

Thermodynamics of trimethylindium adducts of N,N',N'' -trialkyl-1,3,5-triazacyclohexanes †

Donald C. Bradley* and Ian S. Harding

Chemistry Department, Queen Mary and Westfield College, Mile End Road, London, UK E1 4NS

Adducts of formula $\text{InMe}_3 \cdot \text{C}_3\text{H}_6\text{N}_3\text{R}_3$, where $\text{R} = \text{Me}$, Pr^i or Bu^t , have been prepared. The adduct bonding of three lone pairs is shown to be only slightly stronger than a standard one lone-pair adduct bond, and estimated to be between 85 and 90 kJ mol^{-1} . The vapour pressures of these adducts have been determined and interpreted by statistical mechanical techniques to show the presence of disorder within the molecules, both in the alkyl groups and in the adduct bonding. The former is shown to affect the solid phases; its use in modelling the disorder in a crystal structure and in predicting the entropy of phase change to disordered phases is outlined. The latter appears in the liquid and vapour phases and is used to explain melting points and entropies of vaporisation.

The N,N',N'' -trialkyl-1,3,5-triazacyclohexanes (trialkyltriazinanes) are a class of compounds containing three tertiary amine nitrogen atoms linked into a six-membered ring by methylene bridging groups. Alkyl groups on the nitrogen atoms can be axial or equatorial to the ring, within steric constraints, and so the ring has the potential to donate one, two or all three nitrogen lone pairs to a Lewis acid. With alkyl groups in the triequatorial conformation, the three axial lone pairs can become a model for a crystal surface, such as the {111} surface of III–V semiconductors. These semiconductors are often made by metal-organic chemical vapour deposition (MOCVD) using Group III trialkyls, so the interaction between the triazinanes and metal alkyls may be a useful model of what happens during this process.

The first example of a metal alkyl forming an adduct with a triazinane was $\text{InMe}_3 \cdot \text{C}_3\text{H}_6\text{N}_3\text{Et}_3$,¹ but because this adduct was a liquid no statement could be made about the nature of the adduct bonding. This was followed by the structural characterisation of a crystalline adduct with dimethylzinc, $\text{ZnMe}_2 \cdot 2\text{C}_3\text{H}_6\text{N}_3\text{Me}_3$,² where the dimethylzinc bonded to only one equatorial nitrogen lone pair. That the situation might be different for indium was indicated by the diazabicyclo[2.2.2]octane (dabco) adducts of trimethylindium¹ and trimethylgallium.³ The gallium–dabco adduct had trimethylgallium as a typical two-electron acceptor but the trimethylindium was five-coordinate, accepting lone pairs from two different dabco units thereby forming a stable linear polymer.

Since then, a solid adduct with trimethylindium, $\text{InMe}_3 \cdot \text{C}_3\text{H}_6\text{N}_3\text{Pr}^i_3$,⁴ has been prepared and structurally characterised to show that a triazinane can, in fact, act as a three-lone-pair donor, and that indium can become six-coordinate in a trimethylindium complex. The crystal structure showed extensive disorder in the alkyl groups, however, and it was only possible to model this disorder with the help of vapour-pressure measurements, which gave an indication of the extent of disorder present. The data and arguments behind this form the subject of this paper, and the nature of the adduct bond is probed.

Results and Discussion

The trimethylindium adducts of some trialkyltriazinanes have been synthesized by simple mixing of the Lewis acid and base in diethyl ether solution, from which the adduct can be isolated either by crystallisation or removal of solvent and subsequent sublimation *in vacuo*. This method has not worked with tri-

phenyltriazinane, however: even when the solvent is toluene and there is no competing Lewis base, triphenyltriazinane still crystallises from solution without forming an adduct with trimethylindium. This is a reflection of the known poor Lewis basicity of nitrogen lone pairs when adjacent to aromatic systems and has been seen before in other group III alkyl chemistry.⁵ The trimethylindium adducts of the trialkyltriazinanes are now known to contain the alkyl groups methyl (**1**), ethyl¹ (**2**), isopropyl (**3**) and *tert*-butyl (**4**).

Variable-temperature NMR spectroscopy

One aspect of the triazinanes which has been studied in detail is their behaviour during variable-temperature NMR spectroscopy. Two processes have been identified: inversion of the groups around nitrogen (exchange between axial and equatorial conformations) and flipping of the six-membered ring between chair configurations. Coalescences due to nitrogen inversion occur below -100°C ,⁶ while ring inversion produces more accessible coalescences about 80°C higher than this.^{6,7} The ring inversion becomes easier as the bulk of the alkyl groups increases,⁸ the free-energy barrier to ring inversion, ΔG^\ddagger , decreases stepwise by 2.5–3.0 kJ mol^{-1} down the series $\text{R} = \text{Me}$, Et , Pr^i , Bu^t . This has been attributed to the increasing tendency towards planarity of the nitrogen atoms as the size of the substituent is increased.

A detailed study of ring inversion⁶ in trimethyltriazinane has shown the entropy of activation, ΔS^\ddagger , to be $31.4 \text{ J K}^{-1} \text{ mol}^{-1}$. This value has been interpreted in terms of the statistical mechanical relationship $S = R \ln W$ in the following way: of the seven stable methyl-group configurations, only the triequatorial will ring-invert to an unstable configuration. Since the activated state for ring inversion is an envelope configuration, with any of the six possible ring atoms being uniquely out-of-plane, there are thus thirtysix viable activation pathways, (*i.e.* $W = 36$) producing a theoretical entropy of $29.8 \text{ J K}^{-1} \text{ mol}^{-1}$, which compares well with the experimental value.

This work can be extended to the trimethylindium adduct of trimethyltriazinane (**1**). Variable-temperature NMR studies of the adduct have revealed a free-energy barrier to ring inversion, ΔG^\ddagger , of $57.0 \pm 0.2 \text{ kJ mol}^{-1}$ at a coalescence temperature of 280 K. Under similar conditions, the ligand itself gives $\Delta G^\ddagger = 55.2 \pm 0.2 \text{ kJ mol}^{-1}$ at 285 K, which becomes $55.0 \pm 0.2 \text{ kJ mol}^{-1}$ at 280 K. The 2 kJ mol^{-1} difference could easily be attributed to the more pyramidal nature of the nitrogen atoms after adduct formation, but caution must be exercised because the free-energy barrier is a product of not only the enthalpy change but also differences in entropy.

† Non-SI units employed: mmHg \approx 133 Pa, atm = 101 325 Pa.

Table 1 Equations and thermodynamic parameters derived from vapour-pressure data for sublimation of the adducts $\text{InMe}_3 \cdot \text{C}_3\text{H}_6\text{N}_3\text{R}_3$, where R = Me **1**, Prⁱ **3** or Bu^t **4**

Adduct	A^*	B^*	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$
1	4995	14.56	95.6 (1.2)	223.6 (3.8)
3	4573	12.26	87.5 (0.7)	179.6 (2.3)
4	4905	13.02	93.9 (0.9)	194.1 (2.8)

Values in parentheses are statistical errors, σ . * $\log_{10}(P/\text{mmHg}) = -(A/T) + B$.

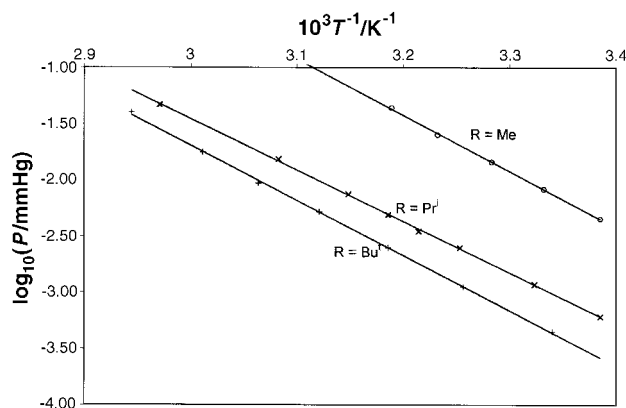


Fig. 1 Plots of $\log P$ vs. $1000/T$ for the adducts $\text{InMe}_3 \cdot \text{C}_3\text{H}_6\text{N}_3\text{R}_3$, where R = Me (**1**), Prⁱ (**3**) or Bu^t (**4**)

The adduct will differ considerably from the free triazinane because the trimethylindium moiety must be associated with only one of the three nitrogen atoms during a ring inversion. (Complete dissociation is unlikely in view of the strength of an indium–nitrogen adduct bond: 83 kJ mol^{-1} for $\text{InMe}_3 \cdot \text{NMe}_3$.)⁹ The three-fold increase this will produce in activation pathways gives an extra $9.1 \text{ J K}^{-1} \text{mol}^{-1}$ to ΔS^\ddagger , requiring an increase of 2.5 kJ mol^{-1} in enthalpy to balance this effect at 280 K. Thus the effect of adduct formation on the enthalpy of activation for ring inversion is to increase it by about 4.5 kJ mol^{-1} . This is caused by both the increasing pyramidal nature of the nitrogen atoms and the change in adduct bonding to indium from three lone-pair donor atoms to one. This is a clear illustration that the formation of extra adduct bonds to trimethylindium beyond the first lone-pair donation results in very little extra bond energy. It then explains the great length of the adduct bonds found in the crystal structures with dabco¹ and triisopropyl-triazinane.⁴

Vapour-pressure measurements

The variation of vapour pressure with temperature for the three solid triazinane adducts is shown in Fig. 1. Equations and thermodynamic parameters derived from these data are presented in Table 1.

The thermodynamic data do not show a gradual change with increasing molecular size, which suggests that more is happening in these compounds than a simple increase in the bulk of ring substituents. In particular, the parameters for the triisopropyl adduct **3** are noticeably lower than for the other two. There is no likely difference that can account for this in the vapour phase, suggesting that the difference lies in the solid phases, with a phase change having occurred in **3** below room temperature. Phase changes in adducts of Group III alkyls are not unknown, having been observed for both amines^{9a} and phosphines.¹⁰

The enthalpy associated with the phase change in compound **3** will be the difference between the measured enthalpy of sublimation (87.5 kJ mol^{-1}) and that expected, based on the results for **1** and **4** (95.6 and 93.9 kJ mol^{-1}), *i.e.* about 7 kJ mol^{-1} . The

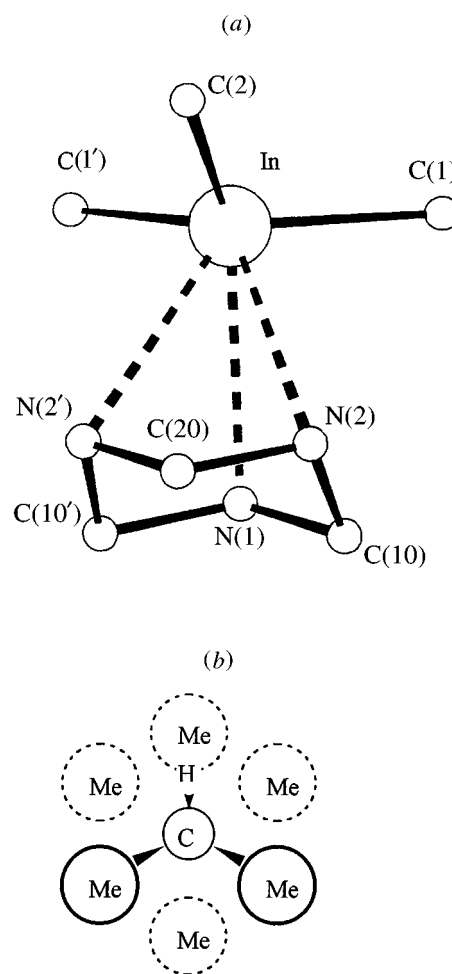


Fig. 2 Crystal structure of $\text{InMe}_3 \cdot \text{C}_3\text{H}_6\text{N}_3\text{Pr}_3$, **3** showing (a) the core, (b) the modelled disorder of the isopropyl groups

same idea can be applied to the entropy, but with less success, because of the large difference between the entropies of sublimation of **1** and **4**. We would anticipate, however, that the result will be closer to that for the *tert*-butyl case, suggesting a value as low as possible between the limits of 14 and $44 \text{ J K}^{-1} \text{mol}^{-1}$. These two parameters are linked, because for an adiabatic change $\Delta H/T = \Delta S$. With a constraint for the phase change to be below 300 K (since it is the disordered phase that is isolated experimentally), the lowest entropy will be about $24 \text{ J K}^{-1} \text{mol}^{-1}$.

Applying statistical mechanics to this value, 18 possible arrangements are indicated, and it was on this basis that the crystal structure of compound **3** was determined (see Fig. 2).⁴ Each isopropyl group was modelled as having six configurations, generated by rotation about the nitrogen–carbon bond. This has generated methyl positions every 60° around the central carbon atom. The success of this model in solving the crystal structure confirms the use of statistical mechanics in interpreting the entropy of these compounds. It also predicts that a similar disorder should be found with *tert*-butyl groups. In this case the six methyl sites can be filled by just two possible arrangements of a *tert*-butyl group associated by a 60° rotation. This will give six possible arrangements per molecule within the crystal structure of **4**, with an associated entropy of $15 \text{ J K}^{-1} \text{mol}^{-1}$.

There is evidence, therefore, that both compounds **3** and **4** exist at room temperature as disordered solid phases, with an ordered phase existing for each at lower temperatures. Since disorder within the alkyl groups does not destroy the solid phase, the principal interactions that hold the molecules together cannot be operating perpendicular to the adduct bond, but must be due to both the alignment of the adduct dipoles themselves and the shorter-range interactions between adjacent molecules which operate in this direction. Only a small increase

Table 2 Thermodynamic parameters for sublimation of the adducts $\text{InMe}_3 \cdot \text{C}_3\text{H}_6\text{N}_3\text{R}_3$, from the ordered and disordered solid phases

Adduct	Disordered phase		Suggested phase change			Ordered phase*	
	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$	T_i/K	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{mol}^{-1}$
1						95.6 (1.2)	223.6 (3.8)
3	87.5 (0.7)	179.6 (2.3)	≈ 290	≈ 7	24	≈ 95	203.6 (2.3)
4	93.9 (0.9)	194.1 (2.8)	≈ 130	≈ 2	15	≈ 95	209.1 (2.8)

Values in parentheses are statistical errors, σ . * Values for adducts **3** and **4** are predicted.

in the enthalpies of sublimation should then occur because of the different equatorial alkyl groups. Thus for **4** an enthalpy difference of about 2 kJ mol^{-1} would be predicted between the ordered and disordered phases to produce similar enthalpies of vaporisation for the ordered phase, but a higher enthalpy is possible. On this basis the phase change in **4** would be expected to occur at around 130 K, though the temperature may be higher if the enthalpy is higher.

The thermodynamic values predicted for sublimations of ordered and disordered phases are presented in Table 2. It is clear from the data that the entropies of sublimation of the ordered phases are still irregular. On the basis of the Sackur–Tetrode equation, a small increase in translational entropy in the vapour phase will be expected down the series which is indeed found between compounds **3** and **4**. The methyl derivative, however, is showing a value approximately $20 \text{ J K}^{-1} \text{mol}^{-1}$ higher. One factor that will contribute to this is the difference in the number of stable arrangements of the triazinane adducts. Study of dipole moments in the ligands¹¹ has shown that only the triequatorial and three monoaxial configurations are possible for *tert*-butyl and isopropyl groups around a triazinane ring, but that the smaller methyl groups can also adopt the three diaxial configurations (as can ethyl groups). Considering the adducts, where trimethylindium can be bonded to any equatorial lone pair, or occupy the axial site if the alkyl groups are all equatorial, then there are 10 arrangements available to **1** (and a further six if the trimethylindium can exist coaxially with a methyl group) compared to four for **3** or **4**. The entropies of sublimation will therefore differ by 7 (or 12) $\text{J K}^{-1} \text{mol}^{-1}$ due to this effect alone. Beyond the arrangements possible within each molecule there will be a further entropy contribution from the mixing of molecules in these different conformations. For **1** there are four (or six) distinguishable conformers, but only two for **3** or **4**. The entropies of mixing will, when the degeneracy is taken into account, differ by about 6 (or 10) $\text{J K}^{-1} \text{mol}^{-1}$.

Another factor which will produce differences between the entropies of vaporisation for compounds of markedly different volatilities is the concentration of the vapour at the projected standard pressure of 1 atm. This effect was first noted by Hildebrand¹² who showed that entropies calculated for different vapours at identical concentrations rather than pressures gave more favourable comparison. The slightly more volatile adduct **1** gives a vapour approximately 12% more concentrated at standard pressure than these of **3** and **4**; correcting this by determining an entropy when all the vapours contain 1 mol per 22.4 dm^3 reduces the noted difference between **1** and the ordered phases of **3** and **4** by a further $1 \text{ J K}^{-1} \text{mol}^{-1}$.

The available configurations (both intramolecular and from mixing) and higher masses of this series of adducts will all contribute to the difference between the entropies found for the triazinanes and the typical value of around $165 \text{ J K}^{-1} \text{mol}^{-1}$ found for simple adducts of trimethylindium by Knudsen effusion.¹³

The volatility of the triethyl derivative **2** has previously been measured by the modified entrainment method (MEM) over the temperature range 69–124 °C. The thermodynamic data derived for this adduct are not discussed here for two reasons: first, since we have shown that the adduct bond strength is

comparable to that of the trimethylamine adduct and that this adduct is known to be dissociating over this temperature range,⁹ there is now doubt over the meaning of the values obtained. Secondly, the approximations introduced by estimating diffusion coefficients for the adduct have produced a vapour-pressure curve at odds with the quoted boiling point of the liquid adduct by a factor of 10. For these reasons the data must be viewed with suspicion when applied to the temperature range considered here.

The adduct itself, with a melting point of 0.5 to 3 °C, is worthy of comment, however. The different ways that disorder has become manifest in the other three adducts will also apply to **2**. Simple rotation of the ethyl groups will produce an entropy change similar to that in **3**, with an appropriate moderate cost of enthalpy. Entropy can also be generated by allowing the molecules to occupy all configurations available to **1** in the vapour, but at a much higher cost of enthalpy, because the rigid solid structure will become disrupted. In the adduct **2** the cumulative entropy of these two effects can match the enthalpy at much lower temperatures than in the other adducts, indicating why **2** has the lowest melting point in the series.

Conclusion

The adduct bonding between trimethylindium and the three nitrogen donor atoms in a triazinane has been shown to be less than 4.5 kJ mol^{-1} stronger than from a simple one-lone-pair donor nitrogen atom. In view of the known strength of such a bond,⁹ a value of between 85 and 90 kJ mol^{-1} is predicted for the adduct bond in compound **1**. This indicates that trimethylindium shows no great preference for bonding to either one or three lone pairs, and so is expected to be quite mobile on a surface rich in lone pairs such as the {111} face of III–V semiconductors.

Differences in the vapour pressure data for compounds **1**, **3** and **4** have shown the presence of two types of intramolecular entropy in these adducts. The first is a disorder within the equatorial alkyl groups, which is particularly great for ethyl and isopropyl groups but also found for *tert*-butyl groups. It is responsible for a change in phase in both **3** and **4** from an ordered to a more disordered crystal structure. The second, larger effect comes from the configurations available in distributing the alkyl groups and the trimethylindium moiety around the axial and equatorial sites of the six-membered ring. It is responsible for the higher-than-normal entropy of sublimation found in these adducts, and is particularly prominent with methyl and ethyl groups. The combination of these two effects accounts for the low melting point of **2**.

Experimental

Standard inert-atmosphere techniques were used for the preparation and characterisation of these compounds, all of which started with the preparation of trimethylindium in ether. Methyl lithium in diethyl ether (Aldrich) was standardised by Gilman titration before use; anhydrous indium trichloride (Johnson Matthey) was used as supplied and diethyl ether (BDH) was distilled off the sodium ketyl of benzophenone and

stored over molecular sieves before use. The *N,N',N''*-trialkyl-1,3,5-triazacyclohexanes were prepared by literature methods¹¹ and satisfactory boiling points and elemental analyses were obtained. Elemental analyses were determined by the Micro-analysis Laboratory, University College, London. The NMR spectra were recorded on a Bruker WP80 FT spectrometer, except for the variable-temperature spectra, where a WP250 FT was used; IR spectra were recorded on a Perkin-Elmer 577 spectrometer over the range 4000–200 cm⁻¹ as Nujol mulls.

Preparations

Trimethylindium solution in ether. Methylindium (21.5 cm³ of 1.80 M solution, 38.6 mmol) was added dropwise to a stirred solution of indium trichloride (2.85 g, 12.9 mmol) in ether (30 cm³) at 0 °C. The solution was allowed to warm to room temperature and the white precipitate filtered off.

Trimethyl(*N,N',N''*-trimethyl-1,3,5-triazinane)indium(III) 1. A solution of trimethylindium (12.9 mmol) in ether was cooled to -78 °C and C₃H₆N₃Me₃ (1.68 cm³, 12.0 mmol) was added dropwise. The solvent was removed *in vacuo*. The remaining solid was sublimed at 10⁻² mmHg from an oil-bath at 45–50 °C onto a cold-finger at -78 °C. Yield 3.24 g (87% based on InCl₃), m.p. 40–41 °C (Found: C, 37.63; H, 8.48; N, 14.00. C₉H₂₄InN₃ requires C, 37.39; H, 8.37; N, 14.53%). ¹H NMR (solvent C₆D₅CD₃): δ 2.92 (2 H, s, CH₂), 2.01 (3 H, s, NCH₃) and -0.16 (3 H, s, InCH₃). IR: 2869s, 2854s, 2801s, 2782 (sh), 2749m, 2732 (sh), 2657m, 1463s, 1379s, 1275m, 1262 (sh), 1242s, 1164m, 1151m, 1117s, 1109s, 1024s, 1001s, 927s, 832m, 803w, 661s, 500w and 485s cm⁻¹.

Trimethyl(*N,N',N''*-triisopropyl-1,3,5-triazinane)indium(III) 3. The compound C₃H₆N₃Pr₃ (1.68 cm³, 12.0 mmol) was added to a solution of trimethylindium (12.9 mmol) in ether and a small amount of white precipitate formed, which increased when the solution was cooled to -78 °C. The supernatant was decanted and the remaining solid dried *in vacuo* then sublimed at 10⁻² mmHg from an oil-bath at 55–65 °C onto a cold-finger at -78 °C. Yield 1.9 g (42% based on InCl₃), m.p. 70–71 °C (Found: C, 48.82; H, 9.93; N, 11.98. C₁₅H₃₆InN₃ requires C, 48.26; H, 9.93; N, 11.26%). The remaining supernatant was concentrated to yield a crop of crystals suitable for analysis by X-ray crystallography. ¹H NMR (solvent C₆D₅CD₃): δ 3.38 (2 H, s, CH₂), 2.80 (1 H, spt, *J* 6.5, NCH), 0.95 [6 H, d, *J* 6.5 Hz, CH(CH₃)₂] and -0.03 (3 H, s, InCH₃). IR: 2950s, 2930s, 2755s, 2700 (sh), 2620 (sh), 2530w (sh), 1361s, 1331m, 1319m, 1302 (sh), 1219s, 1162s, 1120s, 1098s, 1001m, 940 (sh), 931m, 888w, 666s, 502m and 451s cm⁻¹.

Trimethyl(*N,N',N''*-tri-*tert*-butyl-1,3,5-triazinane)indium(III) 4. A solution of trimethylindium (14.4 mmol) in ether was cooled to -78 °C and C₃H₆N₃Bu₃^t (4.2 cm³, 14.4 mmol) was added dropwise. A white precipitate formed which partly dissolved upon warming to room temperature. The solution was recooled and the supernatant decanted. The remaining solid was dried *in vacuo* then sublimed at 10⁻² mmHg from an oil-bath at 70–80 °C. Yield 5.37 g (90% based on InCl₃), m.p. 157–160 °C (Found: C, 51.60; H, 10.05; N, 10.16. C₁₈H₄₂InN₃ requires C, 52.05; H, 10.19; N, 10.12%). ¹H NMR (solvent C₆D₅CD₃): δ 3.45 (2 H, s, CH₂), 1.07 [9 H, s, NC(CH₃)₃] and -0.08 (3 H, s, InCH₃). IR: 3035m, 2855s, 2835 (sh), 2805m, 2780 (sh), 2770m, 2720m, 1480m, 1421w, 1389m, 1366s, 1271s, 1221s, 1200s, 1166s, 1125s, 1048m, 1025m, 1019m, 1010w, 995s, 943s, 682 (sh), 669s (br), 617w, 515w, 461s and 421w cm⁻¹.

Volatility data

Volatility data were recorded by Knudsen effusion, which is described in full elsewhere^{13,14} although a brief outline is presented here.

Table 3 Recorded rates of weight loss, *W'*, and the vapour pressures derived from them for the adducts **1** (*M* = 0.2891), **3** (0.3733) and **4** (0.4154 kg mol⁻¹)

Adduct	<i>T</i> /K	<i>W'</i> /kg s ⁻¹	<i>P</i> /mmHg
1	295.4	1.05 × 10 ⁻⁹	4.50 × 10 ⁻³
	304.6	3.32 × 10 ⁻⁹	1.44 × 10 ⁻²
	313.6	9.95 × 10 ⁻⁹	4.39 × 10 ⁻²
	300.1	1.92 × 10 ⁻⁹	8.26 × 10 ⁻³
	309.4	5.78 × 10 ⁻⁹	2.53 × 10 ⁻²
3	307.4	6.48 × 10 ⁻¹⁰	2.49 × 10 ⁻³
	300.9	3.09 × 10 ⁻¹⁰	1.17 × 10 ⁻³
	295.4	1.61 × 10 ⁻¹⁰	6.06 × 10 ⁻⁴
	313.9	1.26 × 10 ⁻⁹	4.90 × 10 ⁻³
	311.1	9.01 × 10 ⁻¹⁰	3.48 × 10 ⁻³
	317.6	1.92 × 10 ⁻⁹	7.48 × 10 ⁻³
	324.4	3.88 × 10 ⁻⁹	1.53 × 10 ⁻²
	336.6	1.16 × 10 ⁻⁸	4.67 × 10 ⁻²
	339.6	1.05 × 10 ⁻⁸	4.01 × 10 ⁻²
	320.4	1.40 × 10 ⁻⁹	5.20 × 10 ⁻³
4	313.9	6.77 × 10 ⁻¹⁰	2.49 × 10 ⁻³
	332.1	4.67 × 10 ⁻⁹	1.77 × 10 ⁻²
	326.4	2.50 × 10 ⁻⁹	9.38 × 10 ⁻³
	307.1	3.07 × 10 ⁻¹⁰	1.12 × 10 ⁻³
	299.4	1.25 × 10 ⁻¹⁰	4.49 × 10 ⁻⁴

A sample of the compound under investigation, typically 100 mg, was loaded into a sample bottle suspended from a microbalance and hanging inside a vessel fitted with a heating jacket. The whole apparatus was evacuated to below 10⁻⁵ mmHg and the temperature inside the heating jacket monitored with a thermocouple. The technique involves effusion of the molecules through an orifice in the wall of the sample bottle. The compound under investigation exerts its equilibrium vapour pressure on one side of the orifice and on the other side the total pressure is kept negligible. The orifice is small, less than a millimetre in diameter, which reduces the rate of effusion of molecules through it and allows small amounts of compound to be used while maintaining an equilibrium vapour pressure. It also has no significant depth, so it may be approximated to a flat disc. The collision rate of molecules with an area of wall *A*/m² is then the same as the rate of loss of molecules through the orifice, area *A*, which is measured on the microbalance as a mass loss, equation (1) where *Z* is the collision rate per unit area

$$\text{rate of mass loss, } W' = ZmA \quad (1)$$

and *m* the average mass of each species in the vapour (kg per molecule). The rate of mass loss, *W'*, may be equated to the pressure *P* (Pa) within the sample bottle using the simple kinetic theory of gases, since *Z* is given by equation (2) where *k_B* is

$$Z = P/(2\pi mk_{\text{B}}T)^{1/2} \quad (2)$$

Boltzmann's constant (*J K⁻¹*) and *T* is the temperature (K). Since these adducts are associated over the temperature range considered here, *m* = *M*/*N_A* (where *M* = formula mass and *N_A* is Avogadro's number) then equation (3) is obtained.

$$P = \frac{W'}{A} \frac{(2\pi RT)^{1/2}}{M} \quad (3)$$

The approximation of the orifice to a flat disc rather than a tube introduces errors in the theoretical expression for effusion. Allowing for this involves a correction factor which has been studied by Clausing,¹⁵ but this is self-correcting in these experiments since the orifice area is calibrated using mercury and so the factor is incorporated in the area term, *A*. Other sources of error, namely that molecules may diffuse across the surface around the orifice rather than effuse through it and that the rate of weight loss may shift the pressure from the equilibrium value, have also been shown to be negligible.¹³

An area of $4.05 \times 10^{-7} \text{ m}^2$ has been found for the orifice area. The weight losses for the samples at various temperatures are recorded in Table 3, with the vapour pressures derived from them for each adduct.

Acknowledgements

We thank British Telecom Research Laboratories for financial support (to I.S.H.) and the Director of Research, British Telecom, for permission to publish this work.

References

- 1 D. C. Bradley, H. Dawes, D. M. Frigo, M. B. Hursthouse and B. Hussain, *J. Organomet. Chem.*, 1987, **325**, 55.
- 2 M. B. Hursthouse, M. Motevalli, P. O'Brien, J. R. Walsh and A. C. Jones, *J. Mater. Chem.*, 1991, **1**, 139.
- 3 A. M. Bradford, D. C. Bradley, M. B. Hursthouse and M. Motevalli, *Organometallics*, 1992, **11**, 111.
- 4 D. C. Bradley, D. M. Frigo, I. S. Harding, M. B. Hursthouse and M. Motevalli, *J. Chem. Soc., Chem. Commun.*, 1992, 577.
- 5 D. C. Bradley, I. S. Harding, I. A. Maia and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1997, 2969.
- 6 C. H. Bushweller, M. Z. Lourandos and J. A. Brunelle, *J. Am. Chem. Soc.*, 1974, 1591.
- 7 J. M. Lehn, F. G. Riddell, B. J. Price and I. O. Sutherland, *J. Chem. Soc. B*, 1967, 387.
- 8 F. G. Riddell and J. M. Lehn, *Chem. Commun.*, 1966, 375.
- 9 (a) G. E. Coates and R. A. Whitcombe, *J. Chem. Soc.*, 1956, 3351; (b) D. C. Bradley, P. A. Hamilton, I. S. Harding, N. W. Morton, D. W. H. Rankin, H. E. Robertson and J. Vaghjiani, *Proc. R. Soc. London, Ser. A*, 1997, **453**, 2123.
- 10 D. C. Bradley, M. M. Faktor, D. M. Frigo and I. S. Harding, *Chemtronics.*, 1988, **3**, 235.
- 11 R. A. Y. Jones, A. R. Katritzky and M. Snarey, *J. Chem. Soc. B*, 1970, 135.
- 12 J. H. Hildebrand, *J. Am. Chem. Soc.*, 1915, **37**, 970.
- 13 D. C. Bradley, M. M. Faktor and D. M. Frigo, *J. Cryst. Growth*, 1988, **89**, 227.
- 14 M. Knudsen, *Ann. Phys.*, 1910, **32**, 809; *Kinetic Theory of Gases*, Methuen, London and Wiley, New York, 1950.
- 15 P. Clausning, *Ann. Phys.*, 1932, **12**, 961.

Received 6th August 1997; Paper 7/05756C