CONCLUSIONS

1. Electrolytic reduction of 3-formy1-[3]-ferrocenophane and acetylferrocene proceeds through the anion radical formation step.

2. The influence of the structure on the behavior of the anion radicals being formed manifests itself only in nonaqueous solutions, in which the anion radical of acetylferrocene breaks down with rupture of the bond between the metal and the cyclopentadiene ring, whereas the anion radicals of [3]-ferrocenophanes retain the ferrocene structure, the breakdown of which is prevented by the three-carbon bridge.

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CYANOMETHYL DERIVATIVES OF GOLD

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Organic complexes of univalent gold have been known for more than twenty years; however α -functional substituted organogold derivatives are little known. α -Aurated carbonyl compounds have been described previously in [1] and aurated esters of cyanoacetic acid in [2]. The present communication is devoted to the synthesis and chemical properties of organogold derivatives of acetonitrile and dichloroacetonitrile.

Dichloroacetonitrile reacts with tris(triphenylphosphinegold)oxonium borofluoride forming dichlorocyanomethyl(triphenylphosphine)gold (I)

CHCl₂CN + (Ph₃PAu)₃O⁺BF₄^{- $\frac{K_{\bullet}CO_{\bullet}}{THF-H_{\bullet}O}$ Ph₃PAuCCl₂CN (I) 70%}

Under analogous conditions acetonitrile was not aurated by the gold-containing oxonium salt. This is probably connected with the difference in CH acidity of CH_3CN and $CHCl_2CN$. We obtained aurated acetonitrile (II) by another route by the reaction of cyanomethyllithium with the triphenylphosphine complex of gold chloride.

$LiCH_{2}CN + Ph_{3}PAuCl \xrightarrow{}_{-80^{\circ}} Ph_{3}PAuCH_{2}CN$ (II) 67%

In the IR spectra of complexes (I) and (II) the vibrational frequencies of the CN group were displaced by 50 cm⁻¹ towards the low frequency region in comparison with the initial nitriles and appeared at 2220 and 2200 cm⁻¹. It is known that in α -metallated carbonyl compounds also a significant reduction of the stretching vibrational frequency of the CO group was observed in comparison with carbonyl compounds containing no metal [3, 4, 5]. For

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow; M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2818-2824, December, 1983. Original article submitted January 12, 1983.

UDC 542.91:541.49:547.

1'13:546.59

the σ bonded cyanomethyl complexes of platinum cis-L₂Pt(X)CH₂CN the vibrational frequency of the CN group was observed in the region of 2200 cm⁻¹ [6].

In the PMR spectrum of complex (II) splitting was observed for the CH₂ proton signal (δ = 1.64 ppm) as a result of their interaction with the P atom of the triphenylphosphine ligand. The size of the splitting constant ${}^{3}J{}^{3}{}^{1}P{}^{-1}H$ = 12 Hz was typical for phosphine complexes containing an Au-C σ bond [7].

Complexes (I) and (II) differed strongly in their chemical behavior. Thus on reacting (I) with the $AuPPh_3^+$ cation generated by the reaction of $AgBF_4$ and $ClAuPPh_3$, a rapid decomposition of the reaction mixture occurred with the separation of metallic Au and bis(triphenyl-phosphine)gold borofluoride was formed

(I) +
$$Ph_{3}PAu^{+} \xrightarrow{BF_{4}^{-}} [(Ph_{3}P)_{2}Au]^{+}BF_{4}^{-}$$

In this case the $AuPPh_3^+$ cation plays the role of an acceptor of the phosphine ligand. Under analogous conditions $AuPPh_3^+$ split the phosphine ligand from PPh₃AuCN forming [(PPh₃)₂Au]⁺BF₄⁻ and gold cyanide

$$Ph_{3}PAuCN + Ph_{3}PAu^{+} \frac{BF_{4}}{Acetone - THF} [(Ph_{3}P)_{2}Au]^{+}BF_{4}^{-} + AuCN$$

$$70\% \qquad 100\%$$

In difference to (I) aurated acetonitrile (II) reacted with $AuPPh_3^+$ with the formation of binuclear cationic complex (III)

(II) +
$$Ph_3PAu^+ \xrightarrow{BF_4^-}_{Acetone-THF} [(Ph_3PAu)_2CH_2CN]^+BF_4^-$$

(III), 67%

The frequency of the stretching vibration of the CN group (2252 cm⁻¹) in binuclear complex (III) was increased by 52 cm⁻¹ in comparison with the initial complex (II). Such a change in the vCN frequency may be caused both by coordination of the AuPPh₃⁺ cation with the N atom of complex (II) and by the appearance of a cationic center on the C atom in the neighborhood of the CN group (structures (IIIa)-(IIIc).



In the binuclear cationic complexes of Au of the aromatic and alkenyl series investigated by us previously the C atom of the organic radical is bonded with the Au atoms by a twoelectron three-center bond as in structure (IIIb). In the PMR spectrum of (III) there was a doublet for the CH₂ group protons with a splitting constant ${}^{3}J_{31}p_{1-H} = 11$ Hz very closely similar to the analogous value in (II). These data are not in agreement with structures (IIIb) and (IIIc) since the effect of such structures should lead to a change in the multiplicity of the signal and the spin-spin interaction constant (SSIC) of the ¹H and ³¹P nuclei. We considered that structure (IIIa) with coordination of the Au atom to the N atom was the most probable for the binuclear complex (III). This coordination is fairly weak and (III) reacts by transfer of AuPPh₃⁺ cation to other organogold complexes. Thus on interacting (III) with a gold ferrocenyl derivative the binuclear ferrocenyl complex is formed and (II) is regenerated





Fig. 1. Structure of Ph₃PAuCCl₂CN molecule.

Complex (I) reacted readily with KBr giving triphenylphosphinegold bromide in high yield

(I) + KBr
$$\xrightarrow{\text{CHCl}_{\text{s}}-\text{H}_{2}\text{O}}$$
 Ph₃PAuBr 91%

Compound (II) under analogous conditions was stable to the action of KBr. With KCN (I) formed only potassium dicyanaurate in high yield

(I)
$$\xrightarrow{\text{KCN}} \text{K}[\text{Au}(\text{CN})_2]$$

93%

With KCN complex (II) formed a mixture of potassium and methyltriphenylphosphonium dicyanaurates. The source of the CH_3 group when forming phosphonium salts may only be the organic radical of the starting material (II); consequently the given reaction is accompanied by fission of the C-C bond in the CH_2CN radical and rearrangement.*

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$$\begin{array}{c} Ph_{3}PAuCH_{2}CN \xrightarrow{KCN} [Ph_{3}PMe]^{+}[Au(CN)_{2}]^{-} + K[Au(CN)_{2}] \\ (II) & 6\% & 69\% \end{array}$$

Fission of the C-C bond in the organic radical of (II) was also observed in the reaction of (II) with cyclohexene in boiling toluene. As a result of the reaction a product was isolated from the cycloaddition of methylene and the tripenylphosphine complex of the gold ligand



On heating (I) with cyclohexene in toluene or benzene the mixture isolated was of phosphine complexes of gold chloride and cyanide only. Addition products of the carbene to cyclohexene were not detected in the reaction mixture.

It should be noted that complex (I) in difference to (II) was extremely unstable in solution. Thus its benzene solution was stable only for several minutes at room temperature and on heating a benzene solution of (I) for an hour a mixture of AuClPPh₃, AuCN, and Ph₃PO was formed. Under conditions of acid and alkaline hydrolysis the organogold compound (II) was unchanged and we failed to effect conversion of the CN group. Thus the chemical properties of aurated acetonitrile (II) were typical of σ organogold compounds but in aurated dichloroacetonitrile (I) the bond of the CCl₂CN group to AuPPh₃ was so labile that this σ organogold compound recalled complexes of gold halides in chemical behavior.

An X-ray structural investigation carried out by us showed that in complex (I) there were no significant deviations in bond length and size of bond angles from those detected previously in organogold compounds.

^{*}We observed a similar rearrangement in the reaction of NaCN with Ph_3PAuCH_2Cl previously in [8].

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B_{2_3}	0	0	-1,1(2)	0	0,0(4)	1,0(5)	0,9(5)	-0.1(5)	1,2(6)	1,3(5)		_		
B ₁₃	0	0	-1,0(3)	Q	0,3(4)	0, 4(4)	0,0(5)	-0,7(5)	0,8(5)	1,1(5)				
B_{12}	2,22	2,1	4,2(4)	3,0	1,8(4)	3,2(5)	3,5(5)	4,1 (5)	3,0(5)	2,6(5)				
B_{33}	2,58(3)	2,3(2)	4,5(3)	0,4(4)	3,6(5)	3,9(5)	4,6(6)	4,7 (6)	6,9(8)	5,0(6)				
B21	4,43(3)	4,3(1)	7,2 (5)	5,9(6)	3,8(4)	5,9(6)	5,7(6)	5,7 (6)	5,7 (6)	5,3(6)				
B_{11}	4,43 (3)	4,3(1)	7,9(5)	5,9(6)	4,4(5)	5,0(5)	5,9(6)	6,1(6)	4,3(5)	5,0(6)	10(2)†	8(3)†		
N	22839(3)	3363(2)	-982(4)	-1316(7)	-3701 (6)	-4229(6)	-4497 (7)	-4241(6)	-3724(8)	-3441 (7)	-859(39)	-1040(52)		
	0	0	1422(9)	0	303 (10)	1020(13)	1161(13)	568(13)	-137(13)	-271 (13)	2053 (75)	-821(84)		
X	0	0	202(10)	0	-1134(11)	-898(12)	-1823(13)	-2956(13)	-3181(12)	-2282(12)	442 (63)	-1327 (99)		
Atom	Au	વ	CI	ū	C ²	ů	ů,	C	c	C7	Z	U	† <i>B</i> iso.	

Molecule of (1)							
Bond	d, Å	Bond	d, A				
Au-P Au-C ¹ $P-C^2$ C^1-Cl C^2-C^3	$\begin{array}{c} 2,281(5)\\ 2,05(1)\\ 1,82(1)\\ 1,84(1)\\ 1,38(2) \end{array}$	$\begin{array}{c} {\rm C}^2 - {\rm C}^7 \\ {\rm C}^3 - {\rm C}^4 \\ {\rm C}^4 - {\rm C}^5 \\ {\rm C}^5 - {\rm C}^6 \\ {\rm C}^6 - {\rm C}^7 \\ {\rm C}^1 - {\rm C} \\ {\rm C}^- {\rm N} \end{array}$	$\begin{array}{c} 1,39(2)\\ 1,40(2)\\ 1,37(2)\\ 1,35(2)\\ 1,38(2)\\ 1,6(1)\\ 1,0(1) \end{array}$				

TABLE 2. Bond Lengths in the Molecule of (I)

The coordinates of the atoms in the independent portion of the molecule of (I) in the crystal are shown in Table 1, bond lengths in Table 2, and bond angles in Table 3. The molecule of (I) is depicted in Fig. 1 and is located in the crystal in an individual position on axis 3 and is randomized about this axis in three positions with the same population (see Experimental section).

The Au atom in (I) has linear coordination usual for organic derivatives of Au(I). The Au-P distance was 2.281(5) Å virtually in agreement with the values of 2.279(8) Å found in the molecule of methyl(triphenylphosphine)gold MeAuPPh₃ (IV) in [9]. The Au-C¹ bond in (I) at 2.05(1) Å was somewhat shorter than the σ bond Au-C (sp³) in (IV) at 2.12(3) Å and was close to the Au-C (sp²) bond length in the molecule of C₆F₅AuPPh₃ at 2.07(2) Å in [10]. Shortening of the Au-C σ bond in (I) by 0.07 Å may be explained by the greater electron accepting character of the CCl₂CN ligand in comparison with the methyl group.

The C¹ atom of the rotationally disordered dichlorocyanomethyl ligand has the usual tetrahedral sp³ configuration. The length of the C¹-Cl bond at 1.84(1) Å somewhat exceeded the C-Cl distance in halogen derivatives of paraffins at 1.74-1.83, mean 1.77 Å [11] in the gas phase. It should be noted that the appearance of a σ carbon-metal bond in the position α to the C-Cl bond was accompanied by a lengthening of the latter in other cases too {for example to 1.829(9) Å in the structure [N, σ -C₅H₄N(COCHCl)]Pt(Cl)SMe₂ [12]}. The position of the N and C atoms in the CN group were determined with low precision as a result of the randomization and the presence in the structure of the heavy Au atom. The C¹-C and C-N distances were 1.6(1) and 1.0(1) Å, bond angles Au-C¹-C and C¹-C-N were 111(4) and 156(11)° respectively. The nonlinearity of the C-C-N fragment was caused by the large errors in the positions of the N and C atoms and are not statistically significant.

EXPERIMENTAL

The x-ray structural investigation of (I) was carried out at room temperature with a Syntex P2₁ diffractometer (λ MoK_{α}, graphite monochromator, $\theta/2\theta$ scanning, $2\theta \leq 56^{\circ}$). Crystals of (I) were rhombohedral, $\alpha = 12.776(7)$, c = 21.113(9) Å (hexagonal assembly), space group $R\overline{3}$ (from the results of interpreting and refinement), Z = 6, dcalc = 1.907 g/cm³; 1469 independent reflections were measured, and 1453 of them with I > 2 σ were used in the calculations. According to the procedure in [13] a correction was introduced into the absorption allowing for the actual shape of the crystal. The structure of (I) was interpreted by the standard heavy atom method and was refined by a full-matrix least-squares method in isotropic (C and N atoms of the nitrile substituent)-anisotropic approximation. As a result of the disposition of the molecule in a particular position on axis 3 refinement was carried out for two models, a "symmetric" model corresponding to the formula Ph_PAuCCl_3 (which contradicts the elemental composition and data of IR spectroscopy) and a "random" model for a molecule of composition $Ph'_{3}PAuC(CN)Cl_{2}$ containing Cl atoms fixed in a multiplicity of 2/3 and atoms of C and N in the CN fragment with a multiplicity of 1/3 in the independent portion. Refinement of both models with 1413 reflections with F^2 > 4 σ led to a final value of R = 0.072, R_w = 0.088 for the symmetric model and R = 0.069, $R_W = 0.084$ for the random model. The discrepancy of the R factors is statistically significant and in accordance with the Hamilton test [14] indicates with a probability of 99.5% in favor of the random model for (I) with a stoichiometry of $Ph_3PAuC(CN)Cl_2$. All calculations were carried out on an Eclipse S/200 computer with the EXTL program modified by A. I. Yanovskii and R. G. Gerr in the Laboratory of X-Ray Structural Analysis of the Institute of Heteroorganic Compounds, Academy of Sciences of the USSR.

IR spectra were obtained on an IKS-29 instrument (nujol mull) and PMR spectra on a T-60 instrument with an operating frequency of 60 MHz, internal standard being TMS. Analysis of

products by GLC was carried out on a Tsvet-4 instrument with a flame ionization detector, capillary column of length 50 m, and stationary phase PEG-2000.

<u>Dichlorocyanomethyl(triphenylphosphine)gold (I)</u>. Potassium carbonate (0.1 g), water (1 ml), and tris(triphenylphosphinegold)oxonium borofluoride (1.0 g, 0.67 mmole) was added to Cl₂CHCN (0.5 g, 4.6 mmole) in tetrahydrofuran (THF, 30 ml). The reaction mixture was stirred for 1 h at ~1 h at 20°C until complete solution of the oxonium salt. The solution was dried with potassium carbonate, filtered, and the solvent distilled off in vacuum. The residue was dissolved in the minimum quantity of tetrahydrofuran and (I) precipitated with a mixture of petroleum ether—ether (10:1). Yield was 0.8 g (70%) mp 172-173°C. IR spectrum: 2220 cm⁻¹ (CN). Found: C 42.26; H 2.66; Au 34.52; Cl 12.53%. C₂₀H₁₅AuCl₂NP. Calculated: C 42.35; H 2.60; Au 34.72; Cl 12.50%.

<u>Cyanomethyl(triphenylphosphine)gold (II).</u> A suspension of Ph₃PAuCl (5.0 g, 10 mmole) in abs. ether (50 ml) was added in portions with stirring and cooling to -80° C to the lithium derivative of acetonitrile [15] obtained from acetonitrile (1.0 g, 24 mmole) in a stream of Ar. After adding all the suspension the reaction mixture was stirred for 2 h at ~20°C until disappearance of the initial gold chloride. A check on the course of the reaction was carried out by TLC. The reaction mixture was decomposed with water. The organic layer was separated, washed three times with water, and dried over potassium carbonate. After removal of the solvent in vacuum, ethanol (15 ml) was added to the residual oil. The precipitated crystals were filtered off and recrystallized from benzene. Compound (II) (3.4 g, 67%) was obtained having mp 141-142°C. IR spectrum: 2200 cm⁻¹ (CN). PMR spectrum (CH₂Cl₂, δ , ppm): d 1.64 ³J³¹P⁻¹H = 10 Hz. Found: C 47.96; H 3.52; Au 39.10; N 2.76%. Calculated: C 48.11; H 3.45; Au 39.47; N 2.80%.

Interaction of (I) with Triphenylphosphinegold Borofluoride. A solution of AgBF₄ (0.23 g, 1.1 mmole) in acetone (20 ml) was added to a solution of Ph₃PAuCl (0.50 g, 1 mmole) in THF (30 ml). The precipitate of silver chloride was filtered off and the obtained filtrate containing Ph₃PAu⁺BF₄⁻ (1 mmole) was gradually added to the solution of (I) (0.50 g, 0.8 mmole) in a mixture of (40 ml) of THF-ether (1:1). After stirring for 30 min the reaction mixture was filtered from metallic Au and the filtrate diluted with ether. The precipitated bis(triphenylphosphine)gold borofluoride was reprecipitated three times from a mixture of CHCl₃-ether. A yield of 0.42 g (60%) of $[(Ph_3P)_2Au]^+BF_4^-$ was obtained with mp 224-225°C (see 16]).

Interaction of Ph_3PAuCN with Triphenylphosphinegold Borofluoride. A solution of Ph_3 -PAu⁺Bf₄⁻ (1 mmole) in a mixture (30 ml) of THF-acetone (2:1) was added dropwise with stirring to a solution of Ph_3PAuCN (0.5 g, 1 mmole) in THF (5 ml). The resulting yellow precipitate of AuCN was separated and washed with acetone. Yield of AuCN was 0.22 g (~100%), IR spectrum: 2263 cm⁻¹ (CN) (see [17]). From the solution [(Ph_3P_2Au]⁺BF₄⁻ (0.52 g, 70%) was precipitated with an excess of ether and had mp 224-225°C (see [16]).

A small excess of a benzene solution of Ph_3P was added to the AuCN obtained in the present experiment. In this way AuCN dissolved and Ph_3PAuCN with mp 203-204°C (see [18]) was precipitated from the solution with an excess of petroleum ether.

Interaction of Ph_3PAuCH_2CN (II) with Triphenylphosphinegold Borofluoride. A solution of $Ph_3PAu^+BF_4^-$ (1 mmole) in a mixture (30 ml) of THF-acetone (2:1) was added dropwise with stirring to a solution of (II) (0.5 g, 1 mmole) in THF (7 ml). The reaction mixture was diluted with ether (30 ml) and left for 2 h at $-5^{\circ}C$. The precipitated solid was filtered off, washed with ether, and with pentane. The yield of $[NCCH_2(AuPPh_3)_2]^+BF_4^-$ (III) was 0.68 g (65%); it decomposed at 120°C. IR spectrum: 2250 (CN) and 1060 cm⁻¹ (BF₄⁻). PMR spectrum (CHCl₃, δ , ppm): 1.9 d $^{3}J_{31P-1H} = 11$ Hz. Found: C 43.76; H 3.30; Au 37.58%. C₃₈H₂₂AuBF_4NP_2. Calculated: C 43.66; H 3.08; Au 37.60%.

Interaction of $[NCCH_2(AuPPh_3)_2]^+BF_4^-$ (III) with Ferrocenyl(triphenylphosphine)gold. A solution of (III) (0.15 g, 0.15 mmole) in acetone (20 ml) was added to a solution of $C_5H_5Fe-C_5H_4AuPPh_3$ (0.10 g, 0.15 mmole) in benzene (30 ml). After 30 min the reaction mixture was diluted with petroleum ether, the precipitated red solid was filtered off, and washed with benzene. Substance $[C_5H_5FeC_5H_4(AuPPh_3)_2]BF_4^-$ (0.16 g, 91%) with mp 161-163°C (see [19]) was obtained. The solvent was removed in vacuum from the combined organic extracts, the residue was dissolved in benzene, and after adding petroleum ether compound (II) (0.7 g, 92%) was obtained.

<u>Action of KBr on (I) and (II).</u> A solution of (I) (1.0 g, 1.7 mmole) in $CHCl_3$ (60 ml) was stirred for 1 h with a solution of KBr (0.4 g, 3.6 mmole) in water (20 ml). The aqueous

TABLE 3. Bond Angles in the Molecule of (I)*

Angle	ω. deg	Angle	ω, deg	
PAuC ¹ AuPC ² C ² PC ² ' AuC ¹ Cl CC ¹ Au ClC ¹ Cl' Cl'C ¹ C Cl'C ¹ C	180 113,1 (4) 105,6 (6) 112,5 (5) 111 (4) 106,3 (6) 95 (4) 118 (4)	PC ² C ³ PC ² C ⁷ C ³ C ² C ⁷ C ³ C ⁴ C ⁵ C ⁴ C ⁵ C ⁶ C ⁵ C ⁶ C ⁷	122 (1) 118 (1) 120 (1) 120 (1) 120 (1) 120 (1) 120 (1) 121 (1)	
CI'C ¹ C CI"C ¹ C C ¹ CN	95(4) 118(4) 156(11)	C ⁴ C ⁵ C ⁶ , C ⁵ C ⁶ C ⁷ C ² C ⁷ C ⁶	120(1) 121(1) 121(1)	

*The indexes ' and " refer to an atom bound to the atom in question by a rotating operation relative to the axis of symmetry 3 by 120° and 240° respectively.

layer was separated, the chloroform layer washed with water, and dried over potassium carbonate. After removal of the solvent in vacuum the residue was treated with benzene and from the filtrate Ph_3PAuBr (0.9 g, 95%), mp 242-243°C (see [18]) was isolated by adding petroleum ether.

Under analogous conditions starting (II) was isolated in high yield from the reaction of KBr and (II).

Interaction of (I) and (II) with KCN. A solution of (II) (1.0 g, 2 mmole) in benzene (70 ml) was stirred for 2 h with a solution of KCN (0.5 g, 7.6 mmole) in water (10 ml) until disappearance of (I) (check by TLC). The organic layer was separated, dried over potassium carbonate, and the solvent distilled off in vacuum. The solid residue was dissolved in the minimum amount of benzene, filtered, and diluted with petroleum ether. Methyltriphenylphos-phonium dicyanaurate (0.6 g, 6%) with mp 127-128°C (see [8]) was obtained. The aqueous solution was evaporated to dryness and potassium dicyanaurate was extracted from the residue with methyl ethyl ketone. The solution was dried with potassium carbonate and after removal of the solvent in vacuum potassium dicyanaurate (0.4 g, 69%) was obtained, IR spectrum: 2142 cm⁻¹ (CN) (see [20]).

Potassium dicyanaurate (0.44 g, 93%) was obtained by the procedure given above from (I) (1 g, 1.7 mmole).

Interaction of (II) with Cyclohexene. A solution of (II) (0.3 g, 0.6 mmole) and cyclohexene (0.06 g, 7.2 mmole) in abs. toluene (15 ml) was boiled for 40 h. Marked decomposition of (II) occurred on heating with the formation of a gold mirror on the walls of the flask. Norcarane (0.016 g, 28%) was detected in the solution by GLC. From the solution Ph_3PAuCN with mp 203-204°C (see [18]) was isolated on adding petroleum ether.

CONCLUSIONS

1. Triphenylphosphine complexes of cyanomethylgold and dichlorocyanomethylgold have been synthesized.

2. The chemical properties of aurated acetonitrile were typical for σ organogold compounds but aurated dichloroacetonitrile recalled the chemical behavior of complex gold halides

3. The gold atom in the molecule of dichlorocyanomethyl(triphenylphosphine)gold has linear coordination, the bond lengths and angles were typical for organic complexes of univalent gold.

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