

Table IV. Bond Angles (deg)

Au-Ag-O(11)	142.6 (3)	Au-Ag-O(21)	120.6 (3)
O(11)-Ag-O(21)	87.1 (5)	Au-Ag-Au'	93.8 (1)
O(11)-Ag-Au'	101.6 (3)	O(21)-Ag-Au'	107.3 (4)
Ag-Au-C(1)	82.1 (4)	Ag-Au-C(2)	92.7 (4)
C(1)-Au-C(2)	173.9 (5)	Ag-Au-Ag'	86.2 (1)
C(1)-Au-Ag'	89.0 (4)	C(2)-Au-Ag'	87.3 (4)
O(11)-Cl(1)-O(12)	110.2 (10)	O(11)-Cl(1)-O(13)	108.6 (10)
O(12)-Cl(1)-O(13)	109.0 (12)	O(11)-Cl(1)-O(14)	109.9 (10)
O(12)-Cl(1)-O(14)	110.5 (12)	O(13)-Cl(1)-O(14)	108.6 (11)
Ag-O(11)-Cl(1)	118.0 (8)	O(21)-Cl(2)-O(22)	109.2 (8)
O(21)-Cl(2)-O(23)	109.7 (10)	O(22)-Cl(2)-O(23)	110.1 (9)
O(21)-Cl(2)-O(24)	109.2 (9)	O(22)-Cl(2)-O(24)	110.3 (8)
O(23)-Cl(2)-O(24)	108.3 (10)	Ag-O(21)-Cl(2)	145.1 (9)
Au-C(1)-P(1)	112.8 (6)	C(1)-P(1)-C(11)	111.1 (6)
C(1)-P(1)-C(21)	111.4 (6)	C(1)-P(1)-C(31)	109.9 (6)
Au-C(2)-P(2)	115.4 (7)	C(2)-P(2)-C(41)	111.2 (6)
C(2)-P(2)-C(51)	111.5 (6)	C(2)-P(2)-C(61)	111.0 (6)
P(1)-C(11)-C(12)	118.8 (3)	P(1)-C(11)-C(16)	121.2 (3)
P(1)-C(21)-C(22)	119.8 (3)	P(1)-C(21)-C(26)	119.7 (3)
P(1)-C(31)-C(32)	118.0 (4)	P(1)-C(31)-C(36)	122.0 (4)
P(2)-C(41)-C(42)	118.6 (3)	P(2)-C(41)-C(46)	121.3 (3)
P(2)-C(51)-C(52)	118.1 (3)	P(2)-C(51)-C(56)	121.9 (3)
P(2)-C(61)-C(62)	120.3 (3)	P(2)-C(61)-C(66)	119.7 (3)

4569 with $F > 4\sigma(F)$ were used for all calculations (program system SHELXTL). Cell constants were refined from 2θ values of 56 reflections in the range 20–23°. An absorption correction based on ψ -scans was applied (transmissions 0.37–0.66; crystal size 0.45

$\times 0.45 \times 0.4$ mm).

The structure was solved by the heavy-atom method and refined on F to $R = 0.075$ and $R_w = 0.071$ [Au, Ag, Cl, and P atoms anisotropic; phenyl rings as idealized rigid groups with C–C = 1.395 Å and C–H = 0.96 Å; methylene H included by using a riding model; weighting scheme $w^{-1} = \sigma^2(F) + 0.0005F^2$; 168 parameters]. Final atomic coordinates are given in table II (see also Figure 1).

The high-temperature factors of the O atoms and the presence of significant electron density associated with the perchlorate groups probably indicate disorder, but no sensible disorder model could be refined. The corresponding bond lengths and angles of the ClO_4^- groups should therefore be interpreted with caution. These problems are also reflected in the rather high R value.

Single crystals of V could be obtained but lost solvent too readily to permit X-ray analysis. The cell constants of V are $a = 17.5$ Å, $b = 17.1$ Å, $c = 25.25$ Å, and $\beta = 102.5^\circ$ (monoclinic P).

Acknowledgment. We thank the CAICYT (Spain) and the Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: Tables of positional and thermal parameters of calculated hydrogen atoms and anisotropic thermal parameters for IV (2 pages); a listing of structure factor amplitudes for IV (41 pages). Ordering information is given on any current masthead page.

Mercury in Organic Chemistry. 34.¹ Synthesis of Vinylmercurials via Mercuration of Propargylic Amines

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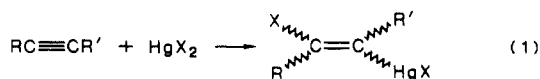
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Received December 8, 1986

Propargylic amines react readily with 1–2 M HgCl_2 in 2–6 M HCl to precipitate the ammonium trichloromercurate, bis(ammonium) tetrachloromercurate, or bis(ammonium) hexachlorodimercurate salts 1–10 in which mercuric chloride has added in a trans manner across the original carbon-carbon triple bond placing the mercury nearer to nitrogen. X-ray crystallographic data on one of each type of these salts are provided.

Introduction

Vinylmercurials have proven to be versatile intermediates in organic synthesis.^{2–4} While a number of methods presently exist for the preparation of vinylmercurials, one of the simplest and most important approaches involves the direct addition of mercury(II) salts to acetylenes (eq 1). For instance, mercuric acetate adds primarily trans



to internal dialkyl-^{5–10} and alkylarylacetylenes^{11,12} and cis

to diphenylacetylene^{5,7,13,14} to afford stable, isolable (β -acetoxyvinyl)mercurials. Mercuric chloride adds to internal acetylenic halides,^{15,16} ethers,^{17–19} alcohols,^{15,20,21}

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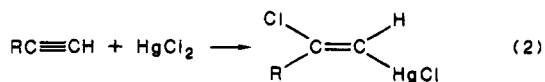
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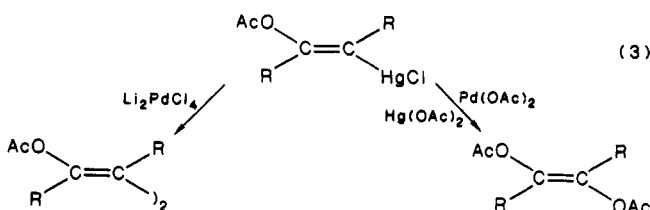
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ketones,²² acids, and esters,²³⁻²⁶ as well as cyclooctyne²⁷ to afford (β -chlorovinyl)mercurials. Mercuric chloride addition to terminal alkynes appears less general but affords addition compounds with acetylene,²⁸⁻³² propyne,³³ vinylacetylene,³³⁻³⁶ and propargylic alcohols^{15,20,21} (eq 2).

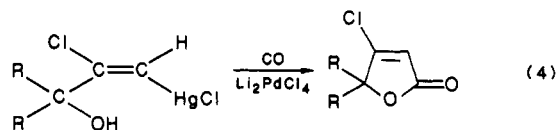


Where the stereochemistry of the mercuric chloride addition reaction has been established, it appears to be exclusively trans, except for cyclooctyne. Our recent work on the mercuration of 4-hydroxy-2-alkyn-1-ones uncovered what appears to be the first case of mercuric chloride cis addition to an acyclic alkyne.³⁷

These vinylmercurials undergo a number of transformations useful in organic synthesis. For example, (β -acetoxyvinyl)mercurials react with palladium salts to afford symmetrical 1,3-dienes³⁸ and ene diacetates¹⁰ (eq 3). The



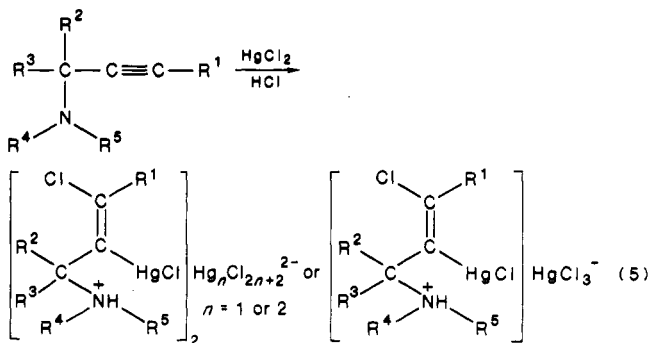
vinylmercurials derived from mercuric chloride and propargylic alcohols can be readily carbonylated to afford excellent yields of β -chlorobutenolides (eq 4).^{20,21} This



transformation encouraged us to look at analogous reactions of propargylic amines as a potential route to lactams. At this time we wish to report our results on the mercuration of propargylic amines.

Results and Discussion

Preparation. Initial attempts to mercurate propargylic amines under conditions similar to those used with propargylic alcohols (aqueous mercuric chloride and sodium chloride)^{15,20,21} resulted in formation of either metallic mercury or copious precipitates of unknown composition, presumed to be polymers. Aqueous solutions of mercuric acetate proved equally unsuccessful. To avoid polymerization via intermolecular aminomercuration and hopefully to protect the amine at the same time, we examined the reaction of propargylic amines with mercuric chloride in aqueous hydrochloric acid. Several different procedures (A through C) varying in the concentrations of HCl and HgCl₂ were eventually developed (see Table I). This approach proved quite successful as white powdery vinylmercurials were observed to slowly precipitate from solution (eq 5). These products were subsequently de-



termined to be either the bis(ammonium) tetrachloromercurate salt ($n = 1$), the corresponding hexachlorodimercurate salt ($n = 2$), or the simple ammonium trichloromercurate salt as discussed later and proven by X-ray crystallography.

A brief examination of the reaction conditions revealed the following features. Vinylmercurial precipitation usually begins within an hour or two and continues for up to 24–48 h. Slightly higher yields and purer products are usually obtained by filtering off the product at intervals of 6, 12, and 24 h as it is being formed. Addition of sodium chloride had little effect on the reaction. Yields with added sodium chloride were generally somewhat lower, and no significant improvement in melting point or purity (as determined by ¹H NMR spectroscopy) was observed.

A wide range of hydrochloric acid concentrations can be employed, with best results generally being obtained by using concentrations of 2–6 M HCl. These concentrations tend to give lower crude yields but purer products. At HCl concentrations of 9–12 M, no vinylmercurial precipitation at all occurred.

Mercuric chloride concentrations of 1–2 M proved most satisfactory. While higher concentrations give higher yields of crude product, the product appears to be less pure. It appears that under those conditions mercuric chloride itself may be precipitating with the vinylmercurial product, as those products tend to give higher mercury analyses than those run at lower mercuric chloride concentrations.

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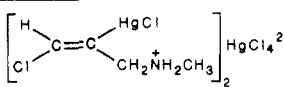
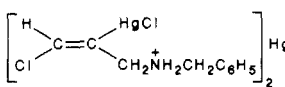
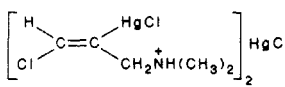
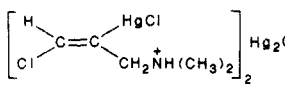
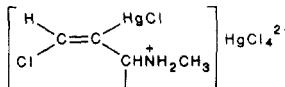
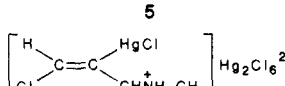
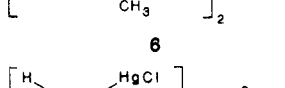
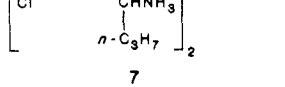
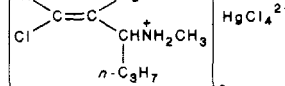
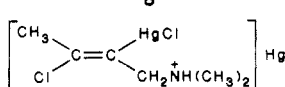
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Table I. Mercuration of Propargylic Amines

entry	amine	proce- dure ^a	vinylmercurial	% yield ^c	mp, °C	elemental anal. ^{b,c}		
						C	H	Hg
1	HC≡CCH ₂ N- HCH ₃	A		53	151-152	9.45 (9.37)	1.32 (1.57)	58.99 (58.67)
			1					
2	HC≡CCH ₂ N- HCH ₂ C ₆ H ₅	A		60	180-181	20.36 (20.39)	2.04 (2.05)	52.19 (51.09)
			2					
3	HC≡CCH ₂ - N(CH ₃) ₂	A		56	141-142	10.24 (11.40)	1.58 (1.91)	58.07 (57.11)
			3					
4		C		34 ^d	151 ^d	9.65 (9.06)	1.60 (1.52)	61.06 (60.55) ^d
			4					
5	HC≡CCHNHCH ₃ CH ₃	A		57	161-163 (165 ^d)	9.65 (11.40)	1.91 (1.97)	57.43 (57.11)
			5					
6		C		38 ^d	163-163.5 ^d	9.45 (9.06)	1.62 (1.52)	60.99 (60.55) ^d
			6					
7	HC≡CCHNH ₂ n-C ₃ H ₇	A		50 9 ^d	118-119 128-130 ^d	13.18 (13.32) 13.18 (13.32)	2.31 (2.29) 2.31 (2.29)	55.01 (55.63) 55.54 (55.63) ^d
			7					
8	HC≡CCHNHCH ₃ n-C ₃ H ₇	A		52	155-155.5	12.60 (15.15)	2.07 (2.54)	55.38 (54.22)
			8					
9	CH ₃ C≡CCH ₂ - N(CH ₃) ₂	B		95	101-102	13.57 (13.32)	2.13 (2.23)	55.34 (55.63)
			9					
10		B		80 ^d	102-102.5 ^d	10.62 (10.65)	1.81 (1.79)	59.26 (59.29) ^d
			10					
11	HC≡CCH ₂ C- H ₂ NH ₂	B	no reaction					

^a Procedure A: 5 mmol of amine, 25 mL of 5 M HCl, and 27.5 mmol of HgCl₂. Procedure B: 5 mmol of amine, 25 mL of 2 M HCl, and 50 mmol of HgCl₂. Procedure C: 5 mmol of amine, 25 mL of 6 M HCl, and 50 mmol of HgCl₂. ^b Observed percentages of C, H, and Hg (calculated percentages). ^c Data are for crude material unless otherwise noted. ^d Data are for recrystallized material.

Alternatively, we may simply be seeing a shift from tetrachloromercurate formation to trichloromercurate or hexachlorodimercurate formation.

It is not clear whether formation of the specific salts is due to the mercuration conditions or recrystallization. Mercuration using a low HgCl₂ concentration (procedure A) always gives rise to the tetrachloromercurate salt, and in one case, recrystallization of the crude material also gave the tetrachloromercurate salt (entry 7). Except for one example (entry 9), the use of higher HgCl₂ concentrations (procedure B or C) tended to give products with a broader melting point range and generally unsatisfactory elemental

analyses for any of the various salts. However, recrystallization of these products from acetonitrile or acetonitrile/benzene gave either the trichloromercurate or hexachlorodimercurate salts. The mercuration of 1-(dimethylamino)-2-butyne using a high HgCl₂ concentration (procedure B) appeared to give the tetrachloromercurate salt as the crude product (entry 9), but recrystallization afforded the trichloromercurate salt (entry 10).

Some representative results are reported in Table I. Contrary to the mercuration of propargylic alcohols which appears limited to symmetrical primary and tertiary alcohols,^{15,20,21} the mercuration of propargylic amines appears

to be a very general reaction. Substitution on both the nitrogen and the carbon skeleton is readily tolerated. The proximity of the amine to the carbon-carbon triple bond is apparently quite important as seen in the last entry in Table I. 4-Amino-1-butyne fails to react under conditions in which a variety of propargylic amines readily react. The higher molecular weight amines 3-(*n*-butylamino)-1-hexyne and 3-(cyclohexylamino)-1-hexyne either failed to react or gave rather impure products respectively using procedure A. This is presumably due to the low solubility of the amine in the aqueous acid medium. Propargylamine and *N*-propargylaniline also gave rather impure products. With the latter compound, this may be due to mercuriation of the highly reactive aromatic ring.

The following relative rates of precipitation were observed using procedure A: $\text{HC}\equiv\text{CCH}_2\text{NHCH}_2\text{C}_6\text{H}_5 > \text{HC}\equiv\text{CCH}(\text{CH}_3)\text{NHCH}_3 > \text{HC}\equiv\text{CCH}_2\text{NHCH}_3 > \text{HC}\equiv\text{CCH}(\text{C}_3\text{H}_7)\text{NHCH}_3 > \text{HC}\equiv\text{CCH}_2\text{N}(\text{CH}_3)_2 > \text{HC}\equiv\text{CCH}_2\text{N}-\text{H}_2 > \text{HC}\equiv\text{CCH}(\text{C}_3\text{H}_7)\text{NH}_2$. While these results do not directly translate into relative rates of reaction, there seems to be a correlation between the basicity of the amine and the rate of precipitation. In general, secondary amines are more basic than primary amines, which are comparable to tertiary amines. This is roughly the observed order of precipitation.

The vinylmercurial salts are most easily recrystallized from acetonitrile or acetonitrile/benzene. A variety of other solvents have been examined but appear less suitable. The compounds appear to decompose in Me_2SO , losing HgCl_2 to regenerate the starting alkyne. In general, fairly good elemental analyses could be obtained on either the crude or the recrystallized salts. Attempts to liberate the free mercurated amines did not appear promising as far as generating organomercurials which might be more easily characterized than the ammonium salts.

Structure Determination. The structure determination of these salts presented a number of problems. The crude products generally gave elemental analyses which were consistent with those expected for either bis(ammonium) tetrachloromercurate salts, $(\text{R}_4\text{N}^+)_2\text{HgCl}_4^{2-}$, bis(ammonium) hexachlorodimercurate salts, $(\text{R}_4\text{N}^+)_2\text{Hg}_2\text{Cl}_6^{2-}$, or ammonium trichloromercurate salts, $(\text{R}_4\text{N}^+)\text{HgCl}_3^-$. It was not until X-ray crystallographic data was obtained that we realized that we were dealing with all three types of salts. The nature of the species perhaps depends on the solvent used for crystallization, as the stability of these species depends very much on solvent polarity.³⁹

The vinylmercurials are characterized in the infrared spectra by olefinic stretching in the 1600 cm^{-1} region and by a very broad amine salt absorption at $2500\text{--}3000\text{ cm}^{-1}$. An additional strong band around 750 cm^{-1} has been assigned to vinyl chloride stretching.

While the infrared spectra is consistent with a vinylmercurial, a more difficult question is the regio- and stereochemistry of these mercuric chloride additions. The ^1H NMR spectra of these compounds provides some useful information with regards to this point. The vinylmercurials derived from terminal acetylenic amines show a peak in the region δ 6.2–6.9 consistent with a vinyl proton which is coupled to ^{199}Hg with $J^{199}\text{Hg-H}$ on the order of 160 Hz. Vinylmercurials derived from addition of mercuric chloride to propargylic alcohols show a geminal coupling of $J^{199}\text{Hg-H} = 128\text{ Hz}$,^{15,21} and the geminal coupling in either *cis*- or *trans*-(β -chlorovinyl)mercuric chloride is similar.⁴⁰

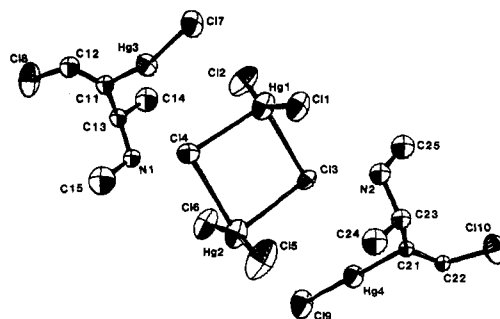


Figure 1. Structure of $(\text{ClHgNC}_5\text{H}_{10}\text{Cl})_2\text{Hg}_2\text{Cl}_6$. Thermal ellipsoids are scaled to enclose 50% of the electron density.

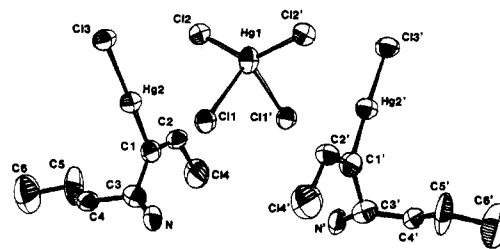


Figure 2. Structure of $(\text{ClHgNC}_6\text{H}_{12}\text{Cl})_2\text{HgCl}_4(\text{C}_6\text{H}_6)\cdot\text{H}_2\text{O}$. The solvent and water molecules are not included. Thermal ellipsoids are scaled to enclose 50% of the electron density.

For the latter two compounds, $J^{199}\text{Hg-H}$ for Hg and H trans to each other is 474.5 Hz while the *cis* coupling is 155 Hz. The $J^{199}\text{Hg-H}$ coupling constants obtained from all of our terminal acetylenic amines are most consistent with a *cis* arrangement of Hg and H, which has been borne out by X-ray crystallography. In other words, mercuric chloride adds to the carbon-carbon triple bond in a *trans* manner placing the mercury nearer to nitrogen. From a mechanistic standpoint, this makes sense, since strong electron withdrawal by the ammonium group should favor this regiochemistry.

In several cases (entries 2, 3, and 8), the crude reaction product appeared to consist of a mixture of products. In addition to the expected product, a second set of resonances was observed in the ^1H NMR spectrum. In addition to minor differences in chemical shifts (0.1–0.2 ppm), there were also differences in the magnitude of the coupling between ^{199}Hg and the vinyl proton. In the second case (entry 3) this amounted to 50–60 Hz. These differences are too small to arise from either *cis* or geminal coupling of isomeric (chlorovinyl)mercuric chlorides, but are close to the values determined for geminal $^{199}\text{Hg-H}$ coupling in bis(β -chlorovinyl)mercurials (60–63 Hz). We, therefore, surmise that the impurities observed in the ^1H NMR spectra of some of our products, as well as the relatively poor elemental analyses obtained for some products are due to the formation of minor amounts of divinylmercurials. We believe that these side products have the same regio- and stereochemistry as the major products shown in Table I. It is possible, however, that these side products are simply arising due to decomposition of the sample in Me_2SO during NMR spectral analysis.

In the one instance in which an internal acetylene was mercurated (entries 9 and 10), analysis of the product by proton NMR spectroscopy was complicated by apparent elimination of HgCl_2 from the product when dissolved in Me_2SO . While the NMR spectral data appeared consistent with the assigned structure, confirmation required X-ray crystallography.

The exact nature of these new organomercurials was not established until we were able to recrystallize three of these compounds, 6, 7, and 10, from acetonitrile or aceto-

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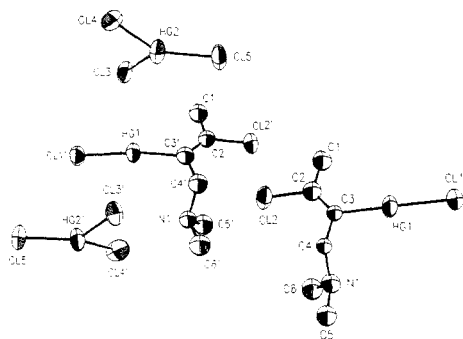


Figure 3. Structure of $(\text{ClC}_6\text{H}_{12}\text{NHgCl})\text{HgCl}_3$. Thermal ellipsoids are scaled to enclose 50% of the electron density. One asymmetric unit (two molecules) is shown here.

nitrile/benzene and determine their structures by X-ray crystallography. The structures of compounds 6, 7, and 10 are shown in Figures 1, 2, and 3, respectively. Note that compound 7 contained one molecule of water and one molecule of benzene after recrystallization. We are not certain if our other organomercurials also retain water in the crude product or water and/or benzene after recrystallization. We did not observe benzene in the ^1H NMR spectra of our other recrystallized organomercurials, and we would not have been able to distinguish the water of crystallization from the water present in the $\text{Me}_2\text{SO}-d_6$ or acetone- d_6 used as a solvent in obtaining all our NMR spectra. Due to the uncertain composition of our organomercurials, we have ignored water and benzene when reporting yields and calculated elemental analyses in Table I. The presence of water and/or benzene may account for certain discrepancies observed in the elemental analyses.

Let us discuss the structure of the anions in our compounds first, since they actually turn out to be more interesting structurally. The structural chemistry of mercuric halides is diverse,⁴¹⁻⁵⁵ including the existence of $\text{Hg}_2\text{Cl}_6^{2-}$,⁴²⁻⁴⁵ HgCl_4^{2-} ,^{46,47} and HgCl_3^{-} ,^{39,41,43} moieties. The structures reported here are noteworthy in that HgCl_2 and HCl complex with the organomercury compounds strongly enough to produce interesting mercury-chlorine complexes with highly distorted anions.

Although the basic framework in structures 6 and 7 is conveniently discussed in terms of discrete cationic and anionic species, it should be noted that the most complete description would be in terms of continuous networks of

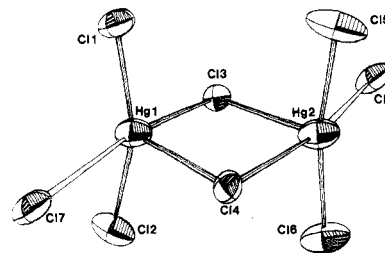


Figure 4. Structure of the $\text{Hg}_2\text{Cl}_6^{2-}$ anion in $(\text{ClC}_5\text{H}_{10}\text{Hg-Cl})_2\text{Hg}_2\text{Cl}_6$ showing the effective coordination about the mercury atoms. This coordination closely approximates the joining of two square pyramids on a common edge.

mercury and chlorine atoms with the organic constituents contributing only secondarily to the crystal packing and coordination. Crystals of compound 10 on the other hand contain more discrete units.

According to the convention devised by Grdenic,⁴² all of the mercury atoms in these structures have characteristic coordination numbers of two. The effective coordination numbers, on the other hand, are in most cases higher, ranging from two to five. Mercury, in the presence of chlorine, has a strong tendency to expand its coordination sphere by taking on additional ligands. The arrangements observed here are unusual.

At first glance, the geometry of the $\text{Hg}_2\text{Cl}_6^{2-}$ group in compound 6 appears to be that of a distorted edge-shared bitetrahedron as reported by Kistenmacher et al.,⁴³ Bats et al.,⁴⁴ Goggin et al.,⁴⁵ and Zhilyaeva et al.,⁴⁶ with effective coordination numbers of four for both mercury atoms. (The effective coordination number is the number of neighbors within a distance that is the sum of the van der Waals radii of the interacting atoms; in the case of Hg^{2+} and Cl^- this distance is 3.30 Å.) The group can, in fact, be reasonably well-described by two nearly perpendicular intersecting planes, one containing Hg1, Hg2, Cl1, Cl2, Cl5, and Cl6 and the other containing Hg1, Hg2, Cl3, Cl4. These least-squares planes have mean-square deviations of 0.0147 and 0.0074 Å, respectively, and an interplanar angle of 94.1°.

On closer examination, however, one sees that the effective coordination number for both Hg1 and Hg2 is five and that the geometry is more like the joining of two square pyramids sharing one of the side edges, with Cl3 forming one apex and Cl4 the other (see Figure 4). The distances Hg1-Cl7 and Hg2-Cl9 are 3.39 (1) and 3.27 (1) Å, respectively (distances and angles are given in Tables VI and VII). The former is only slightly beyond the range of that usually considered for effective coordination, while the latter is within the range. The least-squares planes containing (1) Hg1, Cl1, Cl2, Cl3, Cl7 and (2) Hg2, Cl5, Cl6, Cl4, Cl9 are 3.4° from being parallel, and Cl4 and Cl3 are 8.2° and 6.8° from the vertical through Hg1 and Hg2, respectively.

Furthermore, a comparison of Hg-Cl bond distances between the reported results of Kistenmacher et al.⁴³ (referred to here as compound 11) and the present work (compound 6) reveals significant differences. In both cases, there are two short Hg-Cl interactions [11, average distance = 2.375 (5) Å; 6, average distance = 2.316 (9) Å] and two longer, bridging Hg-Cl interactions for each mercury atom. In 11 the bridging distances have an average value of 2.648 (5) Å, whereas in 6 the respective distances are significantly longer [2.80 (1)-3.02 (1) Å]. This elongation of the mercury-chlorine bonds is apparently due to the additional coordination of Hg1 and Hg2 with Cl7 and Cl9, respectively. The delocalization of the Hg1-Cl3, Hg1-Cl4, Hg2-Cl3, and Hg2-Cl4 bonds has evidently given rise to

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Table II. Crystal Data for 6, 7, and 10

	6	7	10
formula	Hg ₄ Cl ₁₀ N ₂ C ₁₀ H ₂₀	Hg ₃ Cl ₆ O ₁ N ₂ C ₁₈ H ₃₂	Hg ₂ Cl ₅ N ₁ C ₆ H ₁₂
fw	1325.17	1177.86	676.61
a, Å	13.186 (2)	27.679 (4)	10.532 (6)
b, Å	18.501 (2)	8.140 (1)	9.866 (2)
c, Å	11.189 (1)	14.164 (2)	14.093 (7)
β, deg		97.17 (2)	99.23 (6)
V, Å ³	2729.8 (5)	3166.5 (8)	1445.4 (1.1)
Z	4	4	4
cryst system	orthorhombic	monoclinic	monoclinic
space group	<i>Pn</i> 2 ₁ <i>a</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> c
radiatn, λ, Å	0.70964	0.70964	0.70964
ρ(calcd), g/cm ³	3.23	2.47	3.11
abs coeff, μ, cm ⁻¹	234.6	152.02	221.62
temp, K	295.0	295.0	295.0
2θ range, deg	0° ≤ 2θ ≤ 50	0° ≤ 2θ ≤ 50	0° ≤ 2θ ≤ 50
no. of reflns collected	2746	3477	3058
no. of obsd reflns	1979	2439	1572
no. of variables	174	147	181
R (refinement) ^a	4.9	6.1	4.7
R _w (refinement)	7.1	7.3	5.1
decay Correction Based on Reflection Number (X)			
for 6	2253.3 - 0.3346X + 0.00008X ² = I		
for 7	10064.2 - 1.6010X + 0.00026X ² = I		
for 10	I _c (X) = I _o (X)100.16/(100.16 - 0.01607X)		crystal 1: <i>h, k, l</i> data
	I _c (X) = I _o (X)99.59/(99.59 - 0.02234X)		crystal 2: <i>h, k, -l</i> data

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2}.$$

Table III. Refined Atomic Coordinates^a (×10⁴) for (ClHgNC₆H₁₀Cl)₂Hg₂Cl₆ (6)

atom	x	y	z
Hg1	4132 (1)	7600 (0)	5750 (1)
Hg2	3473 (1)	5681 (1)	4286 (1)
Hg3	1286 (1)	8274 (2)	5890 (1)
Hg4	3687 (1)	9982 (2)	5836 (1)
Cl1	4914 (9)	7216 (7)	7490 (10)
Cl2	3615 (11)	8380 (8)	4241 (10)
Cl3	5201 (7)	6611 (6)	4246 (8)
Cl4	2341 (8)	6787 (6)	5759 (9)
Cl5	4088 (13)	5032 (12)	5877 (14)
Cl6	2636 (11)	6110 (10)	2595 (10)
Cl7	2464 (8)	8619 (8)	7325 (10)
Cl8	-1874 (9)	8428 (9)	4220 (12)
Cl9	4917 (9)	9691 (9)	7225 (13)
Cl10	490 (8)	10212 (7)	4213 (10)
N1	754 (25)	8449 (21)	3461 (29)
N11	130 (27)	8203 (21)	4670 (33)
C12	-711 (27)	8449 (21)	5027 (37)
C13	342 (25)	7926 (18)	3389 (30)
C14	947 (42)	8436 (38)	2683 (35)
C15	65 (50)	6693 (49)	3977 (53)
N2	3180 (24)	11310 (17)	3454 (29)
C21	2521 (24)	10254 (18)	4660 (29)
C22	1627 (20)	10096 (15)	5060 (26)
C23	2726 (26)	10565 (20)	3411 (35)
C24	3428 (36)	10067 (24)	2634 (39)
C25	2574 (40)	11840 (22)	4079 (47)

^a Atomic coordinates are given as fractions of the unit cell. In this and succeeding tables, estimated standard deviations are given in parentheses for the least significant digits.

a shortening of the Hg1-Cl1, Hg1-Cl2, Hg2-Cl5, and Hg2-Cl6 bonds and a straightening out of the Cl1-Hg1-Cl2 and Cl5-Hg2-Cl6 bond angles [11, angle Cl-Hg-Cl = 132.2°; 6, angle Cl1-Hg1-Cl2 = 158.8° and angle Cl5-Hg2-Cl6 = 167.3°].

The geometry of the HgCl₄²⁻ anion in compound 7 is roughly tetrahedral with Hg1 lying on a twofold axis and with the angle between the least-squares planes Cl1, Hg1, Cl1' and Cl2, Hg1, Cl2' being 86.6°. Once again there are significant deviations from the previously reported occurrences of this anion. Ferguson et al.⁴⁷ and Mason et al.⁴⁸ report structures in which this anion exhibits a much more regular geometry with bond distance ranges of

Table IV. Refined Atomic Coordinates^a (×10⁴) for (ClHgNC₆H₁₂Cl)₂HgCl₄(C₆H₆)•H₂O (7)

atom	x	y	z
Hg1	5000	6966 (1)	7500
Hg2	4175 (0)	8603 (1)	5211 (0)
Cl1	5208 (2)	9129 (5)	6219 (3)
Cl2	4204 (2)	5989 (6)	6931 (3)
Cl3	4398 (2)	6348 (5)	4360 (3)
Cl4	3541 (3)	1556 (8)	7539 (4)
N	4437 (3)	2797 (18)	5579 (11)
C1	3912 (6)	507 (21)	5957 (12)
C2	3767 (7)	132 (21)	6766 (13)
C3	3910 (7)	2225 (21)	5568 (13)
C4	3635 (7)	2406 (23)	4567 (13)
C5	3093 (8)	2100 (33)	4528 (16)
C6	2824 (10)	2323 (43)	3554 (21)
C7	2444 (21)	2460 (72)	897 (25)
C8	2843 (15)	3052 (45)	647 (35)
C9	2088 (14)	1806 (45)	278 (41)
O1	5000 (0)	7681 (27)	2500 (0)

^a Atomic coordinates are given as fractions of the unit cell.

2.48–2.51 Å and 2.441–2.523 Å, respectively, and bond angle ranges of 98–119° and 102–122°, respectively. Our observed bond distances of 2.387 (5) and 2.643 (4) Å (to Cl1 and Cl2, respectively) and bond angle range of 96.5 (2)–141.1 (2)° are evidence of the perturbation introduced via coordination of Cl1 with Hg2. (Bond distances and angles are given in Tables VI and VII, respectively.) Note that Cl1 is coordinated twice to Hg2 with distances of 3.06 and 3.36 Å, while Cl2 is coordinated only once to Hg2 with a distance of 3.23 Å. Again these distances are all well within the range of effective coordination between mercury and chlorine.

The geometry of the HgCl₃⁻ anion in compound 10 is roughly trigonal, and the ion is discrete, unlike the polymeric (HgCl₃)_n species reported by Kistenmacher,⁴³ the latter showing roughly trigonal-bipyramidal geometry. In compound 11 the equatorial Cl-Hg bond distances are 2.37, 2.39, and 2.54 Å, while the apical Cl-Hg bond distances are 2.98 and 3.11 Å; the angles that the equatorial chlorine atoms make with the mercury atom are 109.9, 108.8, and 141.0°, while the apical ones make 98.7 and 97.6° angles with the equatorial plane. Our observed Hg-Cl bond

Table V. Refined Atomic Coordinates^a ($\times 10^4$) for (C₁₂H₁₂NH₂Cl)HgCl₃ (10)

atom	x	y	z
Hg1 ^b	1087	7 731 (2)	3478
Hg1'	2601 (1)	13 341 (2)	5982 (1)
Hg2	3086 (2)	10 887 (2)	3444 (2)
Hg2'	686 (2)	16 534 (2)	6899 (2)
Cl1	3278 (8)	7 606 (10)	3289 (8)
Cl1'	525 (8)	13 242 (11)	6242 (8)
Cl2	-3159 (9)	7 086 (12)	3764 (9)
Cl2'	7032 (9)	12 945 (13)	6007 (10)
Cl3	2103 (8)	10 491 (12)	4891 (8)
Cl4	1251 (10)	10 583 (12)	2194 (8)
Cl5	5334 (9)	11 055 (13)	3565 (10)
Cl3'	1859 (9)	16 433 (12)	5463 (8)
Cl4'	2361 (13)	16 117 (13)	8235 (10)
Cl5'	-1506 (8)	16 695 (12)	6498 (9)
N1	-876 (27)	10 325 (30)	4173 (23)
N1'	4676 (27)	16 130 (30)	6296 (22)
C1	-1049 (35)	5 520 (40)	3824 (29)
C2	-1483 (35)	6 880 (38)	3726 (28)
C3	-817 (29)	7 927 (33)	3539 (24)
C4	-1296 (28)	9 383 (33)	3363 (23)
C5	-1210 (35)	11 783 (40)	3841 (29)
C6	-1241 (39)	9 945 (46)	5118 (31)
C1'	5140 (38)	11 244 (42)	6332 (31)
C2'	5372 (33)	12 688 (38)	6043 (27)
C3'	4513 (35)	13 645 (38)	5816 (29)
C4'	4908 (38)	15 112 (45)	5541 (30)
C5'	5424 (40)	15 694 (45)	7238 (32)
C6'	5036 (42)	17 484 (43)	5964 (34)

^a Atomic coordinates are given as fractions of the unit cell. ^b The x and z coordinates of this atom were fixed due to polar nature of the space group P₆.

Table VI. Selected Interatomic Distances (Å) for 6, 7, and 10

atoms	distance		
	6	7	10
Hg1-Cl1	2.32 (1)	2.643 (4)	2.37 (1) [2.28 (1)] ^a
Hg1-Cl2	2.32 (1)	2.387 (5)	
Hg1-Cl3	2.86 (1)		3.44 (1) [3.21 (1)]
Hg1-Cl3'			3.06 (1) [3.21 (1)]
Hg1-Cl4	2.80 (1)		3.37 (1) [4.23 (1)]
Hg1-Cl7	3.39 (1)		
Hg2-Cl1		3.065 (5)	3.25 (1) [3.37 (1)]
Hg2-Cl1'		3.360 (4)	
Hg2-Cl2		3.226 (4)	
Hg2-Cl3	2.85 (1)	2.322 (5)	2.46 (1) [2.54 (1)]
Hg2-Cl4	3.02 (1)		2.42 (1) [2.40 (1)]
Hg2-Cl5	2.30 (2)		2.35 (1) [2.29 (1)]
Hg2-Cl6	2.33 (1)		
Hg2-Cl9	3.27 (1)		
Hg3-Cl7	2.32 (1)		
Hg4-Cl9	2.31 (1)		
Hg1-C3			2.03 (3) [2.09 (4)]
Hg2-C1		2.06 (2)	
Hg3-C11	2.05 (4)		
Hg4-C21	2.09 (3)		
Hg1-Hg2			3.76 (1) [4.06 (1)]

^a The values within rectangular brackets correspond to distances between primed atoms (see Table V).

distances in the trigonal plane range from 2.29 to 2.54 Å, and some of the bond angles in this plane are far from being 120°. The Hg2-Cl1 and Hg2'-Cl1' distances of 3.25 and 3.37 Å, respectively, are larger than those in compound 11 and larger than any Hg-Cl distances for compounds 6 and 7; however, these bonds make angles with the respective trigonal planes (Table VII) which seem to indicate that the geometry around Hg2 and Hg2' is best viewed as approximately trigonal pyramidal with the effective coordination number for these atoms being nearly 4.

The organomercury cation of compound 6 is quite normal. As mentioned earlier, the characteristic coordi-

Table VII. Selected Bond Angles (deg) for 6, 7, and 10

atoms	angle		
	6	7	10
Cl1-Hg1-Cl1'		96.5 (2)	
Cl1-Hg1-Cl2	158.8 (5)	105.2 (2)	
Cl1-Hg1-Cl2'		100.5 (2)	
Cl1-Hg1-Cl3	94.3 (4)		83.6 (4) [82.7 (4)] ^a
Cl1-Hg1-Cl4	102.1 (4)		81.2 (4) [74.5 (4)]
Cl2-Hg1-Cl2'		141.1 (2)	
Cl2-Hg1-Cl3	96.5 (4)		
Cl2-Hg1-Cl4	95.2 (4)		
Cl3-Hg1-Cl4	94.8 (3)		67.1 (4)
Cl1-Hg2-Cl3			86.4 (4) [75.7 (4)]
Cl1-Hg2-Cl4			83.0 (4) [92.8 (4)]
Cl1-Hg2-Cl5			90.1 (4) [89.7 (4)]
Cl3-Hg2-Cl4	89.7 (4)		101.0 (4) [103.2 (4)]
Cl3-Hg2-Cl5	93.1 (5)		120.2 (4) [114.0 (4)]
Cl3-Hg2-Cl6	98.9 (4)		
Cl4-Hg2-Cl5	96.2 (5)		137.7 (4) [142.1 (4)]
Cl4-Hg2-Cl6	88.8 (4)		
Cl5-Hg2-Cl6	167.2 (6)		
Hg1-Cl1-Hg2			82.5 (2) [89.8 (2)]
Hg1-Cl3-Hg2			77.3 (2) [89.3 (2)]
Hg1-Cl4-Hg2			79.4 (2) [69.3 (2)]
Cl4-Hg1-C3			94.5 (9) [99.5 (9)]
Cl3'-Hg1-C3			96.9 (9) [99.1 (9)]
Cl3-Hg1-C3			96.8 (9) [92.4 (9)]
Cl1-Hg1-Cl3'			87.7 (4) [87.3 (4)]
Cl3-Hg1-Cl3'			77.9 (4) [79.5 (4)]
Hg2-Cl3-Hg1'			101.5 (2) [128.3 (2)]
Cl7-Hg3-C11	166.4 (11)		
Cl9-Hg4-C21	176.9 (9)		
Hg3-C11-Cl2	115 (3)		
Hg3-C11-Cl3	119 (2)		
Hg4-C21-C22	112 (2)		
Hg4-C21-C23	122 (2)		
Cl13-Hg2-C1		174.6 (5)	
Hg2-C1-C2		116 (1)	
Hg2-C1-C3		120 (1)	
Cl1-Hg1-C3			175.3 (9) [173.6 (9)]
Hg1-C3-C2			120 (2) [120 (3)]
Hg1-C3-C4			113 (2) [117 (3)]

^a Similar to Table VI.

nation numbers for Hg3 and Hg4 are 2. The effective coordination number for Hg3, however, appears to be 4 with $d(\text{Hg3-Cl4}) = 3.07 (1) \text{ \AA}$ and $d(\text{Hg3-Cl1}) = 3.23 (1) \text{ \AA}$. For Hg4 (recalling that the two cationic moieties are approximately related by a pseudoinversion), the Hg4 to Cl3 [3.36 (1) Å] and Hg4 to Cl6 [3.37 (1) Å] distances are just beyond the range of effective coordination.

In previously published structures containing organomercurials similar to those discussed here, Halfpenny et al.⁴⁹ and Atwood et al.⁵⁰ report distances and angles about the mercury atom that are very similar to those found in this investigation. Halfpenny found bond distances of $d(\text{Hg-Cl}) = 2.326 (6) \text{ \AA}$ and $d(\text{Hg-C}) = 2.11 (2) \text{ \AA}$ and a bond angle of $(\text{C-Hg-Cl}) = 172.2 (5)^\circ$. The bond distances and angle reported by Atwood are $d(\text{Hg-Cl}) = 2.317 (5) \text{ \AA}$, $d(\text{Hg-C}) = 2.08 (2) \text{ \AA}$, and $(\text{C-Hg-Cl}) = 177.3 (5)^\circ$. Our results for compound 6 show bond distances of $d(\text{Hg3-Cl7}) = 2.32 (1) \text{ \AA}$, $d(\text{Hg3-C11}) = 2.05 (4) \text{ \AA}$, $d(\text{Hg4-Cl9}) = 2.31 (1) \text{ \AA}$, and $d(\text{Hg4-C21}) = 2.09 (3) \text{ \AA}$ and bond angles of $(\text{Cl11-Hg3-Cl7}) = 166.4 (1)^\circ$ and $(\text{C21-Hg4-Cl9}) = 176.9 (9)^\circ$. Aside from the somewhat lower bond angle about Hg3 (possibly due to the increased coordination) these results are in good agreement with those previously reported.

In the organomercury cation of compound 7, the characteristic coordination number of Hg2 is 2 while the effective coordination number is 4. The bond distances and angle about Hg2, $d(\text{Hg2-Cl3}) = 2.322 (5) \text{ \AA}$, $d(\text{Hg2-C1}) = 2.06 (2) \text{ \AA}$, and $(\text{Cl1-Hg2-Cl3}) = 174.6 (5)^\circ$, are nearly

identical with previously reported values.

In the organomercury cation of compound **10** the characteristic coordination number of the Hg^I and Hg^{I'} atoms is 2 while the effective coordination number seems to be between 3 and 4. Also the bond distances and angle about these atoms (see Tables VI and VII) are nearly identical with previously reported values.

Experimental Section

Equipment, Analyses, and Chemicals. Routine 60-MHz ¹H NMR spectra were obtained on a Varian Model A-60 or a Hitachi Model R-20-B spectrometer. All 100 MHz spectra were obtained on a Varian Model HN-100 spectrometer while the 300-MHz spectra were obtained on a Nicolet NT-300 spectrometer. Chemical shifts were recorded in parts per million from tetramethylsilane internal standard. Mass spectra were obtained from an AEI 902. All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. All elemental analyses were performed by Galbraith Laboratories.

3-Aminoprop-1-yne, 3-(methylamino)prop-1-yne, and 3-(benzylamino)prop-1-yne were purchased from Aldrich Chemical Co., while 3-(methylamino)but-1-yne and 1-(dimethylamino)but-2-yne were obtained from Farchan Division of Story Chemical Co. (now Farchan Labs, Albany International Chemicals Division). All amines obtained commercially were distilled prior to use. Other amines used in this work were prepared as described later.

Synthesis of Amines. Those amines not commercially available were prepared as follows.

3-(Dimethylamino)prop-1-yne was prepared from propargyl bromide according to a published procedure:⁵⁶ bp 80–82 °C; ¹H NMR (CCl₄) δ 2.05 (t, *J* = 3 Hz, 1 H, C≡CH), 2.20 (s, 6 H, CH₃'s), 3.15 (d, *J* = 3 Hz, 2 H, CH₂); IR (CCl₄) 3320 (C≡CH), 3300 (sh) (NH), 2130 (C≡C) cm⁻¹; mass spectrum (70 eV), *m/z* 83 (parent), 43 (base).

3-Chlorohex-1-yne was prepared according to a published procedure:⁵⁷ 50% yield; bp 61–65 °C (100 mmHg); ¹H NMR (neat) δ 0.90 (t, *J* = 7 Hz, 3 H, CH₃), 1.2–2.2 (m, 4 H, CH₂'s), 2.50 (d, *J* = 3 Hz, 1 H, C≡CH), 4.50 (dt, *J* = 3 Hz, *J* = 7 Hz, 1 H, CHCl).

3-Aminohex-1-yne was prepared from 3-chlorohex-1-yne according to a published procedure:⁵⁸ 58% yield; bp 71–72 °C (100 mmHg); ¹H NMR (CCl₄) δ 0.95 (m, 3 H, CH₃), 1.20 (s, 2 H, NH₂), 1.50 (m, 4 H, CH₂'s), 2.10 (d, *J* = 3 Hz, 1 H, C≡CH), 3.40 (m, 1 H, CH); IR (CCl₄) 3400 and 3320 (sh) (NH₂), 3325 (C≡CH), 2140 (C≡C) cm⁻¹; mass spectrum (70 eV), *m/z* 97 (parent), 54 (base).

3-(Butylamino)hex-1-yne was prepared from 3-chlorohex-1-yne according to a published procedure:⁵⁷ 66% yield; bp 68–72 °C (11 mmHg); ¹H NMR (CCl₄) δ 0.90 (m, 6 H, CH₃'s), 1.4 (m, 8 H, CH₂'s), 2.05 (d, *J* = 3 Hz, 1 H, C≡CH), 2.45 (m, 1 H, NH), 2.70 (m, 2 H, CH₂NH), 3.20 (m, 1 H, CHNH); IR (CCl₄) 3310 (sh) (NH), 3295 (C≡CH), 2080 (C≡C), 1025 (CN) cm⁻¹.

3-(Cyclohexylamino)hex-1-yne was prepared from 3-chlorohex-1-yne according to the published procedure for 3-(*n*-butylamino)hex-1-yne:⁵⁷ mp 44–45 °C; ¹H NMR (acetone-*d*₆) δ 0.90 (t, *J* = 7 Hz, CH₃), 0.80–1.80 (aliphatic hydrogens), 2.55 (d, *J* = 3 Hz, C≡CH), 2.70 (m, 1 H, NCH), 3.40 (m, 1 H, C≡CCH), 3.7 (s, 1 H, NH); IR (KBr) 3300 (NH), 2090 (C≡C), 1130 (CN) cm⁻¹; mass spectrum (70 eV), *m/z* (relative intensity) 179 (parent, 1), 136 (48), 99 (11), 69 (100).

3-(Methylamino)hex-1-yne was prepared from 3-chlorohex-1-yne according to the published procedure for 3-(*n*-butylamino)hex-1-yne:⁵⁷ 40% yield; bp 70–72 °C (90 mmHg); ¹H NMR (neat) δ 0.90 (m, 4 H, CH₃ and NH overlapping), 1.50 (m, 4 H, CH₂'s), 2.35 (s, 4 H, C≡CH and CH₃N overlapping), 3.20 (dt, *J* = 3 Hz, *J* = 7 Hz, 1 H, C≡CCH); IR (CCl₄) 3330 (sh) (NH), 3110 (C≡CH), 2090 (C≡C) cm⁻¹; mass spectrum (70 eV), *m/z* 111 (parent), 68 (base).

4-Aminobut-1-yne was prepared according to a published procedure:^{59,60} bp 99 °C; ¹H NMR (CCl₄) δ 0.95 (s, 2 H, NH₂),

1.80 (t, *J* = 3 Hz, 1 H, C≡CH), 2.25 (dt, *J* = 3 Hz, *J* = 7 Hz, 2 H, CH₂C≡C), 2.75 (t, *J* = 7 Hz, 2 H, CH₂N); IR (CCl₄) 3390 and 3300 (sh) (NH₂), 3310 (C≡CH), 2120 (C≡C) cm⁻¹; mass spectrum (70 eV), *m/z* 69 (parent), 43 (base).

3-(Phenylamino)prop-1-yne was prepared from propargyl bromide according to a published procedure:⁵⁶ 30% yield; bp 118–122 °C (12 mmHg); ¹H NMR (CCl₄) δ 2.05 (t, *J* = 3 Hz, 1 H, C≡CH), 3.75 (br s, 3 H, NH and CH₂C≡C overlapping) [after deuterium exchange, δ 3.75 (d, *J* = 3 Hz, 2 H, CH₂C≡C)], 6.4–7.3 (m, 5 H, aryl); IR (CCl₄) 3320 (C≡CH), 3300 (NH), 3070 (ArH), 1610 (Ar), 1325 and 1260 (ArN), 695 (Ar) cm⁻¹; mass spectrum (70 eV), *m/z* 131 (parent), 43 (base).

Mercuriation of Propargylic Amines. The following synthesis of bis[(*E*)-3-chloro-2-(chloromercurio)-1-methylprop-2-enyl]methylammonium tetrachloromercurate(II) (**5**) is representative of that used for procedure A in Table I. For procedures B and C, 25 mL of 2 M HCl plus 50 mmol of HgCl₂ and 25 mL of 6 M HCl plus 50 mmol of HgCl₂ were used, respectively. The procedures used, yields, melting points, and elemental analyses of crude and recrystallized materials are reported in Table I.

Bis[(*E*)-3-chloro-2-(chloromercurio)-1-methylprop-2-enyl]methylammonium Tetrachloromercurate(II) (5**) (Procedure A).** In a 50-mL flask, 7.47 g (27.5 mmol) of mercuric chloride was added to 25 mL of 5 M HCl while stirring magnetically. To this solution was added 0.416 g (5 mmol) of 3-(methylamino)but-1-yne slowly through a syringe. The reaction was stoppered and stirred for 48 h at room temperature. The product was removed intermittently by vacuum filtration and dried in a desiccator under high vacuum: combined yield 57%; mp 161–163 °C, recrystallized mp 165 °C; ¹H NMR (Me₂SO-*d*₆) δ 1.30 (d, *J* = 7 Hz, 3 H, CH₃), 2.40 (s, 3 H, CH₃N), 4.40 (br m, 1 H, CH), 6.37 (s, 1 H, C=CH, *J*¹⁹⁹Hg-H = 158 Hz), 8.25 (br s, 2 H, NH₂⁺); IR (KBr) 3140 (C=CH), 2800 and 2400 (NH₂⁺), 1615 (C=C), 1565 (CN), 738 (CCl) cm⁻¹.

The following compounds have been prepared by using similar procedures.

Bis[(*E*)-3-chloro-2-(chloromercurio)prop-2-enyl]methylammonium Tetrachloromercurate(II) (1**):** procedure A; ¹H NMR (Me₂SO-*d*₆) δ 2.55 (s, 3 H, NCH₃), 3.85 (s, 2 H, CH₂), 6.35 (s, 1 H, C=CH, *J*¹⁹⁹Hg-H = 156 Hz), 8.20 (br s, 2 H, NH₂⁺); IR (KBr) 3130 (C=CH), 2800 and 2400 (NH₂⁺), 1628 (C=C), 1580 (CN), 750 (CCl) cm⁻¹.

Bis[(*E*)-3-chloro-2-(chloromercurio)prop-2-enyl]benzylammonium Tetrachloromercurate(II) (2**):** procedure A; ¹H NMR (Me₂SO-*d*₆) δ 4.00 (s, 2 H, CH₂N), 4.20 (s, 2 H, CH₂Ph), 6.45 (s, 1 H, C=CH, not concentrated enough for *J*¹⁹⁹Hg-H measurement), 7.50 (s, 5 H, aryl), 8.85 (br s, 2 H, NH₂⁺); IR (KBr) 2800–2200 (NH₂⁺), 1600 (arene and C=C), 1565 (CN), 732 (CCl and arene), 690 (arene) cm⁻¹.

Bis[(*E*)-3-chloro-2-(chloromercurio)prop-2-enyl]dimethylammonium Tetrachloromercurate(II) (3**):** procedure A; 300-MHz ¹H NMR (Me₂SO-*d*₆) δ 2.82 (s, 6 H, CH₃'s), 4.05 (s, 2 H, CH₂), 6.59 (s, 1 H, C=CH, *J*¹⁹⁹Hg-H = 155 Hz), 9.03 (br s, 1 H, NH⁺); IR (KBr) 2720 (NH⁺), 1605 (C=C), 1580 (CN), 750 (CCl) cm⁻¹. In addition, the following ¹H NMR spectral peaks were observed for what is assumed to be the divinylmercurial: δ 2.82 (s, 6 H, CH₃'s), 4.17 (s, 2 H, CH₂), 6.37 (s, 1 H, C=CH, *J*¹⁹⁹Hg-H = 47 Hz), 9.53 (br s, 1 H, NH⁺).

Bis[(*E*)-3-chloro-2-(chloromercurio)prop-2-enyl]dimethylammonium Hexachlorodimercurate(II) (4**):** procedure C; the ¹H NMR spectral data are identical with those of compound **3**.

Bis[(*E*)-3-chloro-2-(chloromercurio)-1-methylprop-2-enyl]methylammonium Hexachlorodimercurate(II) (6**):** procedure C; the ¹H NMR spectral data are identical with those of compound **5**.

Bis[(*E*)-3-chloro-2-(chloromercurio)-1-(*n*-propyl)prop-2-enyl]ammonium Tetrachloromercurate(II) (7**):** procedure A; 100-MHz ¹H NMR (acetone-*d*₆) δ 0.95 (t, *J* = 7 Hz, 3 H, CH₃), 1.45 (m, 4 H, CH₂'s), 5.04 (t, *J* = 7 Hz, 1 H, CH), 6.63 (s, 1 H, C=CH, *J*¹⁹⁹Hg-H = 160 Hz), 7.95 (br s, 3 H, NH₃⁺); IR (KBr)

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3200–2880 and 2700–2500 (NH₃⁺), 1590 (sh) (C=C), 1582 and 1492 (CN), 755 (CCl) cm⁻¹.

Bis[*((E)*-3-chloro-2-(chloromercurio)-1-(*n*-propyl)prop-2-enyl)methylammonium] Tetrachloromercurate(II) (8): procedure A; 300-MHz ¹H NMR (acetone-*d*₆) δ 0.97 (t, *J* = 7 Hz, 3 H, CH₃), 1.51 (m, 4 H, CH₂'s), 2.99 (s, 3 H, NCH₃), 4.93 (m, 1 H, CH), 6.89 (s, 1 H, C=CH, *J*¹⁹⁹_{Hg-H} = 156 Hz), 8.08 (br s, 2 H, NH₂⁺); IR (KBr) 2740 and 2720 (NH₂⁺), 1620 (sh) (C=C), 1565 (CN), 740 (CCl) cm⁻¹. In addition, the following ¹H NMR spectral peaks were observed for what is assumed to be the divinylmercurial: δ 1.00 (t, *J* = 7 Hz, 3 H, CH₃), 1.40 (m, 4 H, CH₂'s), 3.06 (s, 3 H, NCH₃), 4.84 (m, 1 H, CH), 6.60 (s, 1 H, C=CH, *J*¹⁹⁹_{Hg-H} = 56 Hz), 8.43 (br s, 2 H, NH₂⁺).

Bis[*((E)*-3-chloro-2-(chloromercurio)but-2-enyl)dimethylammonium] Tetrachloromercurate(II) (9): procedure B; 300-MHz ¹H NMR (Me₂SO-*d*₆) δ 2.38 (s, 3 H, CH₃), 2.77 (s, 6 H, N(CH₃)₂), 4.03 (s, 2 H, CH₂), 8.93 (br s, 1 H, NH⁺); IR (KBr) 2743 (NH⁺), 1618 (C=C), 650 (CCl) cm⁻¹.

[*((E)*-3-Chloro-2-(chloromercurio)but-2-enyl)dimethylammonium] Trichloromercurate(II) (10): procedure B; the ¹H NMR spectral data are identical with those of compound 9.

X-ray Crystallography. Single crystals of compounds 6, 7, and 10 with approximate dimensions 0.22 × 0.24 × 0.26 mm, 0.10 × 0.12 × 0.42 mm, and 0.2 × 0.2 × 0.2 mm, respectively, were adhered to glass fibers (inside a capillary for compound 10) and mounted on goniometer heads. Data were collected at room temperature in all cases on a four-circle diffractometer designed and built in the Ames Laboratory⁶¹ and using monochromated Mo K_α radiation. Several ω-oscillation photographs at various φ settings were taken for each crystal. From these photographs, the settings for 14, 12, and 16 reflections, respectively, were obtained and input into an automatic indexing algorithm.⁶² The resulting reduced cells and reduced cell scalars revealed primitive orthorhombic symmetry for compound 6, C-centered monoclinic symmetry for compound 7, and primitive monoclinic symmetry for compound 10. Crystal data are summarized in Table II. Data were collected from the octants *h,k,l* and *-h,-k,l* for compounds 6 and 7 and from the octants *h,k,l* and *h,k,-l* for compound 10 (see later). The intensities of three axial standard reflections for compounds 6 and 7 and eight reflections for compound 10 were measured every 75 reflections during data collection to monitor decay. Significant decay was observed for compounds 6 and 7 (14 and 24%, respectively). The decay for compound 10 was so severe that *h,k,l* data were collected on one crystal and *h,k,l* data on another (nearly 25% for both crystals of compound 10). The final unit cell parameters and standard deviations were calculated from the tuned angles for 12 (6), 18 (7), and 29 (10) near-axial reflections (15° ≤ 2θ ≤ 36°). For compound 6 the systematic absences *Ok* (*k* + *l* = 2*n* + 1), and *hk*0 (*h* = 2*n* + 1) narrowed the space group choices to the centrosymmetric group *Pnma* or its noncentrosymmetric counterpart *Pn2₁a*. Statistical evidence⁶³ favored the centrosymmetric choice, but the results were somewhat ambiguous. For compound 7 systematic absences of *hkl* (*h* + *k* = 2*n* + 1) and *hOl* (*l* = 2*n* + 1) uniquely defined the space group as the centrosymmetric group *C2/c*. For compound 10 systematic absences of *hol* (*l* = 2*n* + 1) narrowed the space group choices to *Pc* and *P2/c*. A statistical test⁶³ indicated acentric distribution and space group *Pc* was selected. Decay corrections were made on the basis of the observed decrease in standard reflection intensities, and empirical absorption corrections⁶⁴ were made on the basis of observed variations in the intensity distribution as a function of the orientation of the crystal for reflections near χ = 90°. All data were corrected for Lp effects and appropriately averaged (only one octant of data was retained for compound 6 due to excessive decay). The two reduced data sets from the two different crystals of compound 10 were scaled, combined, and then averaged (see below).

Structure Determination and Refinement. As mentioned above, the true space group for compound 6 was not known at the end of data collection. Attempts to find an acceptable initial

model from the patterson map assuming the space group to be *Pnma* failed. With use of a superposition map and the program ALCAMPS,⁶⁵ the space group was indicated to be *Pn2₁a* and a solution was obtained. This structure contains two crystallographically independent cationic moieties with one unique Hg₂Cl₆²⁻ anion. The cations appear to be approximately related by a pseudo- (i.e., noncrystallographic) inversion operation. All mercury positions and some of the chlorine positions were obtained from ALCAMPS, and the remaining non-hydrogen atoms were located from calculated electron density maps.⁶⁶ All positional and thermal parameters were initially refined by using a block-diagonal-matrix least-squares procedure.⁶⁷ All of the mercury and chlorine atoms were allowed to refine anisotropically. Attempts were made to refine the nitrogen and carbon atoms anisotropically, but they failed, presumably due to correlation between the independent cations. All ethylenic hydrogen atom positions were calculated but not varied. A final full-matrix refinement converged at *R* = 4.9%. Finally, the atomic coordinates (Table III) unambiguously ruled out the much more common space group *Pnma*.

All atoms in the cation and the anion for compound 7 were readily identified by the program ALCAMPS from a Patterson superposition map generated by using an Hg–Cl interatomic vector. The benzene solvent and an apparent water molecule were then located in a subsequent electron density map. As in compound 6, all positional and thermal parameters were initially refined by using a block-matrix least-squares procedure. Isotropic refinement converged at *R* = 15.8%. All non-hydrogen atoms were allowed to refine anisotropically, and all ethylenic and methylenic hydrogen atom positions were calculated, but not refined. A final full-matrix refinement converged at *R* = 6.1%.

Three mercury atoms of compound 10 were obtained from a superposition map generated by using a Hg–Cl vector and three vectors which were considered to be single Hg–Hg vectors. The remaining Hg atom and five Cl atoms were then located from a subsequent difference electron density map by using a data set where the relative scaling of the intensities of the two crystals was done by using ~120 common reflections. With these nine atoms a better estimate of relative scaling of the intensities from the two crystals was obtained by a least-squares refinement where only the scale factors were varied, and the resulting combined averaged data were used in the subsequent calculations. The remaining atoms were then located from difference electron density maps. All of the mercury and chlorine atoms were initially refined isotropically and then anisotropically by using the block-diagonal-matrix least-squares procedure. The data did not warrant refinement of the nitrogen and carbon atoms anisotropically. Hydrogen atom positions (except for the ones attached to the nitrogen atoms) were calculated but not varied. A final full-matrix refinement converged at *R* = 4.7%. Again, examination of the coordinates (Table V) unambiguously ruled out *P2/c* as space group.

The atomic scattering factors⁶⁸ for mercury and chlorine were modified for anomalous dispersion effects.⁶⁹

Tables III–V list the positional parameters for all non-hydrogen atoms with averaged isotropic thermal parameters. Anisotropic thermal parameters and the stereoscopic unit cell diagrams are given in the supplementary material.

Acknowledgment. R.C.L., L.D.B. S.V., and C.E.R. gratefully acknowledge the financial support of the National Institutes of Health (GM 24254). The research of J.W.R., M.N.J., and R.A.J. was supported by the U.S. Department of Energy under Contract No. W-7405-Eng-82, Office of Basic Energy Sciences, Materials Science Division.

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CCH(NH-*c*-C₆H₁₁)CH₂CH₂CH₃, 109086-53-5; HC≡CCH₂CH₂NH₂, 14044-63-4; HC≡CCH₂NHC₆H₅, 14465-74-8; HgCl₂, 7487-94-7; propargyl bromide, 106-96-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and stereoscopic unit cell diagrams for 6, 7, and 10 (6 pages); listings of structure factors for 6, 7, and 10 (15 pages). Ordering information is given on any current masthead page.

Formal Nitrogen Hydride Insertion into the Metal-Carbene Bond of Fischer-Type Carbene Complexes

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Received January 29, 1987

A series of imidate complexes [(CO)₅M{NH=C(OR¹)R²}] (M = W, R¹ = Me or Et, R² = Ph; M = W, R¹ = Me, R² = Me; M = Cr, R¹ = Me or Et, R² = Ph) can be prepared by reaction of alkoxyorganocarbene complexes with *S,S*-diphenylsulfilimine, NH=SPh₂. The thiocarbene complex [(CO)₅W{C(SPh)R²}] (R² = Me) similarly gives the corresponding thioimidate complex, but when R² = Ph, [(CO)₅W(NCPh)] (9) is the only product. The heterometallic complex [(CO)₄W{C(OEt)C(OEt)=CS(CH₂)₃S}] also undergoes NH insertion and concomitant chelate ring enlargement. The imidate complex [(CO)₅W{NH=C(OMe)Ph}] (1) is deprotonated by Bu⁻, H⁻, MeO⁻, and RS⁻ to afford the nitrile (9), but with dimethylamine the amidine complex [(CO)₅W{NH=C(NMe₂)Ph}] (13) is formed by aminolysis. The *Z* isomer of 1 and the *E* isomer of 13 are completely characterized by X-ray structure determinations. Crystal data for 1: WC₁₃H₉NO₆, *M*_r 459.07, monoclinic, space group *P*2₁/*c*, *a* = 10.694 (4) Å, *b* = 6.650 (1) Å, *c* = 20.338 (4) Å, β = 92.18 (3)°, *V* = 1445 Å³, *Z* = 4, *D*_{calcd} = 2.11 g cm⁻³. Crystal data for 13: WC₁₄H₁₂N₂O₅, *M*_r 472.118 monoclinic, space group *P*2₁/*c*, *a* = 11.723 (2) Å, *b* = 9.550 (1) Å, *c* = 15.032 (6) Å, β = 105.43 (3)°, *V* = 1622 Å³, *Z* = 4, *D*_{calcd} = 1.93 g cm⁻³. The W-N(sp²) bond lengths are 2.249 (5) and 2.243 (5) Å. Reaction of NH=SPh₂ with [M(CO)₆] (M = Cr or W) produces yellow solutions from which [(CO)₅M(SPh₂)] can be isolated. In the presence of PPh₃ only the monosubstituted phosphine complexes form in less than 50% yields.

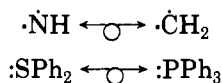
Introduction

The formal insertion of an NH group into a metal-carbene bond is currently receiving attention; e.g., in E. O. Fischer's group, hydroxylamine has been used for the reaction with terminal carbenes¹ whereas we have employed both of the substituted hydrazines H₂NNMe₂ and H₂NNHMe for carbenes that form part of heterometallic ring systems^{2,3} and only the latter for carbene complexes of the type [(CO)₅M{C(OEt)CH₂PPh₃}]³. The main disadvantage of most of these conversions is the unsatisfactory yields due to the formation of various by-products. Note that the Fischer-type chromium carbene complex [(CO)₅Cr{C(OR¹)R²}] (R¹ = R² = Me) gives only the nitrile compound [(CO)₅Cr(CNR²)] with a substituted hydrazine.¹ The NH group has recently been successfully inserted into metal-carbene bonds containing no heteroatoms,⁴ but a similar treatment of alkoxyorganocarbene complexes again affords nitrile complexes.⁵

The present study was undertaken (a) to find a simple quantitative method for introducing an NH unit into the

metal-carbene bond of terminal and chelate carbene donor groups and (b) to establish the susceptibility of the formed imidates (from alkoxyorganocarbene complexes) and thioimidates (from thiocarbene complexes) toward reactions such as deprotonation and aminolysis.

Carbene complexes are converted in high yields into enol ethers and phosphine complexes by treatment with the Wittig reagent CH₂=PPh₃.⁶ The isolobal relationships



that hold between this reagent and the heteroatom carbene complexes, and the fact that SPh₂ coordinates very weakly to group VI metal carbonyls,^{7,8} prompted the use of NH=SPh₂ for NH insertion. The results reported here are of relevance to the recent preparation of ketimine complexes.⁹

Results and Discussion

Reactions of Alkoxyorganocarbene Complexes with Diphenylsulfilimine. Alkoxyorganocarbene pentacarbonyl

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