# Standard Enthalpies of Formation of Li, Na, K and Tl Cyclopentadienyls

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**Keywords:** Thermochemistry / Alkali metals / Heats of formation / Cyclopentadienyl ligands

The enthalpies of formation of lithium, sodium, potassium and thallium cyclopentadienyls were determined by reaction-solution calorimetry as $\Delta_fH^\circ$ [LiCp] = −76.5 ± 2.9 kJ/mol, $\Delta_fH^\circ$ [NaCp] = −39.7 ± 2.5 kJ/mol, $\Delta_fH^\circ$ [KCp] = −83.2 ± 3.2 kJ/mol, and $\Delta_fH^\circ$ [TlCp] = +117.7 ± 1.9 kJ/mol. Using a previously developed model, the enthalpies of formation of RbCp and CsCp were estimated.

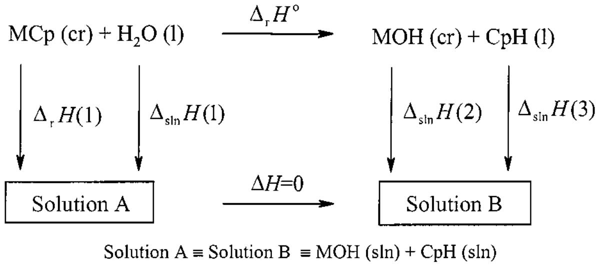
## Introduction

Alkali metal compounds have a major importance in synthetic chemistry.[1] The cyclopentadienyl anion ($C_5H_5^-$, $Cp^-$) can form compounds with almost all metallic elements and is one of the most important ligands in organometallic chemistry.[2−4] The cyclopentadienyl salts of lithium, sodium and potassium have been known for almost a century,[5] and thallium cyclopentadienyl for more than 40 years.[6,7] All of them are basic compounds in organometallic synthesis. Many organometallic compounds whose energetics are known contain one or more Cp ligands and involve MCp (M = Li, Na, K and Tl) reagents in their synthesis.[8−11] However, thermochemical data for these substances are almost absent from literature (a value for TlCp is the exception).[12]

In the present paper the enthalpies of formation of Li, Na, K and Tl cyclopentadienyls were determined by reaction-solution calorimetry, using several different reactions in various environments (water, aqueous hydrochloric acid, ethanol and toluene). These results, together with a previously developed estimation method, allowed us to predict the enthalpies of formation of the Rb and Cs cyclopentadienyls.

## Results and Discussion

Enthalpies of formation of metal cyclopentadienyls were calculated by using Scheme 1 (reaction with water, used for Li, Na and K compounds), Scheme 2 (reaction with 0.1 M HCl, used for all the compounds studied in this paper), Scheme 3 (reaction with ethanol, used for NaCp), and Scheme 4 (reaction with ethanol in toluene, used for NaCp). In these schemes, $\Delta_rH^\circ$ represents the reaction enthalpy with all the compounds in their standard state, $\Delta_rH$ the measured reaction enthalpy, $\Delta_{sln}H(2)$ the dissolution enthalpy of stoichiometric amounts of MOH in $H_2O$, $\Delta_{sln}H(3)$ the dissolution enthalpy of CpH in $H_2O$ + MOH, $\Delta_{sln}H(5)$ the dissolution of MCl in 0.1 M HCl, $\Delta_{sln}H(6)$ the dissolution or mixing of CpH in a 0.1 M HCl + MCl solution, $\Delta_{sln}H(7)$ the dissolution of water in 0.1 M HCl solution, $\Delta_{sln}H(9)$ the dissolution enthalpy of NaOEt in ethanol, $\Delta_{sln}H(10)$ the dissolution enthalpy of CpH in ethanol + NaOEt, $\Delta_{sln}H(11)$ the dissolution enthalpy of EtOH in toluene, $\Delta_{sln}H(12)$ the dissolution enthalpy of NaOEt in toluene + ethanol, and $\Delta_{sln}H(13)$ the dissolution enthalpy of CpH in toluene + ethanol + NaOEt. $\Delta_{sln}H(1)$ (dissolution of water in water), $\Delta_{sln}H(4)$ (dissolution of 0.1 M HCl in 0.1 M HCl), and $\Delta_{sln}H(8)$ (dissolution of ethanol in ethanol) are, obviously, zero.



Scheme 1

As the concentrations of MOH in solution were always very small (about 1 mol of MOH in 4 × $10^5$ mol of water), infinite dilution can be assumed and $\Delta_{sln}H(2)$ can be calculated as −23.49 kJ/mol for lithium hydroxide, −44.50 kJ/mol for sodium hydroxide, and −57.61 kJ/mol for the potassium analogue from the data in Table 1.[13] As cyclopentadiene (CpH) is immiscible with water $\Delta_{sln}H(3)$ was taken as zero.

The enthalpies of formation of aqueous 0.1 M HCl and crystalline metal chlorides are known (Table 1).[13] The dissolution of water in the solvent is negligible (smaller than the detection limit of the apparatus) and even when multiplied by 552 [see Scheme 2 and Equation (2) below] yields a minor contribution to the final $\Delta_rH^\circ$ value (smaller than the experimental error). Therefore, $\Delta_{sln}H(7)$ was neglected. All the other dissolution enthalpies needed were measured or calculated from literature data (Table 2).[13−16]

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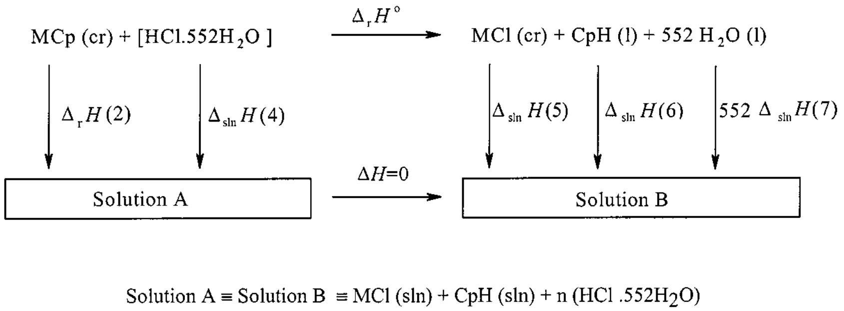
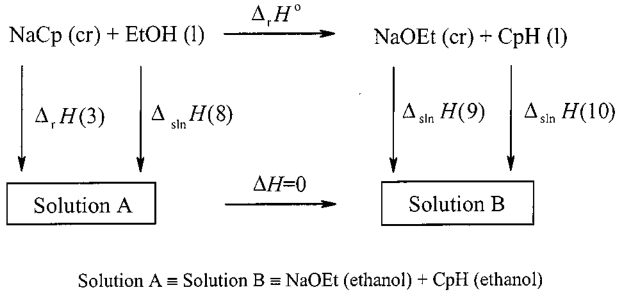
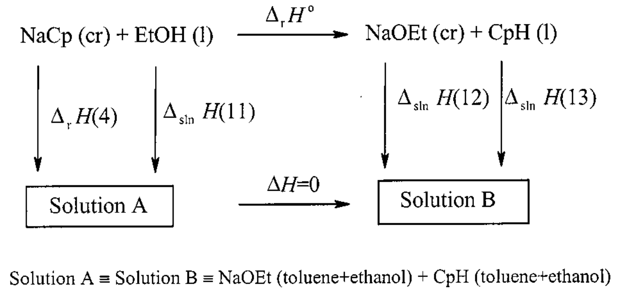


Scheme 2



Scheme 3



Scheme 4

Schemes 1−4 lead to Equation (1)−(4), that allow the calculation of the enthalpies of formation of the metal cyclopentadienyls presented in Table 3.

$$\Delta_fH° (\text{MCp, cr}) = \Delta_fH° (\text{MOH, cr}) + \Delta_fH° (\text{CpH, l}) - \Delta_fH° (\text{H}_2\text{O, l}) - \Delta_rH(1) + \Delta_{sln}H(2) \quad (1)$$

$$\Delta_fH° (\text{MCp, cr}) = \Delta_fH° (\text{MCl, cr}) + \Delta_fH° (\text{CpH, 1}) - \Delta_fH° (\text{HCl·552H}_2\text{O}) - \Delta_rH(2) + \Delta_{sln}H(5) + \Delta_{sln}H(6) + 552\Delta_{sln}H(7) \quad (2)$$

$$\Delta_fH° (\text{NaCp, cr}) = \Delta_fH° (\text{NaOEt, cr}) + \Delta_fH° (\text{CpH, l}) - \Delta_fH° (\text{EtOH, l}) - \Delta_rH(3) + \Delta_{sln}H(9) + \Delta_{sln}H(10) \quad (3)$$

$$\Delta_fH° (\text{NaCp, cr}) = \Delta_fH° (\text{NaOEt, cr}) + \Delta_fH° (\text{CpH, l}) - \Delta_fH° (\text{EtOH, l}) - \Delta_rH(4) - \Delta_{sln}H(11) + \Delta_{sln}H(12) + \Delta_{sln}H(13) \quad (4)$$

For the Li, Na, and K compounds, whose enthalpies of formation were determined from different reactions and thermodynamic cycles, a good agreement between the results is observed (see Table 3, column 3). The recommended values for $\Delta_fH°$(MCp, cr), shown in Table 4, are weighted averages of the data in Table 3.[17]

Table 1. Auxiliary data (T = 298.15 K)

| Compound[a] | $\Delta_fH°$ (kJ/mol) | Reference |
|---|---|---|
| $H_2O$, l | −285.830 | 13 |
| LiOH, cr | −484.93 | 13 |
| $LiOH·100000H_2O$ | −508.423 | 13 |
| LiOH, ai | −508.48 | 13 |
| LiCl, cr | −408.61 | 13 |
| NaOH, cr | −425.609 | 13 |
| $NaOH·\infty H_2O$ | −470.11 | 13 |
| NaOH, ai | −470.114 | 13 |
| NaCl, cr | −411.153 | 13 |
| NaOEt, cr | −411.6 ± 1.9 | 15 |
| KOH,cr | −424.764 | 13 |
| $KOH·\infty H_2O$ | −482.37 | 13 |
| KOH, ai | −482.37 | 13 |
| KCl, cr | −436.747 | 13 |
| TlOH, cr | −238.9 | 13 |
| TlOH, ai | −224.64 | 13 |
| TlCl, cr | −204.14 | 13 |
| $C_5H_6$, l | 105.9 ± 1.5 | 14 |
| $C_2H_5OH$, l | −277.5 ± 0.4 | 14 |
| $C_2H_5OH·\infty H_2O$ | −288.2 ± 0.4 | 14 |
| $HCl·552H_2O$ | −166.596 | 13 |

[a] ai: aqueous solution, ionized substance standard, $m_{\pm}$ = 1 mol/kg; cr: crystalline.

A literature value for the enthalpy of formation of TlCp, $\Delta_fH°$= 99.8 ± 2.5 kJ/mol, was obtained from measurements of the heat of reaction of aqueous TlOH with gaseous $C_5H_6$ at 25°C.[12] Recalculation of this value with more recent auxiliary data leading to 101.7 ± 2.6 kJ/mol,[18] only barely improves the discrepancy with the result in Table 4, 117.7 ± 1.2 kJ/mol. According to Hull and Turnbull, the heat of reaction relies on the mass of TlCp collected. If a small fraction of that mass was lost, the true value of the reaction enthalpy of TlOH with CpH would be less negative and the enthalpy of formation higher, in line with the result in Table 4.

The enthalpies of formation in Table 4 together with literature data,[13,19] were used to calculate the lattice energies ($\Delta_{lat}U°$) of metal cyclopentadienyls, according to Scheme 5. These values are also displayed in Table 4. It is observed that the cyclopentadienyl compounds have a strong ionic character, as their lattice energies are only about 200 kJ/mol lower than the lattice energies for the corresponding hydroxides.[20]

Let us assume a simple ionic model and the Kapustinskii approximation represented by Equation (5).[21]

Table 2. Dissolution enthalpies (T = 298.15 K)

| Compound | $\Delta_{\text{sln}}H(5)$ (kJ/mol)[a] | $\Delta_{\text{sln}}H(6)$ (kJ/mol)[b] | $\Delta_{\text{sln}}H(9)$ (kJ/mol)[c] | $\Delta_{\text{sln}}H(10)$ (kJ/mol)[d] | $\Delta_{\text{sln}}H(11)$ (kJ/mol)[e] | $\Delta_{\text{sln}}H(12)$ (kJ/mol)[e] | $\Delta_{\text{sln}}H(13)$ (kJ/mol)[f] |
|---|---|---|---|---|---|---|---|
| LiCl | −37.60 ± 0.52[g] | | | | | | |
| NaCl | 1.439 ± 0.092[h] | | | | | | |
| KCl | 19.3 ± 2.8 | | | | | | |
| TlCl | 11.2 ± 1.1 | | | | | | |
| CpH | | 5.0 ± 0.3 | | 1.6 ± 0.3 | | | 1.5 ± 1.4 |
| NaOEt | | | −96.3 ± 2.9 | | | −70.4 ± 0.6 | |
| EtOH | | | | | 17.6 ± 0.8 | | |

[a] Dissolution in 0.1 M HCl. – [b] Dissolution in 0.1 M HCl + NaCl; the same value was considered to be the dissolution in 0.1 M HCl + MCl (M = Li, K, Tl) (see ref.[16]). – [c] Dissolution in ethanol. – [d] Dissolution in ethanol + NaOEt. – [e] Dissolution in toluene. – [f] Dissolution in toluene + NaOEt. – [g] Data from ref.[16]. – [h] Calculated from data in ref.[15], considering that the number of mmols of NaCl formed is 0.619 ± 0.033.

Table 3. Reaction enthalpies, and standard enthalpies of formation of metallic cyclopentadienyl salts (T = 298.15 K)

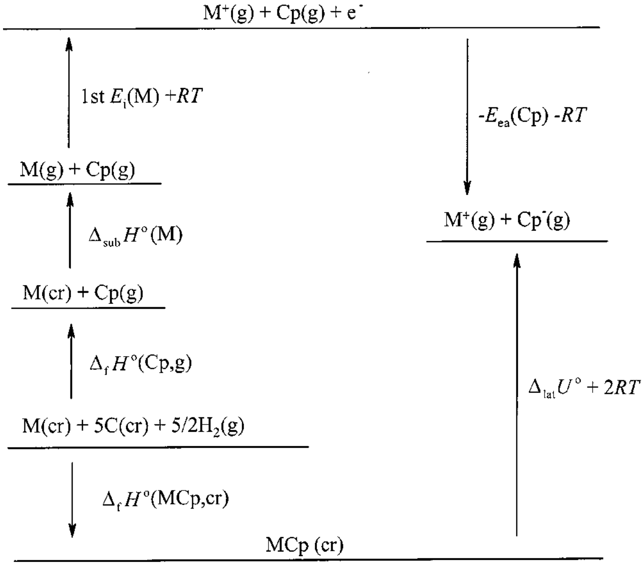
| Metal−Cp | $\Delta_rH$ kJ/mol | $\Delta_fH^o$(MCp, cr) kJ/mol |
|---|---|---|
| LiCp | −40.4 ± 1.7[a] | −76.3 ± 2.3 |
| | −91.5 ± 4.1[b] | −77.2 ± 4.4 |
| NaCp | −38.6 ± 2.5[a],[c] | −39.8 ± 2.9 |
| | −42.4 ± 2.0[a],[d] | −36.0 ± 2.5 |
| | −88.9 ± 1.1[b],[d] | −43.3 ± 1.9 |
| | −82.5 ± 2.8[c],[e] | −40.4 ±4.7 |
| | −72.5 ± 8.5[c],[f] | −42.2 ± 9.0 |
| KCp | −5.8 ± 2.2[a] | −84.8 ± 2.7 |
| | −62.2 ± 3.6[b] | −77.8 ± 4.8 |
| TlCp | −33.1 ± 0.3[b] | +117.7 ± 1.9 |

[a] Reaction with water. – [b] Reaction with 0.1 M HCl. – [c] Batch 1. – [d] Batch 2. – [e] Reaction with ethanol. – [f] Reaction with ethanol in toluene.

Table 4. Enthalpies of formation and lattice energies of cyclopentadienyls salts

| Compound | $\Delta_fH^o$(MCp,cr) kJ/mol | $\Delta_{\text{lat}}U^o$(MCp)[a] kJ/mol |
|---|---|---|
| LiCp | −76.5 ± 2.9 | 823.4 ± 7.5 |
| NaCp | −39.7 ± 2.5 | 710.2 ± 7.4 |
| KCp | −83.2 ± 3.2 | 658.6 ± 7.6 |
| TlCp | +117.7 ± 1.9 | 721.2 ± 7.2 |

[a] $\Delta_fH^o(\text{Cp, g}) = 241 \pm 6$ kJ/mol,[19] $E_{ea}(\text{Cp}) = 174.9 \pm 3.5$ kJ/mol (ref.[19], using only the values from LPES and LPD).



Scheme 5

Table 5. Thermochemical radii calculated or estimated in cyclopentadienyl salts[a] and experimental distances

| MCp | $r_+ + r_-$ | $r_+$[b] | $r_-$ | $d$(M−Cp) |
|---|---|---|---|---|
| LiCp | 262.1 ± 2.4 | 90±1 | 172.1±2.6 | 196.9[c] |
| NaCp | 303.9 ± 3.2 | 116±1 | 187.9±3.4 | 235.7[c] |
| KCp | 327.7 ± 3.8 | 152±1 | 175.7±3.9 | 281.6[c][d] |
| TlCp | 334.2 ± 3.3 | 164±1 | 170.2±3.4 | 319.0[e] |
| RbCp | (332 ± 5) | 166±1 | (166±5) | 297.4[f][g]296.2[f][h] |
| CsCp | (347 ± 5) | 181±1 | (166±5) | 312.3[i] |

[a] Estimated values in parenthesis. – [b] Data from ref.[22]. – [c] Ref.[23]. – [d] Average value. – [e] Ref.[26]. – [f] Ref.[24]. – [g] Average phase I. – [h] Average phase II. – [i] Ref.[25].

$$\Delta_{\text{lat}}U^o = \frac{1.079 \times 10^5 . \nu . Z_+ Z_-}{r_+ + r_-} \tag{5}$$

In this expression, $\nu$ represents the number of ions in the molecule, $Z_+$ and $Z_-$ the charges of the cation and the anion, and $r_+$ and $r_-$ the respective radii in pm. As the ionic radii of $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, and $\text{Tl}^+$ are known,[22] the ionic radius of the cyclopentadienide anion can be derived from the lattice energy in each case (Table 5).

The radii calculated through the above procedure are called "thermochemical radii" [they reproduce lattice energies when introduced in Equation (5)] and should not be interpreted as crystallographic radii. However, some correlation seems to exist and this can be confirmed by comparing the sum $r_+ + r_-$ with the crystallographic distances M−Cp (Table 5).[23–26]

When the values of the thermochemical radius for the $\text{Cp}^-$ ligand are plotted together with the data for $\text{RO}^-$

(R = H, Me, Et)[13,15,16,27,28] a similar trend (with a maximum for sodium) is observed (Figure 1), allowing us to estimate the thermochemical radius for $Cp^-$ in RbCp and CsCp as 166 ± 5 pm.[29] From this value, the lattice energy for RbCp and CsCp can be calculated: $\Delta_{lat}U^o[RbCp] = 650.0 \pm 9.8$ kJ/mol, and $\Delta_{lat}U^o[CsCp] = 621.9 \pm 9.0$ kJ/mol. Finally, the lattice energies and auxiliary data[30] yield (Scheme 5) the enthalpies of formation of the rubidium and caesium compounds: −99 ± 12 kJ/mol and −103 ± 11 kJ/mol, respectively.

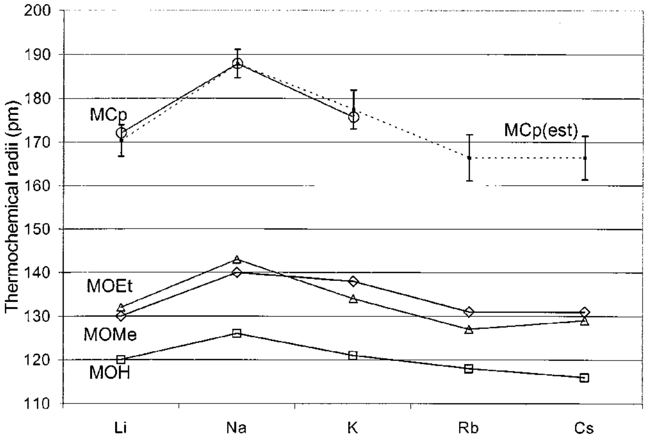


Figure 1. Thermochemical radii of anions ($OH^-$, $OMe^-$, $OEt^-$, and $Cp^-$); estimated values for $Cp^-$ are presented with error bars (for a detailed calculation of these values see the Supporting Information).

The crystallographic M−C distances for $MgCp_2$, 233.9 pm,[31] 234.8 pm[32] in the gas phase and 230.4 pm[33] by X-ray crystallography are comparable to the Na−C distance in NaCp. There exists in the literature a value of 69.3 ± 4.2 kJ/mol for the enthalpy of formation of $MgCp_2$.[34] From this value and an approach similar to the one used for the compounds studied in this paper a thermochemical radius of 183 ± 8 pm for the $Cp^-$ in $MgCp_2$ [35] is obtained, which is in keeping with the value obtained for $Cp^-$ in NaCp (187.9 ± 3.4 pm).

The above results can be used to understand the stability of TlCp in the presence of water or oxygen when compared to other cyclopentadienyl derivatives of Tl or even with InCp.[36−39] TlCp is quite stable in water and reacts only slowly with oxygen.[40] For example, TlCp was found to be more stable than $TlC_5H_4t$Bu or $TlC_5H_4(SiMe_3)$ (which are of similar stability), and of $TlC_5H_4Me$ which is highly air- and water-sensitive. To explain this behaviour it has been argued that TlCp should have a much higher lattice energy than other cyclopentadienyl salts, such as thallium methylcyclopentadienide, due to different molecular symmetries.[41] We note, however, that the reactivity of thallium hydropentalenide in the presence of water is similar to TlCp.[37]

As noticed by Hull and Turnbull,[12] the enhanced stability of TlCp is mainly due to the low affinity of Tl for oxygen and the solubility of TlOH in water. To check this hypothesis, the enthalpy of the reaction in Equation (6) can be calculated for all four compounds studied, using the enthalpies of formation of MCp measured in this work and auxiliary data from Table 1.

$$MC_5H_5(cr) + H_2O(l) \rightarrow MOH(aq) + C_5H_6(l) \qquad (6)$$

The results are −40.2 kJ/mol (Li), −38.7 kJ/mol (Na), −7.4 kJ/mol (K) and 49.4 kJ/mol (Tl). Therefore, only the reaction for TlCp is endothermic. Although the entropy change for this reaction is expected to be positive, the term $T\Delta_rS^o$ at 298.15 K will be much smaller than $\Delta_rH^o$ for TlCp, thus implying that $\Delta_rG^o > 0$.

## Experimental Section

**Materials:** Ethanol (Merck, 99.8%) was pre-dried over calcium sulfate, refluxed over activated magnesium and iodine, and finally distilled. Lithium, sodium, potassium and thallium (Sigma) were kept inside an oxygen- and water-free glove-box and used as supplied. Pentane was distilled over $P_2O_5$ and kept in the glove-box over 4 Å molecular sieves. Tetrahydrofuran was dried over 4 Å molecular sieves, refluxed with sodium and benzophenone, and distilled. Toluene was dried over 4 Å molecular sieves, refluxed with sodium and benzophenone, and distilled. Cyclopentadiene was prepared by cracking the $Cp_2$ dimer under an inert atmosphere, using a Vigreux column, collected at 0° C and used immediately.

**Physical Measurements:** Infrared spectra were obtained on a Perkin−Elmer 577 spectrophotometer with samples mounted as Nujol mulls between KBr plates. Elemental analyses were performed on an automatic analyzer Perkin−Elmer 240 C (C, H). Instrumental neutron activation analysis (INAA) was performed on sodium, using sodium acetate as a standard (for experimental procedure and data processing see, for example, ref.[42]).

**Cyclopentadienyl Salt Syntheses:** The Li, Na, and K compounds are moisture sensitive. Therefore, all syntheses and handling were made inside an oxygen- and water-free (<5 ppm) glove-box or using Schlenk techniques.

The sodium and potassium cyclopentadienyl compounds were synthesised in THF solution according to a literature procedure.[6] The solution was then taken to dryness and the precipitate washed twice with pentane. The resulting compounds were analysed by IR spectroscopy and elemental analysis (C, H). Additionally, the sodium content in NaCp was measured by neutron activation. All analysis found the compounds to be pure.

Lithium cyclopentadienyl was synthesised in THF solution by a similar method to the one used for the sodium and potassium analogues, but instead of metallic lithium we used butyllithium in solution. The final solution was then taken to dryness and the precipitate washed twice with pentane. The resulting compound was analysed by IR spectroscopy and elemental analysis (C, H).

Thallium cyclopentadienyl was synthesised from thallium sulfate, sodium hydroxide, and freshly cracked cyclopentadiene in water, according to a literature procedure.[43] After sublimation the yellow product was analysed by IR spectroscopy and elemental analysis (C, H).

**Reaction-Solution Calorimetry:** The calorimeter used was specially built for the study of oxygen- and water-sensitive compounds, and the experimental procedure was described in a previous paper.[15]

All measurements were made near 298.15 K, and the results are averages of at least four runs. The errors presented are twice the standard deviation of the mean in each case.

**Note added in proof (February 1, 2001):** During publication a previous value of the enthalpy of formation of NaCp (−14±25 J/mol; E. B. Evstigneeva, H. A. Bartolomeeva, T. H. Hukolskai, A. M. Moosu, *Zh. Fiz. Khim.* **1973**, *47*, 2727−2727) was brougth to our attention. Despite the poor quality of the result, their error bar overlaps the experimental value measured in this paper. The reference gives no details concerning the calculation of that value.

## Acknowledgments

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[17] Used formulae (mean, $\bar{x}$, and standard deviation, $\delta\bar{x}$, respectively):

$$\bar{x} = \sqrt{\sum \frac{x_i^2}{\delta_{x_i}^2} \Big/ \sum \frac{1}{\delta_{x_i}^2}}, \quad \delta_{\bar{x}} = \sum \frac{1}{\delta_{x_i}} \Big/ \sum \frac{1}{\delta_{x_i}^2}$$

[18] The enthalpy of formation of crystalline TlCp can be recalculated from the enthalpy of the reaction $TlOH{\cdot}2050H_2O$ + $C_5H_6$ (g) → $TlC_5H_5$(cr) + $H_2O$(l) + 2050 $H_2O$(l), $\Delta_rH = -91.0 \pm 2.1$ kJ/mol, obtained by Hull and Turnbull,[10] and more recent auxiliary data (kJ/mol): $\Delta_fH^o$ (CpH, g) = 134.3 ± 1.5,[12] $\Delta_fH^o(H_2O,\ l) = -285.83$,[11] $\Delta_fH^o(TlOH{\cdot}2050H_2O) = -227.95$,[11] enthalpy of dilution due to formed water (−0.43).[11] The obtained value will be 101.7 ± 2.6 kJ/mol.

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[20] Lattice energies calculated using data from references 11 and 17. $\Delta_{lat}U^o(LiOH) = 1028$ kJ/mol, $\Delta_{lat}U^o(NaOH) = 886$ kJ/mol, $\Delta_{lat}U^o(KOH) = 790$ kJ/mol, $\Delta_{lat}U^o(TlOH) = 876$ kJ/mol.

[21] Kapustinskii noticed that, in the formula for the lattice energy in an ionic model, when dividing the Madelung constants by the number of ions in the molecule the new constant obtained is almost independent of the structure of the lattice. He also assumed that the repulsive part of the energy is 1/9 that of the attractive one and replaced the internuclear equilibrium distance by a sum of two radii ($r_+$ and $r_-$). For a detailed discussion see:D. A. Johnson, *Some Thermodynamic Aspects of Inorganic Chemistry*, 2nd ed., Cambridge University Press, Cambridge, **1982**.

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[29] For the detailed estimation of the values please see the supporting information.

[30] $\Delta_{sub}H^o(Rb) = 80.88$ kJ/mol, 1st $E_i(Rb) = 409.221$ kJ/mol, $\Delta_{sub}H^o(Cs) = 76.065$ kJ/mol, 1st $E_i(Cs) = 381.899$, taken from ref.[11]

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