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# Isocyanide Complexes and (Alkoxy)(*N*-alkylimino)methyl Derivatives of Silver and Their Reactions

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Isocyanide and silver chloride give $[(RNC)AgCl]_n$ complexes. These, or a mixture of $Me_2SAgNO_3$ and isocyanide, react with alcoholic potassium hydroxide affording $[(R'O)(RN{=})CAg]_3$, from which transfer of the organic group on other metals can be accomplished yielding $HgY_2$, ClHgY, $[AuY]_3$, and $(Ph_3P)_2PtClY$, where Y is $(EtO)(p\text{-}CH_3C_6H_4N{=})C-$.

## Introduction

Among the isocyanide complexes of group 1B metals much data are available[2,3] on the preparation and reactivity of copper and gold complexes, while information about silver derivatives is lacking. In the field of gold chemistry, the preparation and reactions of neutral and cationic isocyanide derivatives, RNCAuCl and $[(RNC)_2Au]^+$, respectively, were recently described.[4]

Starting from these species, nucleophilic attack by an alcohol or by an amine afforded "carbene" complexes, according to the reaction patterns (1)–(4), which are in agreement with later reports by other authors,[10,11] or to reaction pattern (5), in place of which other authors[10] found either no reaction or dealkylation of the isocyanide (sealed tube, 60–100°). Further reaction of the carbene complexes A or B takes place according to the reaction pattern (6) or (7), affording cyclic trimers (C)[11,12] or polymers (D).[7] In addition, both reactions 6 and 7 are reversible: indeed protonation[11,12] of C or D affords the carbene complex A or B, respectively.

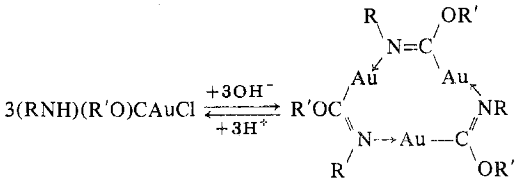
$$\mathrm{RNCAuCl + R'OH = \underset{A}{(RNH)(R'O)CAuCl}} \qquad (1)^{4-6}$$

$$\mathrm{RNCAuCl + R'NH_2 = \underset{B}{(RNH)(R'NH)CAuCl}} \qquad (2)^{5,7}$$

$$\mathrm{[(C_6H_{11}NC)_2Au]^+ + ArNH_2 = [(C_6H_{11}NH)(ArNH)CAu(CNC_6H_{11})]^+} \qquad (3)^{8,9}$$

$$\mathrm{[(RNC)_2Au]^+ + 2R'NH_2 = [\{(RNH)(R'NH)C\}_2Au]^+} \qquad (4)^{8,9}$$

$$\mathrm{[(RNC)_2Au]^+ + 2R'OH = [\{(RNH)(R'O)C\}_2Au]^+} \qquad (5)^{8,9}$$



(6)

C

$$n\mathrm{(RNH)(R'NH)CAuCl} \underset{+n\mathrm{H^+}}{\overset{+n\mathrm{OH^-}}{\rightleftharpoons}} \underset{D}{\mathrm{[(RN{=})(R'NH)CAu]}_n} \qquad (7)$$

In order to get a complete picture inside group 1B, it was decided to extend some of these reactions to silver. The (RNC)AgCl compounds were isolated, but they did not give carbene derivatives, type A or B, while the $[AgC(OR){=}NR']_3$ complexes analogous to C were obtained. These (alkoxy)(alkylimino)methylsilver compounds were found to be useful intermediates for the transfer of the $(R'N{=})(RO)C-$ group to different metals. A preliminary account of this work has already appeared.[13]

## Experimental Section

Reactions were carried out under nitrogen and in the dark because the crude products are often air or (especially) light sensitive. The $(RO)(ArN{=})CAg$ compounds can be obtained from $Me_2SAgNO_3$ or from (ArNC)AgCl according to the procedures described below for compounds VI and VII. Evaporation was always carried out under reduced pressure. Before each reaction solid *p*-tolyl isocyanide (mp ca. 19°) was allowed to thaw at room temperature; it was then measured volumetrically. Analytical data are reported in Table I; NMR data, in Table II.

The starting material, $(Me_2S)AgNO_3$ (I), mp 120–123°, was obtained as a white precipitate (50% yield) from aqueous silver nitrate (15 g, saturated solution) and dimethyl sulfide (70 ml).

**(*p*-Tolyl isocyanide)chlorosilver(I) (II).** Silver chloride (1.5 g, 10.47 mmol) was suspended in chloroform (40 ml) and *p*-tolyl isocyanide was added (2.6 and, shortly afterward, 0.2 ml, 21 mmol), under stirring. To the filtered solution petroleum ether was added (50 ml). After the volume was halved by evaporation, addition of more petroleum ether (30 ml) gave a white compound (1.31 g; 48% on silver). The compound is insoluble in chloroform, dichloromethane, acetone, benzene, alcohol, acetonitrile, and diethyl ether; $\nu(C{\equiv}N)$ at 2160 $cm^{-1}$, Nujol mull.

**(Cyclohexyl isocyanide)chlorosilver(I) (III),** was obtained similarly (48%). It was insoluble in common organic solvents and showed $\nu(C{\equiv}N)$ at 2180 $cm^{-1}$, Nujol mull. Methyl or *p*-nitrophenyl isocyanide did not react under the same conditions, while reaction of $(Me_2S)AgNO_3$ with methyl isocyanide gave an insoluble compound which analyzed as $(MeNC)_2(AgCl)_5$ and which was not further investigated.

**(*n*-Propoxy)(*N*-*p*-tolylimino)methylsilver(I) Trimer (VI).** To a stirred 1-propanol (30 ml) suspension of compound II (405 mg, 1.55 mmol), *p*-tolyl isocyanide (0.21 ml, 1.6 mmol) and, later, potassium hydroxide in 1-propanol (15.8 ml, 5.5 g/l., 1.55 mmol) were added. A brownish precipitate was filtered and extracted with chloroform (30 ml). 1-Propanol (30 ml) was added and the solution was concentrated to yield a white solid (ca. 200 mg), soluble in chloroform and dichloromethane and insoluble in acetone and acetonitrile. Molecular weight: found, 882 (cryoscopy in 3.45% w/w benzene solution), 864 (vapor-phase osmometry, chloroform solution); required, 851.4.

Compounds IV and V were prepared analogously. The methoxy derivative, IV, was insoluble and the ethoxy derivative, V, was sparingly soluble in $CHCl_3$ and $C_6H_6$. For this reason and for the rather limited stability of the solution, no molecular weight determination was carried out for these two compounds.

Table I. Analytical Data

| No. | Compd[a] | Mp, °C | % C | | % H | | % N | |
|---|---|---|---|---|---|---|---|---|
| | | | Calcd | Found | Calcd | Found | Calcd | Found |
| II | $(ArNC)AgCl$ | 153–156 dec | 36.9 | 37.5 | 2.69 | 2.71 | 5.38 | 5.27 |
| III | $(C_6H_{11}NC)AgCl$ | 93–95 | 33.3 | 32.93 | 4.36 | 4.23 | 5.54 | 5.47 |
| IV | $(CH_3O)(ArN{=})CAg$ | 129–130 dec | 42.20 | 41.5 | 3.91 | 3.54 | 5.47 | 5.32 |
| V | $(C_2H_5O)(ArN{=})CAg$ | >60 dec | 44.5 | 45.42 | 4.45 | 4.32 | 5.19 | 5.17 |
| VI | $(n\text{-}C_3H_7O)(ArN{=})CAg$ | >60 dec | 46.50 | 46.40 | 4.92 | 5.00 | 4.92 | 4.92 |
| VII | $(n\text{-}C_4H_9O)(ArN{=})CAg$ | >60 dec | 48.32 | 47.77 | 5.37 | 4.93 | 4.69 | 4.44 |
| VIII | $(CH_3O)(C_6H_{11}N{=})CAg$ | >100 dec | 38.70 | 36.90[b] | 5.65 | 5.00 | 5.65 | 5.30 |
| X | $(C_2H_5O)(ArN{=})CAu$ | | 33.4 | 32.93 | 3.34 | 3.27 | 3.90 | 3.60 |
| XI | $(C_2H_5O)(ArN{=})CPtCl[P(C_6H_5)_3]_2$ | 201–202 | 60.20 | 59.50 | 4.58 | 4.38 | 1.53 | 1.49 |
| XII | $[(C_6H_5)_3Sn]_2O$ | 119–120 | 60.40 | 59.90 | 4.19 | 3.80 | | |
| XIII | $[(C_2H_5O)(ArN{=})C]_2Hg$ | 134–136 | 45.70 | 46.18 | 4.57 | 4.43 | 5.37 | 5.20 |
| XIV | $(C_6H_5)_3PAgCl$ | 284–286 | 53.30 | 53.61 | 3.70 | 3.38 | | |
| XV | $(C_2H_5O)(ArN{=})CHgCl$ | 118–120 | 30.10 | 30.50 | 3.01 | 2.83 | 3.51 | 3.33 |
| | | | | 30.70 | | 2.81 | | 3.34 |

[a] Ar is $4\text{-}CH_3C_6H_4$. [b] See Experimental Section.

Table II. NMR Data[a]

| Compd | Alkoxy group[b] | Aromatic[c] | $p\text{-}CH_3$[d] |
|---|---|---|---|
| V[e] | 8.8 t, 5.87 d | 2.6–3.2 | 7.70 |
| VI[e] | 9.2 t, 8.49 q, 6.0 t | 2.6–3.2 | 7.72 |
| VII | 9.3–8.3 m, 5.94 t | 2.6–3.15 | 7.69 |
| XIII | 8.72 t, 5.91 q | ~3.42 | 7.66 |

[a] $CDCl_3$ solution; Varian NEVA instrument operating at 60 MHz. [b] *J* was ca. 7 Hz; d = doublet, t = triplet, q = quartet, m = multiplet. [c] Always complex. [d] Always singlet. [e] Spectrum recorded at ca. 10°.

Compound V did not react with benzyl chloride, or with 2,4-dinitrochlorobenzene, in chloroform solution at room temperature. Addition of hydrogen chloride in dichloromethane gave a white precipitate, *p*-toluidine hydrochloride. No product could be isolated by reaction of compound V with $(Ph_3P)_2NiCl_2$ or $(Ph_3P)_2CoCl_2$ in chloroform solution.

**(*n*-Butoxy)(*N*-*p*-tolylimino)methylsilver(I) Trimer (VII).** To a stirred suspension of compound I (405 mg, 1.75 mmol) in 1-butanol (20 ml) *p*-tolyl isocyanide (0.24 ml, 1.8 mmol) and then potassium hydroxide (13 ml, 7.69 g/l., 1.8 mmol) in the same solvent were added. The crude brown precipitate was filtered at once and extracted with chloroform (30 ml). On adding 1-butanol to the extract a yellowish solid was obtained which was purified from chloroform–1-butanol, yielding the analytical sample (ca. 250 mg), white. On heating, decomposition was evident from ca. 60°; it is soluble in benzene, chloroform, and dichloromethane. Molecular weight: found, 909 (cryoscopy in 2.65% w/w benzene solution); required, 893.4. The analogous compounds with the ethoxy (V) and *n*-propoxy groups (VI) in place of the *n*-butoxy groups and compound VIII were prepared similarly. The pure compounds are white and their solubility, e.g., in $CHCl_3$, decreases with a decreasing number of carbon atoms in the alkoxy group. Analytical data for compound VIII are not fully satisfactory, because it could not be purified; its formula is assigned by analogy and ir evidence.

**(Triphenylphosphine)(ethoxy)(*N*-*p*-tolylimino)methylgold(I) (IX).** A chloroform solution of triphenylphosphinechlorogold(I) (292 mg, 0.59 mmol) and of compound IV (159 mg, 0.59 mmol) was mixed; silver chloride was filtered away; the solution was evaporated to dryness; the residue was purified twice by dissolving it in diethyl ether (30 ml) and precipitating with petroleum ether (30 ml). The conpound was identified by comparison of its melting point and ir spectrum with those of an authentic sample, prepared[12] independently.

**(Ethoxy)(*N*-*p*-tolylimino)methylgold(I) Trimer (X).** A chloroform solution of (cyclohexyl isocyanide)chlorogold(I) (170 mg, 0.50 mmol) and of compound IV (135 mg, 0.50 mmol) was mixed. Silver chloride was filtered away, the solution was evaporated to dryness, and the oily residue was crystallized from $Et_2O$–petroleum ether (1:1). The silver-free compound was identified by comparison of its ir spectrum with that of a sample prepared according to a general method[12] from (dimethyl sulfide)chlorogold, *p*-tolyl isocyanide, and potassium hydroxide in ethanol.

**Bis(triphenylphosphine)(ethoxy)(*N*-*p*-tolylimino)methylchloroplatinum(II) (XI).** A chloroform solution of *cis*-bis(triphenylphosphine)dichloroplatinum(II) (345 mg, 0.44 mmol) was mixed with a chloroform solution of compound IV (135 mg, 0.50 mmol). After filtering away of the silver chloride, the solution was evaporated to dryness; the orange residue was dissolved in dichloromethane, charcoal was added, and the mixture was stirred 15 hr. To the filtered solution an equal volume of ethanol was added and the whitish precipitate was purified again in the same way, affording the analytical sample.

**Bis(triphenyltin) Oxide (XII).** Triphenylchlorotin(IV) (192 mg, 0.50 mmol) and compound IV (135 mg, 0.50 mmol) were dissolved in chloroform and the solutions were mixed. On concentration of the filtered solution to a small volume, compound XII was obtained (50 mg) and identified through analysis and melting point (lit. mp 122–123°). No attempt was carried out in strictly anhydrous conditions.

**Bis[(ethoxy)(*N*-*p*-tolylimino)methyl]mercury(II) (XIII).** A chloroform solution of compound IV (335 mg, 1.24 mmol) and bis(triphenylphosphine)dichloromercury(II) (500 mg, 0.62 mmol) in the same solvent was mixed. The now turbid solution was evaporated to dryness and the residue was extracted with diethyl ether (three 50-ml portions). The ethereal extract was concentrated to a few milliliters affording crude XIII (200 mg, 61%). It was purified again from diethyl ether to yield the chlorine-free analytical sample, soluble in acetone and chloroform and sparingly soluble in ethanol. The residue (300 mg) left after extraction with diethyl ether was crystallized from pyridine–petroleum ether, affording the mercury-free compound XIV, identified through analytical and spectral data.

Compound XIII was not obtained when mercury(II) chloride replaced its bis(triphenylphosphine) complex.

**(Ethoxy)(*N*-*p*-tolylimino)methyl(chloro)mercury(II) (XV).** (A) Compound XIII (333 mg, 0.64 mmol) was dissolved in ether, and mercury(II) chloride (172 mg, 0.64 mmol) in the same solvent was added. Upon concentration a white precipitate was obtained (ca. 350 mg, 69%), which gave the analytical sample (270 mg) on concentration from a diethyl ether solution (500 ml).

In a similar attempt di-*p*-tolylmercury(II) was used in place of mercury(II) chloride, but no mixed mercury derivative was obtained.

(B) Compound V (500 mg, 1.85 mmol) and mercury(II) chloride (502 mg, 1.85 mmol) were stirred in a diethyl ether (60 ml) suspension. After 0.5 hr, the white solid was filtered and extracted with ether (four 100-ml portions). The solution was concentrated to small volume, affording a white solid (300 mg, 41%) which was crystallized by concentrating its acetone solution.

## Results and Discussion

**Isocyanide Complexes.** Prior to this work only three isocyanide complexes of silver had been described, namely,[14,15] $[L_4Ag]ClO_4$, $[L_4Ag]NO_3 \cdot H_2O$, and $[L_2Ag]NO_3$ ($L = p\text{-}MeC_6H_4NC$). Although other compounds are intermediate[2] in the preparation of isocyanides from silver(I) cyanide and alkyl halide, they have not been characterized.

The compounds LAgCl, where L is $p\text{-}MeC_6H_4NC$ (II) or cyclohexyl isocyanide (III), are easily obtained from silver chloride and a chloroform solution of the isocyanide. A 100% excess of the ligand is necessary to obtain a chloroform-soluble intermediate product; however, on adding hydrocarbons, the solution affords a precipitate which is insoluble in all the

Table III. Comparison of $\nu$(C≡N) Values for Homogeneous Series of Complexes

| Compd | $\nu$(CN), cm$^{-1}$ | Ref |
|---|---|---|
| $[(t\text{-BuNC})_4\text{Rh}]\text{PF}_6$ | 2165 | *a* |
| $[(t\text{-BuNC})_4\text{Ir}]\text{PF}_6$ | 2170 | *a* |
| $[(\text{MeNC})_6\text{Fe}]^{2+}$ | 2234 | *b* |
| $[(\text{MeNC})_6\text{Ru}]^{2+}$ | 2241 | *c* |
| *fac*-$(t\text{-BuNC})_3\text{Cr(CO)}_3$ | 2154, 2112 | *d, h* |
| *fac*-$(t\text{-BuNC})_3\text{Mo(CO)}_3$ | 2155, 2117 | *d, h* |
| *fac*-$(t\text{-BuNC})_3\text{W(CO)}_3$ | 2161, 2114 | *d, h* |
| $(\text{MeNC})\text{Cr(CO)}_5$ | 2173 | *e, i* |
| $(\text{MeNC})\text{Mo(CO)}_5$ | 2173 | *e, i* |
| $(\text{MeNC})\text{W(CO)}_5$ | 2177 | *e, i* |
| *cis*-$(\text{PhNC})_2\text{PdCl}_2$ | 2237, 2222 | *f* |
| *cis*-$(p\text{-MeC}_6\text{H}_4\text{NC})_2\text{PtCl}_2$ | 2254, 2216 | *g* |

[a] J. W. Dart, M. K. Lloyd, R. Mason, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 2039 (1973). [b] G. Fabbri and F. Cappellina, *Ann. Chim. (Rome)*, 48, 909 (1958). [c] D. J. Doonan and A. L. Balch, *Inorg. Chem.*, 13, 921 (1974). [d] R. B. King and M. S. Saran, *ibid.*, 13, 74 (1974). [e] B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, 95, 7517 (1973). [f] F. Canziani, F. Cariati, and U. Sartorelli, *Rend., Ist. Lomb. Accad. Sci. Lett. A*, 98, 564 (1964). [g] F. Bonati and G. Minghetti, *J. Organomet. Chem.*, 24, 251 (1970). [h] Only slight changes of $\nu$(CO) (cm$^{-1}$): 1934, 1861 (Cr); 1946, 1860 (Mo); 1932, 1856 (W). [i] Only slight changes of $\nu$(CO) (cm$^{-1}$): 2068, 1958 (Cr); 2071, 1960 (Mo); 2069, 1956 (W).

Table IV. Comparison of the $\nu$(C≡N) Frequencies of the Known Types of Isocyanide Complexes of Group 1B Metals

| L | M | LMCl | $[\text{L}_2\text{M}]^+$ | $[\text{L}_4\text{M}]^+$ |
|---|---|---|---|---|
| $p\text{-MeC}_6\text{H}_4\text{NC}$ | Ag | 2160[a] | 2195[b] | 2177, 2186 sh[b] |
| $p\text{-MeC}_6\text{H}_4\text{NC}$ | Au | 2220[c] | 2225[c] | |
| $p\text{-MeOC}_6\text{H}_4\text{NC}$ | Cu | 2155[e] | *d, e* | 2169, 2144 sh[e] |
| $p\text{-MeOC}_6\text{H}_4\text{NC}$ | Au | 2265[c] | | |
| $\text{C}_6\text{H}_{11}\text{NC}$ | Ag | 2180[a] | | |
| $\text{C}_6\text{H}_{11}\text{NC}$ | Au | 2241[a] | 2250, 2220 sh[c] | |
| $t$-BuNC | Au | 2250[f] | 2260, 2220 sh[f] | Not obtained[f] |

[a] This work. [b] Reference 15. [c] Reference 4. [d] $\text{L}_2\text{CuCl}$ is not a salt; $\nu$(CN) 2141 cm$^{-1}$. [e] J. Bailey and M. J. Mays, *J. Organomet. Chem.*, 47, 217 (1973). [f] Reference 10.

solvents tried and which analyzes as LAgCl. The intermediate, soluble product might possibly be $\text{L}_2\text{AgCl}$.

The infrared spectrum of the complexes obtained shows all the bands expected for the organic moiety. The coordinated isocyanide stretching frequency is found in a range (2160–2180 cm$^{-1}$) which is typical[2,3] for many other terminal isocyanide complexes of metals but which is surprisingly lower than in the corresponding gold(I) derivatives,[4] LAuCl, the difference amounting to ca. 60 cm$^{-1}$. On this point, it is evident from Table III that the difference between $\nu$(CN) of an $(\text{RNC})_m\text{L}_n\text{M}$ and of an $(\text{RNC})_m\text{L}_n\text{M}'$ complex is generally small provided that the two complexes are homologous and both M and M' belong to the same group in the periodic system. These observations on $\nu$(C≡N) can be correlated with other differences found between copper, or silver, and gold complexes (Table IV). Indeed, while the gold(I) compounds are monomeric, soluble, and two-coordinated, as evidenced by the presence of terminal $\nu$(C≡N) and $\nu$(Au—Cl), the analogous copper and silver compounds are insoluble and do not show any terminal $\nu$(M—Cl). Actually,[16] in $(\text{MeNCCuI})_4$ the copper atoms are four-coordinate through halide bridges. Therefore the silver derivatives are suggested to be polymeric and it can be safely assumed that the silver, or copper, and the gold compounds are homologous only formally.

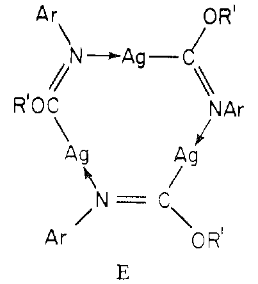
**(Alkoxy)(*N*-arylimino)methylsilver(I), (RO)(ArN═)CAg.** The reaction of the isocyanide complexes II and III, or of silver chloride and an isocyanide, with an alcohol or an amine did not yield any carbene complex, either A or B, according to the reaction pattern (1) or (2). These compounds were not obtained probably owing to the ready rearrangement of the carbene ligand, (RNH)(Y)C:, to the stable isomer, either an alkyl formamidate (RN═CHOR') when Y = OR' or a formamidine (RNHCH═NR') when Y = NHR'. While in the case of the stable gold(I) carbene complexes investigated previously[10,11,17] the rearrangement was found to require the preliminary displacement of the carbene by another ligand, e.g.[17]

$$[\{(\text{ArNH})_2\text{C}\}_2\text{Au}]^+ + \text{Ph}_3\text{P} = [(\text{ArNH})_2\text{CAuPPh}_3]^+ + \text{ArNHCH{=}NAr}$$

in the case of silver(I) the expected carbene complex is probably so unstable that no displacement is needed and the rearrangement is immediate. Indeed, silver chloride has been known[18] to catalyze the addition of alcohols or amines to isocyanides, a reaction which does not take place in the same conditions in the absence of a catalyst.

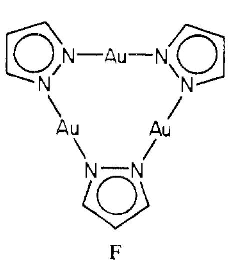
Although gold compounds of type C can be prepared in two steps through the carbene complexes of type A, in the case of silver a different approach must be used which takes advantage of the likely intermediate formation of A before the rearrangement of the organic ligand into a formimidate. Accordingly, addition of alcoholic potassium hydroxide to an alcoholic·suspension of (isocyanide)chlorosilver(I), in the presence of excess isocyanide, affords a precipitate from which (ArN═)(R'O)CAg compounds can be extracted and crystallized. Even the isolation of the isocyanide complexes of silver can be avoided: the same products can be obtained using another silver(I) complex, such as $\text{Me}_2\text{SAgNO}_3$, from which the sulfur ligand can readily be displaced.

The compounds obtained are white solids, sparingly soluble in the usual organic solvents, especially when the group R' is small; they are photosensitive (especially when impure) and generally decompose gradually on heating. Molecular weight determinations (see Experimental Section) indicate that they are trimers. According to the infrared evidence discussed below and by analogy with the formula proposed[12] and accepted[11] for the formally similar gold species C, the trimeric structure E is suggested which allows usual bond angles and coordination numbers to be accepted.

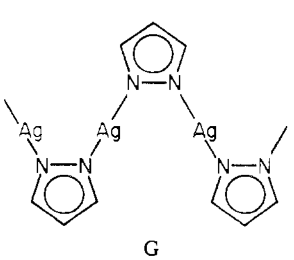


E

These trimeric silver derivatives are more heat and light sensitive than the corresponding gold compounds. This fact agrees with a trend of general stability of certain cyclic compounds (Au > Ag), a trend which can be observed in the aza homologs of the ring system existing in C, namely, in certain metal(I) pyrazolides. Indeed, a trimeric formula was reported[19] also for gold(I) pyrazolides, F, while different structures, e.g., G,[20] were suggested for the corresponding silver compounds.



F



G

The silver compounds IV–VIII (Table I) react with acids:

Table V. Comparison of $\nu$(C=N) Values in the Compounds Containing MC(OR)=NR′ Group(s)

| | Compd[a] | | | | | | |
|---|---|---|---|---|---|---|---|
| | IV–VII | VIII | X | XI | XIII | XV | XVI |
| $\nu$(C=N),[b] cm$^{-1}$ | 1500 | 1540 | 1500 | 1580 | 1600 | 1590,<br>1550 m | 1565 |

[a] See Table I for the numbering; XVI is $Ph_3PAuC(OMe)=NC_6H_4Me$. [b] Nujol mull; all bands are strong unless stated otherwise.

with hydrogen chloride in dichloromethane, silver chloride and $ArNH_3^+Cl^-$ are obtained, while noncoordinating acids (picric or fluoroboric acid) do not yield carbene complexes of type A, as found in the case of gold according to reaction 6.

The compounds do not react with certain organic halides which are generally considered to be reactive, such as benzyl chloride or 2,4-dinitrochlorobenzene. We were unable to isolate any exchange product upon reaction with certain triphenylphosphine complexes such as $(Ph_3P)_2MCl_2$ (M = Co, Ni), while other derivatives react yielding molecules containing a MC(OR′)(=NAr) moiety, here abbreviated as MY, i.e.

$$3Ph_3PAuCl + [AgY]_3 = 3Ph_3PAgCl + [AuY]_3$$

$$C_6H_{11}NCAuCl + [AgY]_3 \rightarrow [AuY]_3$$

$$3\mathit{cis}\text{-}(Ph_3P)_2PtCl_2 + [AgY]_3 = 3AgCl + 3(Ph_3P)_2PtYCl$$

$$3(Ph_3P)_2HgCl_2 + 2[AgY]_3 = 6Ph_3PAgCl + 3HgY_2$$

$$3HgCl_2 + [AgY]_3 = 3AgCl + 3ClHgY$$

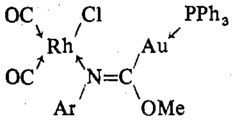
$$HgY_2 + HgX_2 = 2YHgX$$

The last reaction is typical of nearly all the organic derivatives of mercury.

In the case of triphenylchlorotin(IV) a reaction occurred, silver chloride being formed, but $(Ph_3Sn)_2O$ was isolated in place of the expected $Ph_3SnY$, as if the latter compound had undergone hydrolysis.

All the organic compounds of gold, platinum, and mercury thus obtained are white solids and are more stable than the silver-containing parent compounds. They were identified by elemental analyses, by spectral data, and, in the case of gold derivatives, by comparison with samples prepared by an independent route.[12]

The infrared spectra of the compounds containing the >C=N– group show strong and rather broad bands between 1500 and 1600 cm$^{-1}$ (Table V). All the compounds where the lone pair of electrons belonging to the nitrogen atom are not engaged in a donor bond show $\nu$(C=N) in the higher part of the said range: this is observed with compounds **XI**, **XIII**, **XV**, and **XVI**, which are Pt, Hg, Hg, and Au derivatives, respectively. When the nitrogen atom is engaged in a donor bond, $\nu$(C=N) is found in the lower part of the said range: this is the case of compounds for which structure E is suggested (i.e., IV–VIII), where the >C=N– group bridges two identical metal atoms, or of other compounds, where the same group bridges two different metal atoms, e.g.[21]



$\nu$(C=N) 1515 cm$^{-1}$

The last type of complexes obtained, thanks to the donor character of the nitrogen atom of the MC(OR)=NR′ group, is the object of further investigation.

The compounds reported here (IV–VIII), X, XI, XIII, and XV) constitute a new class of stable and synthetically useful $\sigma$-bonded derivatives of metals.

**Registry No.** II, 41676-86-2; III, 55145-55-6; IV, 41676-87-3; V, 41676-88-4; VI, 41676-89-5; VII, 55145-56-7; VIII, 55145-57-8; IX, 37131-39-8; X, 55145-58-9; XI, 41685-45-4; XIII, 41422-37-1; XIV, 52495-09-7; XV, 55145-54-5; XVI, 33637-36-4; $(Me_2S)AgNO_3$, 15171-27-4; 1-propanol, 71-23-8; 1-butanol, 71-36-3; triphenylphosphinechlorogold(I), 14243-64-2; (cyclohexyl isocyanide)chlorogold(I), 43067-26-1; *cis*-bis(triphenylphosphine)dichloroplatinum(II), 15604-36-1; bis(triphenylphosphine)dichloromercury(II), 14494-85-0; mercury(II) chloride, 7487-94-7.

## References and Notes

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