hydrogen atoms were not located in this determination, and their location and the nature of their bonding has since been the subject of much conjecture and study, an X-ray study of the tri-*p*-tolylphosphine analogue casting no further light in this respect.[3] During the course of the present work, hydrogen atoms have been located for the tris(dimethylamino)phosphine analogue, $[P(NMe_2)_3CuH]_6$, by a low-temperature study,[4] while bridging hydrogen atoms have been located by refinement in binuclear $[MeC(CH_2PPh_2)_3]CuH_2Cu[(Ph_2PCH_2)_3CMe]$.[5] We have approached the problem of locating hydrogen atoms in the triphenylphosphine hexamer by seeking improvement of crystal quality through recrystallization under different conditions and from different solvent systems. From tetrahydrofuran ($(CH_2)_4O$ = thf) we have been able to isolate crystals of a new thf-solvated phase of the hexamer that produced diffraction data of the quality and extent necessary to enable both the location and refinement of the hydrogen atoms. A structure determination undertaken on crystalline material of different habit in a similar reaction mixture was found to be isomorphous with the previously studied dmf-solvated phase[2] but shown structurally to be most likely an oxo-bridged hydrolysis product. Crystalline material obtained from a further series of reactions in thf in the presence of excess reducing agent and triphenylphosphine has proved to be a novel pentameric copper cluster compound. We report the results of these structural studies here.

Experimental Section

Preparation of Compounds. $[(PPh_3)CuH]_6$ (1). The synthesis and general characterization of this compound are well-known,[6] and the experiments described here constitute procedural variations with a view of maximizing crystal size and quality. Typically, copper(I) chloride (0.5 g, 0.005 mol) was stirred in 10 mL of dry thf under argon and triphenylphosphine (1.3 g, 0.005 mol) added. An initial white precipitate formed ($[(PPh_3)_3(CuCl)_2]$ from solid-state ^{31}P NMR data). The mixture was stirred continuously while K-Selectride (5 mL of 1.0 M in thf, 0.005 mol (Aldrich)) was added, the precipitate dissolving to give a deep red solution. This was filtered, and the volume of the filtrate was reduced to ca. 50% under vacuum and then cooled to −20 °C. After several days crystals of the compound formed as large dark red hexagonal plates. One of these was mounted in a capillary and used for the structure determination.

Solid-state ^{31}P NMR spectra of this compound revealed a broad, essentially featureless peak centered at −10 ppm.

$[(PPh_3)_6Cu_6H_4O]$ (1a). A crystal of different habit, obtained on another occasion under similar recrystallization conditions, was found to be isomorphous with the previously characterized dmf-solvated structure but was subsequently characterized tentatively as a partially hydrolyzed product.

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