A ^{197}Au Mössbauer Study of a Series of Isocyanide, Carbene, or Methanide Derivatives of Gold. The Crystal Structure of *trans,trans*- and *cis,cis*-[(Carbene)$_2$Au]ClO$_4$ and of *cis,trans*-(Carbene)AuCl (Carbene = *p*-MeC$_6$H$_4$NHCOEt)

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^{197}Mössbauer spectra were recorded for a homogeneous series of two-coordinate organogold(I) and four-coordinate organogold(III) complexes: LAuCl, [L$_2$Au]$^+$ (where L may be Ar—NC or a carbene such as (Ar—NH)$_2$C or (Ar—NH)(EtO)C, Ar being *p*-tolyl), [L$_2$AuI$_2$]$^+$ (where L is a carbene), [(Ar—N=)(EtO)CAu]$_3$, and [(Ar—N=)(Ar—NH)C—Au]$_n$. The Mössbauer parameters are dominated by the σ donor properties of the ligands used; they are sensitive to the immediate environment of the gold atom and not to the geometrical isomerism found in the carbene derivatives investigated. Such isomerism, detected in solution by NMR, was confirmed by X-ray crystal structure determinations carried out on the trans,trans (**7tt**) and cis,cis (**7cc**) steric isomers of {[(*p*-MeC$_6$H$_4$NH)(EtO)C]$_2$Au}ClO$_4$ (**7**, C$_{20}$H$_{26}$N$_2$O$_6$ClAu) as well as on another isomer, (*cis,trans*-MeC$_6$H$_4$NH)(EtO)CAuCl (**5**, C$_{10}$H$_{13}$NOClAu (**5ct**)). Compounds **7tt**, **7cc**, and **5ct** crystallize in the triclinic system of space group $P\bar{1}$. **7tt**: a = 11.686 (3) Å, b = 11.257 (4) Å, c = 11.258 (4) Å, α = 112.5 (5)°, β = 102.5 (4)°, γ = 112.2 (6)°, Z = 2. **7cc**: a = 13.493 (5) Å, b = 9.283 (6) Å, c = 9.978 (5) Å, α = 94.0 (4)°, β = 107.4 (3)°, γ = 99.6 (3)°, Z = 2. **5ct**: a = 10.000 (3) Å, b = 12.953 (4) Å, c = 9.680 (3) Å, α = 90.9 (4)°, β = 108.0 (4)°, γ = 88.8 (3)°, Z = 4. Comparison between Mössbauer spectra, NMR spectra, and X-ray crystal structures reveals some limitation of the techniques employed when each alone is considered, while these together provide a satisfactory characterization and suggest that the amount of Au-C π bonding in our compounds is negligible.

Introduction

During the recent years the chemistry of gold has been extensively investigated.[1,2] In addition to intrinsic scientific interest, the relevance of this field is due to the several uses of certain compounds, for example, as pharmaceutical products[3] or catalysts,[4] as well as to some theoretical aspects of the bonding.[5] As a result, several reviews[6,7] and a monograph[8] on parts of the subject have become available.

Although the ^{197}Au Mössbauer spectroscopy has some disadvantages such as the short half-life of the ^{197}Pt isotope and the low recoil-free fraction, it has been increasingly used in studies of the nature of bonding and of the structures of gold compounds. The available results were summarized in reviews[7-9] to which some more recent papers[10-12] should be added to obtain a panorama of the use of Mössbauer spectroscopy in the chemistry of gold.

Since we have obtained and characterized several sets of new types of gold compounds,[13-18] it seemed interesting to study a homogeneous series of these molecules by Mössbauer spectroscopy, X-ray diffraction, and carbon-13

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Table I. Isomer Shifts (IS), Electric Quadrupole Splittings (QS), and Average Full Line Width at Half-Maximum (*W*) Derived from Mössbauer Spectra at 4.2 K

	IS^{b,c}	QS^{c}	*W*^{c}
1 (ArNCAuCl)	2.00 (1)	7.61 (1)	1.90 (3)
2 [(ArNC)$_2$Au]ClO$_4$	2.65 (3)	9.51 (3)	1.93 (8)
3 [(ArNC)$_2$Au]BF$_4$	2.77 (3)	9.33 (3)	1.90 (1)
4 {[(ArNH)$_2$C]AuCl}	3.00 (1)	7.62 (1)	1.94 (1)
5 {[(ArNH)(EtO)C]AuCl}	2.90 (1)	7.36 (1)	1.97 (2)
6 {[(ArNH)$_2$C]$_2$Au}BF$_4$	4.45 (1)	10.73 (1)	2.01 (2)
7 {[(ArNH)(EtO)C]$_2$Au}ClO$_4$	4.55 (2)	10.61 (2)	1.95 (3)
8 [(ArN=)(EtO)CAu]$_3$	3.90 (1)	8.28 (1)	2.14 (1)
9 [(ArN=)(ArNH)CAu]$_x$	4.05 (1)	8.88 (1)	2.11 (2)
10 {[(ArNH)$_2$C]$_2$AuI$_2$}BF$_4$·$^3/_4$Et$_2$O	2.96 (1)	6.44 (1)	1.96 (2)
11 {[(ArNH)(EtO)C]$_2$AuI$_2$}ClO$_4$·$^1/_4$Et$_2$O	3.22 (1)	6.61 (1)	1.94 (1)

[a] Ar = p-MeC$_6$H$_4$. [b] With respect to ^{197}Au(Pt) source. [c] In mm/s.

NMR spectra. The ligands vary from an isocyanide to the corresponding substituted carbene (Ar—NH)(X)C: and then to the methanide group (Ar—N=)(X)C$^-$, where Ar is p-tolyl and X is either NH-Ar or EtO. The compounds investigated include both ionic, [L$_2$Au]$^+$, and covalent species, LAuCl, and mononuclear and polynuclear complexes such as [(Ar—N=)(X)CAu]$_n$. Previous investigations were concerned with only a few covalent isocyanide derivatives such as (RNC)AuCl where R is phenyl, p-anisyl, or cyclohexyl and one carbene complex, (MeOC$_6$H$_4$NH)$_2$CAuCl.[19]

Experimental Section

The compounds were prepared as already described,[13-18] and their identity was checked through melting point determination, elemental analyses (C, H, N), and infrared and proton NMR spectra.

The ^{197}Pt activity feeding the 77.3 keV Mössbauer transition was produced by irradiation of the enriched ^{196}Pt metal. Both source and absorber were kept at 4.2 K; a sinusoidal velocity waveform and an intrinsic Ge detector were used. The reported shifts are given with respect to the Au(Pt) source. The isomer shift data taken from the literature were converted to this scale by using the value given in the ref 20. Depending upon the compound, absorbers with a ^{197}Au content of 50–200 mg/cm^2 were used. A typical Mössbauer spectrum is shown in Figure 1 while the Mössbauer parameters are listed in the table 1.

The proton NMR spectra of the compounds here reported were carried out for identification purposes only, and they agree with the spectra already published. Figure 2 shows a flow sheet of the preparation of the gold compounds investigated. The carbon-13 NMR spectra in Table II were obtained in deuteriochloroform solution with a Bruker 90 spectrometer.

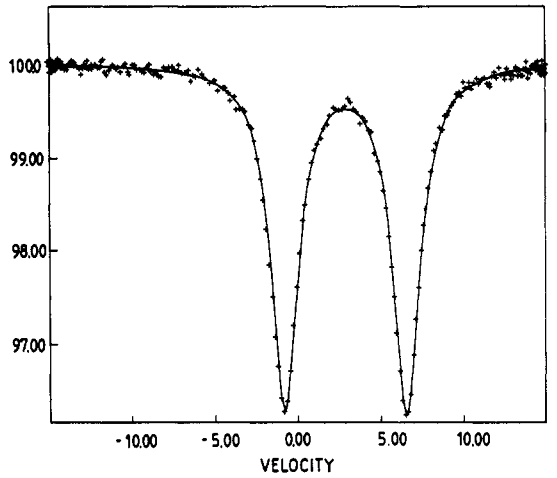

Figure 1. Mössbauer spectrum of (p-MeC$_6$H$_4$NH)(EtO)CAuCl.

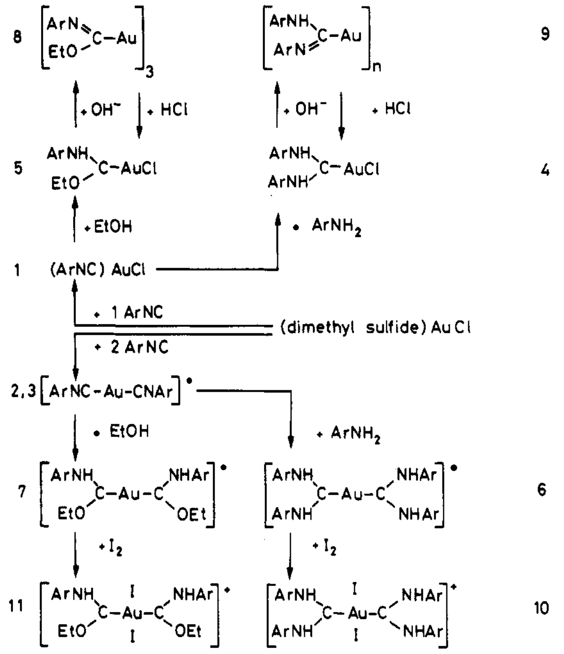

Figure 2. Flow sheet showing the preparation of the gold compounds investigated. The covalent compounds are in the upper part and the ionic ones in the lower part.

Crystallographic Analyses. The crystallographic data are listed in the Table III. Intensity data were collected in an air-conditioned room at 22 ± 1 °C on a four-circle Philips PW 1100 diffractometer with a graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) in the range $2 < \theta < 25°$ using the θ–2θ scan mode. Lorentz and polarization corrections were applied. The structures were solved by using three-dimensional Patterson and Fourier syntheses; least-squares refinements on F were

Table II. Carbon NMR Data^{a} (δ, J in Hz)

	ArNC	ArNC^{b}	ArNCAu-Cl	(ArNC)$_2$-Au$^+$	(ArNH)$_2$C-AuCl	(ArNH)-(EtO)-CAuCl	(ArNH)$_2$-CAu$^+$	[(ArNH)-(EtO)-C]$_2$Au$^+$	trimer	[(ArNH)-(EtO)-C]$_2$AuI$_2$$^+$
NC (^1J(NC))	163.8 (5.7)	165.1 (5.4)	121.9^{c} (15)	*d*	160.7,^{e} 159.1^{f}	205.8	203	220.0,^{e} 223.3^{f}	199.5	175.2
ipso-C (^1J(NC))	124.3 (13.4)	124.3 (13.4)	140.9^{c} (27)	*d*	139.0, 131.7^{g} 136.4	137.1^{g}	137.6^{g}	138.4,^{e,g} 137.5^{f,g} 137.7,^{e,g} 138.7^{f,g}	134.2	131.4 134.7
ortho-C	126.3	126.2	126.8	127.6	123.6, 125.9 123	122.8	123	122.9,^{e} 125.2^{f}	124.4	125.8 125.2
meta-C	130.2	130.1	130.6	130.6	129.7, 131.2 129.8	129.6	129.4	129.8,^{e} 130.0^{f}	128.9	130.0 131.2
para-C	139.9	139.7	142.6	143.3	136.9, 137.4^{g} 137.0	133.7^{g}	136.1^{g}	133.7,^{e,g} 133.9^{f,g}	144.6	139.5 137.2
para-CH$_3$	21.5	21.1	21.6	21.5	21.0^{e} 21.2^{f}	21.0	20.9	21.2	21.0	21.1 21.2
CH$_3$						15.1		15.5,^{e} 15.3^{f}	15.4	
CH$_2$						74.9		74.0,^{e} 73.2^{f}	69.3	

[a] CDCl$_3$ solution unless otherwise stated; Ar = p-MeC$_6$H$_4$. [b] CCl$_4$/CD$_3$CN/Me$_4$Si = 75:23:2.[21] [c] Very weak and broad. [d] Not detected; see text. [e] More intense set of signals. [f] Less intense set of signals. [g] These assignments can be exchanged.

Table III. Crystallographic Data

	{[*cis*,*trans*-(ArNH)(EtO)C]AuCl}	{[*trans*,*trans*-(ArNH)(EtO)C]$_2$Au}-ClO$_4$	{[*cis*,*cis*-(ArNH)(EtO)C]$_2$Au}$^+$
unit cell	triclinic	triclinic	triclinic
formula	$C_{10}H_{13}NOClAu$	$C_{20}H_{26}N_2O_6ClAu$	$C_{20}H_{26}N_2O_6ClAu$
fw, amu	395.6	622.9	622.9
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	10.000 (3)	11.686 (3)	13.493 (5)
b, Å	12.953 (4)	11.257 (4)	9.283 (6)
c, Å	9.680 (3)	11.258 (4)	9.978 (5)
α, deg	90.9 (4)	112.5 (5)	94.0 (4)
β, deg	108.0 (4)	102.5 (4)	107.4 (3)
γ, deg	88.8 (3)	112.2 (6)	99.6 (3)
V, Å^3	1192.2 (5)	1148.4 (6)	1165.8 (6)
Z	4	2	2
d_{calcd}, g/cm^3	2.20	1.80	1.77
cryst dimens, mm	0.25 × 0.25 × 0.30	0.30 × 0.30 × 0.20	0.30 × 0.20 × 0.40
no. of reflctns measd	5333	5159	4097
data used, $I > 3\sigma(I)$	2864	3524	3078
R	0.089	0.077	0.0818
μ cm^{-1}	108.1	56.5	55.6

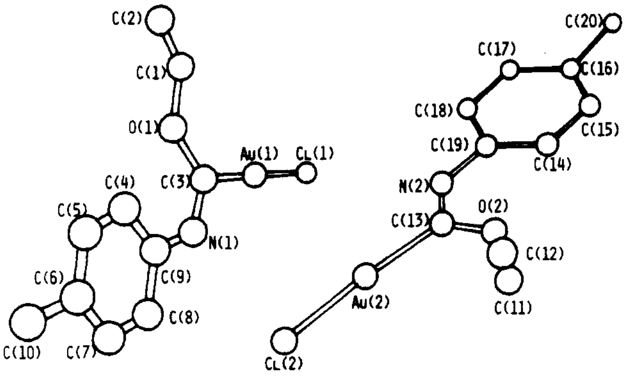

Figure 3. Diagram of the molecular structure of *cis*,*trans*-(*p*-MeC_6H_4NH)(EtO)CAuCl (**5ct**).

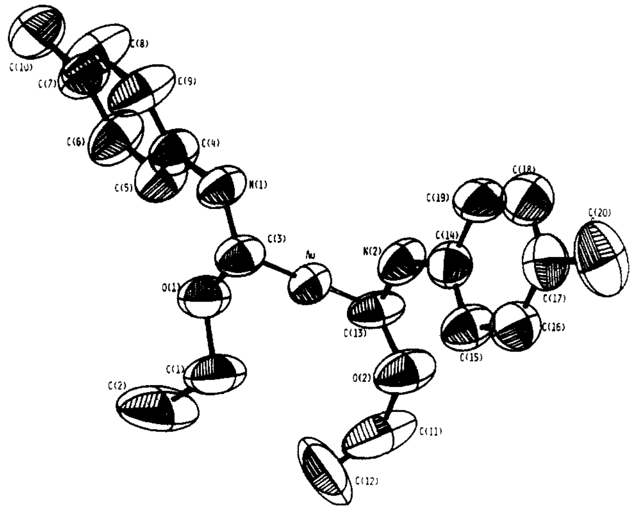

Figure 4. Ortep plot for [*cis*,*cis*-(*p*-MeC_6H_4NH)(EtO)C]$_2$Au$^+$ cation (**7cc**).

computed with an unitary weighting scheme. The non-hydrogen atoms of **5ct**, of the **7cc** cation, and the gold atoms of the **7tt** isomer were refined anisotropically and the others isotropically. The hydrogen atoms were calculated but not refined. The final atomic coordinates are reported in the Table IV and the bond distances and angles in Table V. The molecular diagrams for **5ct** and the Ortep plot for the **7cc** cation are reported in Figures 3 and 4, respectively, together with the atomic labeling scheme. Only the molecular diagram for the **7tt** isomer is reported in Figure 5 because its atoms (gold excepted) were refined isotropically.

The most significant data obtained from the AuCON and *p*-tolyl least-squares planes are reported in Table VI.

Results and Discussion

Crystal Structures. The X-ray crystal structures were carried out on **5ct**, the cis,trans isomer of compound 5 [(ArNH)(EtO)CAuCl], on **7tt**, and on **7cc**, respectively the trans,trans and the cis,cis isomers of compound 7 ([{(ArNH)(EtO)C}$_2$Au]ClO$_4$).

The structure of **5ct** (Figure 3) consists of covalent molecules with intermolecular Au···Au interactions and N···Cl at 3.327 (7) and 3.22 (1) Å. Coordination around the gold atoms is nearly linear, the Cl–Au–C bond angles being 171 (1)° and 175 (1)°; the gold–chlorine and gold–carbon bonds are 2.315 (9) or 2.38 (1) and 1.98 (3) or 2.04 (4) Å, respectively.

The structures of both isomers of compound 7 (cf. Figures 4 and 5) consist of bis(carbene) cations and perchlorate anions. The **7cc** isomer may be stabilized by the presence of two hydrogen bonds between the perchlorate oxygen and the carbene nitrogen atoms at 2.83 (1) and 2.97 (1) Å. The presence of hydrogen bonding coincides with a very weak intermolecular Au···Au interaction of 3.415 (2) Å in the **7cc** isomer against 5.60 (1) Å in the **7tt** species where only van der Waals forces are operating.

The different conformation of the **7tt** and of the **7cc** isomers is shown by the values of the dihedral angles reported in Table VI: the angle between the two Au,C,O,N

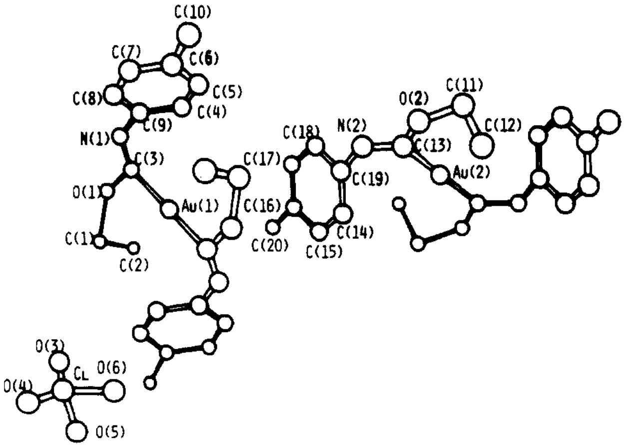

Figure 5. Diagram of the molecular structure of {[*trans*,-*trans*-(*p*-MeC_6H_4NH)(EtO)C]$_2$Au}ClO$_4$ (**7tt**).

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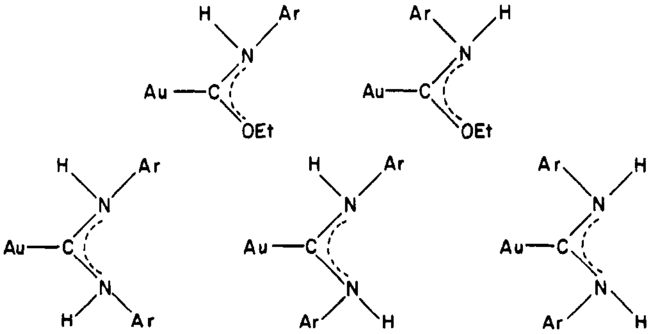
Table IV. Final Atomic Coordinates with Esd's in Parentheses

	{[*cis,trans*-(ArNH)(EtO)C]AuCl}			{[*trans,trans*-(ArNH)(EtO)C]$_2$Au}-ClO$_4$			{[*cis,cis*-(ArNH)(EtO)C]$_2$Au}ClO$_4$		
atom	*x*/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*
Au(1)	0.5888 (1)	0.6537 (1)	0.5576 (1)	0.5000	1.0000	0.5000^a	0.4198 (1)	0.1190 (1)	1.0183 (1)
Cl(1)	0.5135 (9)	0.6486 (8)	0.3062 (9)						
O(1)	0.573 (3)	0.625 (3)	0.856 (3)	0.742 (2)	0.952 (2)	0.516 (2)	0.248 (1)	−0.119 (2)	1.048 (1)
N(1)	0.790 (2)	0.652 (2)	0.848 (3)	0.539 (2)	0.735 (2)	0.388 (2)	0.227 (1)	−0.074 (2)	0.829 (2)
C(1)	0.424 (4)	0.619 (5)	0.791 (4)	0.832 (6)	1.133 (6)	0.628 (6)	0.303 (2)	−0.082 (4)	1.203 (2)
C(2)	0.352 (4)	0.630 (7)	0.882 (7)	0.968 (7)	1.162 (8)	0.616 (8)	0.229 (4)	−0.161 (5)	1.273 (3)
C(3)	0.659 (3)	0.645 (3)	0.772 (3)	0.597 (4)	0.883 (4)	0.466 (4)	0.289 (2)	−0.042 (2)	0.965 (2)
C(4)	0.813 (3)	0.634 (3)	1.108 (3)	0.311 (2)	0.634 (2)	0.397 (1)	0.062 (1)	−0.145 (1)	0.640 (1)
C(5)	0.904 (3)	0.610 (3)	1.245 (4)	0.169 (2)	0.542 (2)	0.325 (1)	−0.031 (1)	−0.245 (1)	0.565 (2)
C(6)	1.043 (3)	0.599 (3)	1.274 (3)	0.108 (2)	0.453 (2)	0.180 (1)	−0.054 (1)	−0.381 (1)	0.613 (2)
C(7)	1.101 (3)	0.615 (3)	1.154 (4)	0.187 (2)	0.457 (2)	0.102 (1)	0.016 (1)	−0.416 (1)	0.735 (2)
C(8)	1.009 (3)	0.628 (4)	1.019 (4)	0.329 (2)	0.548 (2)	0.173 (1)	0.109 (1)	−0.316 (1)	0.809 (2)
C(9)	0.872 (3)	0.637 (3)	0.995 (4)	0.391 (2)	0.637 (2)	0.321 (1)	0.132 (1)	−0.180 (1)	0.762 (2)
C(10)	1.141 (4)	0.573 (3)	1.430 (3)	−0.041 (3)	0.355 (4)	0.089 (4)	−0.154 (2)	−0.495 (4)	0.528 (3)
Au(2)	0.7937 (2)	0.8396 (1)	0.5083 (2)	1.0000	1.0000	0.0^a			
Cl(2)	0.9706 (9)	0.739 (1)	0.652 (1)						
O(2)	0.659 (3)	1.031 (3)	0.370 (3)	1.233 (2)	1.221 (2)	0.290 (2)	0.619 (1)	0.326 (2)	1.192 (2)
N(2)	0.534 (4)	0.895 (3)	0.273 (3)	1.038 (2)	1.149 (2)	0.304 (2)	0.568 (1)	0.339 (2)	0.972 (2)
C(11)	0.792 (4)	1.091 (6)	0.462 (7)	1.333 (6)	1.260 (6)	0.214 (6)	0.604 (3)	0.251 (4)	1.319 (3)
C(12)	0.764 (6)	1.160 (7)	0.581 (9)	1.377 (6)	1.156 (7)	0.194 (6)	0.552 (3)	0.320 (6)	1.395 (5)
C(13)	0.646 (5)	0.922 (3)	0.354 (5)	1.089 (4)	1.125 (4)	0.203 (4)	0.545 (2)	0.281 (3)	1.068 (2)
C(14)	0.414 (5)	1.047 (3)	0.138 (6)	0.811 (2)	0.915 (2)	0.178 (2)	0.717 (1)	0.570 (1)	1.101 (2)
C(15)	0.304 (6)	1.086 (4)	0.025 (6)	0.670 (2)	0.845 (2)	0.131 (2)	0.797 (1)	0.683 (1)	1.097 (2)
C(16)	0.198 (5)	1.023 (4)	−0.057 (5)	0.608 (2)	0.930 (2)	0.157 (2)	0.813 (1)	0.709 (1)	0.968 (2)
C(17)	0.206 (5)	0.915 (4)	−0.024 (4)	0.687 (2)	1.086 (2)	0.229 (2)	0.749 (1)	0.621 (1)	0.843 (2)
C(18)	0.323 (5)	0.875 (3)	0.096 (5)	0.828 (2)	1.156 (2)	0.276 (2)	0.668 (1)	0.508 (1)	0.847 (2)
C(19)	0.428 (4)	0.942 (3)	0.173 (4)	0.890 (2)	1.070 (2)	0.291 (2)	0.652 (1)	0.482 (1)	0.976 (2)
C(20)	0.070 (4)	1.052 (4)	−0.176 (5)	0.460 (3)	0.864 (4)	0.098 (3)	0.905 (3)	0.933 (4)	0.960 (5)
Cl(2)				0.2515 (8)	0.4545 (9)	0.7049 (9)	0.3953 (5)	0.1805 (8)	0.5937 (6)
O(3)				0.323 (5)	0.429 (6)	0.611 (5)	0.326 (2)	0.207 (3)	0.449 (3)
O(4)				0.186 (7)	0.304 (7)	0.599 (7)	0.264 (2)	0.123 (3)	0.639 (2)
O(5)				0.231 (5)	0.434 (5)	0.826 (5)	0.414 (2)	0.326 (3)	0.682 (4)
O(6)				0.214 (7)	0.553 (8)	0.686 (7)	0.424 (3)	0.083 (4)	0.587 (3)

[a] Occupancy Parameter 0.5

planes I/II is 119.8° vs. 6.0° and the angle between the Au,C,O,N plane and the neighbor *p*-tolyl plane I/III (or II/IV) is 118.5° vs. 32.7° (or 116.7 vs. 19.4°).

Mononuclear Gold(I) Compounds. The Mössbauer parameters, isomer shifts, IS, electric quadrupole splittings, QS, and average full line width at half-maximum, *W*, are reported in Table I. All the line widths (except those of the polynuclear compounds **8** and **9**) are close to the observed minimum of 1.87 (3) mm/s. The spectrum of each compound consists of a quadrupole-split doublet, indicating the presence of only one distinguishable good site in the mononuclear compounds even if, in the case of the carbene complexes, different isomers



are known to be present in the sample used. The isomers were detected independently in solution by proton or by carbon-13 NMR spectra (Table II) in the samples of compound **4** or **7** actually used in this work for Mössbauer measurements. It is interesting to note that the crystal structures of **7tt** and **7cc**, both being isomers of the compound **7**, were resolved by using different crystals obtained from the same solution of the analytical sample after recording proton and carbon-13 NMR spectra. In the case of compound **5**, where both isomers were isolated by fractional crystallization,[13] suitable crystals for X-ray structure determination were available only for the **5ct** isomer.

The geometrical isomers of the same carbene complex exhibited indistinguishable Mössbauer parameters because the Mössbauer effect is generally the result of a short-range interaction and, therefore, is not sensitive to a type of geometric isomerism which takes place at a significant distance from the gold nucleus: three atoms away in our case. By comparison, carbon-13 NMR spectra are more sensitive to changes in fairly remote environments, so that isomerism is detected even when Mössbauer spectra are blind to it. But even the high sensitivity of carbon-13 NMR spectroscopy may be insufficient for routine characterization of certain organogold compounds. For example, in the case of compounds **1**–**3** the signals of the isocyano carbon and of the ipso-carbon nuclei could not be detected with certainty or even found. In addition, the same signals could not be found in the spectrum of (*p*-anisyl isocyanide)chlorogold(I), another known compound, and they are the weakest in the spectrum of *p*-tolyl isocyanide, both in deuteriochloroform or in a solvent mixture.[21]

Relevant IS and QS literature data are plotted in Figure 6 for a series of covalent, two-coordinate gold(I) compounds of the type (ligand)AuCl. It can be seen that a widely spread cluster is formed by the compounds where the C-donating ligand contains a carbon in the formal oxida-

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Table V. Significant Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses

	5ct	7tt	7cc
	Bond Distances		
Au(1) - Cl(1)	2.315 (9)		
Au(2) - Cl(2)	2.283 (10)		
Au(1) - C(3)	1.98 (3)	2.03 (3)	2.02 (2)
Au(2) - C(13)	2.04 (4)	1.92 (3)	1.97 (2)
O(1) - C(3)	1.37 (4)	1.43 (3)	1.31 (3)
O(2) - C(13)	1.43 (5)	1.43 (3)	1.32 (2)
O(1) - C(1)	1.43 (5)	1.64 (4)	1.49 (3)
O(2) - C(11)	1.56 (6)	1.62 (5)	1.55 (4)
C(1) - C(2)	1.30 (8)	1.54 (6)	1.51 (6)
C(11) - C(12)	1.54 (11)	1.41 (5)	1.37 (7)
N(1) - C(3)	1.29 (3)	1.33 (3)	1.34 (2)
N(2) - C(13)	1.21 (5)	1.39 (3)	1.32 (3)
C(6) - C(10)	1.56 (4)	1.48 (3)	1.54 (30)
C(16) - C(20)	1.48 (6)	1.46 (3)	1.57 (4)
N(1) - C(9)	1.42 (4)	1.46 (2)	1.43 (2)
N(2) - C(19)	1.34 (5)	1.45 (2)	1.45 (2)
Cl(2) - O(3)		1.49 (5)	1.43 (3)
Cl(2) - O(4)		1.39 (6)	1.46 (3)
Cl(2) - O(5)		1.52 (5)	1.51 (3)
Cl(2) - O(6)		1.40 (7)	1.41 (4)
	Bond Angles		
Cl(1)-Au(1)-C(3)	175 (1)		
Cl(2)-Au(2)-C(13)	171 (1)		
C(3)-Au(1)-C(13)			178 (1)
Au(1)-C(3)-O(1)	123 (2)	123 (2)	129 (1)
Au(2)-C(13)-O(2)	114 (3)	128 (2)	129 (2)
N(1)-C(3)-O(1)	113 (3)	110 (3)	111 (2)
N(2)-C(13)-O(2)	114 (4)	101 (3)	109 (2)
C(1)-O(1)-C(3)	121 (3)	117 (3)	116 (2)
C(11)-O(2)-C(13)	126 (3)	118 (3)	116 (2)
O(1)-C(1)-C(2)	115 (3)	98 (4)	105 (2)
O(2)-C(11)-C(12)	113 (4)	103 (4)	115 (3)
C(3)-N(1)-C(9)	136 (3)	122 (2)	131 (2)
C(13)-N(2)-C(19)	134 (4)	116 (2)	134 (2)
N(1)-C(9)-C(4)	123 (2)	123.1 (9)	123 (1)
N(2)-C(19)-C(14)	128 (4)	122.0 (9)	117 (1)
N(1)-C(9)-C(8)	115 (3)	116.9 (9)	117 (1)
N(2)-C(19)-C(18)	113 (4)	118.0 (9)	123 (2)
C(5)-C(6)-C(10)	122 (3)	125 (1)	120 (2)
C(15)-C(16)-C(20)	129 (5)	122 (1)	118 (2)
C(7)-C(6)-C(10)	121 (3)	115 (1)	120 (2)
C(17)-C(16)-C(20)	113 (4)	117 (1)	121 (2)
O(3)-Cl(2)-O(4)		68 (3)	113 (1)
O(3)-Cl(2)-O(5)		141 (3)	107 (2)
O(3)-Cl(2)-O(6)		104 (3)	98 (2)
O(4)-Cl(2)-O(5)		99 (3)	109 (2)
O(4)-Cl(2)-O(6)		122 (4)	116 (2)
O(5)-Cl(2)-O(6)		114 (3)	112 (2)

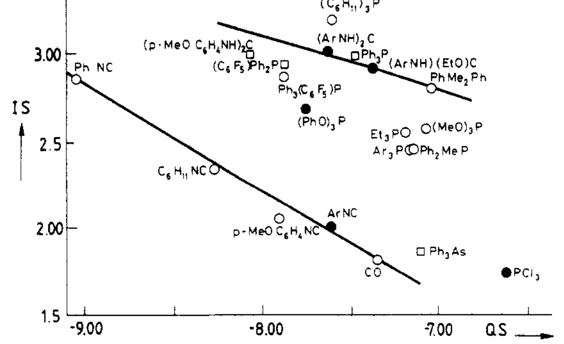

Figure 6. Mössbauer data for covalent LAuCl compounds. The ligand L as reported Ar is *p*-tolyl: ○, from ref 7 or 19, ●, from Table I, and □, from ref 19.

Table VI. Orthogonalized Least-Squares Planes, Dihedral Angles (deg), and Individual Deviations (Å) for the Isomers Reported in This Paper

plane no.	atoms defining the plane
I	Au(1), C(3), O(1), N(1)
II	Au(2), C(13), O(2), N(2)
III	C(4), C(5), C(6), C(7), C(8), C(9), C(10)
IV	C(14), C(15), C(16), C(17), C(18), C(19), C(20)

	dihedral angles		
	cis, trans	trans,trans	cis,cis
I-II	75.8	119.8	6.0
I-III	14.3	118.5	32.7
I-IV	70.7	3.5	14.3
II-III	81.3	1.9	26.6
II-IV	5.1	116.7	19.4
III-IV	76.5	115.4	44.7

	individual deviations		
	cis,trans	trans,trans	cis,cis
	Plane I		
Au(1)	-0.004	-0.008	0.008
O(1)	-0.005	-0.010	0.011
C(1)	0.068	0.183	0.111
C(2)	0.424	-0.327	0.433
C(3)	0.015	0.029	-0.029
C(4)	0.021	0.993	-0.660
N(1)	-0.006	-0.011	0.010
C(10)	-0.901	-0.459	-0.098
	Plane II		
Au(2)	0.018	0.001	
O(2)	0.021	0.001	-0.007
C(11)	-0.152	0.367	0.067
C(12)	1.109	-0.899	1.327
C(13)	-0.069	-0.001	0.017
C(14)	-0.085	-0.983	0.382
N(2)	0.030	0.001	-0.006
C(20)	-0.141	0.421	-0.184

tion state of +2, namely, isocyanides, carbenes or carbon monoxide. This region overlaps largely with that occupied by the (tertiary phosphine)chlorogold(I) and by the (tertiary arsine)chlorogold(I) species, in agreement with the soft character of all these ligands, which are bonded to the gold(I) atom through P, As, or one carbon donor atom. This qualitative trend is in agreement with the absence of a relevant π bonding interaction in these isocyanide, carbene, or carbon monoxide complexes of gold(I). Independent confirmation of the absence of a significant amount of π bonding comes from the X-ray crystal structure[22] determination carried out on {[(*trans,trans*-MeC$_6$H$_4$NH)$_2$C]$_2$Au}BF$_4$ (6), where the Au-C distance, 2.02 (1) Å, is typical of a single bond. The same absence is also evidenced by the Au-C bond lengths in the X-ray crystal structures here reported: 1.97 (2) and 2.02 (2) Å in **7cc**, 1.92 (3) and 2.03 (3) Å in **7tt**, and 1.98 (3) and 2.04 (4) Å in **5ct**.

The electrical field gradient (EFG) in Au(I) complexes arises from the 6p$_z$ rather than from the 5d$_{xz,yz}$ electron populations.[23,24] This determines a negative sign for the EFG as verified in the case of K[Au(CN)$_2$].[23] Since the quadrupole moment of the ^{197}Au nuclear ground state is positive, the sign of the electric quadrupole splitting is negative with—presumably—a vanishing asymmetric parameter for all the linear complexes 1-9 of Table I.

Upon complex formation the σ bonding involves electronic population of the unfilled 6s,6p hybrid orbitals of gold(I) from the ligands. Consequently the s-electron

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Table VII. Comparison of Experimental Quadrupole Splittings (in mm/s) with Values Predicted by the Partial Quadrupole Splitting Model

	QS^a	L^b	QS^c
1 [ArNCAuCl]	(–) 7.61 (1)		–7.20 (6)
2 [$(ArNC)_2Au]^+$	(–) 9.51 (3)	–2.38 (3)	
3 [$(ArNC)_2Au]^+$	(–) 9.33 (3)		–9.52 (6)
4 [$(ArNH)_2CAuCl$]	(–) 7.62 (1)		–7.20 (6)
5 [(ArNH)(EtO)CAuCl]	(–) 7.36 (1)		–7.74 (6)
6 {$[(ArNH)_2C]_2Au\}^+$	(–) 10.73 (1)		–10.60 (2)
7 {$[(ArNH)(EtO)C]_2Au\}^+$	(–) 10.61 (2)	–2.65 (1)	

^{a}Experimental value. A negative sign is assumed for V_{zz}.[24,25] ^{b}Derived pqs by using QS = 4[L] for $[L_2Au]^+$ complexes ($D_{\infty h}$ symmetry). ^{c}Calculated value by using QS = 4[L] or 2{[L_1] + [L_2]} for $[L_1L_2Au]^+$ complexes ($C_{\infty v}$ symmetry).

density at the gold nucleus increases. The isomer shift values increase on going from Ar–NC to (Ar–NH)(EtO)C and to $(Ar–NH)_2C$ in the LAuCl series while for the same ligand L, the isomer shift values are larger for the $[LAuL]^+$ than for the LAuCl complexes (Table I). Figure 6 shows that there is an approximately linear correlation between the IS and QS parameters for th[illegible]o LAuCl series: L = phenyl, *c*-hexyl, or *p*-anisyl iso[illegible]le and carbon monoxide in the lower part and [illegible] $(MeOC_6H_4NH)_2C$, $(MeC_6H_4NH)_2C$, and $(MeC_6H_4$[illegible]EtO)C in the upper part of the figure. Assuming that [illegible]oth series the binding properties of the fixed Cl ligand do not change appreciably and that, consequently, the changes in the Mössbauer parameters are mainly due to the L ligand, one concludes that the σ donor properties dominates both the IS and QS parameters. If one assumes a simple molecular orbital model in which the σ bonding is into the empty $6s,6p_z$ and π back-bonding from the filled $5d_{xz},5d_{yz}$ orbitals the two types of bonding influence the quadrupole splitting in opposite directions, such that QS becomes more positive with decreasing the $6p_z$ contribution and (or) with decreasing the $5d_{xz}$ contribution. The existence of the nearly linear correlations for the two groups of ligands thus indicates that within each group mainly σ bonding is responsible for the changes of IS and QS.

The application of the partial quadrupole splitting (pqs) model[25] to rationalize the electric quadrupole splitting of the gold(I) compounds is generally not successful because of the s—p rehybridization effects resulting from the trans influence. Nevertheless, the pqs model will be used here to verify in the mononuclear complexes 1–7 whether it is consistent with the presence of linear coordination, established through X-ray crystal structures for 5, 7, and 6[22] as well as for another isocyanide complex of gold(I), MeNCAuCl.[26] To this end the pqs for Ar–NC (–2.38 (3) mm/s) is derived from the splitting of $[(Ar–NC)_2Au]ClO_4$ (QS = –9.51 (3) mm/s) and the pqs for (Ar–NH)(X)C (–2.65 (1) mm/s), where X is either Ar–NH or EtO, from $\{[(Ar–NH)(EtO)C]_2Au\}ClO_4$ (QS = –10.61 (2) mm/s). With use of these data and the already available pqs value for chlorine (–1.22 (5) mm/s),[25] the QS values of the Table VII are obtained. The agreement between observed and calculated values of QS (Table VII) is considered to support the linear coordination assumed for all compounds 1–7 and verified for some of them. In addition, it should be noted that assumption of two-coordination even for those compounds where a gold–gold interaction seems to be present (e.g., those, like **5ct**, having an Au···Au separation smaller than ca. 3.4 Å) means that such an interaction has no sensible influence on the Mössbauer parameters.

The relative bonding ability of the ligands may be expressed in a semiquantitative form by the σ donor ability of the ligands derived from both the IS and QS splitting data. For this purpose we have used the procedure of ref 27 (Table VIII). In this way one reaches the following conclusions on the bonding properties and the charge distribution of the ligands here investigated in the $[LAuL]^+$ complexes: (1) the σ donor ability of the ligands obeys the relation Ar–NC < $(Ar–NH)_2C$ < (Ar–NH)(EtO)C; (2) the ligands Ar–NC, $(Ar–NH)_2C$, and (Ar–NH)(EtO)C are better s than p_z donors; (3) the carbenes (Ar–NH)(X)C where X = Ar–NH or OEt do not differ much in their s as well as p donor properties, but both are better s donors than ArNC.

Polynuclear Gold(I) Compounds. The X-ray crystal structure determination carried out[28] on the trimeric compound 8 indicates small differences in the environment of the three gold atoms, as well as inter- and intramolecular Au···Au interactions. Owing to these, the ring is puckered rather than planar as expected if the nitrogen and carbon atoms of the ring had sp^2 and the gold atoms had sp hybrid orbitals. Moreover, although the three Au—C [1.93 (3), 1.95 (2), and 1.97 (3) Å] and the three Au—N distances [2.04 (2), 2.02 (2), and 2.04 (2) Å] are undistinguishable, one of the three AuC=N double-bond lengths, 1.22 (3) Å, is different from the other two, 1.38 (4) and 1.37 (4) Å, indicating a slightly different environment for one of the three atoms of gold.

The Mössbauer spectrum of compound 8 shows only one resolved quadrupole doublet, the line width (*W*) of which, however, is somewhat larger than normal for the compounds listed in Table I. The Mössbauer line width for the polynuclear compound 9 is similar to that of the trimer 8. These findings agree with the idea that the individual gold sites in both compounds are slightly different, but not sufficiently so as to yield resolved, individual quadrupole doublets.

The similarity of IS and *W* for compounds 8 and 9 requires only a similarity in the local environment around the gold atoms; it does not mean that 9 has the same trimeric structure as ascertained for 8. Indeed, the latter is soluble in organic solvents, while the former is insoluble, in agreement with the suggested oligomeric or polymeric nature.[16]

It is tempting to associate the stability, in general terms, of 8 and 9, of their homologues, and of other trimeric molecules as well (such as 2-pyridylgold(I),[29] (1-methylbenzimidazol-2-yl)gold(I),[30] or tris(μ-[bis(3,5-trifluoromethyl)pyrazolato-*N,N'*]}trigold(I)[31]) with some form of π bonding involving, e.g., $5d_{xz}$, $5d_{xy}$ orbitals of gold and the unfilled π^* C=N orbitals. The nonplanarity of 8, however, rules out an electron delocalization over the entire nine-membered ring.

Other trimeric gold(I) derivatives with the general formula[32] Au_3(μ-pyrazolato-*N,N'*)$_3$or Au_3(μ-pyrazolato-*N*,-

Table VIII. Derivation of the σ-Bonding Parameters from $[L_2Au]^+$ Complexes^a Following Ref 27

ligand	IS^{a,b}	QS^b	$\Delta n_s{}^c$	$p_z{}^c$	σ^c
Cl^d	1.72	6.13	0.22	0.27	0.25
ArNC	3.88 (4)	9.51 (3)	0.48 (4)	0.48 (3)	0.45 (7)
$(ArNH)_2C$	5.68 (2)	10.73 (1)	0.71 (2)	0.48 (1)	0.59 (3)
(ArNH)(EtO)C	5.78 (3)	10.61 (2)	0.72 (3)	0.47 (2)	0.60 (5)

^{a}Reference to gold metal. ^{b}From Table I. $^c\Delta n_s$ = IS/8; p_z = QS/22.37; $\sigma = (\Delta n_s + p_z)/2$. ^{d}In $AuCl_2^-$ from ref 27.

$N')_3I_2$ were investigated by Mössbauer spectroscopy[10a] and found to have even larger line widths than those of the spectra of **8** or **9**. It is not possible to compare the Mössbauer parameters of **8** and **9** with other suitable gold(I) compounds having a similar arrangement of ligands because such Mössbauer data have not been reported in the literature. The best candidate for such a comparison may be the linear $(Au—C{\equiv}N)_n$ (IS = 2.30 and QS = 7.95 mm/s) since in this compound the gold has one unsaturated carbon and one unsaturated nitrogen as donor ligands.

Gold(III) Derivatives. An X-ray crystal structure determination established that a trans square-planar coordination about the gold center is present in the cation $\{[(ArNH)_2C]_2AuI_2\}^+$ (no. 10 in Table I). The bonding involves $5d6s6p^2$ hybridization, and the Au–C bonds have been reported to be almost pure σ bonds.[33] Similar assumptions can be made by analogy for cation **11**.

The Mössbauer parameters of cations **10** and **11** are typical of covalent compounds containing gold(III). The parameters are close to those of another covalent species having two unsaturated C ligands and two iodine atoms around the gold(III) coordination center, namely, $[Au(CN)_2I_2]^-$.[34] The EFG, which would be negative for a d_{z^2} electron configuration, changes sign from negative to positive owing to the population of the Au p_x and p_y orbitals[24] in covalent Au(III) complexes. So a positive sign for the quadrupole coupling constant is expected for complexes **10** and **11**.

On complex formation not only the quadrupole coupling increases but also the isomer shift becomes more positive. Its value increases with the σ donor properties of the ligands. On comparing cations **10** and **11** it may be observed from the Mössbauer parameters that (Ar–NH)(EtO)C is a better σ donor than $(ArNH)_2C$, in agreement with the behavior of these ligands in the gold(I) complexes.

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Registry No. 1, 43067-30-7; 2, 43067-35-2; 3, 58299-95-9; 4, 50870-66-1; 5, 101835-35-2; 6, 58320-41-5; 7, 58299-90-4; 8, 55145-58-9; 9, 51032-35-0; 10, 58919-38-3; 11, 58919-44-1.

Supplementary Material Available: Tables of least-squares of planes and listings of the structure factors amplitudes with thermal parameters (53 pages). Ordering information is given on any current masthead page.

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Radicals of C_7-Polyolefin Cobalt Complexes: Electrochemistry, Reaction Routes, and Structure of a Resulting Dimer

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The reduction and oxidation of several cyclopentadienyl (Cp) cobalt complexes with π-bonded C_7-polyolefin ligands have been studied by electrochemical methods. The cycloheptadienyl complex $CpCo(\eta^5\text{-}C_7H_9)^+$ is reversibly reduced to a neutral radical which undergoes a slow dimerization reaction with a rate constant of $k = 1.35 \pm 0.23\ M^{-1}\ s^{-1}$ as measured by cyclic voltammetry. X-ray crystallographic studies of the dimer confirmed that coupling took place at the C_7 ligand. The dimer crystallizes in the space group $P\bar{1}$ with $a = 6.577$ (1) Å, $b = 12.152$ (2) Å, $c = 12.693$ (2) Å, $\beta = 100.90$ (1)°, and $Z = 2$. $CpCo(\eta^4\text{-}C_7H_8)$ is reduced to a reactive monoanion that undergoes protonation and further reduction to yield $CpCo(\eta^4\text{-}C_7H_{10})$. $CpCo(\eta^4\text{-}C_7H_{10})$ is also reduced electrochemically, but its radical anion is very unstable and no product analysis was performed. However, $CpCo(\eta^4\text{-}C_7H_{10})$ gives a cation radical upon one-electron oxidation that is stable enough to be characterized by electron spin resonance spectroscopy.

Introduction

The (η^5-cyclopentadienyl)cobalt (CpCo) moiety has been useful as a template to facilitate the study of reactions of coordinated polyolefins with electrophiles and nucleophiles.[1-4] Since CpCo (polyolefin) complexes often display reversible electron-transfer reactions,[5] we sought to use electrochemistry to prepare CpCo (polyolefin) radicals in

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