Chemistry of gold(I, III) complexes with organic ligands as potential MOCVD precursors for fabrication of thin metallic films and nanoparticles

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Table 1. Thermal properties of [R_3PAuCN] [133].

PR_3	T_m, °C	Yield, %	Mass loss, %	ΔT, °C	Volatile products	Residue
$PCycl_3$	143	78	60.30	290–430	$Cycl_3P$, CN^-	Au
$PCyclPh_2$	170	82	59.85	210–415	$CyclPh_2P$, CN^-	Au
PEt_3	108	73	42.00	255–405	Et_3P, CN^-	Au
PPh_3	202	90	58.64	280–490	Ph_3P, CN^-	Au
$PAllPh_2$	139	60	48.21	200–440	$AllPh_2P$, CN^-	Au
CEP	121	71	38.25	220–500	CEP, CN^-	Au
PNp_3	263	75	69.18	270–544	Np_3P, CN^-	Au
P(*p*-Tol)$_3$	185	85	61.98	260–520	*p*-Tol, CN^-	Au
P(*m*-Tol)$_3$	154	86	61.87	220–500	*m*-Tol, CN^-	Au
P(*o*-Tol)$_3$	240	81	57.50	250–385	*o*-Tol, CN^-	AuCN
AuCN	---	70	11.5	350–700	CN^-	Au

Table 2. DTA data for the complexes of dimethylgold(III) with β-diketones, β-iminoketones, β-monothioketones and β-thioimines [108-112, 118].

Organic ligand	R	R’	$T_{m.}$, °C	T^{a}, °C	
			DTA/ He	DTA /He	DTA /H_2
R-CO-CH_2-CO-R’	CH_3	CH_3	76	145	125
	CH_3	CF_3	35	140	125
	$C(CH_3)_3$	CF_3	75	150	140
	$C(CH_3)_3$	$C(CH_3)_3$	74	200	160
	CH_3	C_6H_5	46	150	140
	C_6H_5	CF_3	66	80	75
	C_6H_5	C_6H_5	115	155	150
R-CNH-CH_2-CO-R’	CH_3	CH_3	66	190	160
	CH_3	CF_3	103	250	150
	$C(CH_3)_3$	CF_3	61	300	175
	CH_3	C_6H_5	57	200	165
R-CS-CH_2-CO-R’	CH_3	CH_3	48	77	--
	CH_3	CF_3	85	85	--
R-CS-CH_2-CNH-R’	CH_3	CH_3	--	168	--
	CH_3	CF_3	--	-	--

[a]decomposition onset temperatures of the complexes in the condensed phase

Table 3. Coefficients of the equation lg$P$ = A – B/T and thermodynamic parameters of sublimation of dimethylgold(III) β-diketonates [147].

Complex[a]	ΔT, K	A	B	ΔH_T^o, kJ/mol	ΔS_T^o, J/(mol·K)
$Me_2Au(acac)$	297–312	13.5	4995	95.3±2.9	203.1±9.2
$Me_2Au(thd)$	295–323	18.8	6622	126.6±1.3	304.3±4.2
$Me_2Au(bac)$	348–390	9.6	4524	86.5±1.7	128.3±4.2
$Me_2Au(i\text{-}acac)$	297–328	13.1	5087	97.4±3.8	195.6±12.1

[a]acac = $CH_3C(O)CHC(O)CH_3$, thd = $(CH_3)_3CC(O)CH\ C(O)C(CH_3)_3$, bac = $CH_3C(O)CHC(O)C_6H_5$, i-acac = $CH_3C(O)CHC(NH)CH_3$.

Table 4. Saturated vapor pressure of dimethylgold(III) with β-diketones [148, 149]

Me_2Au(ttfac) [148]		Me_2Au(ftfac) [148]		Me_2Au(btfac) [149]	
T, ºC	*P*, Torr	*T*, ºC	*P*, Torr	*T*, ºC	*P*, Torr
80	$1.2 \cdot 10^{-2}$	40	$3.1 \cdot 10^{-4}$	80	$2.0 \cdot 10^{-2}$
100	$5.9 \cdot 10^{-2}$	60	$3.8 \cdot 10^{-3}$	90	$4.1 \cdot 10^{-2}$
110	$1.2 \cdot 10^{-1}$	80	$2.8 \cdot 10^{-2}$	100	$8.3 \cdot 10^{-2}$
120	$2.4 \cdot 10^{-1}$	100	$1.6 \cdot 10^{-1}$	120	$3.1 \cdot 10^{-1}$
		110	$3.8 \cdot 10^{-1}$		
		120	$6.4 \cdot 10^{-1}$		

Table 5. Thermodynamic parameters of sublimation of dimethylgold(III) complexes with carboxylate, salicylaldiminate and quinolinate ligands.

Complex	ΔT, K	A	B	ΔH_T^o, kJ/mol	ΔS_T^o, J/(mol·K)
$[Me_2Au(OAc)]_2$	26–59	14.2	5280	100.9±0.8	216.7±1.5
$[Me_2Au(OOCCF_3)]_2$	26–52	14.9	5421	103.6±2.9	229.9±7.7
$[Me_2Au(Piv)]_2$	28–50	15.3	5701	109.1±2.1	273.1±7.1
$[Me_2Au(OBz)]_2$	94–130	17.7	8080	103.6±2.9	229.9±7.7
$Me_2Au(Sal{=}N{-}Me)$	58–87	15.9	6480	154.5±1.5	283.4±3.2
$Me_2Au(Sal{=}N{-}i\text{-}Pr)$	48–78	15.6	6211	123.9±0.8	250.0±1.6
$Me_2Au(Sal{=}N{-}Cy)$	65–111	16.9	7351	118.8±2.7	243.2±6.2
$Me_2Au(Sal{=}N{-}Ph)$	71–141	16.7	7420	140.6±2,2	268.1±5.1
$Me_2Au(OQ)$	81–114	14.6	6341	141.9±1,2	264.3±2.7
$Me_2Au(SQ)$	86–128	13.3	6300	121.2±1,9	224.1±4.6

Table 6. Temperatures of decomposition onset and main products of thermal decomposition of dimethylgold(III) complex vapors on heated surfaces at $P = 10^{-6}$ Torr [117, 138, 139].

Complex	T, °C (±5)	Main products of thermal decomposition
$[Me_2Au(OAc)]_2$	> 70	CH_3COOH, C_2H_6, CO_2
$[Me_2Au(Piv)]_2$	> 60	*t*-BuCOO*t*-Bu, *t*-BuCOOH, C_2H_6, CO_2
Me_2Au(Sal=N–Me)	> 120	EtSal=N–Me, MeSal=N–Me, HSal=N–Me
Me_2Au(Sal=N–*i*-Pr)	> 110	EtSal=N–*i*-Pr, MeSal=N–*i*-Pr, HSal=N–*i*-Pr

Table 7. Temperature ranges and main gaseous products of thermolysis of dithiophosphate complexes of dimethylgold(III).

Complex	ΔT, °C (±10)	Main gaseous products of thermolysis
$Me_2AuS_2P(OMe)_2$	160-200	$MeS_2P(OMe)_2$, $(MeS)_2$, $HP(OMe)_2$, C_2H_6, C_2H_4
$Me_2AuS_2P(OEt)_2$	150-200	$HS_2P(OMe)_2$, $(EtS)_2$, POMe, C_2H_6, C_2H_4
$Me_2AuS_2P(i\text{-}Bu)_2$	170-250	$HS_2P(i\text{-}Bu)_2$, $(i\text{-}BuS)_2$ and/or i-$BuBu_2PHS$, Me_4P_2 and/or $(EtS)_2$, $Me_2AuS_2PH_2$, C_4H_8

Table 8. Gold precursors used in CVD processes.

Precursor	Film composition	Deposition temperature, °C	Ref.
$Me_2Au(hfac)$	100% Au, 0% C	225–275	[165]
$Me_2Au(tfac)$	100% Au, 0% C	200–300	[134]
$Me_2Au(acac)$	95% Au, 5% C	200–300	[134]
$MeAu(PMe_3)$	96% Au, 4% C	200	[137]
$Me_3Au(PMe_3)$	95% Au, 5% C	200	[137]
$CF_3Au(PMe_3)$	no data	no data	[129]
$(CF_3)_3Au(PMe_3)$	no data	no data	[129]
$[Me_2AuOSiMe_3]_2$	95–97% Au	135–150	[160, 168]
MeAu(CNMe)	83% Au, 10% C	200	[62, 137]

Table 9. Composition of films deposited from different precursors according to XPS analysis [62].

Precursor	Element	Content, %
$MeAu(PMe_3)$	Au	71.22
	C	28.78
after Ar etching for 3 min.	Au	95.50
	C	3.80
	O	0.69
$Me_3Au(PMe_3)$	Au	65.61
	C	32.81
after Ar etching for 3 min.	O	1.59
	Au	95.32
	C	4.68
MeAu(CNMe)	Au	52.93
	C	36.81
	O	5.25
	N	5.01
$Me_3CC{\equiv}CAu(PMe_3)$	Au	37.64
	C	59.70
	O	2.66