Breaking through the Thermodynamics "Wilds" of Metal–Organic Chemical Vapor Deposition Precursors: Metal *tris*-Acetylacetonates

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Table S1. Saturated vapor pressures of Al(acac)$_3$, Cr(acac)$_3$, and In(acac)$_3$ obtained by the transpiration method: p_i – from the experimental data and $p_{calc.}$ – from the corresponding equation (p_{ref} = 1 Pa, standard uncertainty $u(p_i) = 0.05 \cdot p_i$).

T, K [a]	P_a, Pa [b]	m, mg [c]	υ(Ar/N$_2$), dm^3 h^{-1} [d]	V(Ar/N$_2$), dm^3 [e]	T_a, K [c]	p_i, Pa	$p_{calc.}$, Pa
			Al(acac)$_3$, $P2_1/c$				
			series 1 (NIIC SB RAS)				
		$\ln(p/p_{ref}) = \dfrac{399.8}{R} - \dfrac{144677.5}{RT} - \dfrac{65.2}{R}\ln\dfrac{T}{298.15}$					
421.0	100525	7.38	3.733	0.933	295.2	59.8	56.8
425.3	100525	9.84	3.719	0.930	295.2	80.0	79.7
456.1	101325	25.73	1.040	0.260	295.2	743	730
460.0	101325	31.89	1.035	0.259	295.2	924	944
422.5	101325	11.43	4.050	1.38	295.2	62.5	64.0
440.0	101325	16.12	2.000	0.500	295.2	243	240
382.0	102792	16.44	4.063	71.1	295.7	1.75	1.79
418.3	101325	11.98	4.005	2.00	295.2	45.3	45.8
428.1	101325	12.67	4.004	1.00	295.2	95.7	98.9
436.8	101325	12.97	2.134	0.534	295.2	184	190
398.8	101058	10.72	4.004	9.01	295.2	9.00	8.70
405.3	100258	10.24	4.002	5.00	295.2	15.5	15.4
448.9	100258	30.59	2.021	0.505	295.2	456	449
379.2	101325	12.50	4.005	72.1	295.2	1.31	1.35
386.7	100792	10.06	4.003	26.0	295.2	2.93	2.83
			series 2 (University of Rostock)				
		$\ln(p/p_{ref}) = \dfrac{393.4}{R} - \dfrac{142213.4}{RT} - \dfrac{65.2}{R}\ln\dfrac{T}{298.15}$					
411.9	99458	24.00	2.269	6.96	295.2	26.1	26.0
425.0	99458	14.42	2.269	1.51	296.2	72.4	73.0
439.3	99458	14.30	1.872	0.499	296.2	218	210
381.6	99992	15.70	4.160	67.3	295.2	1.76	1.74
399.1	99992	19.00	4.255	17.1	295.2	8.41	8.82
416.7	99992	15.50	4.119	3.02	296.2	39.0	38.5
434.9	102792	20.80	2.816	1.03	296.2	153	153
394.0	103058	13.90	4.240	19.9	296.2	5.31	5.57
444.6	103591	21.00	1.269	0.529	295.2	301	304
454.9	103591	33.10	1.235	0.412	295.2	608	605
378.4	103591	14.60	5.162	82.0	294.2	1.34	1.28

Cr(acac)$_3$, $P2_1/c$

series 1 (NIIC SB RAS)

$$\ln(p/p_{\mathrm{ref}}) = \frac{391.6}{R} - \frac{146931.9}{RT} - \frac{65.3}{R}\ln\frac{T}{298.15}$$

471.7	101458	31.51	2.021	0.505	296.2	438	417
458.1	101458	12.22	2.007	0.502	296.2	171	173
465.0	101458	19.84	2.016	0.504	296.2	277	272
410.6	101458	12.40	4.010	18.0	295.2	4.83	4.70
407.7	101458	10.41	4.008	20.0	295.2	3.65	3.66
420.4	101458	11.79	4.006	8.01	295.2	10.3	10.7
444.2	101458	11.91	4.000	1.33	295.2	62.7	65.7
455.1	101458	12.52	2.503	0.626	295.2	140	141
477.0	101458	40.76	2.004	0.501	295.2	568	579
395.0	101458	10.97	4.006	67.1	295.2	1.15	1.16
400.9	101458	10.10	2.058	34.5	295.2	2.06	2.00

series 2 (University of Rostock)

$$\ln(p/p_{\mathrm{ref}}) = \frac{398.6}{R} - \frac{150436.4}{RT} - \frac{65.3}{R}\ln\frac{T}{298.15}$$

400.8	101992	16.30	3.974	73.8	295.2	1.55	1.61
421.0	101725	21.30	4.769	14.9	295.2	10.0	9.53
440.4	101725	9.10	3.906	1.43	295.2	44.6	44.3
459.8	101725	12.10	1.600	0.482	295.2	176	179
470.2	99458	13.50	1.059	0.265	293.2	356	357

In(acac)$_3$, $Pbca$

$$\ln(p/p_{\mathrm{ref}}) = \frac{411.1}{R} - \frac{153285.7}{RT} - \frac{65.1}{R}\ln\frac{T}{298.15}$$

435.6	99992	13.24	3.934	1.31	294.2	59.9	63.3
412.5	103058	14.15	3.214	9.11	296.2	9.28	9.06
429.2	102792	13.11	3.225	2.15	296.2	36.42	37.8
407.9	103591	10.36	3.353	10.1	294.2	6.11	5.98
389.4	99992	10.33	1.286	59.3	295.2	1.04	1.00
384.2	100525	6.96	0.949	75.0	296.2	0.555	0.587
395.4	99992	9.51	1.293	32.3	296.2	1.76	1.83
399.4	100125	11.34	1.114	24.5	296.2	2.76	2.69
418.7	101992	10.44	3.091	3.86	295.2	16.1	15.63
423.6	101992	10.80	3.088	2.57	295.2	25.0	23.7

[a] Saturation temperature, standard uncertainty $u(T) = 0.5$ K.

[b] Atmospheric pressure, standard uncertainty $u(P_a) = 133$ Pa.

[c] Mass of transported compound cooled at the ambient temperature T_a, standard uncertainty $u(m) = 5\cdot10^{-5}$ g.

[d] Velocity of argon or nitrogen flow, standard uncertainty $u(v(\mathrm{Ar})) = 0.02\cdot v(\mathrm{Ar})$.

[e] Volume of the gas transported at the ambient temperature T_a and the atmospheric pressure P_a during experiments.

Table S2. The results of the vapor pressure measurements of the Al(acac)$_3$ by Knudsen effusion method with mass spectrometric registration of the gas phase composition: p_i – from the experimental data and $p_{calc.}$ – from the corresponding equation (p_{ref} = 1 Pa). [a] .

	Al(acac)$_3$, $P2_1/c$	
	series 3 (NIIC SB RAS)	
	$\ln(p/p_{\text{ref}}) = \dfrac{413.4}{R} - \dfrac{151052.1}{RT} - \dfrac{65.2}{R}\ln\dfrac{T}{298.15}$	
T, K	p_i, Pa	p_{calc}, Pa
427.0	80.4	77.9
429.0	99.5	91.6
434.0	130	136
382.0	1.21	1.24
390.0	3.07	2.80
402.0	8.36	8.87
414.0	24.1	26.1

[a] Standard uncertainty u is $u(T)$ = 1.0 K; relative standard uncertainty for vapor pressure $u_r(p_i)$ = $0.10 \cdot p_i$.

Table S3. Compilation of data on molar heat capacities $C_{p,m}^o$ and heat capacity differences for *tris*(acetylcetonato)metal(III) complexes at 298.15 K (in J·K^{-1}·mol^{-1}) [a]

.Complex	$C_{p,m}^o$(cr) [a]	$-\Delta_{cr}^g C_{p,m}^o$ [b]	[M] [c]	$C_{p,m}^o$(l) [d]	$-\Delta_l^g C_{p,m}^o$ [e]
1	2	3	4	5	6
Al(acac)$_3$	429.6±0.6 [1]	65.2	15.9	460.6	130.3
Cr(acac)$_3$	430.3±0.6 [1]	65.3	16.6	461.3	130.5
Sc(acac)$_3$	425.1±0.9 [2]	-64.5	11.4	456.1	129.2
Fe(acac)$_3$	429.9±0.9 [3]	-65.2	16.2	460.9	130.4
Ir(acac)$_3$	423.34±1.1 [1]	-64.2	9.6	454.3	128.7
V(acac)$_3$	418.3±0.8 [2]	-63.5	4.6	449.3	127.4
Mn(acac)3	424.5±0.8 [2]	-64.4	10.8	455.5	129.0
Co(acac)$_3$	409.0±0.8 [2]	-62.1	-4.7	440.0	125.0
Ru(acac)$_3$	428.3±0.2 [1]	-65.0	14.6	459.3	130.0
Rh(acac)$_3$	442±3.0 [4]	-67,1	28.3	473.0	133.6
	429.0±8.0 [f]	**65.1±1.2** [f]	**11.8±8.2** [f]		

[a] Values were obtained by adiabatic calorimetry except Rh(acac)$_3$ for which the value was get from DSC [4].

[b] Calculated according to equations (6).

[c] Assessed as [M] = $C_{p,m}^o$(cr) − 3[acac], where [acac] = 137.9 J·K^{-1}·mol^{-1} (see text).

[d] The contribution 31 J·K^{-1}·mol^{-1} was derived from experimental data on $C_{p,m}^o$(liq) and $C_{p,m}^o$(cr) for ferrocene [5] and was assumed to be valid for *tris*(acetylacetonato)metal(III) complexes.

[e] Calculated as $-\Delta_l^g C_{p,m}^o = 10.58 + 0.26 C_{p,m}^o(l)$ as suggested by Chickos et al. [6, 7].

[f] Values in bold are weighted mean ones. The uncertainty was used as the weighing factor. Uncertainties are expressed as expanded uncertainties at a level of confidence of 0.95 (k=2).

The $\Delta_{cr}^l H_m^o(T_{fus})$ values have been adjusted to 298.15 K with Equations (S1,S2) [7]:

$$\{\Delta_{cr}^l H_m^o(T_{fus}/K) - \Delta_{cr}^l H_m^o(298.15\ K)\}/(J\cdot mol^{-1}) = \Delta_{cr}^g C_{p,m}^o\ [(T_{fus}/K) - 298.15] - \Delta_l^g C_{p,m}^o\ [(T_{fus}/K) - 298.15] \quad (S1)$$

$$\{\Delta_{cr}^{l}S_{m}^{o}(T_{fus}/K) - \Delta_{cr}^{l}S_{m}^{o}(298.15\ K)\ \}/(J\cdot mol^{-1}\ K^{-1}) = \Delta_{cr}^{g}C_{p,m}^{o}\ln\frac{T_{fus}/K}{298.15} - \Delta_{l}^{g}C_{p,m}^{o}\ln\frac{T_{fus}/K}{298.15}, \tag{S2}$$

where $\Delta_{cr}^{g}C_{p,m}^{o}$ and $\Delta_{l}^{g}C_{p,m}^{o}$ have been taken from Table S3. Uncertainties in the temperature adjustment of fusion enthalpies from T_{fus} to the reference temperature are estimated to account with 30 % to the total adjustment [8]. The resulted $\Delta_{cr}^{l}H_{m}^{o}$ (298.15 K)/ $\Delta_{cr}^{l}S_{m}^{o}$(298.15 K) values are listed in Table S4.

Table S4. Compilation of available experimental fusion temperatures and standard molar enthalpies of fusion, $\Delta_{cr}^{l}H_{m}^{o}(T_{fus})$, and calculated from these data entropies of fusion, $\Delta_{cr}^{l}S_{m}^{o}(T_{fus})$, for *tris*(acetylacetonato)metal(III) complexes [a].

Complex	T_{fus}, K	$\Delta_{cr}^{l}H_{m}^{o}(T_{fus})$, kJ·mol⁻¹	$\Delta_{cr}^{l}S_{m}^{o}(T_{fus})$, J·mol⁻¹ K⁻¹	$\Delta_{cr}^{l}H_{m}^{o}$(298.15 K), [b] kJ·mol⁻¹	$\Delta_{cr}^{l}S_{m}^{o}$(298.15 K), [b] J·mol⁻¹ K⁻¹	Ref
Al(acac)₃	463.7	35.2±0.6	75.9±1.3	24.4±3.3	47.1±6.4	[9]
	469	35.0±2.0	74.6±4.3	23.9±3.9	45.1±7.4	[10]
	460	32.7±0.3	71.1±0.7	22.2±3.2	42.8±6.1	[10]
	466.7±0.2	32.7±0.3	71.1±0.7	22.2±3.2	42.8±6.1	[11]
	467.8	(28.7±1.3)	(61.4±2.8)	(17.6±3.6)	(32.0±6.5)	[12]
				23.2±1.7 [c]	**44.4±3.3** [c]	this work
Cr(acac)₃	488.9±0.5	34.0±0.3	69.5±0.6	21.6±3.7	37.3±6.5	[11]
	486	35.9±1.0	73.9±2.1	23.6±3.8	42.0±6.8	[9]
	494	35.2±0.2	71.3±0.4	22.4±3.8	38.3±6.6	[10]
	487	(28.1±1.3)	(57.7±2.7)	(15.8±3.9)	(25.7±6.4)	[13]
	489	(28.0±1.0)	(57.3±2.0)	(15.6±3.9)	(25.0±6.2)	[2]
				22.5±2.2 [c]	**39.1±3.8** [c]	this work
Sc(acac)₃	460	28.8±1.0	62.6±2.2	18.3±3.3	34.6±6.2	[2]
	461.2±0.3	25.6±0.5	55.5±1.1	15.1±3.3	27.3±5.8	[14]
				16.7±2.3 [c]	**30.7±4.2** [c]	[15], this work
Fe(acac)₃	461	34.1±0.9	74.0±2.0	23.5±3.3	45.6±6.4	[10]
	458.8	30.1±0.5	65.6±1.1	19.6±3.2	37.5±6.1	[9]
				21.5±2.3 [c]	**41.4±4.4** [c]	[16], this work
Mn(acac)₃	421.9	27.7±1.0	65.7±2.4	**19.7±2.6**	**43.2±5.7**	[9]
Ru(acac)₃	503.9	25.0±0.6	49.6±1.2	**11.4±4.1**	**15.0±5.4**	[17]

[a] Uncertainties in this table are expressed as expanded uncertainties at a level of confidence of 0.95 (k=2). Values in parenthesis were excluded from the consideration as doubtful.

[b] The enthalpies and entropies of fusion $\Delta_{cr}^{l}H_{m}^{o}/\Delta_{cr}^{l}S_{m}^{o}$ at T_{fus} were adjusted to 298.15 K (see Equations (S1, S2)). Uncertainties in the temperature adjustment of fusion enthalpies from T_{fus} to the reference temperature are estimated to account with 30 % to the total adjustment [8].

[c] Weighted mean value. We used the experimental uncertainty as the weighing factor.

Table S5. The experimental vapor pressure points for Mn(acac)$_3$ and Co(acac)$_3$ obtained by Knudsen effusion method with mass spectrometric registration of the gas phase composition which were used for the estimation of volatility in [18] but not published in original literary source [a].

Mn(acac)$_3$		Co(acac)$_3$	
T, K	p_i, Pa	T, K	p_i, Pa
340.0	0.003	350.0	0.008
347.0	0.009	356.0	0.015
351.0	0.013	362.0	0.031
359.0	0.033	379.0	0.179
364.0	0.075	388.0	0.433
372.0	0.160	392.0	0.634
376.0	0.304	408.0	2.61
386.0	0.946	415.0	5.11
396.0	2.27		
400.0	3.18		

[a] Standard uncertainty u is $u(T)$ = 1.0 K; relative standard uncertainty for vapor pressure $u_r(p_i)$ = $0.15 \cdot p_i$.

Table S6. Compilation of enthalpies, $\Delta_{cr,l}^g H_m^o$, and entropies, $\Delta_{cr,l}^g S_m^o$, of phase transitions available for *tris*(acetylacetonato)metal(III) complexes at 298.15 K [a].

Complex	M, g	$\Delta_{cr}^g H_m^o$ [b], kJ·mol^{-1}	$\Delta_l^g H_m^o$, [b] kJ·mol^{-1}	$\Delta_{cr}^g S_m^o$ [b], J·mol^{-1} K^{-1}	$\Delta_l^g S_m^o$ [b], J·mol^{-1} K^{-1}
1	2	3			
Al(acac)$_3$	324.30	123.9±0.9	104.2±1.6 100.7±1.9 **102.7±1.2** [c]	236.4±1.6	199.4±6.2 192.0±3.7 **193.9±3.2** [c]
Cr(acac)$_3$	349.32	129.6±0.9	111.1±2.0 107.1±2.4 **109.5±1.5** [c]	236.2±1.7	206.1±6.7 197.1±4.2 **199.6±3.6** [c]
In(acac)$_3$	412.14	134.0±2.9		250.4±5.2	
Sc(acac)$_3$	342.28	126.4±1.1	111.3±5.0 109.7±2.5 **110.0±2.2** [c]	236.7±2.7	208.5±8.6 206.0±5.0 **206.6±4.3** [c]
Fe(acac)$_3$	353.17	130.6±1.7	110.8±8.9 109.1±2.9 **109.3±2.8** [c]	244.4±3.3	226±20 203.0±5.5 **204.6±5.3** [c]
Ir(acac)$_3$	489.54	136.8±1.4		234.3±2.8	
Mn(acac)$_3$	421.9	131.3±3.1	111.6±4.0	249.6±5.8	206.4±8.1
Co(acac)$_3$	356.26	129.2±2.6		241.0±6.0	
Ru(acac)$_3$	398.39	137.4±1.6	126.0±4.4	238.3±3.9	223.3±6.7
Rh(acac)$_3$	400.23	135.7±1.1		230.5±2.5	
				238±8 [d]	**205±12** [d]

[a] Uncertainties in this table are expressed as expanded uncertainties at a level of confidence of 0.95 (k=2).

[b] From Table 2, columns 5 and 6, in bold.

[c] Vaporization enthalpy and entropy values are calculated as average weighted value of both figures in bold in Table 2 (columns 5 and 6).

[d] Average weighted value.

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