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BIS(ALKYLAMINO)CARBENE COMPLEXES OF GOLD(I) AND RELATED COMPOUNDS

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SUMMARY

Primary amines, RNH_2 react with (*p*-tolyl isocyanide)chlorogold(I), to give two-coordinate $[(Ar{-}NH)(R{-}NH)C]AuCl$ or four-coordinate $[(Ar{-}NH)(R{-}NH)C]_2(R{-}NH_2)_2Au_2Cl_2$ carbene complexes. Geometrical isomers are identified in solutions of the former type, by NMR spectroscopy. Both types of product react with bases to give insoluble $[(Ar{-}N{=})(R{-}NH)CAu]_x$ species, related to the known trimers, $[(Ar{-}N{=})(RO)CAu]_3$.

INTRODUCTION

Alcohols react with isocyanide complexes of gold(I) to yield [(alkoxy)(arylamino)carbene]chlorogold(I) compounds[1,2], *i.e.*:

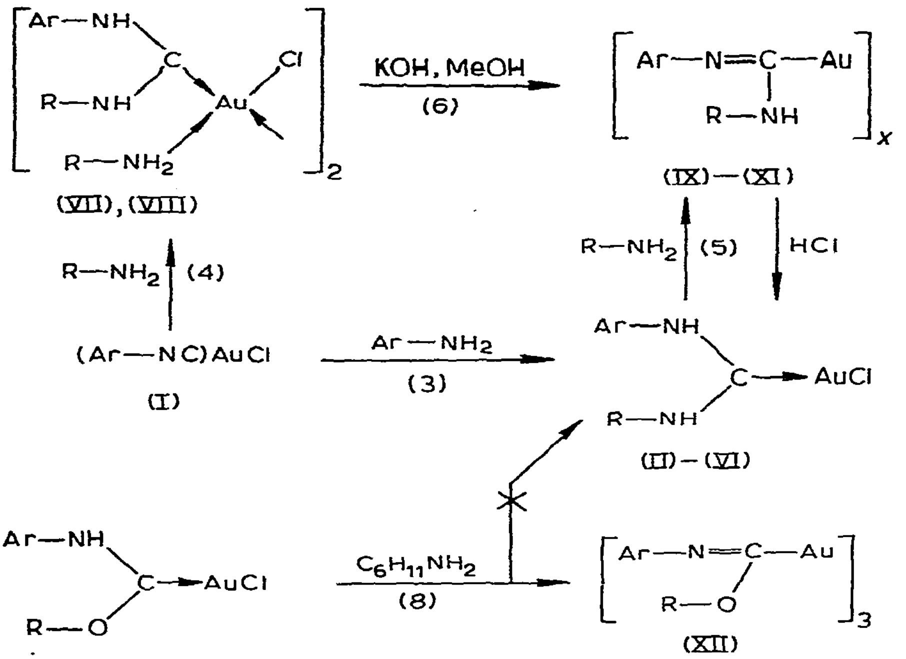
$$(R{-}NC)AuCl + R'{-}OH \rightarrow [(R{-}NH)(R'{-}O)C]AuCl \qquad (1)$$

Because no other carbene complex of an element with a d^{10} configuration is known, except those of mercury(II)[3,4], obtained by different routes, reaction (1) was extended to other nucleophiles, such as amines. We report here the preparation and properties of bis(arylamino)carbene and of (alkylamino)(arylamino)carbene complexes of gold(I), prepared according to (3) or (4) (*cf.* Scheme 1). It was found possible to deprotonate the products according to (5) or (6), and so obtain compounds of a type related to those already described[5] which can also be obtained by deprotonation[6,7]:

$$[(R{-}NH)(R'{-}O)C]AuCl + OH^- \rightarrow Cl^- + H_2O + \tfrac{1}{3}[(R{-}N{=})(R'{-}O)CAu]_3 \qquad (2)$$

RESULTS AND DISCUSSION

The reaction between an amine and (*p*-tolyl isocyanide)chlorogold(I) gives either bicoordinate (II)–(VI) or four-coordinate (VII)–(VIII) complexes. The former are obtained when an aromatic amine, even in excess, is employed and the reaction requires a few days of stirring in diethyl ether when *p*-methyl-, *p*-methoxy-, or *p*-fluoroaniline are used. Sterically hindered amines, such as 2,6-dimethyl- or 2,6-diisopropylaniline, require refluxing in diisopropyl ether. The latter type of compound, SCHEME 1



	R
(II)	p-MeC$_6$H$_4$
(III)	p-MeOC$_6$H$_4$
(IV)	p-FC$_6$H$_4$
(V)	o,o'-Me$_2$C$_6$H$_3$
(VI)	o,o'-(Me$_2$CH)$_2$C$_6$H$_3$
(VII)	C$_6$H$_5$CH$_2$

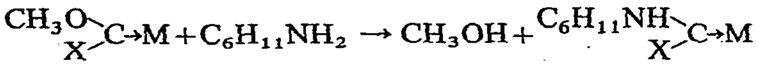
	R
(VIII)	C$_6$H$_{11}$
(IX)	p-MeC$_6$H$_4$
(X)	o,o'-(Me$_2$CH)$_2$C$_6$H$_3$
(XI)	C$_6$H$_{11}$
(XII)	CH$_3$

(Ar=p-CH$_3$C$_6$H$_4$)

(VII) and (VIII), is obtained when a relatively basic amine, such as cyclohexylamine or benzylamine, is employed.

In the attempt to obtain four-coordinate complexes, the bicoordinated compounds (II) and (VI) were treated with cyclohexylamine, but (IX) or (X) were obtained as the respective products, that is, the amine acted simply as a base. The stronger base, potassium hydroxide in methanol, reacts with (VII) to give (XI) similar to (IX) and to (X).

Certain aminocarbene complexes [where $M=(CO)_5Cr$ and $X=CH_3$ or C_6H_5] may be prepared as follows[8]:



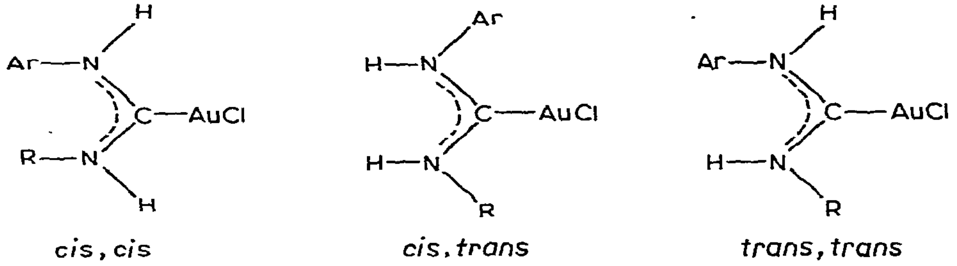
$$\begin{matrix}\mathrm{CH_3O}\\ \mathrm{X}\end{matrix}\!>\!\mathrm{C{\to}M}+\mathrm{C_6H_{11}NH_2}\rightarrow \mathrm{CH_3OH}+\begin{matrix}\mathrm{C_6H_{11}NH}\\ \mathrm{X}\end{matrix}\!>\!\mathrm{C{\to}M} \qquad (7)$$

The same reaction was attempted here, with $M=AuCl$ and $X=NH\text{–}C_6H_4CH_3$, but, instead of the expected carbene complex, cyclohexylammonium chloride and the cyclic molecule (XII) were obtained, according to (8).

The products are air-stable solids, and generally sparingly soluble or nearly insoluble in organic solvents, even when a cyclohexyl or a 2,6-diisopropylphenyl group is present. They are rather light sensitive, especially when crude or in solution, so that purification steps must be carried out as quickly as possible. Decomposition is evidenced by the appearance of a violet tinge, which may also develop after prolonged standing of purified samples.

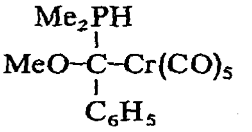
The compounds were identified by elemental analyses (Table 1), infrared spectra, and, whenever possible, by NMR spectra and molecular weight determinations.

The bicoordinate gold(I) carbene complexes can exist as geometrical isomers if the CN bond order is significantly higher than 1.0. This bond order may be related to the value of the CN stretching frequency (around 1550 cm^{-1}, intense, often broad and asymmetric, a value comparable to that found[9] in metal dithiocarbamates where the CN bond order is intermediate between 1.0 and 2.0). Consequently the NMR spectra (see Experimental), in $CDCl_3$ or in CD_3COCD_3, show more signals than would be expected for only one isomer, at least in the cases where R=Ar=p-CH_3-C_6H_4, (II), R=p-$CH_3OC_6H_4$ and Ar=p-$CH_3C_6H_4$, (III). For these compounds a ca. 1/2 mixture of either *cis, cis* or *trans, trans* and *cis, trans* isomer accounts for the observed spectra. When Ar=p-$CH_3C_6H_4$ and R=p-FC_6H_4, (IV), or R=o,o'-$(Me_2CH)_2C_6H_3$, (VI), the available data do not permit a choice between a mixture of *cis, cis* plus *trans, trans* isomers or a single isomer, *cis, trans*, which is probably favoured in the case of (VI) owing to the bulky *ortho*-substituents.

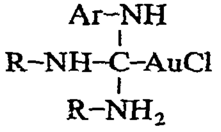


cis, cis *cis, trans* *trans, trans*

The four-coordinate compounds, (VII) and (VIII), show a complex infrared spectrum without any absorption in the range of the terminal ν(Au–Cl) in contrast with the bicoordinate species reported here (324–332 cm^{-1}) and with the (alkoxy)(arylamino)carbene derivatives described elsewhere[1,2]. A further structure, to be compared with the phosphorus ylide complexes recently reported[10], *i.e.*:



$$\begin{array}{c} Me_2PH \\ | \\ MeO\text{–}C\text{–}Cr(CO)_5 \\ | \\ C_6H_5 \end{array}$$



$$\begin{array}{c} Ar\text{–}NH \\ | \\ R\text{–}NH\text{–}C\text{–}AuCl \\ | \\ R\text{–}NH_2 \end{array}$$

can be ruled out because it does not explain the strong absorption at ca. 1550 cm^{-1} and requires a Au–Cl stretching vibration.

TABLE 1

ANALYTICAL AND OTHER DATA

Compound	M.p. (dec.) (°C)	Cryst. from	Mol. wt. found (calcd.), (in $CHCl_3$)	Analyses found (calcd.) (%)				
				C	H	N	Au[a]	Cl[b]
(II) $[(4\text{-}CH_3C_6H_4NH)_2C]AuCl$	162 (ca. 160)	CH_2Cl_2/Pet. ether		39.22 (39.40)	3.15 (3.50)	5.98 (6.12)	44.0 (43.2)	7.36 (7.77)
(III) $[(4\text{-}CH_3C_6H_4NH)(4\text{-}CH_3OC_6H_4NH)C]AuCl$	154 (ca. 148)	$CHCl_3$/Pet. ether + Et_2O(6/6+1)	520 (473)	38.17 (38.20)	3.38 (3.39)	5.83 (5.94)		
(IV) $[(4\text{-}CH_3C_6H_4NH)(4\text{-}FC_6H_4NH)C]AuCl$	181	CH_2Cl_2/Pet. ether		36.13 (36.50)	2.61 (2.82)	5.81 (6.08)		
(V) $\{(4\text{-}CH_3C_6H_4NH)[2,6\text{-}(CH_3)_2C_6H_3NH]C\}AuCl$	191 (ca. 191)	CH_2Cl_2/Et_2O	425 (470)	40.27 (40.80)	3.46 (3.82)	5.92 (5.95)		
(VI) $\{(4\text{-}CH_3C_6H_4NH)(2,6\text{-}[(CH_3)_2CH]_2C_6H_3NH)C\}AuCl$	190 (ca. 188)	Et_2O	600 (527)	45.68 (45.60)	4.92 (4.94)	5.14 (5.31)		
(VII) $\{[(4\text{-}CH_3C_6H_4NH)(C_6H_5CH_2NH)C](C_6H_5CH_2NH_2)AuCl\}_2$	108 (ca. 105)	CH_2Cl_2/Pet. ether	475 (564)	47.40 (46.90)	4.13 (4.44)	7.60 (7.45)		
(VIII) $\{[(4\text{-}CH_3C_6H_4NH)(C_6H_{11}NH)C](C_6H_{11}NH_2)AuCl\}_2$	149 (ca. 146)	CH_2Cl_2/Pet. ether	500 (548)	43.48 (43.80)	5.97 (6.02)	7.39 (7.66)	36.7 (36.00)	6.40 (6.50)
(IX) $\{[(4\text{-}CH_3C_6H_4NH)(4\text{-}CH_3C_6H_4N{=})C]Au\}_x$	154			43.35 (43.00)	3.71 (3.58)	6.78 (6.88)	47.00 (46.70)	0.10 0.0
(X) $\{[(4\text{-}CH_3C_6H_4N{=})(2,6\text{-}[(CH_3)_2CH]C_6H_3NH)C]Au\}_x$	183			49.0 (50.00)	5.1 (4.82)	5.71 (5.71)	39.9 (40.20)	
(XI) $\{[(4\text{-}CH_3C_6H_4N{=})(C_6H_{11}NH)C]Au\}_x$				41.16 (40.90)	4.45 (4.62)	6.59 (6.80)		

[a] Determined as ash. [b] Determined as AgCl after melting the sample in $NaNO_3/K_2CO_3$.

Products (IX)–(XI), obtained by action of bases on carbene complexes, are white stable solids, unaffected by water, and nearly insoluble in organic solvents, so that no NMR spectra or molecular weight determinations could be made. Characterization rests on analytical data, infrared spectra, reaction with HCl (see Scheme 1) to yield the starting material, together with the analogy with the trimeric [(alkoxy)-(arylimino)methyl]gold(I) species. The compounds (IX)–(XI) are unlikely to be high polymers because they have a small but definite solubility; it is tempting to consider them as trimers, by analogy with compound (XII).

In particular, the infrared spectrum shows a ν(C=N$^+$) (1518 cm^{-1}), lower than in the starting compounds, [(Ar–NH)(R–NH)C]AuCl, (ca. 1550 cm^{-1}), in the related[5] [$(C_6H_{11}N=)(CH_3O)CAu]_3$ (1535 cm^{-1}) or in $(Ph_3P)AuC(OCH_3)(=NAr)$[11] (1565–1580 cm^{-1}). In addition, the band assigned to δ(NH) is found at ca. 1600 cm^{-1} as in the carbene complexes, *e.g.* (II) where deuteration was carried out (*cf.* Experimental).

EXPERIMENTAL

The starting material, (*p*-tolyl isocyanide)chlorogold(I), (I), was prepared according to the literature[2,12]. All compounds were kept *in vacuo* (ca. 0.1 mm Hg) till constant weight, and were always stored in the dark, although they are not necessarily photosensitive when pure. All evaporations were carried out under reduced pressure. Infrared spectra were recorded on a Perkin–Elmer 457, and NMR spectra on a Perkin–Elmer R-10 instrument. Molecular weight determinations were carried out at 37° on a Mechrolab osmometer by Mrs. M. Bonfà.

[Bis(p-tolylamino)carbene]chlorogold(I), (II)

Compound (I) (1.46 g) was suspended in diethyl ether (50 ml) and *p*-toluidine (0.89 g) was added. The reaction vessel was protected from daylight by a sheet of black paper, and the mixture was stirred for three days, then filtered, to yield the crude product (1.73 g). This solid was dissolved in chloroform (13 ml) and upon slow addition of petroleum ether a white precipitate was obtained, which was repurified in the same way to give an analytically pure sample (0.63 g). The product which was a nonelectrolyte in acetone, was sparingly soluble in methanol and in acetone. IR spectrum (nujol mull): 3270 m and 3240 s (br), 3140 w, 3080 w, 3060 w, 1600 s, 1550 s(br), 1518 s, 1465 s, 1414 m, 1372 s, 1328 s, 1304 m, 1270 m, 1228 m, 1081 w, 1078 w, 1012 w, 1025 w, 940 w, 819 s, 798 w, 753 m, 700 m, 640 w, 572 w, 539 m, 517 s, 503 m, 493 m, 479 w, 324 s. NMR spectrum ($CDCl_3$): 7.75 and 7.63 singlets, ca. 1/2, *p*-CH_3, 6 H; 2.4–3.1, multiplet, aromatic, 8 H; 0.55, 0.95 and 2.02 τ, singlets, NH, ca. 1/1/1, 2H.

A sample (200 mg) was stirred with D_2O (4 ml) for a week, and was then dried in a desiccator over P_4O_{10}. The bands at 3240, 1600, 753 and 700 cm^{-1} almost completely disappeared, and two new bands, at 2400 and 1210 cm^{-1}, were observed in the sodium chloride range.

[(p-Tolylamino)(p-anisylamino)carbene]chlorogold(I), (III)

(III) was obtained similarly. ν_{max}(nujol mull) at 3250 and 1600 (N–H), ca. 1550 or 1510 (C=N$^+$) and 325 cm^{-1} (Au–Cl). NMR spectrum ($CDCl_3$): 7.62 and

7.74, singlets, ca. 1/2, *p*-CH_3, 3H; 6.20 and 6.30, singlets, ca. 1/2, *p*-CH_3O, 3H; 2.4–3.3, complex, aromatic, 8H; 0.55, 0.99 and 2.05 τ, singlets, ca. 1/1/1, NH, ca. 2H.

[(*p-Tolylamino*)(*p-fluoroanilino*)*carbene*] *chlorogold*(*I*), (*IV*)

(IV) was prepared similarly. ν_{max}(nujol mull) at 3260 m, 1610 w, 1600 w (NH), ca. 1560 s or 1510 s ($C{=}N^+$), and 322 m cm^{-1} (Au–Cl). NMR spectrum (C_3D_6O): 7.63 and 7.66, overlapping singlets, *p*-CH_3, 3H; ca. 2.0–3.0, complex, aromatic, 8H; ca. +0.4 and −0.10 τ, broad, NH, not integrated.

[(*2,6-Dimethylanilino*)(*p-tolylamino*)*carbene*] *chlorogold*(*I*), (*V*)

(V) was obtained as described for compound (VI), after 9 h reflux; it is sparingly soluble in chloroform. ν_{max}(nujoll mull) at 3310 m, 3220 m (br), and 1590 m (NH), ca. 1550 s, asymm. ($C{=}N^+$), and 330 cm^{-1} (Au–Cl).

[(*2,6-Diisopropylanilino*)(*p-tolyamino*)*carbene*] *chlorogold*(*I*), (*VI*)

A mixture of (I) (1.06 g) and 2,6-diisopropylaniline (1.07 ml) in diisopropyl ether (50 ml) were refluxed 24 h under nitrogen, with stirring. The product (1.37 g) was filtered off, and crystallized by concentration of a cold solution in diethyl ether (500 ml), to yield an analytically pure sample (0.70 g). ν_{max}(nujol mull): 3320 m, 3230 s,(br); 1590 w, 1545 s, asymm., 1512 m, 1465 s, 1380 m, 1363 s, 1345 m, asymm., 1310 m, 1258 w, 1222 w, 1182 w, 1175 w, 1112 w, 1060 w, 1019 w, 942(sh), 938 w, 847 w, 818 m, 808 m, 797 w, 725 w, 710 w, 658 m, 632 w, 593 w, 552 w, 538 w, 503 w, 482 w, 450 w, 332 m. NMR spectrum ($CDCl_3$): 7.78 and 7.81, doublets, *J* 7.0 Hz, 12H, CH_3 of the isopropyl groups; 7.70, singlet, 3H, *p*-CH_3; 6.5–7.0, five broad signals (probable septet), 2H, $-\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$; 2.5–3.0 complex, 7H, aromatic protons; 0.6 τ, singlet, 1–2H, NH. The last signal disappeared upon shaking the sample with D_2O.

Bis[(*p-tolylamino*)(*benzylamino*)*carbene*] *bis*(*benzylamine*)-*μ-dichlorodigold*(*I*), (*VII*)

(VII) was obtained in a similar way to compound (VIII) after 14 h reflux. ν_{max} at 3240 w, 3200 m, ca. 3040 m, ca. 1600 m (NH), and 1555 cm^{-1} ($C{=}N^+$). NMR spectrum (C_3D_6O): 7.68, singlet, *p*-CH_3; 6.51 and 6.06, singlets, CH_2; 2.4–2.9 τ, complex, aromatic protons; no NH signal was observed.

Bis[(*p-tolyamino*)(*cyclohexylamino*)*carbene*] *bis*(*cyclohexylamine*)-*μ-dichlorodigold* (*I*), (*VIII*)

Compound (I) (0.51 g) was suspended in diethyl ether and cyclohexylamine (0.40 ml) was added: a white cloudy precipitate formed in the ethereal phase. After stirring the suspension for 70 h under nitrogen in the dark, the white solid (0.55 g) was filtered off, and was dissolved in dichloromethane (45 ml). The solution was concentrated to ca. 15 ml, and petroleum ether was added (40 ml). Upon concentration a white solid formed, which was purified twice in the same way to afford an analytically pure sample (0.37 g). The compound had $\Lambda = 3.7$ and 4.0 $ohm^{-1} \cdot cm^2 \cdot mole^{-1}$ in acetone at a concentration of 0.8 and 0.4×10^{-3} *M* respectively.

Infrared spectrum (nujol mull): 3520 w, 3440 vw, 3220 s, 3180 s, 3050 s; 1600 m, 1555 s(br), 1505 s, 1460 m, 1440 s, 1380 w, 1370 w, 1330 w, 1302 w, 1292 vw, 1253 w, 1170 vw, 1156 vw, 1100 m, asym., 1090(sh), 1070 m, 1055(sh), 822 vw, 807 s, ca. 790 m, ca. 605 w, 508 m. NMR spectrum ($CDCl_3$): broad envelopes at

8.0–9.0 and 6.2, cyclohexyl; broad signals at 0.85 and 1.0, NH; 2.5–3.2, complex, aromatic; 7.63 τ, singlet, p-CH_3.

(N-p-Tolylamino)(N-p-tolylimino)methylgold(I), (IX).

Compound (II) (0.90 g) was suspended in diethyl ether (50 ml) and treated with cyclohexylamine (0.45 ml). The reaction mixture was stirred under nitrogen in the dark for 20 h and then filtered. The resulting solid (1.04 g) was stirred with acetone (250 ml) for 2 h and the violet, insoluble residue (80 mg) was discarded. On adding water (ca. 6 ml) to the solution, a white precipitate was obtained (0.56 g). Infrared spectrum: 3260 w, ca. 1590 w, 1518 s, 1502 s, 1460 m, 1376 m, 1362 w, 1312 w, 1228(sh), 1218 w, 1109 w, 1018 w, 938 w, 850(sh), 812 s, 760 w, 718 w, 708 w, 671 w, ca. 610 w, 547 w, 530 vw, 512 w, 487 w.

Reaction of (IX) with HCl. Compound (IX) (0.339 g), methanol (40 ml) and a few drops of hydrochloric acid in methanol (1/5 v/v) were stirred together for 0.5 h. The clear, pale yellow solution was evaporated to dryness and the oily residue was stirred under petroleum ether overnight. The solid which formed was crystallized twice from chloroform/petroleum ether, to yield material identified as (II) by its m.p. 158° and IR spectrum.

(N-2,6-Diisopropylanilino)(N-p-tolylimino)methylgold(I), (X)

(X) obtained similarly, was sparingly soluble in organic solvents. ν_{max} 3280 w, 1590 w (NH), 1520 (C=N)cm^{-1}.

(N-Cyclohexylamino)(N-p-tolylimino)methylgold(I), (XI)

Compound (VIII) (0.72 g) in methanol (60 ml) and KOH in methanol (8.8 ml; 0.16 *M*) were stirred together under nitrogen, in the dark for 3.5 h. The white resulting product was filtered off, was stirred under water (40 ml) for 15 min, then refiltered and dried to constant weight over P_4O_{10}. ν_{max} at ca. 3240 w (br), and 1600 w (br) (NH), 1518 (C=N); no band between 250 and 400 cm^{-1}.

Trimeric [(p-tolylimino)(methoxy)methyl]gold(I), (XII)

A mixture of [(p-tolylamino)(methoxy)carbene]chlorogold(I)[1,2] (0.49 g), diethyl ether (50 ml), and cyclohexylamine (0.45 ml) were stirred under nitrogen 2 h. The filtered product (0.54 g) was dissolved in CH_2Cl_2 and the solution was concentrated to small volume to give a white precipitate (340mg). This was dissolved in $CHCl_3$ and methanol (130+80 ml). Upon concentration the product was obtained and identified by m.p. (188°), (mixed m.p. with the sample obtained in a different way[7]), IR and NMR spectra.

The mother liquor was evaporated to dryness and the oily residue was taken up with diethyl ether. The white solid which formed was purified by sublimation (110°/0.02 mm Hg) and identified by comparison with the infrared spectrum of an authentic sample of cyclohexylammonium chloride.

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