catalyze the condensation reactions of coordinated alkylaminophosphines are in progress.

Acknowledgment. Support by National Science Foundation Grants CHE-7909497 and CHE-8312856, the University of Colorado Computing Center, and a Chinese Ministry of Defense fellowship to H.-J.C. is gratefully acknowledged.

Registry No. **1**, 103711-89-3; **2**, 103711-90-6; **3**, 82991-18-2; **4**, 103711-91-7; **5**, 103711-92-8; **6**, 103711-93-9; **7**, 103711-94-0; *fac*-$(PCl_3)_3Mo(CO)_2$, 19195-96-1; PCl_3, 7719-12-2.

Supplementary Material Available: Listings of thermal parameters, positional and thermal parameters for hydrogen atoms, structural parameters, planes, equations and deviations from planes, and torsion angles and a crystal packing diagram (6 pages); a table of structure factors (2 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Marquette University, Milwaukee, Wisconsin 53233

Mass Spectra and ^{9}Be NMR Spectra of Partially Fluorinated β-Diketonate Complexes of Beryllium

Joan C. Kunz, Manoranjan Das,[1] and Daniel T. Haworth*

Received February 24, 1986

Numerous mass spectral studies of metal complexs of β-diketonates have appeared, with acetylacetonate complexes being the most extensively studied.[1-6] Comparative studies on the effect of the metal[4b,5] and on the influence of the R group of the β-diketonate ligand[8] on the mass spectral fragmentation patterns have also been reported. However, data are sparse on the mass spectra of beryllium β-diketonates,[4] with no results reported on fluorinated β-diketonate–beryllium complexes.

We describe here the mass spectra of several fluorinated β-diketonate–beryllium complexes, having methyl, phenyl and aryl substituents. Transfer of a fluorine atom from ligand to metal is observed, which follows from hard–soft acid–base theory.

The ^{9}Be NMR spectra of the complexes are also reported. Some trends in the chemical shifts of the compounds can be discerned. The ^{1}H, ^{13}C, and ^{19}F NMR spectra of these same β-diketonate beryllium complexes have already been reported.[9]

Results and Discussion

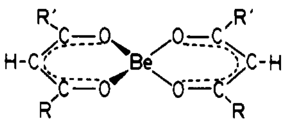

Figure 1. Structure of the beryllium–β-diketonate complexes. The geometry at beryllium is tetrahedral.

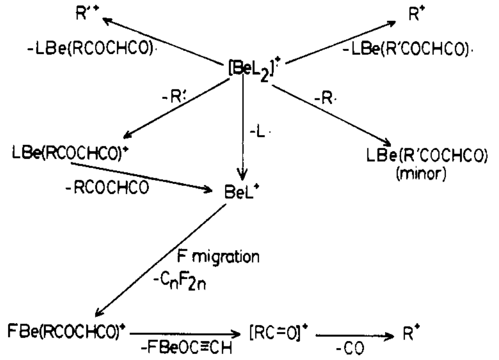

Figure 2. Major fragmentation pathways observed in the mass spectra of the partially fluorinated β-diketone complexes of beryllium.

Table I. Mass and Relative Intensity of Molecular Ions of $Be(RCOCHCOR')_2$

compd no.	R	R′	M^+ *m/e*	rel intens, %
1	CH_3	CF_3	315	30.8
2	C_6H_5	CF_3	439	36.0
3	2′-C_4H_3S	CF_3	451	32.1
4	2′-C_4H_3O	CF_3	419	37.3
5	C_6H_5	C_2F_5	539	13.3
6	2′-C_4H_3S	C_2F_5	551	10.6
7	C_6H_5	C_3F_7	639	4.9
8	2′-C_4H_3S	C_3F_7	651	6.0

The structure of the beryllium β-diketonate complexes is shown in Figure 1, with the substituent groups listed in Table I. The geometry at the beryllium atom is tetrahedral with the formal symmetry as D_{2d} for $Be(acac)_2$ and $Be(hfac)_2$, and C_2 for the unsymmetrically substituted β-diketonate beryllium complexes. Thus these latter chelates are rendered dissymmetric.[9] The appearance of the mass spectra of these complexes is simplified by there being only single isotopes for beryllium and fluorine, and major isotopes for carbon, oxygen, and hydrogen that have only minor contributions from secondary isotopes. Thus, the spectra appear stark, with a single peak for each ion in the spectrum. The molecular ion is observed for each complex. The mass and relative intensity of the molecular ions for each complex are listed in Table I. The relative intensities of prominent ions are given in Table II. The major fragmentation pathways are shown in Figure 2.

Initial fragmentation of the molecular ion proceeds by loss of R′, the fluorinated substituent on the diketone ligand. Peaks appear at masses corresponding to $M^{\bullet+} - R$, which is the loss of the nonfluorinated substituent. However, these peaks are either quite small (compounds **1–4**, **6**, **8**) or they are absent altogether (compounds **5** and **7**). Loss of a CF_3 radical is preferred to loss of a CH_3 radical due to higher stability of the CF_3 radical.[2] This trend appears to be general for fluorinated ligands over nonfluorinated ones. Indeed, the stability of the phenyl radical compared to $\cdot C_2F_5$ or $\cdot C_3F_7$ is so small that $M^{\bullet+} - R$ is not observed for compounds **5** and **7**. The parent ion may cleave at the same bond, but in an alternate fashion as shown in Figure 2, creating R'^+ and LBe(RCOCHCO)·. However, rupture of this bond appears to favor formation of $LBe(RCOCHCO)^+$ and R′ over this alternate cleavage as demonstrated by a comparison of the intensities of R'^+ and $M^{\bullet+} - R'$ listed in Table II.

The next major peak in the mass spectrum at higher mass corresponds to $M^+ - L$, where one β-diketonate ligand has been lost from the parent. Loss of an entire ligand, as a radical, is commonly observed in β-diketonate–metal complexes.[2-7] Loss of the ligand as a radical creates an even electron ion, BeL^+, which is then susceptible to fragmentation by loss of neutral even-electron species.[3] This general phenomenon is observed in the mass spectra

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(1) Current address: Department of Chemistry, Garyounis University, Benghazi, Libya.

(2) Mehrotra, R. C.; Bohra, R.; Gaur, O. P. *Metal β-Diketonates and Allied Derivatives*; Academic: New York, 1978. Macklin, J.; Dudek, G.; *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 403 and references therein.

(3) Clobes, A. L.; Morris, M. L.; Koob, R. D. *Org. Mass Spectrom.* **1971**, *5*, 633 and references therein.

(4) (a) Patel, K. S.; Rinehart, K. L., Jr.; Bailer, J. C., Jr. *Org. Mass Spectrom.* **1970**, *3*, 1239. (b) Lacey, M. I.; MacDonald, C. G.; Shannon, J. S. *Org. Mass Spectrom.* **1968**, *1*, 115. (c) Bhasin, S. K.; Umapathy, P.; Seng, D. N. *J. Indian Chem. Soc.* **1972**, *49*, 1113.

(5) Das, M. *Inorg. Chim. Acta* **1983**, *77*, L65 and earlier references therein.

(6) Reichert, C.; Bancroft, G. M.; Westmore, J. B. *Can. J. Chem.* **1970**, *48*, 1362. Reichert, C.; Westmore, J. B. *Can. J. Chem.* **1970**, *48*, 3213. Bancroft, G. M.; Reichert, C.; Westmore, J. B. *Inorg. Chem.* **1968**, *7*, 870. Bancroft, G. M.; Reichert, C.; Westmore, J. B. *Inorg. Chem.* **1969**, *8*, 474. Reichert, C.; Westmore, J. B. *Inorg. Chem.* **1969**, *8*, 1012.

(7) (a) Das, M. J. *Inorg. Nucl. Chem.* **1981**, *43*, 3412. (b) Das, M.; Livingstone, S. E. *Aust. J. Chem.* **1975**, *28*, 1513.

(8) Rubesch, M.; Clobes, A. L.; Morris, M. L.; Koob, R. D. *Org. Mass. Spectrom.* **1971**, *5*, 237.

(9) Haworth, D. T.; Das, M. *J. Fluorine Chem.* **1984**, *26*, 331.

0020-1669/86/1325-3544$01.50/0

Table II. Relative Intensities of Prominent Ions in the Mass Spectra of β-Diketonate–Beryllium Complexes

R	R′	M$^{\cdot+}$	M$^{\cdot+}$ – R′	M$^{\cdot+}$ – L	FBe(RCOCHCO)$^+$	RCO$^+$	R$^+$	R′$^+$
CH_3	CF_3	31	100	30	69	96		97
C_6H_5	CF_3	36	69	55	59	100	68	43
C_4H_3S	CF_3	32	54	62	59	100	11	44
C_4H_3O	CF_3	37	71	47	100	59	4	42
C_6H_5	C_2F_5	13	37	13	29	100	48	15
C_4H_3S	C_2F_5	11	28	20	35	100	6	22
C_6H_5	C_3F_7	5	23	2	6	100	30	7
C_4H_3S	C_3F_7	6	21	4	5	100	4	12

Table III. ^{9}Be NMR Chemical Shift Data for Be(RCOCHCOR′)$_2$

R	R′	$\delta(^9Be)$	R	R′	$\delta(^9Be)$
CH_3	CF_3	3.14	C_4H_3S	C_2F_5	3.66
C_6H_5	CF_3	3.74	C_6H_5	C_3F_7	3.14
C_4H_3S	CF_3	3.22	C_4H_3S	C_3F_7	3.15
C_4H_3O	CF_3	3.26	CH_3	CH_3	2.97
C_6H_5	C_2F_5	3.64	CF_3	CF_3	3.58

of β-diketones and their metal complexes, especially for fluorinated or partially fluorinated β-diketones and their complexes. For the beryllium complexes in this study, formation of the even-electron BeL$^+$ ion is followed by transfer of a fluorine atom to beryllium and loss of a fluorine-containing even-electron neutral species. When R′ is CF_3, :CF_2 is lost, giving the ion [FBe(RCOCHCO)]$^+$. When R′ is C_2F_5, C_2F_4 is lost, generating the same ion. Minute peaks for :CF_2 loss are observed, leading to the [FBe(RCOCHCOCF$_2$)]$^+$ ion, but these are understandably of very low intensity in view of the stability of the alkene C_2F_4 over the neutral carbene CF_2. When R′ is C_3F_7, C_3F_6 is lost, with no or only trace peaks observed for :CF_2 and C_2F_4 losses.

The migration of a fluorine atom from the ligand to the metal has precedent in the metal complexes of fluorinated β-diketonates of some transition metals[3,6] beryllium,[4] alkaline earths,[7a] group 13 metals,[7a] lanthanides,[5,7b] tin,[7a] and zinc[6]. Other transition metals, such as copper,[6] do not show fluorine migration in their fluorinated β-diketonate complexes. Hard–soft acid–base theory, and class a and class b metal designations have been invoked[5,7] to explain these observations. It is not unexpected then to find the "hard" fluoride migrating to the "hard" Be^{2+}.

The base peak in most of the spectra examined corresponds to RCO$^+$, as seen in Table II. The formation of RCO$^+$ can be explained by loss of the neutral even-electron species FBe(COCH) from [FBe(RCOCHCO)]$^+$ as shown in Figure 2. The RCO$^+$ ion is particularly stable when R is phenyl or thienyl, due to resonance stabilization of the charge over the ion fragment framework. RCO$^+$ further degrades by loss of CO. The intensities of the resulting R$^+$ ion are given in Table II. One notes that the intensity of R$^+$ is generally less than that of R′$^+$, except when R is phenyl, again due to the resonance stability of the phenyl cation. Contributions to the intensity of the R$^+$ peak would certainly include R$^+$ formation from decomposition of RCO$^+$, and from cleavage of the nonfluorinated substituent on the ligand from M$^{\cdot+}$ to generate R$^+$ and LBe(R′COCHCO)·.

The ^{9}Be NMR spectra of these complexes are characterized by a single sharp resonance. The chemical shifts are given in Table III. The width at half-height is ca. 6 Hz when R′ is CF_3 or CH_3. When R′ is C_2F_5 or C_3F_7, the half-height line width increases to ca. 10 Hz. The cause of this change is uncertain but it may be due to minor through-space interactions with the fluorine atoms on the ends of R′ with beryllium.

The range of measured chemical shifts for the β-diketonate complexes (+2.96 to +3.66 ppm) fit into the range for four-coordinate ^{9}Be centers as previously established (ca. –2 to +6 ppm).[10] These data agree with the crystallographically established 4-coordinate tetrahedral geometry at beryllium.[9]

The ^{9}Be NMR chemical shift for Be(acac)$_2$ is 2.97 ppm and it has the most shielded resonance of the beryllium–β-diketonate complexes studied. Due to a total chemical shift range of only 0.77 ppm for the compounds observed, care must be taken in interpreting the chemical shift data in terms of any definite trends. Substitution of a CF_3 group for a CH_3 group results in an upfield shift of the beryllium resonance for Be(tfac)$_2$. A futher upfield shift is noted for Be(hfac)$_2$. This deshielding trend at beryllium is consistent with the electron-withdrawing ability of the CF_3 groups. Keeping the R group constant and varying the R′ group from CF_3 to C_2F_5 to C_3F_7, one observes a reversal of this trend when R is phenyl. Likewise when R is 2′-thienyl the ^{9}Be NMR resonance increases from 3.22 to 3.66 ppm when R′ is CF_3 and C_2F_5, respectively, but decreases when R′ is C_3F_7 to 3.15 ppm. This latter chemical shift variation indicates that the electronegativity of the substituent is not always the primary effect in determining the direction of the chemical shift. For example, the electronegativity of the X group in a series of C_5H_5BeX compounds has a small effect on the deshielding at the beryllium atom as compared to the paramagnetic ring current of the η^5-C_5H_5 ring.[10a] An explanation of these possible trends reported here must await further study with theoretical calculations.

Experimental Section

The β-diketonates and their beryllium complexes listed in Table I were prepared as previously described.[9] Be(acac)$_2$ was obtained from Alfa Products, and Be(hfac)$_2$ was a gift from Professor Gaines. Mass spectra were obtained on a Finnegann 4000 gas chromatograph/EI-CI. ^{9}Be NMR spectra were recorded in $CDCl_3$ at ambient temperature at approximately 0.1 M concentration on a Bruker AM-500 at 70.278 MHz using a 5.0-μs pulse width and a pulse delay of 111.3 μs between scans over a 5600-Hz window. Chemical shifts were referenced to Be(H$_2$O)$_4{}^{2+}$(aq).

Acknowledgment. The authors thank W. Schulze, of Miller Brewing Co., Inc., for the mass spectral data. The authors also thank Professor D. Gaines, Drs. T. Hill and B. Adams, and G. Edvenson at the University of Wisconsin—Madison for the ^{9}Be NMR spectra.

Registry No. **1**, 13939-10-1; **2**, 14052-07-4; **3**, 13928-05-7; **4**, 13928-06-8; **5**, 93595-66-5; **6**, 93595-67-6; **7**, 93595-68-7; **8**, 93595-69-8; Be, 7440-41-7.

---

(10) (a) Gaines, D. F.; Coleson, K. M.; Hillenbrand, D. F. *J. Magn. Reson.* **1981**, *44*, 84. (b) Lindman, B.; Forsen, S. *in NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978.

Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36849

Can the Bis(diboranyl) Structure of B_4H_{10} Be Observed?

Michael L. McKee

Received February 18, 1986

Two recent theoretical studies[1,2] have appeared on the relative stability of the known "butterfly" C_{2v} structure of B_4H_{10} (**2**) and the unknown bis(diboranyl) C_2 structure of B_4H_{10} (**1**). Given the prediction of nearly equal stability, it is perhaps unusual that the bis(diboranyl) structure has not been observed. The purpose of the present note is to explore theoretically the potential energy

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(1) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1981**, *20*, 4452.
(2) Morris-Sherwood, B. J.; Hall, M. B. *Chem. Phys. Lett.* **1981**, *84*, 194.

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