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Error or exemption to the rule?
Development of a diagnostic check for thermochemistry of metal-organic compounds

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Table S1 Compilation of phase transition parameters and heat capacities of imidazolium based ionic liquids (IL)

IL	$C_{p,m}^{o}$(cr)(298 K)	$C_{p,m}^{o}$(liq)(298 K)	$\Delta_{cr}^{l} C_{p,m}^{o}$
	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}
[C_2C_1Im][Br]	207.5 [1]	245.0 [1]	-38
[C_2C_1Im][NO_3]	262.1 [2]	293.4 [2]	-31

Table S2 Compilation of available experimental fusion temperatures and enthalpies $\Delta_{cr}^{l}H_{m}^{o}(T_{fus})$ for *tris*(β-diketonato)iron(III) complexes.[a]

Complex	T_{fus}/K	Ref.	$\Delta_{cr}^{l}H_{m}^{o}(T_{fus})$/kJ·mol^{-1}	$\Delta_{cr}^{l}H_{m}^{o}$(298.15 K)[b] /kJ·mol^{-1}
$Fe(acac)_3$	454	Ref. 3	(25.9±0.5)	
	461	Ref. 4	34.1±0.9	
	462	Ref. 5	(22.6±0.5)	
	460	Ref. 6	(25.3±1.0)	
	459	Ref. 6	30.1±0.5	
	459 [c]		31.0±0.9[d]	20.5±3.3
$Fe(Meacac)_3$	461	Ref. 7	31.8±3.0[e]	19.7±4.7
$Fe(tfac)_3$	388	Ref. 8		
	387	Ref. 9		
	389	Ref. 10		
	391	Ref. 11		
	389 [c]		38.0±5.5 [f]	31.2±5.4 [g]
$Fe(hfac)_3$	327	Ref. 12		
	331	Ref. 10		
	331	Ref. 13		
	328	Ref. 14		
	329 [c]		31.3±3.6 [f]	28.5±3.5 [g]
$Fe(ba)_3$	493	Ref. 10		
	498	Ref. 15		
	497	Ref. 16		
	496 [c]		34.2±3.0 [e]	17.4±5.9
$Fe(dbm)_3$	548	Ref. 17		
	530	Ref. 12		
	538	Ref. 13		
	538	Ref. 10		
	539 [c]		37.3±3.0 [e]	12.2±8.1
$Fe(thd)_3$	440	Ref. 18		
	437	Ref. 19		
	437	Ref. 9		
	438 [c]		30.8±5.9 [f]	14.6±3.4 [g]

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

[b] The enthalpies of fusion, $\Delta_{cr}^{l}H_{m}^{o}$, at T_{fus} were adjusted to 298.15 K (see Eq. 6). 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.[20]

[c] Average value.

[d] Weighted mean value. We used the experimental uncertainty as the weighing factor. Values in parenthesis were excluded from the calculation of the mean.

[e] Calculated by the multiplication of the fusion temperature, T_{fus}, with the *Walden constant* 69±2 J·K^{-1}·mol^{-1} with uncertainty assessed to be ±3.0 kJ·mol^{-1}

[f] The enthalpies of fusion, $\Delta_{cr}^{l}H_{m}^{o}$, at 298.15 K derived as the difference between experimental sublimation and vaporization enthalpies (see Table 1, column 5, values in bold) were adjusted to T_{fus}. Uncertainties in the temperature adjustment of fusion enthalpies from the reference temperature to T_{fus} are estimated to account with 30 % to the total adjustment. [20]

[g] The enthalpies of fusion, $\Delta_{cr}^{l}H_{m}^{o}$, at 298.15 K were calculated as the differences $\Delta_{cr}^{g}H_{m}^{o}$(298.15 K) - $\Delta_{l}^{g}H_{m}^{o}$(298.15 K) (see Eq. 7) taken from Table 1 (column 5, values in bold).

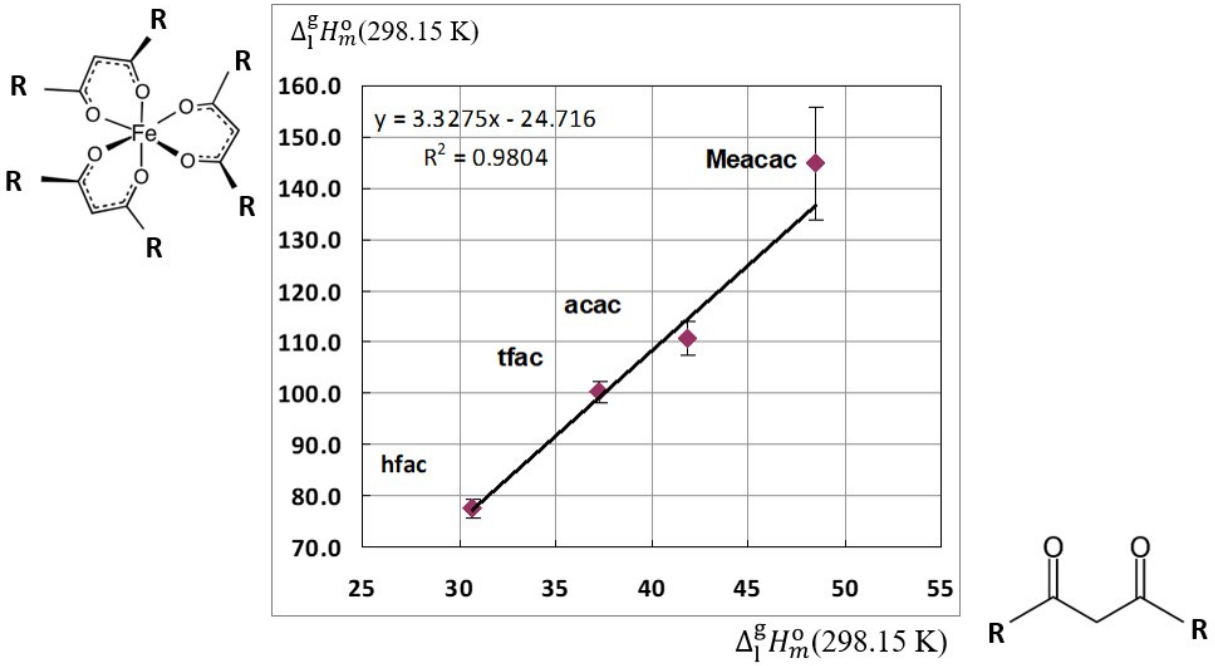

Fig. S1. Correlation of vaporization enthalpies of ligand molecules with vaporization enthalpies of *tris*(β-diketonato)iron(III) complexes at 298.15 K

Table S3 Compilation of vaporization enthalpies, $\Delta_{l}^{g}H_{m}^{o}$(298.15 K), used for parametrization of the group-additivity method (in kJ·mol^{-1})[a]

compound	$\Delta_{l}^{g}H_{m}^{o}$(298.15 K)	Ref.
trans-4,6-dimethyl-1,3-dioxane	42.5±0.6	Ref. 21
benzene	33.9±0.1	Ref. 22
cyclohexene	33.6±0.2	Ref. 23
cyclohexane	33.1±0.2	Ref. 23
toluene	38.1±0.1	Ref. 22
methylcyclohexene	35.4±0.2	Ref. 23
1,2,3-trimethylbenzene	49.1±0.2	Ref. 23
1,2,3-trimethylcyclohexane	43.3±0.5	Table S4
trifluoromethylbenzene	37.7±0.2	Ref. 23
biphenyl	65.5±0.8	Ref. 24
tert-butylbenzene	47.5±0.4	Ref. 25
ferrocene	60.9±1.9	Ref. 26

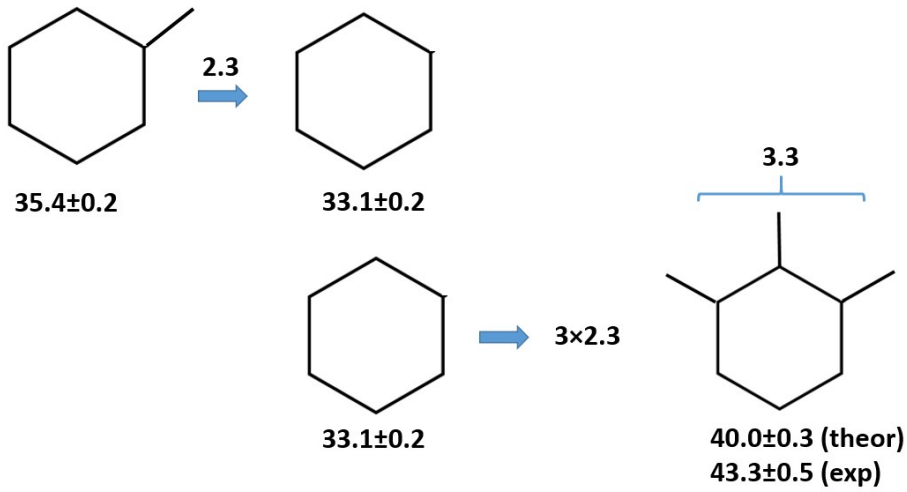

Fig. S2 Estimation of the [1,2,3-CH_3] group contribution from arrangement of three *CH_3*-groups in the sequence 1,2,3 on the r aliphatic ring, based on vaporization enthalpies (in kJ·mol^{-1}) of 1,2,3-trimethylcyclohexane, cyclohexane, and methylcyclohexane (see Table S3)

Table S4 Correlation of vaporization enthalpies, $\Delta_l^g H^o_m$(298.15 K), of substituted cyclohexanes with their Kovats´s indices on OV-101.

	J_x [a]	$\Delta_l^g H^o_m(298.15\ K)_{exp}$ [b]	$\Delta_l^g H^o_m(298.15\ K)_{calc}$ [c]	Δ [d]
Compound		kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
cyclohexane	654.6	33.1	32.7	0.4
methylcyclohexane	719.4	35.4	35.6	-0.2
ethylcyclohexane	830.1	40.6	40.4	0.2
1,2-dimethylcyclohexane (*trans*)	795.1	38.4	38.9	-0.5
1,2-dimethylcyclohexane (*cis*)	825.0	39.7	40.2	-0.5
1,3-dimethylcyclohexane (*cis*)	775.0	38.3	38.0	0.3
1,2,3-trimethylcyclohexane	**897.7**		**43.3**	
1,4-dimethylcyclohexane (*trans*)	776.7	38.0	38.1	-0.1
n-propylcyclohexane	926.4	45.1	44.6	0.5
1,3-dimethylcyclohexane (*trans*)	802.2	39.2	39.2	0.0
1,4-dimethylcyclohexane (*cis*)	802.2	39.1	39.2	-0.1
1,3,5-trimethylcyclohexane	835.0	40.2	40.6	-0.4

[a] Data on OV-101.[27]
[b] Experimental data from ref. 23.
[c] Calculated using equation:
$\Delta_l^g H^o_m(298.15\ K)\ /(kJ\cdot mol^{-1}) = 4.17+0.0436\times J_x$ with ($R^2 = 0.987$) (Eq. S1)
[d] Difference between experimental and calculated by Eq. S1 values.

It is well established, that the vaporization enthalpies correlate linearly with Kovats`s indices[28] in different homologous series of alkanes, alcohols, aliphatic ethers, alkylbenzenes[29] or in a series of structurally parent compounds. We have collected Kovats´s indices for a series alkyl-

substituted cyclohexanes, reported for the OV-101 capillary column[27] (see Tables S3-S4) for correlation with $\Delta_l^g H^o_m$(298.15 K) values of alkyl-substituted cyclohexanes with well-established experimental vaporization data[23]. As expected, the selected set of the $\Delta_l^g H^o_m$(298.15 K) values have linearly correlated with J_x values:

$$\Delta_l^g H^o_m(298.15\ \text{K})\ /(\text{kJ}\cdot\text{mol}^{-1}) = 4.17+0.0436\times J_x \text{ with } (R^2 = 0.987) \qquad \text{(S1)}$$

This correlation has been used to estimate $\Delta_l^g H^o_m$(298.15 K) = 43.3 kJ·mol^{-1} for 1,2,3-trimethylcylohexane (see Table S4) in order obtain specific correction to vaporization enthalpy of the six-membered ring, which have been applied for calculation of vaporization enthalpy of $Fe(Meacac)_3$ (see Table 5)

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