$\{Pt[C(O)CF_3](O_2CCF_3)[P(C_6H_5)_3]\}_2$. Tris(triphenylphosphine)platinum(0), 0.81 g, 0.5 ml of trifluoroacetic anhydride, and 10 ml of benzene were mixed *in vacuo*. After 2 hr at room temperature, the colorless mixture was evaporated to dryness and the colorless product washed with ether; 85% yield. The product was recrystallized from benzene-*n*-hexane.

$[Pt[P(C_6H_5)_3]_2(C_2H_4)]$. A continuous flow of ethylene was maintained through a suspension of carbonatobis(triphenylphosphine)platinum(II), 1.5 g, in 40 ml of ethanol at 25°. In a period of 20 min 18 ml of 0.1 *M* $NaBH_4$ in ethanol solution was added. The resulting white suspension was stirred for an additional 2 hr under ethylene at 25°. Filtration gave 1.33 g of product, 100% yield, whose infrared spectrum, melting point, and reactivity were the same as those of an authentic sample.[20] The product was washed with ethanol, water, and ethanol and then dried *in vacuo*. If sufficient reaction time is not allowed, some of the carbonato complex will remain. This results in a product which is not completely soluble in benzene.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and to the University Organized Research Fund for partial support of S. F. S. and L. W. We wish to thank Dr. A. L. Ternay for valuable discussions.

Registry No. Ia, 51293-04-0; Ib, 51293-05-1; Ic, 51293-06-2; Id, 51293-07-3; Ie, 51293-08-4; IIa, 51293-09-5; IIb, 51364-35-3; IIc, 51293-10-8; IIIa, 51293-11-9; IIIb, 51293-12-0; IVa, 51364-36-4; IVb, 51293-13-1; V, 51293-14-2; VI, 51293-15-3; VIIa, 51293-16-4; VIIb, 51293-17-5; VIIIa, 51293-18-6; VIIIb, 51293-19-7; IX, 51293-20-0; X, 51293-21-1; XI, 51293-22-2; XII, 23868-38-4; *trans*-$\{IrCl(CO)[P(C_6H_5)_3]_2\}$, 15318-31-7; *trans*-$\{IrBr(CO)[P(C_6H_5)_3]_2\}$, 15842-08-7; *trans*-$\{IrCl(CO)[PCH_3(C_6H_5)_2]_2\}$, 15318-32-8; $CF_3C(O)OC(O)CF_3$, 407-25-0; $C_2F_5C(O)OC(O)C_2F_5$, 356-42-3; $CH_3C(O)OC(O)CH_3$, 108-24-7; *trans*-$\{IrCl(N_2)[P(C_6H_5)_3]_2\}$, 21414-18-6; $CF_3C(O)Cl$, 354-32-5; CF_3I, 2314-97-8; $Pt[P(C_6H_5)_3]_2C_2H_4$, 12120-15-9; $Pt[P(C_6H_5)_3]_3$, 13517-35-6; perfluorosuccinic anhydride, 699-30-9; perfluoroglutaric anhydride, 376-68-1; ethylene, 74-85-1; carbonatobis(triphenylphosphine)platinum, 17030-86-3.

Contribution from the CNR Laboratory, Istituto di Chimica Generale dell'Universita, 20133 Milan, Italy

Trimeric (Alkoxy)(alkylimino)methylgold(I) Compounds, $[(RO)(R'N=)CAu]_3$

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Received July 6, 1973 AIC305000

The title compounds are stable, not cluster-type molecules, having an enneaatomic and probably planar cycle. They are prepared by action of potassium hydroxide in an alcohol on a mixture of an isocyanide and a gold(I) complex, such as Me_2SAuCl or Ph_3PAuCl; alternatively they are obtained by deprotonation of a carbene complex, $[(RO)(R'NH)C]AuCl$, which is re-formed when the trimer is treated with hydrochloric acid.

The reaction of aromatic isocyanides in alcoholic potassium hydroxide with phosphine complexes of metals such as platinum,[1,2] palladium,[3] or gold[1,4] yields compounds containing the -C(OR)=NR′ group, *e.g.*

$$(Ph_3P)AuCl + ROH + KOH + Ar-NC = (Ph_3P)AuC(OR)=NAr + KCl + H_2O$$

$$(Ph_3P)_2PtCl_2 + 2ROH + 2KOH + 3Ar-NC = Ph_3P + 2KCl + 2H_2O + (Ph_3P)(Ar-NC)Pt[C(OR)=NAr]_2$$

While extending the reaction to other isocyanides, we obtained a new phosphine-free compound, *i.e.*,[5] $[Au-C(OMe)=NC_6H_{11}]_3$. This is a discrete coordination polymer and is likely to be one of the few polynuclear gold compounds not containing a cluster of metal atoms.[6] Here we describe a general synthesis of complexes having the formula $[Au-C(OR)=NR']_3$, where R′ is an aliphatic, cycloaliphatic, alkylaromatic, or aromatic group. The similar, less stable silver(I) derivatives have been briefly described recently.[7]

Experimental Section

$(Me_2S)AuCl$,[8] $(RNC)AuCl$,[9] and $(Ph_3P)AuCl$[10] were prepared according to published methods. Evaporation was always carried out under reduced pressure. All the analytical samples were dried to constant weight under vacuum (*ca.* 0.1 Torr). All the reactions were carried out at room temperature.

Reaction 1. This was carried out as described elsewhere.[5]

Reaction 2: (Methoxy)(*N*-*p*-tolylimino)methylgold(I) Trimer (V). To a stirred suspension of $(Me_2S)AuCl$ (2.59 g, 8.7 mmol) in methanol (30 ml) *p*-tolyl isocyanide (1.13 ml, 8.7 mmol) and, later, potassium hydroxide (0.50 g, 8.7 mmol) in methanol (50 ml) were added. After 0.5 hr the solution was evaporated to dryness, and the residue was extracted with chloroform. On concentration the extract afforded a precipitate, which was crystallized from chloroform-ether to afford the analytical sample. When compound I was prepared, the extraction was carried out with hot CH_2Cl_2 in place of $CHCl_3$. When compound VII was prepared, the methanol suspension was filtered, and the precipitate was stirred under water overnight, filtered again, washed with acetone, with ether, and then with hot $CHCl_3$ until the washings were colorless. While the other compounds gave colorless crystals, VII is a brownish powder.

Reaction 3: [(Methoxy)(methylimino)carbene]chlorogold(I) (X). To a stirred suspension of compound I (426.8 mg) in methanol (20 ml) aqueous hydrochloric acid (1 ml) in the same solvent (9 ml) was added. After 2 hr the solution was concentrated to a small volume to afford a precipitate; this was dissolved in CH_2Cl_2, the solution was concentrated, and the analytical sample was obtained after addition of ether.

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Table I

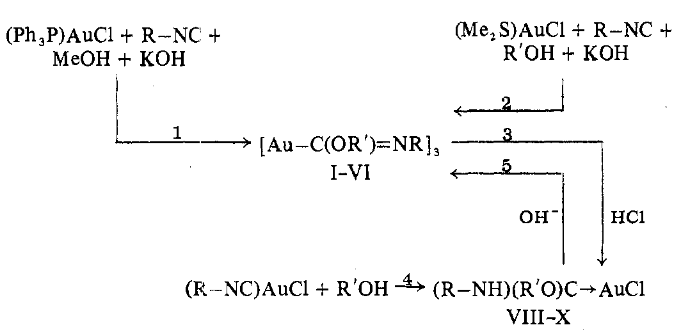
Compd[a]		Pattern	Mp, °C	Analyses[b]				Ir[d] and nmr[e] data
				% C	% H	% N	Mol wt[c]	
Au–C(OR′)=NR								
(I)	$R' = Me$	2	150	12.92	2.18	5.10	870	1565 br (C=N), 1125 br (C–OR)
	$R = Me$			13.37	2.20	5.20	807	7.0 s (CH_3), 5.90 s (OCH_3)
(II)	$R' = Me$	2	161–162 dec	17.57	2.94	4.97	860	1530 br (C=N), 1125 br (C–OR)
	$R = Et$			16.92	2.82	4.94	850	8.7 t (CH_2-$C\mathit{H}_3$), 6.55 q ($C\mathit{H}_2$-CH_3), 6.0 s (OCH_3)
(III)	$R' = Me$	2	163–164 dec	31.90	2.84	4.05	935	1540 br (C=N), 1129 br (C–OR)
	$R = CH_2Ph$			31.25	2.89	4.06	1035	6.65 s (CH_2), 5.60 s (OCH_3), 2.80 m (C_6H_5)
(IV)[f]	$R' = Me$	1, 2, 5	160 dec	28.60	4.00	4.10	1055	1510 br (C=N), 1129 br (C–OR)
	$R = C_6H_{11}$			28.80	4.00	4.20	1011	8.32 br (C_6H_{10}), 5.99 s (OCH_3), 5.70 br [$C\mathit{H}(CH_2)_5$]
(V)[g]	$R' = Me$	2, 5	181–183 dec	31.52	2.61	3.85	1070	1510 br (C=N), 1130 br (C–OR)
	$R = p\text{-}MeC_6H_4$			31.23	2.90	4.06	1035	7.65 s (p-CH_3), 6.10 s (OCH_3), 3.1–2.8 m (C_6H_4)
(VI)	$R' = Me_2CH$	2	115–116 dec	36.22	3.65	3.87		1500 br (C=N), 1100 br (C–OR)
	$R = p\text{-}MeC_6H_4$			35.35	3.74	3.74		
Cl–Au←C(OR′)NHR								
(VIII)	$R' = Me$	3	210–211 dec	25.40	3.87	3.67	375	3400 br (N–H), 1569 br
	$R = C_6H_{11}$			25.73	4.02	3.75	374	8.9–8.1 br (C_6H_{10}), 6.3–6.0 br [$C\mathit{H}(CH_2)_5$], 5.7 s (OCH_3)
(IX)	$R' = Me$	3, 4		28.7	2.80	3.71		3210 (N–H), 1565 (asym), 330 (Au–Cl)
	$R = CH_2Ph$			28.3	2.88	3.67		5.86 s (OCH_3), 5.11 d (J = 7 Hz) (CH_2), 2.72 s (C_6H_5), 1.84 br (N–H)
(X)	$R' = Me$	3	129–130 dec	11.75	2.08	4.48		3290 br (N–H), 1585 br
	$R = Me$			11.80	2.20	4.50		7.09 s (CH_3), 5.75 s (OCH_3), 0.6–1.4 br (N–H)

[a] Compounds I, II, V, VI, VIII, and X were crystallized from CH_2Cl_2-Et_2O; compound III was recrystallized from CH_2Cl_2, IV from $CHCl_3$–MeOH, and IX from Et_2O. [b] The first row of data for each compound is "found" and the second row is "calculated." [c] Vapor pressure in $CHCl_3$ at 37°. In addition the parent ion was detected in the mass spectra of I, II, and IV: L. F. Zerilli and M. Landi, to be submitted for publication. [d] First row of data for each compound; Nujol mull; all bands are strong unless otherwise stated. [e] Second row of data for each compound; $CDCl_3$ solution; τ units. [f] Oxygen: calcd, 4.7%; found, 5.31%. [g] Gold: calcd, 57.2%; found, 57.0%.

Reaction 4: [(Methoxy)(benzylamino)carbene]chlorogold(I) (IX). (Benzyl isocyanide)chlorogold(I)[11] (0.40 g) and methanol (10 ml) were refluxed 2 days. After evaporation of the filtered solution to dryness, the oily residue was dissolved in diethyl ether, where it is sparingly soluble. The analytical sample was obtained on concentration (0.15 g).

Reaction 5: (Methoxy)(*N*-*p*-tolylimino)methylgold(I) Trimer (V). To a methanol solution (50 ml) of [(methoxy)(*p*-tolylamino)carbene]-chlorogold(I)[12] (0.456 g) 0.16 *M* potassium hydroxide in methanol (7.5 ml) was added. A white precipitate formed at once. After 2 hr of stirring the filtered solution was shaken with methanol, scratched, filtered, and crystallized from chloroform–ether.

Scheme I



Results and Discussion

Reaction 1 (see Scheme I) was carried out at room temperature and $[Au{-}C(OMe){=}NC_6H_{11}]_3$ (IV), was readily isolated. When aromatic isocyanides were used, the phosphine ligand was not displaced and those $(Ph_3P)AuC(OR){=}NAr$ compounds[4] were obtained which can be prepared also[7] from $(Ph_3P)AuCl$ and $[Ag{-}C(OR){=}NR']_3$. When a rather labile ligand, *e.g.*, Me_2S, was present in the starting material, the $[Au{-}C(OR){=}NR']_3$ compounds, I-VI, were obtained in good yields according to pattern 2, which is the most convenient among those tried. The same compounds could be obtained also by action of alkali on an [(alkoxy)(alkylamino)-carbene]chlorogold(I) complex: according to pattern 5 both potassium hydroxide in methanol and cyclohexylamine in chloroform afforded compound IV or V. Pattern 5 is limited, however, because the carbene complexes where R is an aliphatic group cannot be prepared according to reaction 4; they were prepared from $[Au{-}C(OR){=}NR']_3$ and hydrochloric acid according to reaction 3.

Compounds I-VI were identified through analyses, infrared and nmr spectra, and molecular weight determinations. Compound VII is insoluble, could not be purified, and gave unsatisfactory analyses; its identification rests on the infrared spectrum.

The infrared spectra showed all the required absorptions: a strong ν(C=N) above 1500 cm^{-1}, a strong ν(C–OR) at 1100-1200 cm^{-1}, and strong vibrations at *ca.* 400-500 cm^{-1} where ν(Au–C) is expected. There was no evidence for any N–H, O–H, or C≡N stretching vibration. The nmr spectra are simple (see Table I) and support the formulas proposed.

Compounds I-VII are rather stable; they are unaffected by carbon monoxide (1 atm; 25°), triphenylphosphine, various solvents at room temperature, or boiling pyridine, from which some of them could be crystallized. They are sparingly soluble in organic solvents and the solutions are stable at least for a short time. The compounds were immediately attacked by hydrochloric acid according to reaction 5, giving the carbene complexes VII-IX. The behavior is different from that observed[4] in the case of $(Ph_3P)Au{-}C(OMe){=}NC_6H_4CH_3$, where the same attack led to $(Ph_3P)AuCl$ and to *p*-tolylammonium chloride; in the same case the attack

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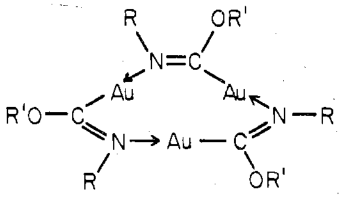
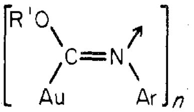
(12) F. Bonati and G. Minghetti, *Syn. Inorg. Metal-Org. Chem.*, **1**, 299 (1970).

can be limited and a carbene complex is isolated only if an acid with a noncoordinating anion is used (*e.g.*, picric acid).[13]

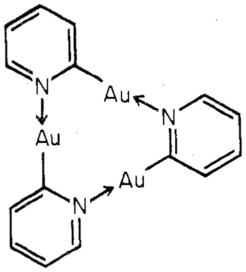
The carbene complexes VII-X belong to a known class of complexes.[11,12,14] They showed the expected ν(NH), δ(NH) plus ν(C=N), and ν(AuCl) in the 3200-3300, 1550-1600, and 330 cm^{-1} ranges, respectively. Although they might give geometrical isomers, no evidence of them was found in the nmr spectra. The molecular weight determinations (see Table I) prove that the compounds I-VI should be formulated as trimers. In the absence of an X-ray crystal structure determination a planar enneaatomic ring structure is hypothesized for these compounds, while a polymeric structure is likely for the highly insoluble compound VII. A very similar planar arrangement of atoms was assigned to α-pyridylgold(I), obtained[6] from (triphenylarsine)chlorogold(I) and 2-pyridyllithium, although in this case no molecular weight determination could be carried out.



I-VI



VII



If the usual bond distances and angles are assumed, the gold-gold distances in the planar enneaatomic ring are likely to be *ca.* 3.3 Å, thus leaving no opportunity for a metal-metal bond.[15,16]

Ultraviolet spectra were recorded in chloroform solution. Compound IV, $[C_6H_{11}N{=}C(OMe)Au]_3$, showed a band at 264 nm (ϵ 10,500), while the related species $[(C_6H_{11}NH)(MeO)C]AuCl$ and $(C_6H_{11}NC)AuCl$ are transparent in the range afforded by the solvent. The $-\ddot{N}{=}C{<}$ chromophore is known[17] to absorb around 220-240 nm (n → σ^* transition), while the ternary iminium salts, *e.g.*, $Me_2CCH_2CMe{=}NH^+CH_2$ or quinolizidine perchlorate, are transparent[18,19] above 220 nm, the expected $\pi \rightarrow \pi^*$ transition lying well below this value.

In $CHCl_3$ solution no band is expected in the case of the above-mentioned isocyanide or carbene complex; the absorption shown by compound IV may be explained by the effect of three $>\overset{+}{N}{=}C{<}$ groups in a ring. In fact conjugation of an iminium group with another unsaturated group shifts the absorption maximum to considerably longer wavelength, *e.g.*,[18] to 250 nm in $CH_3CH{=}CH_2CH{=}N^+Et_2$ or to 247 nm in $CH_2CH{=}CHCH{=}NH^+$.

The stability of compounds I-VI might be due to back-donation, from filled 5d orbitals of gold to unfilled π^* orbitals of the C=N bond, and/or to overlap,[20] among p_z orbitals on C, N, and Au atoms, both phenomena producing electron delocalization in the planar ring. Nevertheless another effect, *i.e.*, the good donor character[13] of the nitrogen atom of the $-C(OR){=}NR'$ group, is likely to be more important.

Registry No. I, 51239-99-7; II, 51240-00-7; III, 51240-01-8; IV, 38333-31-2; V, 50989-80-5; VI, 51240-02-9; VIII, 51240-36-9; IX, 43081-31-8; X, 51240-37-0; $(Me_2S)AuCl$, 29892-37-3; *p*-tolyl isocyanide, 7175-47-5; methanol, 67-56-1; (benzyl isocyanide)chlorogold(I), 43067-27-2; [(methoxy)(*p*-tolylamino)carbene]chlorogold(I), 35843-71-1.

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