

**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<sub>3</sub>PAuCN] [133].

PR <sub>3</sub>	T <sub>m</sub> , °C	Yield, %	Mass loss, %	ΔT, °C	Volatile products	Residue
PCycl <sub>3</sub>	143	78	60.30	290–430	Cycl <sub>3</sub> P, CN <sup>-</sup>	Au
PCyclPh <sub>2</sub>	170	82	59.85	210–415	CyclPh <sub>2</sub> P, CN <sup>-</sup>	Au
PEt <sub>3</sub>	108	73	42.00	255–405	Et <sub>3</sub> P, CN <sup>-</sup>	Au
PPh <sub>3</sub>	202	90	58.64	280–490	Ph <sub>3</sub> P, CN <sup>-</sup>	Au
PAllPh <sub>2</sub>	139	60	48.21	200–440	AllPh <sub>2</sub> P, CN <sup>-</sup>	Au
CEP	121	71	38.25	220–500	CEP, CN <sup>-</sup>	Au
PNp <sub>3</sub>	263	75	69.18	270–544	Np <sub>3</sub> P, CN <sup>-</sup>	Au
P( <i>p</i> -Tol) <sub>3</sub>	185	85	61.98	260–520	<i>p</i> -Tol, CN <sup>-</sup>	Au
P( <i>m</i> -Tol) <sub>3</sub>	154	86	61.87	220–500	<i>m</i> -Tol, CN <sup>-</sup>	Au
P( <i>o</i> -Tol) <sub>3</sub>	240	81	57.50	250–385	<i>o</i> -Tol, CN <sup>-</sup>	AuCN
AuCN	---	70	11.5	350–700	CN <sup>-</sup>	Au

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

Organic ligand	R	R'	$T_m, ^\circ\text{C}$	$T^a, ^\circ\text{C}$	
			DTA/ He	DTA /He	DTA /H <sub>2</sub>
R-CO-CH <sub>2</sub> -CO-R'	CH <sub>3</sub>	CH <sub>3</sub>	76	145	125
	CH <sub>3</sub>	CF <sub>3</sub>	35	140	125
	C(CH <sub>3</sub> ) <sub>3</sub>	CF <sub>3</sub>	75	150	140
	C(CH <sub>3</sub> ) <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	74	200	160
	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	46	150	140
	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	66	80	75
	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	115	155	150
R-CNH-CH <sub>2</sub> -CO-R'	CH <sub>3</sub>	CH <sub>3</sub>	66	190	160
	CH <sub>3</sub>	CF <sub>3</sub>	103	250	150
	C(CH <sub>3</sub> ) <sub>3</sub>	CF <sub>3</sub>	61	300	175
	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	57	200	165
R-CS-CH <sub>2</sub> -CO-R'	CH <sub>3</sub>	CH <sub>3</sub>	48	77	--
	CH <sub>3</sub>	CF <sub>3</sub>	85	85	--
R-CS-CH <sub>2</sub> -CNH-R'	CH <sub>3</sub>	CH <sub>3</sub>	--	168	--
	CH <sub>3</sub>	CF <sub>3</sub>	--	-	--

<sup>a</sup>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)  $\beta$ -diketonates [147].

Complex <sup>a</sup>	$\Delta T$ , K	A	B	$\Delta H_T^o$ , kJ/mol	$\Delta S_T^o$ , J/(mol·K)
Me <sub>2</sub> Au(acac)	297–312	13.5	4995	95.3±2.9	203.1±9.2
Me <sub>2</sub> Au(thd)	295–323	18.8	6622	126.6±1.3	304.3±4.2
Me <sub>2</sub> Au(bac)	348–390	9.6	4524	86.5±1.7	128.3±4.2
Me <sub>2</sub> Au(i-acac)	297–328	13.1	5087	97.4±3.8	195.6±12.1

<sup>a</sup>acac = CH<sub>3</sub>C(O)CHC(O)CH<sub>3</sub>, thd = (CH<sub>3</sub>)<sub>3</sub>CC(O)CH C(O)C(CH<sub>3</sub>)<sub>3</sub>, bac = CH<sub>3</sub>C(O)CHC(O)C<sub>6</sub>H<sub>5</sub>,  
i-acac = CH<sub>3</sub>C(O)CHC(NH)CH<sub>3</sub>.

**Table 4.** Saturated vapor pressure of dimethylgold(III) with  $\beta$ -diketones [148, 149]

Me <sub>2</sub> Au(tfac) [148]		Me <sub>2</sub> Au(ftfac) [148]		Me <sub>2</sub> Au(btfac) [149]	
<i>T</i> , °C	<i>P</i> , Torr	<i>T</i> , °C	<i>P</i> , Torr	<i>T</i> , °C	<i>P</i> , Torr
80	1.2·10 <sup>-2</sup>	40	3.1·10 <sup>-4</sup>	80	2.0·10 <sup>-2</sup>
100	5.9·10 <sup>-2</sup>	60	3.8·10 <sup>-3</sup>	90	4.1·10 <sup>-2</sup>
110	1.2·10 <sup>-1</sup>	80	2.8·10 <sup>-2</sup>	100	8.3·10 <sup>-2</sup>
120	2.4·10 <sup>-1</sup>	100	1.6·10 <sup>-1</sup>	120	3.1·10 <sup>-1</sup>
		110	3.8·10 <sup>-1</sup>		
		120	6.4·10 <sup>-1</sup>		

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

Complex	$\Delta T$ , K	A	B	$\Delta H_T^\circ$ , kJ/mol	$\Delta S_T^\circ$ , J/(mol·K)
$[\text{Me}_2\text{Au}(\text{OAc})]_2$	26–59	14.2	5280	100.9±0.8	216.7±1.5
$[\text{Me}_2\text{Au}(\text{OOCF}_3)]_2$	26–52	14.9	5421	103.6±2.9	229.9±7.7
$[\text{Me}_2\text{Au}(\text{Piv})]_2$	28–50	15.3	5701	109.1±2.1	273.1±7.1
$[\text{Me}_2\text{Au}(\text{OBz})]_2$	94–130	17.7	8080	103.6±2.9	229.9±7.7
$\text{Me}_2\text{Au}(\text{Sal}=\text{N}-\text{Me})$	58–87	15.9	6480	154.5±1.5	283.4±3.2
$\text{Me}_2\text{Au}(\text{Sal}=\text{N}-i\text{-Pr})$	48–78	15.6	6211	123.9±0.8	250.0±1.6
$\text{Me}_2\text{Au}(\text{Sal}=\text{N}-\text{Cy})$	65–111	16.9	7351	118.8±2.7	243.2±6.2
$\text{Me}_2\text{Au}(\text{Sal}=\text{N}-\text{Ph})$	71–141	16.7	7420	140.6±2.2	268.1±5.1
$\text{Me}_2\text{Au}(\text{OQ})$	81–114	14.6	6341	141.9±1.2	264.3±2.7
$\text{Me}_2\text{Au}(\text{SQ})$	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 ( $\pm 5$ )	Main products of thermal decomposition
$[\text{Me}_2\text{Au}(\text{OAc})]_2$	> 70	$\text{CH}_3\text{COOH}$ , $\text{C}_2\text{H}_6$ , $\text{CO}_2$
$[\text{Me}_2\text{Au}(\text{Piv})]_2$	> 60	$t\text{-BuCOO}t\text{-Bu}$ , $t\text{-BuCOOH}$ , $\text{C}_2\text{H}_6$ , $\text{CO}_2$
$\text{Me}_2\text{Au}(\text{Sal}=\text{N}-\text{Me})$	> 120	$\text{EtSal}=\text{N}-\text{Me}$ , $\text{MeSal}=\text{N}-\text{Me}$ , $\text{HSal}=\text{N}-\text{Me}$
$\text{Me}_2\text{Au}(\text{Sal}=\text{N}-i\text{-Pr})$	> 110	$\text{EtSal}=\text{N}-i\text{-Pr}$ , $\text{MeSal}=\text{N}-i\text{-Pr}$ , $\text{HSal}=\text{N}-i\text{-Pr}$

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

Complex	$\Delta T, ^\circ\text{C}$ ( $\pm 10$ )	Main gaseous products of thermolysis
$\text{Me}_2\text{AuS}_2\text{P}(\text{OMe})_2$	160-200	$\text{MeS}_2\text{P}(\text{OMe})_2$ , $(\text{MeS})_2$ , $\text{HP}(\text{OMe})_2$ , $\text{C}_2\text{H}_6$ , $\text{C}_2\text{H}_4$
$\text{Me}_2\text{AuS}_2\text{P}(\text{OEt})_2$	150-200	$\text{HS}_2\text{P}(\text{OMe})_2$ , $(\text{EtS})_2$ , $\text{POMe}$ , $\text{C}_2\text{H}_6$ , $\text{C}_2\text{H}_4$
$\text{Me}_2\text{AuS}_2\text{P}(i\text{-Bu})_2$	170-250	$\text{HS}_2\text{P}(i\text{-Bu})_2$ , $(i\text{-BuS})_2$ and/or $i\text{-BuBu}_2\text{PHS}$ , $\text{Me}_4\text{P}_2$ and/or $(\text{EtS})_2$ , $\text{Me}_2\text{AuS}_2\text{PH}_2$ , $\text{C}_4\text{H}_8$



**Table 8.** Gold precursors used in CVD processes.

Precursor	Film composition	Deposition temperature, °C	Ref.
Me <sub>2</sub> Au(hfac)	100% Au, 0% C	225–275	[165]
Me <sub>2</sub> Au(tfac)	100% Au, 0% C	200–300	[134]
Me <sub>2</sub> Au(acac)	95% Au, 5% C	200–300	[134]
MeAu(PMe <sub>3</sub> )	96% Au, 4% C	200	[137]
Me <sub>3</sub> Au(PMe <sub>3</sub> )	95% Au, 5% C	200	[137]
CF <sub>3</sub> Au(PMe <sub>3</sub> )	no data	no data	[129]
(CF <sub>3</sub> ) <sub>3</sub> Au(PMe <sub>3</sub> )	no data	no data	[129]
[Me <sub>2</sub> AuOSiMe <sub>3</sub> ] <sub>2</sub>	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 <sub>3</sub> ) after Ar etching for 3 min.	Au	71.22
	C	28.78
	Au	95.50
	C	3.80
	O	0.69
Me <sub>3</sub> Au(PMe <sub>3</sub> ) after Ar etching for 3 min.	Au	65.61
	C	32.81
	O	1.59
	Au	95.32
	C	4.68
MeAu(CNMe)	Au	52.93
	C	36.81
	O	5.25
	N	5.01
Me <sub>3</sub> CC≡CAu(PMe <sub>3</sub> )	Au	37.64
	C	59.70
	O	2.66