that we have identified. It also remains to be established to what extent the chemistry that we have identified is relevant to the catalysis by **1** of the hydrogenation of other (notably polar) substrates such as ketones, nitriles, and esters.[16]

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Registry No. 1, 74981-90-1; **2**, 84800-50-0; **3**, 84774-77-6; **5**, 84751-07-5; **6**, 84751-08-6; **7**, 84751-09-7; [RuH(PPh$_3$)$_2$B] (B = cyclohexadiene), 84751-10-0; anthracene, 120-12-7.

---

[16] (a) Grey, R. A.; Pez, G. P.; Wallo, A.; Corsi, J. *J. Chem. Soc., Chem. Commun.* **1980**, 783–784. (b) Grey, R. A.; Pez, G. P.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *103*, 7536–7542.

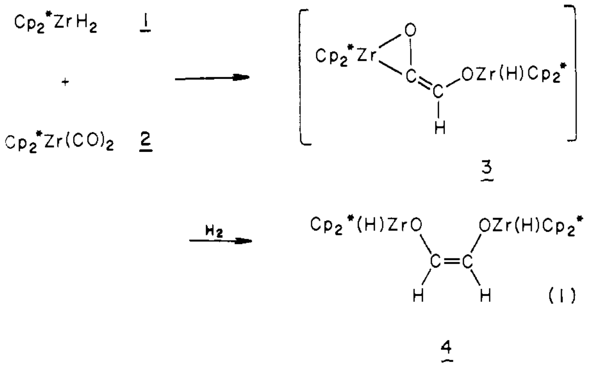
Synthesis and Structure of Ketene Complexes of Permethylzirconocene and Their Hydrogenation to Zirconium Enolate Hydrides

Eric J. Moore, Daniel A. Straus, Justine Armantrout,
Bernard D. Santarsiero,[1] Robert H. Grubbs,* and
John E. Bercaw*[2]

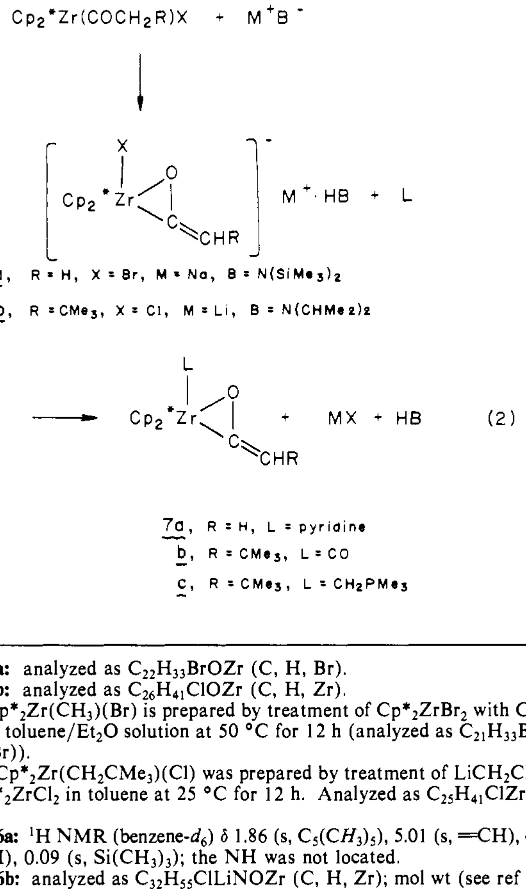
Contribution No. 6742 from the Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

Received October 12, 1982

The reduction of carbon monoxide by Cp*$_2$ZrH$_2$ (**1**, Cp* = η^5-C$_5$Me$_5$) is complex and yields a variety of products depending on reaction conditions.[3] Whereas the mechanism leading to *trans*-(Cp*$_2$ZrH)$_2$(μ-OCH=CHO) from **1** and free CO is relatively well established, the steps leading to *cis*-(Cp*$_2$ZrH)$_2$(μ-OCH=CHO) (**4**) from **1**, Cp*$_2$Zr(CO)$_2$ (**2**), and H$_2$ are largely speculative. The favored scheme[3] involves initial attack of **1** at a carbonyl ligand of **2**[4] followed by carbene–carbonyl coupling affording coordinated "zirconoxy" ketene **3**, which undergoes hydrogenation to **4** (eq 1). The cis geometry of this enediolate product was proposed to result from (i) the structure of **3** in which the bulky Cp*$_2$ZrO moieties are sterically constrained in a cis arrangement and (ii) its stereospecific hydrogenation to **4**.[3,5] Recently a general route to titanocene and zirconocene ketene complexes, dehydrohalogenation of haloacyl compounds, has been developed.[6] Application of this methodology to the permethylzirconocene system has led to isolation of monomeric, Lewis base adducts of Cp*$_2$Zr(C,O-η^2-R$_2$C=CO). We report the results of a structure determination for Cp*$_2$Zr(py)(C,O-η^2-H$_2$C=CO) (py = pyridine) and the stereochemistry of the hydrogenation of the *tert*-butyl ketene complex, which bears on the proposed CO reduction mechanism.



The requisite haloacyl compounds Cp*$_2$Zr(COCH$_3$)(Br) (**5a**)[7] and Cp*$_2$Zr(COCH$_2$CMe$_3$)(Cl) (**5b**)[8] were prepared by carbonylation of the corresponding haloalkyl complexes.[9,10] Deprotonation of **5a** with NaN(SiMe$_3$)$_2$ or **5b** with LiN(CHMe$_2$)$_2$ in toluene affords the soluble anionic halo ketene compounds **6a**[11] or **6b**.[12] The ^{1}H NMR parameters for **6a** and **6b** are similar to those reported for the analogous anionic complex (Cp$_2$Zr(COCH$_2$)CH$_3$)Na$^+$·Et$_2$O (Cp = η^5-C$_5$H$_5$).[6] The ionic ligands of **6a** and **6b** are readily displaced by a variety of neutral donors to yield the neutral ketene complexes **7a**,[14] **7b**,[15] and **7c**[16] (eq 2).



---

[1] Myron A. Bantrell Fellow, 1981–1983.

[2] Camille and Henry Dreyfus Teacher–Scholar, 1977–1982.

[3] Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

[4] Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218.

[5] The reaction of asymmetric ketenes such as Me$_3$SiCH=C=O with (Cp*$_2$ZrN$_2$)$_2$N$_2$ gave only ketene-coupled metallacyclic products, whereas the reduction of such ketenes by **1** gives enolate hydrides, nonstereospecifically. Moore, E. J.; Bercaw, J. E., manuscript in preparation.

[6] (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499. (b) Straus, D. A. Ph.D. Thesis, California Institute of Technology, 1983.

[7] **5a:** analyzed as C$_{22}$H$_{33}$BrOZr (C, H, Br).

[8] **5b:** analyzed as C$_{26}$H$_{41}$ClOZr (C, H, Zr).

[9] Cp*$_2$Zr(CH$_3$)(Br) is prepared by treatment of Cp*$_2$ZrBr$_2$ with CH$_3$MgBr in toluene/Et$_2$O solution at 50 °C for 12 h (analyzed as C$_{21}$H$_{33}$BrZr (C, H, Br)).

[10] Cp*$_2$Zr(CH$_2$CMe$_3$)(Cl) was prepared by treatment of LiCH$_2$CMe$_3$ with Cp*$_2$ZrCl$_2$ in toluene at 25 °C for 12 h. Analyzed as C$_{25}$H$_{41}$ClZr (C, H, Zr).

[11] **6a:** ^{1}H NMR (benzene-d_6) δ 1.86 (s, C$_5$(C*H*$_3$)$_5$), 5.01 (s, =CH), 4.01 (s, =CH), 0.09 (s, Si(CH$_3$)$_3$); the NH was not located.

[12] **6b:** analyzed as C$_{32}$H$_{55}$ClLiNOZr (C, H, Zr); mol wt (see ref 13), 430 (mol wt calcd 561); ^{1}H NMR (benzene-d_6) δ 1.90 (s, C$_5$(C*H*$_3$)$_5$), 4.19 (s, CH), 2.43 (m, NCH), 1.40 (C(CH$_3$)$_3$), 0.83 (d, $^3J_{HH}$ = 6.6 Hz, C(CH$_3$)$_3$), the NH proton was not located; ^{13}C{^{1}H} NMR (benzene-d_6) δ 189.37 (COZr), 115.28 (*C*$_5$(CH$_3$)$_5$), 102.79 (=*C*HC(CH$_3$)$_3$), 45.68 (*C*H(CH$_3$)$_2$), 32.71 (*C*(CH$_3$)$_3$), 32.59 (C(*C*H$_3$)$_3$), 22.88 (CH(*C*H$_3$)$_2$), 12.13 (C$_5$(*C*H$_3$)$_5$); IR (Njuol) ν(NH) 3250 cm^{-1}.

[13] Molecular weight analysis of **6b** and **7c** were determined via isothermal distillation using the Signer method. See: Signer, R. *Justus* Liebigs *Ann. Chem.* **1930**, *478*, 246. The molecular weight of **6b** was low for a monomeric complex and is probably due to labile ligand dissociation. No free diisopropylamine was observed in the ^{1}H NMR spectrum of **6b**.

[14] **7a:** ^{1}H NMR (THF-d_8) δ 1.60 (C$_5$(CH$_3$)$_5$), 9.26 (s, py), 8.43 (s, py), 7.91 (m, py), 7.56 (m, py), 4.57 (d, $^2J_{HH}$ = 1.6 Hz, CH), 3.51 (d, $^2J_{HH}$ = 1.6 Hz, CH); ^{13}C NMR (THF-d_8) δ 205.2 (t, $^2J_{CH}$ = 8 Hz, COZr), 153.0 (d, $^1J_{CH}$ = 182 Hz, py), 151.0 (d, $^1J_{CH}$ = 189 Hz, py), 139.1 (d, $^1J_{CH}$ = 166 Hz, py), 126.2 (d, $^1J_{CH}$ = 162 $^1J_{CH}$ py), 124.6 (d, $^1J_{CH}$ = 164 Hz, py), 115.1 (s, *C*$_5$(CH$_3$)$_5$), 72.8 (dd, $^1J_{CH}$ = 160.2 Hz, $^1J_{CH}$ = 148.4 Hz, CH$_2$), 11.67 (q, $^1J_{CH}$ = 125.0 Hz, C$_5$(*C*H$_3$)$_5$).

[15] **7b** could only be obtained as a dark green oil. Purity by ^{1}H NMR was 80%. ^{1}H NMR (benzene-d_6) important peak δ 4.49 (s, CH); ^{13}C{^{1}H} NMR (benzene-d_6) δ 228.0 (CO), 176.2 (COZr), 91.1 (CH(CMe$_3$)); IR (benzene) ν(CO) 1987 cm^{-1}.

[16] **7c:** analyzed as C$_{30}$H$_{51}$OPZr (C, H, P. Zr); mol wt (ref 13) 582 (mol wt calcd 550); important ^{1}H NMR (benzene-d_6) δ 4.22 (s, CH), 0.97 (d, $^2J_{PH}$ = 14 Hz, P(CH$_3$)$_3$), −0.43 (d, $^2J_{PH}$ = 13.2 Hz, ZrCH$_2$); ^{31}P{^{1}H} NMR (benzene-d_6, external H$_3$PO$_4$) δ 26.59 (P); ^{13}C{^{1}H} NMR (benzene-d_6) δ 186.85 (d, $^3J_{PC}$ = 7.8 Hz, COZr), 13.97 (d, $^1J_{PC}$ = 48.8 Hz, P(CH$_3$)$_3$).

0002-7863/83/1505-2068$01.50/0

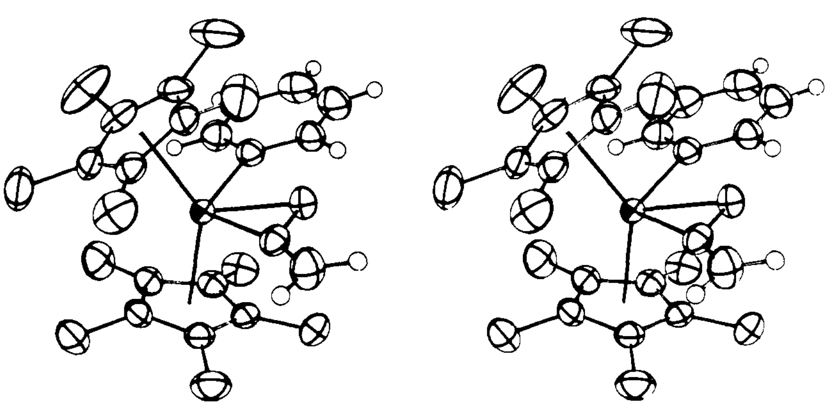


Figure 1. Stereoscopic view of $Cp^*_2Zr(py)(C,O\text{-}\eta^2\text{-}H_2C{=}CO)$.

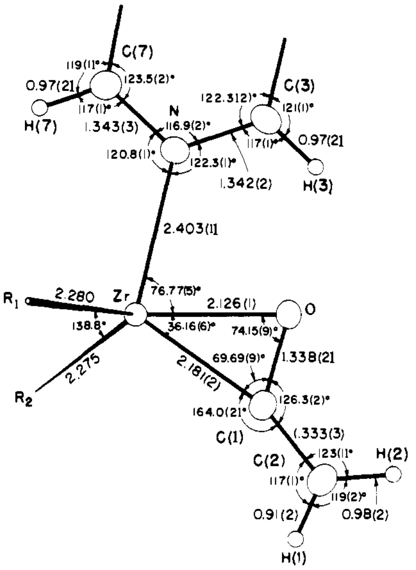
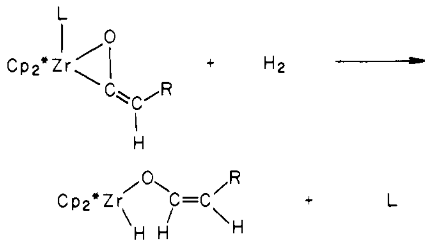


Figure 2. Skeletal view of $Cp^*_2Zr(py)(C,O\text{-}\eta^2\text{-}H_2C{=}CO)$ showing important bond lengths and angles.

Crystals of **7a** suitable for an X-ray structure determination[17] were obtained from diethyl ether. Figure 1 shows the molecular structure, and a skeletal view of the immediate ligation about zirconium with relevant bond distances and angles is given in Figure 2. As expected, the normal covalent bonding between both C and O for **7a** results in a weakened C=O bond and relatively shorter Zr–O distance as compared to these same parameters for $Cp_2Zr(COCH_3)(CH_3)$.[18] The C(1)–C(2) distance of 1.333 (3) Å and coplanarity of C(1), C(2), H(1), and H(2) are representative of a double-bonded $C{=}CH_2$ arrangement. The structures of **7b** and **7c** are expected to be closely analogous with the *tert*-butyl group substituted for H(2), the sterically less encumbered position. This assignment is supported by structural studies of the closely related compound $Cp^*_2Zr(H)[C,O\text{-}\eta^2\text{-}(PMe_3)HC{=}CO)]$, which does exhibit a cis arrangement of Cp^*_2ZrO and PMe_3 groups.[19]

The bulky pentamethylcyclopentadienyl ligands apparently prevent dimerization, which has been observed for the parent $Cp_2Zr(C,O\text{-}\eta^2\text{-}R_2C{=}CO)$ complexes[6] and for $[Cp_2M(Ph_2C{=}CO)]_2$ (M = Ti, Zr).[20] The more soluble, monomeric compounds **7a–c** react rapidly with H_2 (1 atm) at 25 °C to afford the enolate hydride compounds **9a**[21] and **9b**[22] (eq 3). In accord with the



(3)

9a, R = H
b, R = CMe$_3$

proposed stereospecificity of the hydrogenation (eq 1), the enolate geometry of **9b** is >96% cis, as deduced from the vinylic H–H coupling constant ($^3J_{HH}$ = 7.9 Hz).

Since **9b** (and **4**) decomposes before isomerization, we were unable to confirm that the trans isomer of **9b** is thermodynamically favored. However it was demonstrated that the trans isomer of a closely related compound was more stable; treatment of **9b** with CH_3I affords $Cp^*_2Zr(I)(OCH{=}CHCMe_3)$ (**10**),[23] which does isomerize to the trans isomer (eq 4).

These results clearly support the key postulates dictating a cis geometry of $(Cp^*_2ZrH)_2(\mu\text{-}OCH{=}CHO)$ (**4**) in eq 1. Results supporting the proposed step in which the carbene and carbonyl ligands couple to generate a coordinated ketene will be reported

---

[17] **7a**, crystal data: space group $P2_1/n$ ($h0l$ absent for $h + l$ odd, $0k0$ absent for k odd). Lattice constants were obtained by least-squares refinement of 30 2θ values ($33 < 2\theta < 49°$), where each 2θ value was an average of $\pm 2\theta$ values: a = 17.4069 (13) Å, b = 16.1841 (14) Å, c = 8.6076 (7) Å, β = 91.946 (9)°, V = 2423.5 (6) Å^3, Z = 4. Data were collected on a locally modified Syntex $P2_1$ diffractometer with graphite monochromator and Mo Kα radiation (λ 0.71069 Å) in three shells: 1213 reflections ($\pm h, -k, +l$) with $2\theta < 30°$, 7727 reflections ($\pm h, +k, +l$) with $2\theta < 56°$, and 1323 reflections ($\pm h, -k, +l$) in the range $56 < 2\theta < 60°$. The total, 10263, yielded an averaged data set of 7034 reflections. The three check reflections indicated no decomposition, and the data were reduced to F^2 and corrected for absorption (μ = 0.462 mm^{-1}). The Zr atom position was derived from the Patterson map, and the subsequent Fourier map phased on the Zr atom revealed the remaining non-hydrogen atoms. Least-squares refinement of atomic coordinates and U's, minimizing $\sum w(F_o^2 - (F_c/k)^2)^2$ with weights $w = (\sigma_{F^2}{}^2 + (0.02 \times \text{scan counts})^2)^{-1}$ gave $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.059$. The hydrogen atoms, located from difference maps, were included in the model with U = 0.10 Å^2 for ring 1 and U = 0.076 Å^2 for ring **2**, and refinement of all non-hydrogen atoms, pyridine hydrogen atoms, and carbene hydrogen atoms using all the data led to R_F = 0.045 (the sums including 6542 reflections with $F^2 > 0$), R_F = 0.030 (the sums including 5026 reflections with $F_o^2 > 3\sigma_{F^2}$), and the goodness of fit = 1.53 (299 parameters in two blocks: scale factor and Gaussian amplitudes in one block and coordinates in the other).

[18] Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc. Dalton Trans.* **1977**, 1946.

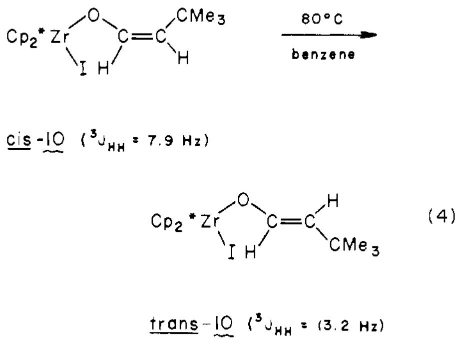
[19] Santarsiero, B. D.; Moore, E. J.; Bercaw, J. E., manuscript in preparation.

[20] (a) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1978**, *17*, 2995. (b) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 462.

[21] **9a:** ^1H NMR (benzene-d_6) δ 1.94 ($C_5(CH_3)_5$), 6.80 (dd, $^3J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 5.9 Hz, CHO), 6.14 (s, ZrH), 4.16 (d, $^3J_{HH}$ = 13.7 Hz, CH), 3.95 (d, $^3J_{HH}$ = 5.9 Hz, CH); $^{13}C\{^1H\}$ NMR (benzene-d_6) δ 154.2 (CHO), 118.3 ($C_5(CH_3)_5$), 89.4 (CH_2), 11.8 ($C_5(CH_3)_5$).

[22] **9b:** analyzed as $C_{26}H_{42}OZr$ (C, H, Zr); ^1H NMR (benzene-d_6) δ 1.97 (s, $C_5(CH_3)_5$), 6.26 (d, $^3J_{HH}$ = 7.9 Hz, CHO), 6.23 (s, ZrH), 3.94 (d, $^3J_{HH}$ = 7.9 Hz, CHCMe$_3$), 1.32 (s, C(CH_3)$_3$); IR (Nujol) ν(C=C, enolate) 1630, ν(ZrH) 1537 cm^{-1}.

[23] *cis*-**10**: ^1H NMR (benzene-d_6) δ 1.88 (s, $C_5(CH_3)_5$), 6.07 (d, $^3J_{HH}$ = 7.9 Hz, CHO), 4.03 (d, $^3J_{HH}$ = 7.9 Hz, CHCMe$_3$), 1.29 (s, $C(CH_3)_3$). *trans*-**10**: ^1H NMR (benzene-d_6) δ 1.93 (s, $C_5(CH_3)_5$), 6.37 (d, $^3J_{HH}$ = 13.2 Hz, CHO), 4.85 (d, $^3J_{HH}$ = 13.2 Hz, CHCMe$_3$), 1.08 (s, $C(CH_3)_3$).



cis-10 ($^3J_{HH}$ = 7.9 Hz)

(4)

trans-10 ($^3J_{HH}$ = 13.2 Hz)

in a forthcoming article.[24] The reactivity of these and related ketene complexes is under further investigation.[25]

Acknowledgment. Financial support from the National Science Foundation (CHE-8024869, J.E.B.; CHE-7904814, R.H.G.) is gratefully acknowledged. R.H.G. also acknowledges financial support from The Department of Energy.

Supplementary Material Available: Bond distances and angles (Table I) and labeling scheme (Figure 3) (2 pages). Ordering information is given on any current masthead page.

---

[24] Barger, P. T.; Santarsiero, B. D.; Bercaw, J. E., manuscript in preparation.

[25] Ho, S. C.; Straus, D. A.; Grubbs, R. H., work in progress.

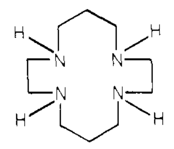
Standard Enthalpies of Sublimation and Vaporization of 1,4,8,11-Tetraazacyclotetradecane and 1,4,8,11-Tetraazaundecane. Gas-Phase Macrocyclic Enthalpy

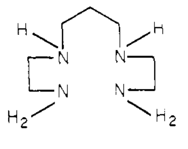
R. M. Clay,* S. Corr, G. Keenan, and W. V. Steele

Chemistry Department, University of Stirling
Stirling FK9 4LA, Scotland, U.K.

Received November 17, 1982

In an earlier paper,[1] the standard enthalpies of formation and solution of 1,4,8,11-tetraazacyclotetradecane (L_1) and 1,4,8,11-tetraazaundecane (L_2) were reported, and in the absence of experimental data, the values of the enthalpies of sublimation and vaporization, respectively, were estimated. A torsion-effusion, weight-loss apparatus has been constructed and calibrated.[2] This apparatus allows the determination of very low vapor pressures and has been used to evaluate the enthalpies of sublimation and vaporization of L_1 and L_2. The significance of these results is discussed below.


L_1


L_2

The apparatus is similar to that described by de Kruif and van Ginkel[3] and in general is suitable for compounds with vapor pressures between 0.1 and 10 Pa (see Figure 1). Typically, the effusion cell is loaded with approximately 200 mg of the compound mixed with silver turnings to promote thermal equilibrium. The apparatus is then evacuated to a pressure of 100 Pa, and in the torsion mode, the electric compensating circuit is set to zero. The pressure is then further reduced to below 0.1 Pa. In the weight-loss mode, the system is then left overnight for the balance to come to rest before measurements begin. After equilibration at each temperature, simultaneous resistance (temperature), voltmeter (torsion), or microbalance outputs are recorded on a 16K Pet microcomputer interfaced to the system. In the weight-loss mode, the readings are taken at precisely time intervals.

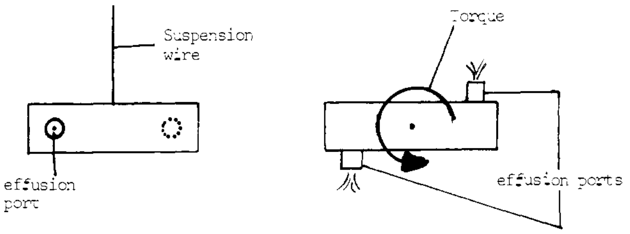


Figure 1. Sketch of effusion cell.

Table I. Vapor Pressure Data for L_1 and L_2

L_1		L_2	
T, K	*P*, Pa	*T*, K	*P*, Pa
352.26	0.040	332.38	0.61
359.99	0.107	335.38	0.81
360.29	0.110	335.53	0.84
361.40	0.131	339.37	1.24
367.31	0.254	341.99	1.645
368.84	0.309	343.65	1.93
371.87	0.425	346.69	2.60
372.34	0.453	347.66	2.87

Scheme I

$$\begin{tikzcd}
ML_2^{2+}(g) \arrow[d, "\Delta H^h(ML_2^{2+})"] & + & L_1(g) \arrow[r, "\Delta H_{gas}"] \arrow[d, "\Delta H^h(L_1)"] & ML_1^{2+}(g) \arrow[d, "\Delta H^h(ML_1^{2+})"] & + & L_2(g) \arrow[d, "\Delta H^h(L_2)"] \\
ML_2^{2+}(aq) & + & L_1(aq) \arrow[r, "\Delta H_{mac}"] & ML_1^{2+}(aq) & + & L_2(aq)
\end{tikzcd}$$

Dissolved air was removed from L_2, which is a liquid at room temperature, by repeated solidification and fusion of the sample under vacuum, and the sample was then transferred to the cooled cell as a solid.

In the weight-loss, or Knudsen mode, first formulated by Knudsen, the vapor pressure of the sample is given by the expression[4]

$$P = \frac{\dot{m}}{A}\left(\frac{2\pi RT}{M}\right)^{1/2}\frac{3l + 8r}{8r}\,\frac{1}{1 + 0.48r/2\lambda}$$

where P = pressure (Pa), $\dot{m}$ = rate of mass loss from cell (kg s^{-1}), A = cross-sectional area of the effusion port (m^2), M = molecular mass of the effusing species (kg), l = depth of the effusion port (m), r = radius of the effusion port (m), and λ = mean free path of effusing species = $(kT/\sqrt{2}\pi\sigma^2)(1/P)$ [σ = collision diameter (m)].

In the torsion-effusion mode, as the molecules effuse from the cell, the suspension wires are subject to a torque that is directly proportional to the vapor pressure of the sample. This torque is counterbalanced by passing a current through a coil mounted directly above the cell. The current required to bring the cell back to the zero point is determined as a voltage drop across a standard resistance. The vapor pressure is then given by

$$P = C'I$$

where C' contains only apparatus constants and is determined by

---

[1] R. M. Clay, M. Micheloni, P. Paoletti, and W. V. Steele, *J. Am. Chem. Soc.*, **101**, 4119 (1979).

[2] R. M. Clay and W. V. Steele, manuscript in preparation.

[3] C. G. de Kruif and C. H. D. van Ginkel, *J. Phys. E: Sci. Instrum.* **6**, 766 (1973).

[4] S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976, p 26.

0002-7863/83/1505-2070$01.50/0