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SYNTHESIS AND REACTIONS OF CYANO-PENTAFLUOROPHENYL AURATE(I) AND -(III)

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Summary

The preparation of $Q[Au(C_6F_5)_n(CN)_m]$ (Q = bulky cation; $n = 1$ or 3, $m = 1$; $n = 2$, $m = 2$) is described and the following reactions are reported: (a) with inorganic acids (HCl or HBF_4) to give $[Au(C_6F_5)_n(CN)_mHOEt_2]$ ($n = 1$ or 3, $m = 1$; $n = 2$, $m = 2$), (b) with $[Me_3O][BF_4]$ to give isocyanides which react with methylamine to give carbene $[Au(C_6F_5)_n(CN)_m\{C(NHMe)_2\}]$; and (c) with gold complexes containing readily replaceable ligands to give binuclear (Au—CN—Au) or polynuclear (Au—CN—M) (M = Au or Ag) cyano-bridged complexes. Addition of neutral ligands (Py, Phen or PPh_3) to the polynuclear complexes leads to mononuclear complexes $[AgL_n][Au(C_6F_5)_2(CN)_2]$ (L = neutral ligands, $n = 2$ or 3). The assignment of the structures are based on the IR spectra of the complexes.

Introduction

The few hitherto known cyano-organogold complexes belong to two types: (1) Tetranuclear derivatives [1—3] $[AuR_2(CN)]_4$ (R = alkyl) whose CN-groups are bridging two gold centers [4]. Addition of neutral ligands leads to cleavage of these bridges and thus to the mononuclear complexes $AuR_2(CN)L$ (R = Me; L = 2,3-dimethyl-1,8-naphthyridine [5], PPh_3 [3,6]), whilst careful warming (heating) of $[AuR_2(CN)]_4$ leads to [2,7] polymeric materials $[R_2Au(CN)_2Au]_m$. (2) Monomeric derivatives of the types $[AuR_2(CN)L]$ (R = C_6F_5; L = PPh_3 [8], $AsPh_3$ [9]), $[AuEt_2(CN)_2]^-$ [2,10] and $[Au(C_6F_5)(CN)]^-$ [11].

In the present paper we describe the preparation of two new cyano-organoaurate(III) anions, $[Au(C_6F_5)_3(CN)]^-$ and $[Au(C_6F_5)_2(CN)_2]^-$. The reactions of the already-known gold(I) derivative $[Au(C_6F_5)CN]^-$ and of the new anionic gold(III) complexes with HBF_4, $[Me_3O][BF_4]$ and $AgClO_4$ are furthermore studied. The cyano complexes are finally used as N-ligands for the synthesis of some bi- and poly-nuclear complexes.

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Results and discussion

(a) Synthesis of cyano-pentafluorophenylaurate

The reaction of the precursors $Au(C_6F_5)_n(tht)$ (n = 1 or 3; tht = tetrahydrothiophene) with KCN (eq. 1):

$$Au(C_6F_5)_n(tht) + KCN \rightarrow tht + K[Au(C_6F_5)_n(CN)] \quad (1)$$

leads to solutions from which the gold(III) complex $K[Au(C_6F_5)_3(CN)]$ (IIb) can be crystallized by evaporation. The gold(I) derivative gives non-crystallizable oils, but well-crystallized compounds can be obtained by addition of solutions of a salt with a bulky cation $QClO_4$ (Q = $[BzPh_3P]^+$ (Bz = benzyl)) [11,12] (eq. 2).

$$K[Au(C_6F_5)_n(CN)] + QClO_4 \rightarrow KClO_4 + Q[Au(C_6F_5)_n(CN)] \quad (2)$$

(I, n = 1; IIa, n = 3)

The salt $Q[Au(C_6F_5)_2(CN)_2]$ (Q = NBu_4) can be obtained by an exchange reaction according to eq. 3

$$trans\text{-}Q[Au(C_6F_5)_2Cl_2] + 2\ NaCN \rightarrow 2\ ClNa + Q[Au(C_6F_5)_2(CN)_2] \quad (3)$$

(III)

The anion in III must be the *trans*-isomer, because it shows a single band due to ν(C≡N) at 2170m cm^{-1}, along with another single band (at 795s cm^{-1}) assignable to the X-sensible mode of XC_6F_5 [13,14].

Refluxing of acetone solutions of III (for 4 h) leads to complete isomerization to the *cis*-derivative, as has been reported for other dihaloaurate(III) [11]. Evaporation of these solutions yields non-crystallizable oils. The same happens if the *cis*-derivative is synthesized directly (eq. 3) starting from the *cis*-dichloro derivative, even if another cation is used (K^+ or $BzPh_3P^+$). However, the solutions exhibit two bands due to ν(C≡N) at 2175m and 2150m cm^{-1} along with another two (at 800m and 785m cm^{-1}) assignable to the X-sensitive mode of XC_6F_5, which confirms the presence of the *cis*-isomer.

(b) Reactions of the cyanoaurate with inorganic acids

The reaction of complexes I, IIb and III in Et_2O with an excess of the acid HA (A = Cl or BF_4) takes place according to eq. 4.

$$Q[Au(C_6F_5)_3(CN)] + HA \xrightarrow{Et_2O} QA + Au(C_6F_5)_3(CN)HOEt_2 \quad (4)$$

(IV)

Of the possible complexes only IV can be isolated as a white solid, whilst the other two reactions give non-crystallizable oils. In the resulting complex the band due to ν(C≡N) is displaced towards higher energies (90 cm^{-1}) relative to the parent compound (Table 1). Acetone solutions of IV are acidic, and their conductivity is that of an 1/1 electrolyte. The IR spectra of these solutions show ν(C≡N) again at 2180 cm^{-1}. All this seems to support its formulation as $[Et_2OH]^+$ $[Au(C_6F_5)_3(CN)]^-$. The molecular weight of IV (osmometric in chloroform) is only a little lower than that calculated for the formula weight, indi-

TABLE 1

ANALYTICAL DATA FOR COMPLEXES I—XXIV

Complex		Yield (%)	M.p. (°C)	Anal. found(calcd.) (%)				Λ_M (ohm^{-1} cm^2 mol^{-1})	Mol.wt. found(calcd.)	ν(CN) (cm^{-1})
				C	H	N	Au			
I	$BzPh_3P[Au(C_6F_5)(CN)]$	55	140	52.10 (51.69)	3.00 (2.98)	1.71 (1.88)	27.05 (26.49)	112	—	2140m
IIa	$BzPh_3P[Au(C_6F_5)_3(CN)]$	80	150	49.30 (49.05)	2.20 (2.06)	1.38 (1.30)	19.12 (18.28)	107	—	2175m
IIb	$K[Au(C_6F_5)_3(CN)]$	75	>260	30.40 (29.90)	—	2.19 (1.83)	25.85 (25.80)	117	—	2180mw
III	$Bu_4N[Au(C_6F_5)_2(CN)_2]$	87	120	43.78 (43.65)	4.37 (4.40)	5.47 (5.09)	24.09 (23.86)	106	—	2185m
IV	$Au(C_6F_5)_3(CN)HOEt_2$	20	165	34.73 (34.56)	1.51 (1.39)	1.90 (1.75)	25.41 (24.64)	120	705 (799)	2265s
V	$Et_3HN[Au(C_6F_5)_3(CN)]$	85	130	36.93 (36.34)	2.17 (1.95)	3.36 (3.39)	24.50 (23.83)	130	—	2175m
VI	$Et_3HN[Au(C_6F_5)(CN)]$	79	180 (dec.)	32.26 (31.72)	2.78 (3.28)	5.20 (5.69)	40.52 (40.01)	132	—	2140m
VII	$Et_3HN[Au(C_6F_5)_2(CN)_2]$	79	135 (dec.)	35.14 (35.05)	2.65 (2.35)	6.40 (6.13)	29.32 (28.74)	100	—	2180m
VIII	$Au(C_6F_5)(CNMe)$	60	130	24.05 (23.72)	0.89 (0.75)	3.54 (3.46)	48.82 (48.62)	6	420 (405)	2265vs
IX	$Au(C_6F_5)_3(CNMe)$	51	115	32.93 (32.50)	0.70 (0.41)	1.65 (1.89)	27.21 (26.65)	8	752 (739)	2295vs
X	$Au(C_6F_5)_2(CN)(CNMe)$	48	193 (dec.)	30.25 (30.11)	0.60 (0.50)	4.80 (4.68)	33.20 (32.93)	3	615 (598)	2185mw 2310vs
XI	$Au(C_6F_5)[C(NHMe)_2]$	67	85	24.92 (24.78)	1.91 (1.85)	6.35 (6.42)	45.40 (45.16)	3	442 (436)	1580s
XII	$Au(C_6F_5)_3[C(NHMe)_2]$	85	98	32.82 (32.75)	1.10 (1.05)	3.54 (3.64)	25.93 (25.57)	3	795 (770)	1605s
XIII	$Au(C_6F_5)_2(CN)[C(NHMe)_2]$	36	175 (dec.)	29.60 (30.54)	1.73 (1.28)	7.02 (6.68)	31.70 (31.30)	12	—	2190mw 1625s
XIV	$BzPh_3P[(C_6F_5)_3AuCNAu(C_6F_5)]$	60	141	41.38 (41.66)	1.80 (1.54)	1.10 (0.97)	27.10 (27.33)	110	—	2190m
XV	$(C_6F_5)_3AuCNAuPPh_3$	50	210	37.65 (37.55)	1.40 (1.28)	1.30 (1.18)	32.72 (33.29)	6	1115 (1183)	2225m

TABLE 1 (continued)

ANALYTICAL DATA FOR COMPLEXES I–XXIV

Complex		Yield (%)	M.p. (°C)	Anal. found(calcd.) (%)				Λ_M (ohm^{-1} cm^2 mol^{-1})	Mol.wt. found(calcd.)	ν(CN) (cm^{-1})
				C	H	N	Au			
XVI	$(C_6F_5)_2(CN)AuCNAuPPh_3$	70	153 (dec.)	36.78 (36.87)	1.69 (1.45)	2.72 (2.69)	38.21 (37.79)	17	1060 (1042)	2242m 2185vw
XVII	$BzPh_3P\{(\mu\text{-}CN)[Au(C_6F_5)]_2\}$	86	125	40.73 (41.21)	2.20 (2.00)	1.30 (1.26)	36.10 (35.57)	128	—	2195ms
XVIII	$BzPh_3P\{(\mu\text{-}CN)[Au(C_6F_5)_3]_2\}$	65	75	41.28 (41.94)	1.31 (1.25)	0.90 (0.79)	22.75 (22.18)	130	—	2210ms
XIX	$[(C_6F_5)_2Au(CN)_2Ag]_n$	90	230 (dec.)	24.98 (24.33)	—	4.13 (4.05)	—	58	—	2238m
XX	$[Ag(py)_2][Au(C_6F_5)_2(CN)_2]$	57	198	33.44 (33.94)	1.42 (1.18)	6.61 (6.60)	—	98	—	2175w
XXI	$[Ag(phen)_2][Au(C_6F_5)_2(CN)_2]$	87	238 (dec.)	44.19 (43.41)	1.61 (1.53)	8.26 (7.91)	—	106	—	2175w
XXII	$[Ag(PPh_3)_3][Au(C_6F_5)_2(CN)_2]$	90	206	55.97 (55.27)	3.80 (3.07)	1.51 (1.90)	—	86	—	2190w
XXIII	$[(C_6F_5)_2Au(CN)_2Au]_n$	45	206 (dec.)	21.87 (21.55)	—	3.73 (3.59)	50.41 (50.49)	—	—	2240m
XXIV	$[Au(PPh_3)_2][Au(C_6F_5)_2(CN)_2]$	75	270 (dec.)	46.45 (46.03)	2.67 (2.32)	2.29 (2.15)	31.05 (30.19)	91	—	2175w

cating that CN···$HOEt_2$ interaction via hydrogen bridges is likely, both in the solid state and in $CHCl_3$ solution. The IR spectrum does not show the bands due to ν(N—H) [15], but exhibits an absorption at 3600m(br) cm^{-1} which is assignable to ν(OH).

Complex IV reacts with NEt_3 according to eq. 5 to give V, which exhibits a

$$Au(C_6F_5)_3CNHOEt_2 + NR_3 \rightarrow [Et_3HN][Au(C_6F_5)_3(CN)] \quad (5)$$

(V)

band due to ν(C≡N) at 2175 cm^{-1}. This shows that complex V does not show the type of interaction between the cation and anion postulated for complex IV.

The solutions which are obtained if I and III are brought into reaction according to eq. 4, show the bands due to ν(CN) at 2110s cm^{-1} or, respectively, 2205m and 2175m cm^{-1}. Though the oils obtained upon evaporating could not be crystallized, it seems that both I and III undergo protonation, but III only at one of the CN groups. If NEt_3 is added to either of these solutions (eq. 5) the anionic complex $[Et_3NH][Au(C_6F_5)(CN)]$ (VI) or $[Et_3NH][Au(C_6F_5)_2(CN)_2]$ (VII) can be isolated (Table 1). VII must be the *trans*-isomer, since its IR spectrum shows a single band (at 795s cm^{-1}) due to XC_6F_5.

(c) Isocyanide and carbene complexes

The methylation of complexes I, IIa and III with $[Me_3O][BF_4]$ (eq. 6) gives the corresponding isocyanide complexes (VIII—X):

$$Q[M^*—CN] + [Me_3O][BF_4] \rightarrow M^*—CNMe + Me_2O + QBF_4 \quad (6)$$

($M^* = (C_6F_5)Au$, $(C_6F_5)_3Au$, $(C_6F_5)_2(CN)Au$)

As before, only one of the two CN group of III undergoes reaction, even if an excess of $[Me_3O][BF_4]$ is used.

Complexes VIII—X are white air- and moisture-stable solids at room temperature. They are non-conducting in acetone and monomeric in $CHCl_3$ (Table 1). In their IR spectra the band due to ν(CN) is shifted towards higher energies relative to the parent compounds, which is in accordance with previous observations on analogous complexes [16,17].

The isocyanides VIII—X react readily with methylamine to give the corresponding carbene (XI—XIII) (eq. 7):

$$M^*—CN—Me + NH_2Me \rightarrow M^*—C(NHMe)(NHMe) \quad (7)$$

These are white air- and moisture-stable solids, which are non-conducting and monomeric (Table 1). Their IR spectra exhibit a band due to ν(CN) at about 1590 cm^{-1}, characteristic of carbene [18,19].

(d) Complexes I, IIa and III as N-donor ligands

The terminal nitrogen atom in the cyano complex can act as a donor [14],

and can even displace other ligands (eq. 8, 9, 10)

$$Q[Au(C_6F_5)CN] + Au(C_6F_5)_3(tht) \rightarrow tht + Q[(C_6F_5)Au{-}CN{-}Au(C_6F_5)_3] \quad (8)$$

(XIV)

$$Q[Au(C_6F_5)_3CN] + Au(OClO_3)PPh_3 \rightarrow (C_6F_5)_3Au{-}CN{-}AuPPh_3 + QClO_4 \quad (9)$$

(XV)

$$Q[Au(C_6F_5)_2(CN)_2] + Au(OClO_3)PPh_3 \rightarrow$$

$$\rightarrow (C_6F_5)_2(CN)Au{-}CN{-}AuPPh_3 + QClO_4 \quad (10)$$

(XVI)

Although the reaction between IIa and $Au(C_6F_5)(tht)$ should lead to an isomer of XIV, the resulting product is undistinguishable from XIV (the IR spectra and melting points are the same).

Cyano-bridged binuclear aurate can also be prepared (eq. 11) by precipitating half of the CN of the precursors (I or IIa) as AgCN:

$$2\,Q[M^*{-}CN] + AgClO_4 \rightarrow AgCN + Q[M^*{-}CN{-}M^*] \quad (11)$$

(XVII, $M^* = (C_6F_5)Au$; XVIII, $M^* = (C_6F_5)_3Au$)

In the spectra of complexes XIV, XV, XVII and XVIII, the single band due to $\nu(C{\equiv}N)$ is shifted towards higher energies relative to the mononuclear complexes containing terminal CN. In the spectrum of XVII two bands are observed, though only one of them is shifted towards higher energies. A single band at 800m cm^{-1} points to the *trans*-configuration of the two C_6F_5 groups.

The reaction (1/1) of III with $AgClO_4$ does not follow eq. 11 but leads to precipitation of a white air- and moisture-stable solid (XIX). This does not contain terminal CN groups since its single band due to $\nu(CN)$ is displaced towards higher energies. It also shows a single absorption at 802 cm^{-1} assignable to XC_6F_5. Because of its insolubility in benzene, dichloromethane, chloroform, diethyl ether and n-hexane it is assumed to be a polymeric species, formed according to eq. 12.

$$Q[Au(C_6F_5)_2(CN)_2] + AgClO_4 \rightarrow QClO_4 + \frac{1}{x}[NC\underset{\displaystyle C_6F_5}{\overset{\displaystyle C_6F_5}{Au}}CNAg]_x \quad (12)$$

(XIX)

The treatment of suspensions of XIX in CH_2Cl_2 with Py, Phen, or PPh_3 causes complete dissolution of XIX and formation of $[AgL_n][Au(C_6F_5)_2(CN)_2]$ (XX, $n = 2$ (Py); XXI, $n = 2$ (phen); XXII, $n = 3$ (PPh_3)). Complexes XX—XXII are air- and moisture-stable solids, which behave as (1/1) electrolytes in acetone. They show a single band due to $\nu(CN)$ in the 2190—2175 cm^{-1} region, along with a single band assignable to the C_6F_5X sensitive mode at 800—790 cm^{-1} and should therefore be the *trans*-isomers.

The (1/1) reaction of III with $Au(OClO_3)(tht)$ leads to the precipitation of $[(C_6F_5)_2Au(CN)_2Au]_n$ (XXIII), similar to XIX, whose spectrum shows a single

band assignable to ν(CN) bridge at 2240 cm^{-1} along with a single band at 795 cm^{-1} due to the C_6F_5X sensitive mode. This points as for XIX to a *trans* configuration of the aryl groups. It is noteworthy that a *cis*-geometry for the R groups has been proposed for the derivatives $[R_2Au(CN)_2Au]_n$ (R = Et, n-Pr) obtained by thermal decomposition of $[R_2AuCN]_4$ [2,6]. Complex XXIII dissolves upon addition of PPh_3, to give $[Au(PPh_3)_2][Au(C_6F_5)_2(CN)_2]$ (XXIV), an 1/1 electrolyte, whose anion retains the *trans*-configuration (single bands at 2175w and 795m cm^{-1}).

Experimental

IR spectra were recorded (over the range 4000—200 cm^{-1}) on a Perkin—Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in 5×10^{-4} *M* acetone solutions with a Philips PW 9501/01 conductimeter. Molecular weights were measured in chloroform solutions with a Hitachi Perkin—Elmer 115 osmometer. C, N and H analyses were carried out with a Perkin—Elmer 240 microanalyzer Au was determined by ashing the samples in a crucible together with an aqueous solution of hydrazine.

The yields, melting points, C, H, N and Au analyses, conductivities, molecular weights, as well as, the ν(CN) of the novel complexes are listed in Table 1.

Preparation of the complexes

$BzPh_3P[Au(C_6F_5)_n(CN)]$ (n = 1 or 3). 0.066 g (1 mmol) of KCN was added to a solution of 1 mmol of $Au(C_6F_5)_n$(tht) [12,20] in 30 ml of methanol and the solution was stirred for 4 h at room temperature. After addition of 0.46 g (1 mmol) of $[BzPh_3P]ClO_4$ and stirring for 30 min the solution was evaporated to dryness and the white residue was treated with dichloromethane. The $KClO_4$ was filtered off and the filtrate was concentrated to ~5 ml. Addition of hexane led to the separation of the white complex I or IIa, which was recrystallized from dichloromethane/hexane.

IIb was obtained similarly, though without adding $[BzPh_3P]ClO_4$.

trans-$Bu_4N[Au(C_6F_5)_2(CN)_2]$. 0.074 g (1.5 mmol) of NaCN were added to a solution of 0.42 g (0.5 mmol) of *trans*-$Bu_4N[Au(C_6F_5)_2Cl_2]$ in 50 ml of acetone and the mixture was stirred for 18 h at room temperature. After filtering off the precipitated NaCl, the solution was evaporated to dryness and the residue was extracted with 30 ml of dichloromethane. The excess of NaCN was removed, the filtrate was evaporated to dryness and the white residue was recrystallized from dichloromethane/hexane to give white crystals of III.

A similar process, but starting from *cis*-$Bu_4N[Au(C_6F_5)_2Cl_2]$ led to *cis*-Bu_4N-$[Au(C_6F_5)_2(CN)_2]$ as an oil, which could not be crystallized.

$Au(C_6F_5)_3(CN)HOEt_2$. Addition of an excess of HBF_4 or HCl (0.5 ml) to a solution of IIa (0.2 g, 0.19 mmol) in 15 ml of ether at 0°C led to the precipitation of $[BzPh_3P]A$ (A = BF_4 or Cl). After 15 min stirring the precipitate was filtered off and the filtrate was evaporated to dryness. The resulting oil was destroyed vigorous stirring with hexane, and complex IV was recrystallized from ether/hexane.

A similar process, but starting from complex I or III led to $Au(C_6F_5)(CN)$-

$HOEt_2$ or $Au(C_6F_5)_2(CN)_2HOEt_2$ as oils, which could not be crystallized.

$Et_3HN(M^*—CN)$ ($M^* = (C_6F_5)Au$, $(C_6F_5)_3Au$ or $(C_6F_5)_2(CN)Au$). An equimolecular amount of Et_3N was added to solutions of 0.2 mmol of each of the three above described complexes in 20 ml of dichloromethane. The solution was stirred for 30 min at room temperature, then evaporated to dryness. Recrystallization of the residue from dichloromethane/hexane gave white crystals of V, VI or VII, respectively.

$Au(C_6F_5)_n(CNMe)$ ($n = 1$ or 3). 0.054 g (0.36 mmol) of $[Me_3O]BF_4$ was added to solutions of 0.36 mmol of I or IIa in 30 ml of dichloromethane and the solution was refluxed for 6 h. It was then evaporated to dryness, and the residue was treated with 25 ml of ether. The insoluble $[BzPh_3P]BF_4$ was filtered off. Evaporation to dryness and recrystallization from dichloromethane/hexane afforded the white complex VIII or IX.

$Au(C_6F_5)_2(CN)(CNMe)$. A solution of 0.054 g (0.36 mmol) of $[Me_3O]BF_4$ and 0.15 g (0.18 mmol) of III in 40 ml of dichloromethane was refluxed for 10 h. Evaporation of the solvent led to the white complex X, which was washed with 5 ml of dichloromethane and recrystallized from acetone/hexane.

$M^*—C(NHMe)_2$ ($M^* = (C_6F_5)Au$; $(C_6F_5)_3Au$ or $(C_6F_5)_2(CN)Au$). 0.4 mmol of methylamine was added to a solution of 0.2 mmol of I, IIa or III, in 20 ml of chloroform, and the mixture was stirred for 2 h at room temperature. The solution was evaporated to dryness to leave the white complexes XI, XII or XIII, which were recrystallized from dichloromethane/hexane.

$BzPh_3P[(C_6F_5)_3AuCNAu(C_6F_5)]$. A solution of 0.21 g (0.2 mmol) of IIa and 0.071 g (0.2 mmol) of $Au(C_6F_5)$(tht) [12] in 20 ml of methanol was stirred at room temperature for 2 h. Evaporation to dryness gave the white XIV, which was recrystallized from dichloromethane/hexane.

$M^*—CNAuPPh_3$ ($M^* = (C_6F_5)_3Au$ or $(C_6F_5)_2(CN)Au$). A solution of 0.38 mmol of $Au(OClO_3)(PPh_3)$ [21] in 20 ml of dichloromethane was added to 0.38 mmol of IIa or III and the mixture was stirred at room temperature for 3 h. Evaporation to dryness afforded a white solid, which was treated with 15 ml of ether. The $[BzPh_3P]ClO_4$ or $[Bu_4N]ClO_4$ was filtered off, and the filtrate was evaporated to dryness to give XV or XVII, which were recrystallized from dichloromethane/hexane.

$BzPh_3P\{\mu\text{-}CN)[Au(C_6F_5)_n]_2\}$ ($n = 1$ or 3). 0.041 g (0.2 mmol) of $AgClO_4$ was added to a solution of 0.4 mmol of I or IIa in 20 ml of dichloromethane and the mixture stirred at room temperature for 1 h. The precipitated AgCN was removed and the filtrate evaporated to dryness. The residue was treated with 15 ml of ether, the $[BzPh_3P]ClO_4$ was filtered off, and the filtrate was evaporated to dryness to give white crystals of XVII or XVIII, which were recrystallized from dichloromethane/hexane.

$[(C_6F_5)_2Au(CN)_2Ag]_n$. Addition of 0.041 g (0.2 mmol) of $AgClO_4$ to a solution of 0.165 g (0.2 mmol) of III in a mixture of 20 ml of dichloromethane and 20 ml of ether gave rise to precipitation of the white complex XIX, which was filtered off and washed with dichloromethane.

$[AgL_n][Au(C_6F_5)_2(CN)_2]$ ($L = Py$, $n = 2$; $L = Phen$, $n = 2$; $L = PPh_3$, $n = 3$). Addition of pyridine (0.4 mmol), *o*-phenantroline (0.4 mmol) or triphenylphosphine (0.6 mmol) to a suspension of 0.138 g (0.2 mmol) of XIX in 30 ml of dichloromethane led to formation of a clear solution which was stirred for

15 min at room temperature and partly evaporated (to ~8 ml). Addition of hexane led to the precipitation of XX, XXI or XXII, which were recrystallized from dichloromethane/hexane.

$[(C_6F_5)_2Au(CN)_2Au]_n$. 0.41 g (0.5 mmol) of III was added to a solution of 0.5 mmol of $Au(OClO_3)$(tht) in dichloromethane (10 ml)/ether (10 ml) (prepared by treating AuCl(tht) [22] with $AgClO_4$ at −20°C). The solution was slowly allowed to warm to room temperature (ca. 30 min) and stirred for another 30 min. The white precipitate of XXIII was filtered off and washed with dichloromethane.

$[Au(PPh_3)_2][Au(C_6F_5)_2(CN)_2]$. 0.078 g (0.3 mmol) of triphenylphosphine was added to a suspension of 0.117 g (0.15 mmol) of XXIII in 30 ml of dichloromethane. The resulting solution was stirred for 30 min at room temperature then evaporated to dryness, and the residual was recrystallized from dichloromethane/hexane.

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