Enthalpies of Sublimation of $M(\eta^5\text{-}C_5H_5)_2Cl_2$ (M = Ti, Zr, Hf, V, Nb, W) Complexes

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The standard molar enthalpies of sublimation of $M(\eta^5\text{-}C_5H_5)Cl_2$ (M = Ti, V, Zr, Nb, Hf, and W) compounds, at 298.15 K, were determined by the Knudsen effusion method to be: 124.4±2.9 kJmol^{-1} (M = Ti), 108.5±4.6 kJmol^{-1} (M = Zr), 110.2±2.9 kJmol^{-1} (M = Hf), 140.1±7.4 kJmol^{-1} (M = V), 127.4±4.4 kJmol^{-1} (M = Nb), and 120.7±8.6 kJmol^{-1} (M = W). The results obtained show a tendency to linearly decrease with increasing metal atomic radius.

Introduction

The study of bent metallocenes has generated a wealth of fundamental chemistry and some major commercial applications (e.g. new Ziegler-Natta catalysts for the production of polyethylene and polypropylene).[1] These studies have also raised an increasing number of questions about the energetics of reactivity and bonding in these complexes as one tries to rationalise the observed reactions and molecular structures.[2]

The enthalpies of sublimation of $M(\eta^5\text{-}C_5H_5)_2Cl_2$ (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W) complexes are of considerable importance in the study of the energetics of transition metal-ligand bonds. Bis(cyclopentadienyl) compounds, $M(\eta^5\text{-}C_5H_5)_2L_n$ (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W; L = H, halogen, CO, alkyl, alkene, aryl, alkoxide, thiolate, phosphane, etc.; $n = 1-3$), have been extensively used as models for investigating the general trends of M−L bond dissociation enthalpies in group 4−6 transition metals.[3−9] Absolute M−L bond dissociation enthalpies in these complexes can, in principle, be obtained by calculating the enthalpy of reaction (1) from the gas phase enthalpies of formation of $M(\eta^5\text{-}C_5H_5)_2L_n$, $M(\eta^5\text{-}C_5H_5)_2$, and L:

$$M(\eta^5\text{-}C_5H_5)_2L_n\,(g) \rightarrow M(\eta^5\text{-}C_5H_5)_2\,(g) + nL\,(g) \quad (1)$$

$$DH^o(M-L) = \Delta_fH^o[M(\eta^5\text{-}C_5H_5)_2, g]/n + \Delta_fH^o(L, g) - \Delta_fH^o[M(\eta^5\text{-}C_5H_5)_2L_n, g]/n \quad (2)$$

where $DH^o(M-L)$ denotes a bond dissociation enthalpy for $n = 1$ and a mean bond dissociation enthalpy for $n = 2$ or 3.

Unfortunately, although many $\Delta_fH^o[M(\eta^5\text{-}C_5H_5)_2L_n, g]$ and $\Delta_fH^o(L, g)$ values are available,[3−9] the enthalpies of formation of the $M(\eta^5\text{-}C_5H_5)_2$ fragments are not known. In order to overcome this problem, all $DH^o(M-L)$ values reported up to now for $M(\eta^5\text{-}C_5H_5)_2L_n$ compounds have been anchored in the mean M−Cl bond dissociation enthalpies of the corresponding dichlorides. This has been done by considering reaction (3) and Equation 4:

$$M(\eta^5\text{-}C_5H_5)_2L_n\,(g) + 2\,Cl\,(g) \rightarrow M(\eta^5\text{-}C_5H_5)_2Cl_2\,(g) + nL\,(g) \quad (3)$$

$$DH^o(M-L) = 2\,DH^o(M-Cl)/n + \Delta_fH^o[M(\eta^5\text{-}C_5H_5)_2Cl_2, g]/n + \Delta_fH^o(L_n, g) - \Delta_fH^o[M(\eta^5\text{-}C_5H_5)_2L_n, g]/n - 2\Delta_fH^o(Cl, g)/n \quad (4)$$

The calculation of $DH^o(M-L)$ from Equation 4 requires knowledge of the values of $DH^o(M-Cl)$ and $\Delta_fH^o[M(\eta^5\text{-}C_5H_5)_2Cl_2, g]$. The M−Cl bond dissociation enthalpies in $M(\eta^5\text{-}C_5H_5)Cl_2$ have been estimated from the corresponding values in the homoleptic molecules MCl_x.[3−5,8] The enthalpies of formation of $M(\eta^5\text{-}C_5H_5)_2Cl_2$ in the gaseous state can be derived from Equation 5.

$$\Delta_fH^o[M(\eta^5\text{-}C_5H_5)_2Cl_2, g] = \Delta_fH^o[M(\eta^5\text{-}C_5H_5)_2Cl_2, cr] + \Delta_{sub}H^o[M(\eta^5\text{-}C_5H_5)_2Cl_2] \quad (5)$$

The enthalpies of sublimation of $M(\eta^5\text{-}C_5H_5)_2Cl_2$ are therefore needed to calculate $DH^o(M-L)$ from Equation 4.

The $\Delta_{sub}H^o[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ values are also interesting since they are directly related to the intermolecular forces that dictate the solid state structures of the $M(\eta^5\text{-}C_5H_5)_2Cl_2$ compounds. They can therefore be useful in the development of methods for predicting crystal structures or enthalpies of sublimation of organometallic compounds based on atom-atom potential calculations.[10] The ability to predict crystal structures has of course a major impact in areas of great current chemical research activity, such as crystal engineering,[11] while the enthalpy of sublimation and vapour pressures of organometallic compounds are important in, for example, the design of chemical vapour deposition (CVD) processes.[12]

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Only the enthalpies of sublimation of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$, $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$, and $Hf(\eta^5\text{-}C_5H_5)_2Cl_2$ have been measured up to now,[8,9,13,14] and some discrepancies exist in cases where more than one independent result has been reported. The importance of $\Delta_{sub}H^o[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ for the research topics mentioned above led us to undertake their systematic determination for group 4−6 transition metals.

Results and Discussion

The enthalpies of sublimation of the $M(\eta^5\text{-}C_5H_5)_2Cl_2$, compounds were derived from vapour pressure versus temperature measurements, using three different Knudsen effusion apparatuses.[15−18] For M = Ti, Zr, Hf, V, and W, the vapour pressures, p (Table 1), were determined as a function of the temperature, T, from the mass of sample, m, lost by the cell during the time t, according to:[19]

$$p = \frac{m}{AtK_C}\sqrt{\frac{2\pi RT}{M}} \tag{6}$$

where M is the molar mass of the effusing vapour, A is the area of the effusion hole, R is the gas constant, and K_C is the Clausing factor given by Equation 7.[19]

$$K_C = \frac{8r}{3l + 8r} \tag{7}$$

In Equation 7, l and r represent the thickness and the radius of the effusion hole, respectively. The vapour pressure data in Table 1 were fitted to the Clausius−Clapeyron Equation 8.[20]

$$\ln p = -\frac{a}{T} + b \tag{8}$$

and the enthalpies of sublimation of the dichloride complexes at the mean temperature, T_m, of the experiments were obtained as $\Delta_{sub}H^o(T_m) = aR$, where R is the gas constant. The values of $\Delta_{sub}H^o(T_m)$, and of the constants a and b in Equation 8 are indicated in Table 2. The uncertainties quoted correspond to σt_s, where σ is the standard error and t_s the Student's factor for a 95% confidence level.[21] Plots of Equation 8 for $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$, $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$, $Hf(\eta^5\text{-}C_5H_5)_2Cl_2$, $V(\eta^5\text{-}C_5H_5)_2Cl_2$, and $W(\eta^5\text{-}C_5H_5)_2Cl_2$ are shown in Figure 1. The lines for the titanium, zirconium and hafnium complexes are based on the values of the corresponding a and b constants for the global results in Table 2.

In the case of $Nb(\eta^5\text{-}C_5H_5)_2Cl_2$, the mass of compound effusing from the Knudsen cell was monitored with a quartz crystal resonator detector.[17,18] If a thin film of any substance is deposited on the surface of a quartz crystal resonator, a shift Δf, of the main resonance frequency, f, is observed, which is a function of the mass of the coating, m.[22] Under the conditions of our experiment, the rate of change of the resonance frequency of the quartz crystal, v, with the time, t, is proportional to the rate of effusion of the compound from the cell, m/t:[17,18]

$$v = \frac{\Delta f}{t} = C_f\frac{m}{t} \tag{9}$$

where C_f is a proportionality constant. Equations 6 and 9 lead to:

$$p = \frac{v}{C_f AK_C}\sqrt{\frac{2\pi RT}{M}} \tag{10}$$

and, therefore, according to Equations 8 and 10, a plot of $\ln(vT^{1/2})$ against $1/T$ should give a straight line:

$$\ln(vT^{1/2}) = -\frac{a}{T} + b' \tag{11}$$

of slope $a = \Delta_{sub}H^o(T_m)/R$, and ordinate b. By fitting Equation 11 to the v and T data given in Table 1 for $Nb(\eta^5\text{-}C_5H_5)_2Cl_2$ it was possible to derive the values of a, b', and

Table 1. Vapour pressures of $M(\eta^5\text{-}C_5H_5)_2Cl_2$ compounds

$Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ [a]			$Zr(\eta^5\text{-}C_5H_5)_2Cl_2$				$Hf(\eta^5\text{-}C_5H_5)_2Cl_2$			$V(\eta^5\text{-}C_5H_5)_2Cl_2$		$Nb(\eta^5\text{-}C_5H_5)_2Cl_2$		$W(\eta^5\text{-}C_5H_5)_2Cl_2$	
T/K	p/Pa hole 1	p/Pa hole 3	T/K	p/Pa hole 1	p/Pa hole 2	p/Pa hole 3	T/K	p/Pa hole 1	p/Pa hole 3	T/K	p/Pa hole 4	T/K	10^2v/s^{-2} hole 5	T/K	p/Pa hole 4
399.30	0.1141	0.1089	377.74	0.2261	0.2077	0.2062	366.21	0.1408	0.1327	459.8	0.1374	388.6	0.32964	466.5	0.0302
400.82	0.1377	0.1297	379.19		0.2565	0.2519	369.19	0.1825	0.1736	462.2	0.1664	390.1	0.38306	470.7	0.0408
402.34	0.1453	0.1524	380.85	0.3081	0.2947	0.2900	372.20	0.2395	0.2384	465.1	0.2045	391.7	0.44764	472.2	0.0442
405.25	0.1873	0.1918	382.10	0.3096	0.3142	0.2996	375.10	0.3180	0.3032	468.3	0.2426	393.2	0.50993	473.1	0.0448
407.30	0.2286	0.2265	383.62	0.3765	0.3565	0.3565	378.20	0.4240	0.4053	470.0	0.2829	394.7	0.57993	477.8	0.0604
409.75	0.2900	0.2877	385.35	0.4370	0.3869	0.3873	381.17	0.5232	0.5105	471.9	0.3306	396.2	0.71288	478.3	0.0660
412.35	0.3680	0.3573	386.84	0.4982	0.4616	0.4846	384.25	0.7234	0.7047	477.1	0.4859	397.7	0.76842	482.9	0.0808
414.55	0.4219	0.4157	388.08	0.5087	0.5433	0.5154	387.18	0.9023	0.8920	477.5	0.4916	399.1	0.88632	485.3	0.0933
417.42	0.5412	0.5173	389.57	0.6387	0.5849	0.5895						400.7	1.00661		
420.40	0.6959	0.6784	391.16		0.6499	0.6902						402.3	1.21577		
422.32	0.8054	0.7817	392.65	0.8133	0.7635	0.7339						403.6	1.28136		
424.05	0.9222	0.9178										405.0	1.53338		

[a] Hole dimensions: (1) $A = 0.596\ mm^2$, $r = 0.436$ mm, $l = 0.049$ mm; (2) $A = 0.754\ mm^2$, $r = 0.490$ mm, $l = 0.049$ mm; (3) $A = 0.862\ mm^2$, $r = 0.524$ mm, $l = 0.049$ mm; (4) $A = 0.440\ mm^2$, $r = 0.374$ mm, $l = 0.0209$ mm.

Table 2. Values of the constants in Equations 8 and 11 and enthalpies of sublimation of the $M(\eta^5\text{-}C_5H_5)_2Cl_2$ compounds at the average temperature of the experiments (T_m)

M	Hole no.	T_m/K	a	b[a] or b[b]	$\Delta_{sub}H^o(T_m)$/kJmol^{-1}
Ti	1	411.68	14307±334	33.66±0.82	
	3	411.68	14244±281	33.49±0.69	
	Global results	411.68	14275±211	33.58±0.52	118.7±1.8
Zr	1	385.20	12633±1116	31.95±2.88	
	2	385.20	12343±821	31.15±2.13	
	3	385.20	12591±805	31.79±2.08	
	Global results	385.20	12511±517	31.60±1.33	104.0±4.3
Hf	1	376.70	12669±360	32.62±0.95	
	3	376.70	12892±333	33.18±0.88	
	Global results	376.70	12781±287	32.90±0.77	106.3±2.4
V	4	468.7	15824±795	32.42±1.69	131.6±6.6
Nb	5	396.8	14729±470	35.17±1.18	122.5±3.9
W	4	475.9	13464±935	25.38±1.96	111.9±7.8

[a] See Equation 8, for M = Ti, Zr, Hf, V, W. − [b] See Equation 11, for M = Nb.

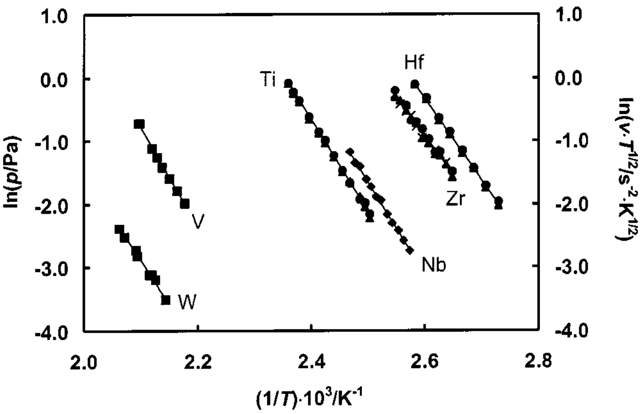

Figure 1. Plots of the Clausius−Clapeyron equation for the $M(\eta^5\text{-}C_5H_5)_2Cl_2$ (M = Ti, Zr, Hf, V, W) compounds and of $\ln(vT^{1/2})$ versus $1/T$ for $Nb(\eta^5\text{-}C_5H_5)_2Cl_2$ (see text). (•) − hole 1, (×) − hole 2, (▲) − hole 3, (■) − hole 4, (◆) − hole 5

$\Delta_{sub}H^o(T_m)$ indicated in Table 2. The uncertainties quoted were calculated as described above for the other complexes. A representation of $\ln(vT^{1/2})$ versus $1/T$ for $Nb(\eta^5\text{-}C_5H_5)_2Cl_2$, based on the a and b constants in Table 2, is also shown in Figure 1.

The enthalpies of sublimation of the $M(\eta^5\text{-}C_5H_5)_2Cl_2$ compounds, at 298.15 K, were derived from:

$$\Delta_{sub}H^o(298.15\ K) = \Delta_{sub}H^o(T_m) + \Delta_{sub}C_p^o(298.15 - T_m) \qquad (12)$$

by using the $\Delta_{sub}H^o(T_m)$ data in Table 2 and an estimated value $\Delta_{sub}C_p^o = -(50\pm20)$ JK^{-1}mol^{-1}.[23] The results obtained are shown in Table 3.

As mentioned in the Introduction, only the enthalpies of sublimation of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$,[8,9,13,14] $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$,[8,9,13,14] and $Hf(\eta^5\text{-}C_5H_5)_2Cl_2$[8,9,13] had been previously measured. Correction of the reported values from their reference temperatures to 298.15 K, using Equation 12 and $\Delta_{sub}C_p^o = -(50\pm20)$ JK$^{-}\cdot^{1}$mol^{-1}, led to the results in Table 3. Note, however, that the information needed to recalculate the corresponding uncertainties using the Student's factor is lacking in the literature. The errors in the published data included in Table 3 may, therefore, be underestimated relative to those quoted for our values. Table 3 shows that the standard molar enthalpies of sublimation of $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$, $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$, and $Hf(\eta^5\text{-}C_5H_5)_2Cl_2$ proposed in this paper agree, within the experimental error, with those obtained by Balducci et al.[13] and by Rabinovich et al.,[8,9] using effusion methods. Our value for $\Delta_{sub}H^o[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ is also in good agreement with a mass spectrometric result published by Kiser et al.[14] A large discrepancy exists, however, between the $\Delta_{sub}H^o[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ value reported by Kiser et al.[14] and those obtained by us and other authors. The enthalpy of sublimation of $\Delta_{sub}H^o[W(\eta^5\text{-}C_5H_5)_2Cl_2]$ in Table 3 is also ca. 16 kJmol^{-1} higher than an estimate of 104.6±4.2 kJmol^{-1} reported by Tel'noi et al.[8]

Finally, it is interesting to note that a linear least squares analysis of a representation of the $\Delta_{sub}H^o[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Ti, Zr, Hf, V, Nb, W) values reported in this paper versus the atomic radii of the metals, r_M,[24] (Table 3), leads to (Figure 2):

$$\Delta_{sub}H^o[M(\eta^5\text{-}C_5H_5)_2Cl_2]/\text{kJmol}^{-1} = -0.972(r_M/\text{pm}) + 263.3 \qquad (13)$$

with a regression coefficient of 0.9. Equation 13 reproduces the experimental $\Delta_{sub}H^o[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ values with a maximum error of 10 kJmol^{-1}, and predicts that $\Delta_{sub}H^o[Ta(\eta^5\text{-}C_5H_5)_2Cl_2]$ = 124±10 kJmol^{-1}, and $\Delta_{sub}H^o[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ = 131±10 kJmol^{-1}. Attempts to measure the enthalpies of sublimation of $Ta(\eta^5\text{-}C_5H_5)_2Cl_2$, and $Mo(\eta^5\text{-}C_5H_5)_2Cl_2$ in the Lisbon laboratory failed due to decomposition of the samples before a measurable mass loss from the Knudsen cell could be obtained.

Conclusion

The enthalpies of sublimation of the $M(\eta^5\text{-}C_5H_5)_2Cl_2$ compounds reported in this paper (*i*) decrease from the first to the second transition series, (*ii*) remain almost constant from the second to the third transition series, and (*iii*) decrease across a transition series. This trend shows a remarkably good linear correlation with the atomic radii of the metals. The significance of this correlation to the nature of the intermolecular potentials in these molecules needs to

Table 3. Enthalpies of sublimation of the $M(\eta^5\text{-}C_5H_5)_2Cl_2$ compounds, at 298.15 K, in $kJ mol^{-1}$,[a] and atomic radii of the metals (r_M) in pm[b]

Group 4	Group 5	Group 6
M = Ti (r_M = 144.8) 124.4±2.9 (this work) 102±13[c] 120.2±3.7[d] 118.9±3.5[e]	**M = V** (r_M = 132.1) 140.1±7.4 (this work)	
M = Zr (r_M = 160) 108.5±4.6 (this work) 103±13[c] 105.6±3.1[d] 106.7±3.1[e]	**M = Nb** (r_M = 142.9) 127.4±4.4 (this work)	**M = Mo** (r_M = 136.2) (131±10)
M = Hf (r_M = 156.4) 110.2±2.9 (this work) 107.3±2.4[c] 106.4±2.8[d]	**M = Ta** (r_M = 143) (124±10)	**M = W** (r_M = 137) 120.7±8.6 (this work)

[a] Values in parentheses were estimated from Equation 13. – [b] Ref.[24]. – [c] Ref.[14]. – [d] Ref.[8,9]. – [e] Ref.[13].

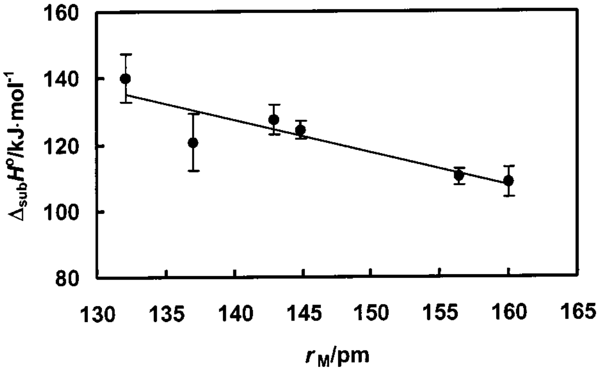

Figure 2. Enthalpies of sublimation of the $M(\eta^5\text{-}C_5H_5)_2Cl_2$ compounds, at 298.15 K, versus the atomic radii, r_M of the metals

be investigated. The obtained $\Delta_{sub}H^o[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ data will also enable an improvement in the reliability of bond dissociation enthalpies derived for bis(cyclopentadienyl) compounds, which are one of the most important model systems used to study the systematics of bonding energetics in transition metal compounds.

Experimental Section

General: All syntheses were carried out under argon atmosphere, by standard Schlenk techniques. Solvents were dried as recommended by Perrin et al.[25] and distilled and stored under argon atmosphere. The $W(\eta^5\text{-}C_5H_5)_2H_2$ used in the preparation of $W(\eta^5\text{-}C_5H_5)_2Cl_2$ was synthesised as described by Green and Knowles[26] and purified by sublimation at 353 K and 0.13 Pa.

C, H, N elemental analysis were performed with a Carlo Erba 1106 elemental analyser. Infrared spectra were obtained with a Perkin–Elmer 683 spectrophotometer calibrated with polystyrene film. Band intensities are referred to as following: vs, very strong; s, strong; m, medium; w, weak.

Materials: $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ was prepared as recommended by Samuel[27] and purified by sublimation at 333 K and 0.13 Pa. – $C_{10}H_{10}Cl_2Ti$: calcd. C 48.24, H 4.05; found C 48.20, H 4.03. – IR (KBr, cm^{-1}): 3120 m, 1445 s, 1375 w, 1028 m, 1015 s, 874 m, 820 vs.

$Zr(\eta^5\text{-}C_5H_5)_2Cl_2$ was synthesised as described in the literature[27–29] and purified by sublimation at 363 K and 1.3 Pa. – $C_{10}H_{10}Cl_2Zr$: calcd. C 41.09, H 3.45; found C 41.03, H 3.47. – IR (KBr, cm^{-1}): 3100 m, 1865 w, 1760 w, 1660–1640 w, 1435 s, 1360 m, 1115 m, 1065 w, 1020–1015 vs, 935–920 w, 860–840 vs, 815 vs.

$Hf(\eta^5\text{-}C_5H_5)_2Cl_2$ (Aldrich, 98%) was purified by sublimation at 390 K and 0.13 Pa. – $C_{10}H_{10}Cl_2Hf$: calcd. C 31.64, H 2.65; found C 31.59, H 2.62. – IR (KBr, cm^{-1}): 3115 m, 1440 s, 1367 w, 1023 s, 1013 s, 855–840s, 814 vs.

$V(\eta^5\text{-}C_5H_5)_2Cl_2$ (Aldrich, 95%) was purified by sublimation at 463 K and 0.13 Pa. – $C_{10}H_{10}Cl_2V$: calcd. C 47.65, H 4.00; found C 47.59, H 3.94. – IR (KBr, cm^{-1}): 3100 m, 1450 m, 1370 w, 1015–1025 w, 1013 s, 890 w, 830 vs.

$Nb(\eta^5\text{-}C_5H_5)_2Cl_2$ was synthesised as described in the literature[30] and purified by sublimation at 363 K and 1.3 Pa. – $C_{10}H_{10}Cl_2Nb$: calcd. C 40.85, H 3.43; found C 40.60, H 3.68. – IR (KBr, cm^{-1}): 3100 m, 1435 m, 1360 w, 1260 w, 1120 w, 1070 w, 1020 s, 870 m, 820 vs.

The method of preparing $W(\eta^5\text{-}C_5H_5)_2Cl_2$ [31] was adapted from that given by Cooper and Green.[32] Dropwise addition of chloroform to a solution of $W(\eta^5\text{-}C_5H_5)_2H_2$ in toluene, under argon atmosphere, at room temperature, gave green crystals of $W(\eta^5\text{-}C_5H_5)_2Cl_2$. These were washed with diethyl ether and dried at room temperature in a filter funnel connected to a water aspirator pump. The product obtained was washed with dichloromethane in a Soxhlet apparatus for 24 h, until colourless extracts were observed, and dried under vacuum (318 K, 1.3 Pa). – $C_{10}H_{10}Cl_2W$: calcd. C 31.20, H 2.62; found C 31.40, H 2.60. – IR (KBr, cm^{-1}): 3110 m, 1430 m, 1360 w, 1265 vw, 1110 vw, 1010 m, 875 m, 835 s, 800 m, 585 w.

Apparatus: The Knudsen effusion apparatus used in the Porto laboratory to measure the vapour pressures of the complexes $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$, $Zr(\eta^5\text{-}C_5H_5)_2Cl_2$, and $Hf(\eta^5\text{-}C_5H_5)_2Cl_2$ has been reported.[15] This apparatus enables the simultaneous operation of three Knudsen cells. In the present work, the effusion holes had a thickness of 0.049 mm, and the areas were 0.596 mm^2 (hole 1), 0.754 mm^2 (hole 2), and 0.862 mm^2 (hole 3). The cells were immersed in a silicone oil bath whose temperature was controlled to within ±0.001 K using a Tronac PTC 40 thermostat. The temperature of the sample was assumed to be identical to the temperature of the bath, which was measured to ±0.01 K with an Amarell calibrated mercury thermometer. In a typical experiment, each cell was charged with ca. 300 mg of sample and the observed mass loss was determined to $\pm10^{-5}$ g with a Mettler H54 balance. The duration of the runs varied from 3 h to 6 h and the corresponding mass losses from the cell varied between 10 mg and 30 mg.

In the Lisbon laboratory, the vapour pressures of V(η^5-C_5H_5)$_2$$Cl_2$ and W(η^5-C_5H_5)$_2$$Cl_2$ were measured with the Knudsen effusion setup previously described.[16] The temperature range of the apparatus was, however, extended up to ca. 650 K by replacement of the water bath with a Termolab tubular furnace surrounding the brass block containing the effusion cell. The temperature of the furnace was controlled to ±0.1 K by a Eurotherm 902P thermostatic unit and a K type thermocouple placed in contact with the inner wall of the furnace. The equilibrium temperature inside the cell was assumed to be identical to the temperature of the brass block. This temperature was measured with a Tecnisis 100 Ω platinum resistance thermometer embedded in the block and connected in a four wire configuration to a Keithley 2000 multimeter. The average of all temperature readings acquired during a constant 10 s interval was stored in the buffer memory of the multimeter. The mean value of the total number of readings accumulated by the multimeter during a run was taken as the corresponding sample temperature. The bronze cell used in the experiments[16a][16b] had an effusion hole with an area of 0.440 mm^2, and a thickness of 0.0209 mm. In a typical run, the cell was charged with ca. 250 mg of sample and the observed mass loss was determined to $\pm10^{-5}$ g with a Sartorius 2474 balance. The duration of the experiments varied between ca. 21 h and 23 h for V(η^5-C_5H_5)$_2$$Cl_2$, and 18 h and 25 h for W(η^5-C_5H_5)$_2$$Cl_2$. The corresponding sample mass losses from the cell were in the ranges ca. 15 mg − 56 mg and 4 mg − 13 mg, respectively.

The compound Nb(η^5-C_5H_5)$_2$$Cl_2$ was studied using an improved version[18] of the Knudsen effusion apparatus with a quartz crystal microbalance detector, described by Burkinshaw and Mortimer.[17] The cylindrical Knudsen cell with an external diameter of 13 mm, an internal diameter of 6 mm, and a depth of 8 mm, was made of steel. The cell was closed by screwing on a steel lid containing a central effusion hole. The hole has the shape of diverging conical orifice with the smaller section (0.8 mm diameter) facing the interior of the cell. The complete cell was screwed into an electrically heated cylindrical steel block, inside the vacuum chamber of an Edwards 306 vacuum coating unit, equipped with a Edwards FTM3 film thickness monitor incorporating a water cooled quartz crystal resonator (6 MHz). The temperature of the block was controlled to ±0.1 K by an Eurotherm 815 unit. The temperature of the sample was measured by a Labfacility P100/0620 platinum resistance thermometer screwed to the bottom of the effusion cell. The vapour effusing from the Knudsen cell condensed on the quartz crystal resonator which was positioned above the effusion hole. The changes in the oscillation frequency of the crystal were monitored as a function of time by a Philips Frequency Counter PM. The pressure inside the vacuum chamber was maintained at ca. $6{\cdot}10^{-5}$ Pa by an Edwards system consisting of an E2M12 rotary pump and a E04 diffusion pump with a liquid nitrogen trap. In the study of Nb(η^5-C_5H_5)$_2$$Cl_2$ the cell was initially charged with ca. 200 mg of compound, and the temperature of the furnace was raised until the rate of sublimation corresponded to a rate of frequency change, v, greater than ca. 10 Hz min^{-1}. When equilibrium was established the frequency counter readings were acquired as a function of time for 45−60 min. The experiment was repeated at successively higher temperatures separated by ca. 2 K.

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[1] For leading references see: [1a]*Comprehensive Organometallic Chemistry* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, **1982**. − [1b]*Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**. − [1c]*Metallocenes: Synthesis, Reactivity, Applications* (Eds.: A. Togni, R. L. Alterman), Wiley-VCH, Weinheim, **1998**.

[2] For leading references see: [2a]*Metal-Ligand Bonding Energetics in Organotransition Metal Compounds* (Ed.: T. J. Marks), Polyhedron Symposium-in-Print, *7*, **1988**. − [2b]*Bonding Energetics in Organometallic Compounds* (Ed.: T. J. Marks), ACS Symposium Series 428, American Chemical Society, Washington, **1990**. − [2c]*Energetics of Organometallic Species* (Ed.: J. A. Martinho Simões), NATO ASI Ser., Ser. C, Vol. 367, Kluwer, Dordrecht, **1992**. − [2d]S. P. Nolan, in *Encyclopedia of Inorganic Chemistry* (Ed.: R. B. King), John Wiley, Chichester, **1994**, Vol. 1, 307−318. − [2e]P. B. Dias, M. E. Minas da Piedade, J. A. Martinho Simões, *Coord. Chem. Rev.* **1994**, *135/136*, 737−807.

[3] G. Pilcher, H. A. Skinner in *The Chemistry of the Metal-Carbon Bond* (Eds.: F. R. Hartley, S. Patay), John Wiley, New York, **1982**, Chapter 2.

[4] A. R. Dias, J. A. Martinho Simões, *Polyhedron* **1988**, *16/17*, 1531−1544.

[5] J. A. Martinho Simões, J. L. Beauchamp, *Chem. Rev.* **1990**, *90*, 629−688.

[6] H. P. Diogo, J. A. Simoni, M. E. Minas da Piedade, A. R. Dias, J. A. Martinho Simões, *J. Am. Chem. Soc.* **1993**, *115*, 2764−2774.

[7] J. A. Martinho Simões, *Organometallic Thermochemistry Data* in NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Eds.: W. G. Mallard, P. J. Linstrom), National Institute of Standards and Technology, Gaithersburg, February 2000, (http://webbook.nist.gov/chemistry).

[8] V. I. Tel'noi, I. B. Rabinovich, *Russ. Chem. Rev.* **1977**, *46,* 689−705.

[9] I. B. Rabinovich, V. P. Nistratov, V. I. Tel'noi, M. S. Sheiman, *Thermochemical and Thermodynamic Properties of Organometallic Compounds*, Begell House, New York, **1999**.

[10] See, for example, [10a] A. J. Pertsin, A. I. Kitaigorodsky, *The Atom-Atom Potential Method. Applications to Organic Molecular Solids*, Springer Verlag, Berlin, **1987**. − [10b] *Theoretical Aspects and Computer Modelling of the Molecular Solid State*, (Ed.: A. Gavezzotti), John Wiley, Chichester, **1997**.

[11] *Crystal Engineering: From Molecules and Crystals to Materials* (Eds.: D. Braga, F. Grepioni, A. G. Orpen) NATO Science Series C, Vol. 538, Kluwer, Dordrecht, **1999**.

[12] See, for example, [12a] *The Chemistry of Metal CVD*, (Ed. T. T. Kodas, M. J. Hampden-Smith), John Wiley, New York, **1994**. − [12b] H. D. Kaesz, A. Zinn, L. Brandt, in *Encyclopedia of Inorganic Chemistry* (Ed.: R. B. King), John Wiley, Chichester, **1994**, Vol. 4, 2205−2219. − [12c] H. O. Pierson, *Handbook of Chemical Vapour Deposition (CVD)*, 2nd Ed., Noyes Publications, New Jersey, **1999**.

[13] G. Balducci, G. Bardi, G. de Maria, R. Gigli, *VII All-Union Calorimetry Conference*, Moscow, Russia, **1977**, 33−34.

[14] R. W. Kiser, J. G. Dillard, D. L. Dugger, *Adv. Chem. Ser.* **1968**, *72*, 153−180.

[15] M. A. V. Ribeiro da Silva, M. J. S. Monte, *Thermochim. Acta* **1990**, *171*, 169−183.

[16] [16a]J. C. G. Calado, A. R. Dias, M. E. Minas da Piedade, J. A. Martinho Simões, *Rev. Port. Quim.* **1980**, *22*, 53−62. − [16b] H. P. Diogo, M. E. Minas da Piedade, A. C. Fernandes, J. A. Martinho Simões, M. A. V. Ribeiro da Silva, M. J. S. Monte, *Thermochim. Acta* **1993**, *228*, 15−22. − [16c] R. C. Santos, *Tese de Doutoramento*, Instituto Superior Técnico, Lisboa, Portugal, **2000**.

[17] P. M. Burkinshaw, C. T. Mortimer, *J. Chem. Soc., Dalton Trans.* **1984**, 75−77.

[18] J. M. Gonçalves, *Tese de Doutoramento*, Universidade do Porto, Porto, Portugal, **1996**.

[19] See for example, [19a] S. Dushman, *Scientific Foundations of Vacuum Technique*, Wiley, New York, **1949**. − [19b] E. D. Cater, *The Effusion Method at Age 69: Current State of the Art*, in Proceedings of the 10th Materials Research Symposium on Characterization of High Temperature Vapors and Gases, Vol. I, (Ed.: J. Hastie) National Bureau of Standards Special Publication 561/1, Washington, **1979**, 3−36.

[20] See for example, J. D. Cox, G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, **1970**.

[21] G. A. Korn, T. M. Korn, *Mathematical Handbook for Scientists and Engineers*, McGraw-Hill, New York, **1968**.

[22] G. Z. Sauerbrey, *Z. Phys.* **1959**, *155*, 206−222.

[23] J. B. Pedley, University of Sussex, personal communication as cited in reference 13. The error of ±20 $JK^{-1}mol^{-1}$ was assumed in the present paper.

[24] J. Emsley, *The Elements*, 2nd ed. (revised), Clarendon Press, Oxford, **1992**

[25] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd Ed., Pergamon, Oxford, **1980**.

[26] M. L. H. Green, P. J. Knowles, *J. Chem. Soc., Perkin Trans. 1* **1973**, 989−991.

[27] E. Samuel, *Bull. Soc. Chim. Fr.* **1966**, *11*, 3548−3564.

[28] E. Samuel, R. Setton, *C. R. Hebd. Seances Acad. Sci.* **1962**, *254*, 308−309.

[29] H. P. Diogo, *Tese de Doutoramento*, Instituto Superior Técnico, Lisboa, Portugal, **1993**.

[30] L. E. Manzer, *Inorg. Chem.* **1977**, *16*, 525−528.

[31] M. E. Minas da Piedade, *Tese de Doutoramento*, Instituto Superior Técnico, Lisboa, Portugal, **1988**.

[32] R. L. Cooper, M. L. H. Green, *J. Chem. Soc. (A)* **1967**, 1155−1160.

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