In this connection it is of interest that the reduction of tetraphenylporphineiron(III) chloride by chromium(II) in benzene solution produces $CrCl^{2+}$. Evidently this reaction, too, proceeds *via* an anion-bridged transition state.[22]

The effect of added anions on the rate of reduction of $Fe^{III}TpyP$ by vanadium(II) has also been studied.[13,14] In these experiments the anions were added to the porphyrin solutions only. Since the measured reduction rates were greater than the rate of water loss from the hexaaquovanadium(II) ion,[17] the added anions cannot be bridging the two metal centers in the transition state. This situation is thus similar to the one for $Co^{III}TMpyP$. Yet the catalytic effects observed for the reduction of $Fe^{III}TpyP$ by vanadium(II) are comparable to those observed for the reduction of $Fe^{III}TpyP$ by chromium(II) and much larger than those observed for the reduction of $Co^{III}TMpyP$ by chromium(II). This observation further demonstrates that it is necessary that the anion be bonded to the metal center of the porphyrin for large anion effects to be observed.

Finally, the rate of the inverse acid path is also enhanced by added chloride and thiocyanate ions. An ambiguity concerning the nature of the reactants again arises: the reactants could either be the ion pair $CoP(H_2O)(OH),X^-$ and Cr^{2+} or be $CoP(H_2O)(OH)$ and the chromium(II) complex CrX^+, for the reaction of either pair of reactants could yield the hydroxide-bridged transition state. The relatively small effect of chloride on the inverse acid path ($k_1'/k_0' = 3$) shows that the hydroxide-bridged transition state benefits less from the presence of a chloride ion than does the transition state in the acid-independent reaction ($k_1/k_0 = 30$); by contrast, the hydroxide-bridged transition state derives relatively more benefit from the presence of a thiocyanate ion ($k_2'/k_1' = 1 \times 10^2$, $k_2/k_1 = 6 \times 10$). This comparison provides mild evidence for the operation of a hydroxide and thiocyanate doubly bridged mechanism. In such a mechanism, hydroxide might bridge the two metal centers while thiocyanate coupled the chromium to the porphyrin ring system. This effect could be synergistic in the sense that the hydroxide coordinated to the cobalt could withdraw electrons from the porphyrin ring system thereby making it more positive and a better site for attachment of the nucleophilic sulfur atom of thiocyanate. Addition of a second thiocyanate ion to the transition state appears to benefit the acid-independent and the inverse acid paths about equally.

In conclusion, these studies show that different mechanisms operate in the chromium(II) reductions of tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) and tetrakis(pyridyl)porphineiron(III). The reduction of the iron(III) complex is much more sensitive to the effect of added anions than is the reduction of the cobalt(III) complex, a result which we have rationalized in terms of the ease of substitution at the two metal centers. Coordination to the metal center of the porphyrin system seems to be required for the operation of large anion effects; conversely, when the axial sites on the metal center are blocked (by nonbridging ligands), the effect of added anions is relatively small. This conclusion is consistent with the effect of anions on the rate of reduction of ferricytochrome *c* by chromium(II); the anion effects observed in this system are smaller when both iron-protein bonds are intact than when one of the iron-protein bonds is intact and the other broken.[23]

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Registry No. $Co^{III}TMpyP$, 51329-41-0; $Fe^{III}TpyP$, 51371-92-7; Cr^{2+}, 22541-79-3.

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Mass Spectrometry of Square-Planar Rhodium(I)-β-Diketonate Complexes

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A number of square-planar monovalent rhodium-β-diketonate coordination compounds have been investigated by both low-resolution and high-resolution mass spectrometry. Fragmentation patterns were studied on the basis of the exact isotopic masses and intensities obtained by use of the computerized TPEAKS program. The composition of ions could thus be accurately determined and new insights of the fragmentation patterns of previously investigated compounds were obtained. Attention has also been focused on the mass spectroscopy of complexes with two bulky bidentate ligands. The mass spectra are simple and the presence of the metal atom plays an important role in the fragmentation paths of the ligands observed. The general course of fragmentation is rationalized in terms of the stability of the ions formed and follows established trends in rhodium organic chemistry. Intramolecular rearrangements involving the metal atom have been proposed. Diastereoisomeric rhodium complexes have also been investigated and for the first time chemical ionization mass spectra of square-planar d^8 transition metal complexes have been obtained.

Introduction

Mass spectrometry of metal complexes has received increased attention in recent years.[2-4] Most of the work reported is concerned with investigations of complexes containing monodentate ligands such as CO, olefins, or group V

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[1] Fellow of the Intra-Science Research Foundation, 1971-1975.

[2] (a) M. I. Bruce, *Advan. Organometal. Chem.*, **6**, 273 (1968); (b) M. Cais and M. S. Lupin, *ibid.*, **8**, 211 (1970).

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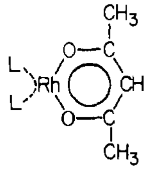
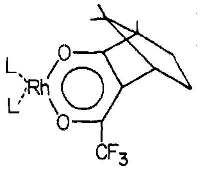
donor molecules. The fragmentation pattern of such metal complexes is relatively simple and consists of successive losses of the monodentate ligands from the metal ion. Consequently, mass spectrometry is merely used for the exact determination of molecular weights and composition of the complexes. For some time, however, more complicated molecules have been studied[5-8] and some interesting conclusions have emerged concerning certain trends in organometallic chemistry.

We were interested in mass spectrometry of complexes containing one or two bidentate chelating moieties bonded to the metal. Emphasis has been focused on the question of how the fragmentation course is directed as a result of the presence of the metal atom. It can be assumed that the positive charge brought about upon electron ionization (EI) will be generally centered on the metal atom. However, stable ions might result if this charge is allowed to delocalize within appropriate metal ligand molecular orbitals. On the basis of this assumption, plausible ligand-rhodium ion structures will be assigned to abundant peaks in the mass spectra of organometallic rhodium compounds.

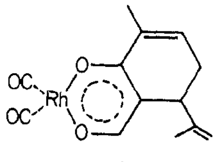
The square-planar rhodium(I)-β-diketonate coordination compounds **1-4** have been measured by both low-resolution and high-resolution mass spectrometry. The following features led to the choice of compounds **1-4** for mass spectrometric investigations: the chelates exhibit high volatility, are thermally very stable, and may be easily prepared and purified. Due to the absence of multiple isotopes of rhodium, well-defined spectra are observed (as an example, see the EI mass spectrum of **4c** in Figure 1) in which the loss of hydrogen atoms may be unequivocally determined. Previous investigations[10] have shown that all complexes gave abundant molecular ions and have very simple fragmentation patterns upon electron impact. No associations were detected in the mass spectra.



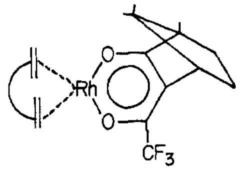
di(ligand)rhodium acetylacetonates (acac)
1a, L = CO
b, L = C_2H_4



di(ligand) rhodium 3-trifluoroacetylcamphorates (tfaCam)
2a, L = CO
b, L = C_2H_4



dicarbonylrhodium 3-formylcarvonate
3



di(olefin)rhodium 3-trifluoroacetylcamphorates
4a, diolefin = NOR[9]
b, diolefin = COD[9]
c, diolefin = DCP[9]
d, diolefin = CAR[9]

Experimental Section

The acetylacetonate rhodium complexes **1a** and **1b** were prepared according to established methods.[11,12] Complexes **2a**, **2b**, and **4a-d** were obtained from the appropriate ligand-rhodium dimer and barium bis(3-trifluoroacetylcamphorate).[10]

Preparation of Dicarbonylrhodium(I) 3-Formylcarvonate, 3. This compound was obtained by a homogeneous exchange reaction of the lead salt of 3-formylcarvone with dicarbonylrhodium chloride in chloroform as described similarly for **2a**.[10] 3-Formylcarvone was prepared according to the method employed in ref 13. It is a pale yellow liquid of bp 65° at 5 × 10^{-3} mm; n^{23}D 1.5310; yield 23%. The lead salt was prepared as follows. To a solution of 379 mg (1 mmol) of $Pb(OCOCH_3)_2 \cdot 3H_2O$ in 20 ml of H_2O was added 5 ml of concentrated NH_3. To this mixture was then added 356 mg (2 mmol) of crude 3-formylcarvone in 20 ml of CH_3OH. The yellow precipitate was filtered off and washed several times with water followed by acetone. The product was air-dried; yield 484 mg. A 484-mg sample of the crude lead salt of 3-formylcarvone and 175 mg (0.5 mmol) of $(CO)_4Rh_2Cl_2$ were allowed to react in 30 ml of $CHCl_3$ for 15 min. The mixture was filtered and the solvent removed *in vacuo*. The residue was chromatographed with $CHCl_3$ on inactivated alumina. Removal of the solvent resulted in dark brown crystalline **3**; yield 295 mg (88%). Further purification was accomplished by sublimation at 50° and 5 × 10^{-3} mm with some decomposition occurring. Dark dichroic crystals separated on the probe, mp 69° (uncor). *Anal.* Calcd for $RhC_{13}H_{13}O_4$: mol wt, 335.9859; C, 46.46; H, 3.90; Rh, 30.62. Found: mol wt, 335.9894 (high-resolution mass spectrum); C, 46.72; H, 3.95; Rh, 30.49. The following infrared absorption maxima were obtained in KBr: 2900 (m), 2075 (vs), 2020 (vs), 1650 (m), 1575 (vs), 1440 (w), 1410 (m), 1375 (w), 1348 (s), 1262 (m), 1223 (w), 1192 (w), 1173 (w), 1053 (w), 903 (s) cm^{-1}. All complexes are stable, volatile, and colored (yellow to red) and are obtained pure by sublimation under high vacuum at 50-120°. Thermogravimetric analysis of **2a** showed that the compound sublimed without decomposition at temperatures between 100 and 250° at 1 atm of N_2 (mp 131°).[14]

High-resolution mass spectra were obtained for each one of the nine compounds. All of the accurate masses found for the hypothetical ion structures agreed to within ±3 millimass units (mmu) with the theoretically accurate masses.

Low resolution (EI) mass spectra were obtained with an LKB 9000 mass spectrometer. Samples were introduced *via* a direct-introduction probe. Mass spectrometer settings were as follows: ion source temperature, 270°; probe temperature, 40-100°; accelerating voltage, −3.5 kV; electron energy, 70 eV.

The high-resolution mass spectrometer employed in this work was a CEC (Du Pont) 21-110B (Lot 9). This instrument was also modified for chemical ionization (CI) mass spectrometry (*vide infra*). Samples were introduced into the ion-source block by means of a direct-introduction probe. Settings were as follows: ion source, 90-110°; accelerating voltage, −8 kV; electron energy, 70 eV. A photographic emulsion placed in the focal plane served as the ion detector. Perfluorokerosene was used as the internal mass standard. All accurate masses were obtained by measuring the ion density profiles on the

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[9] Key: COD, 1,5-cyclooctadiene; NOR, norbornadiene; DCP, dicyclopentadiene; CAR, carvone.

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[14] V. Schurig and Z. Halmos, unpublished data.

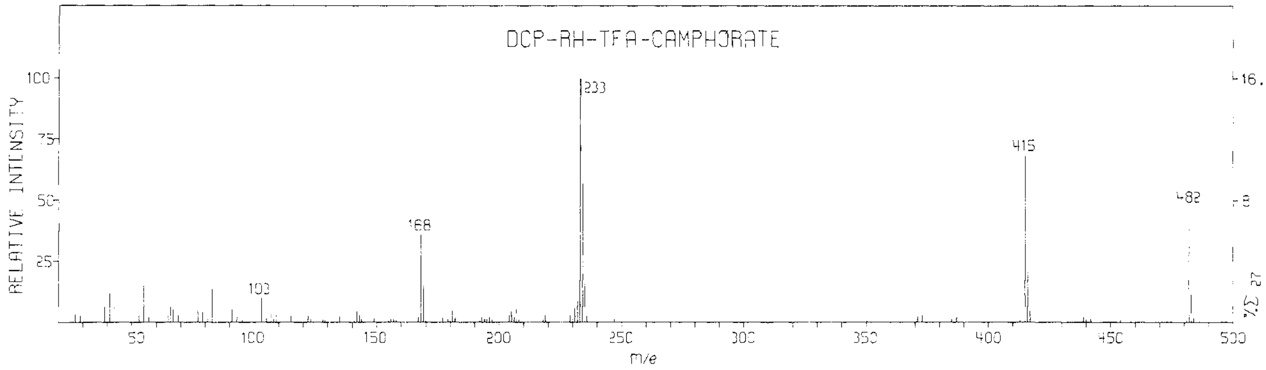
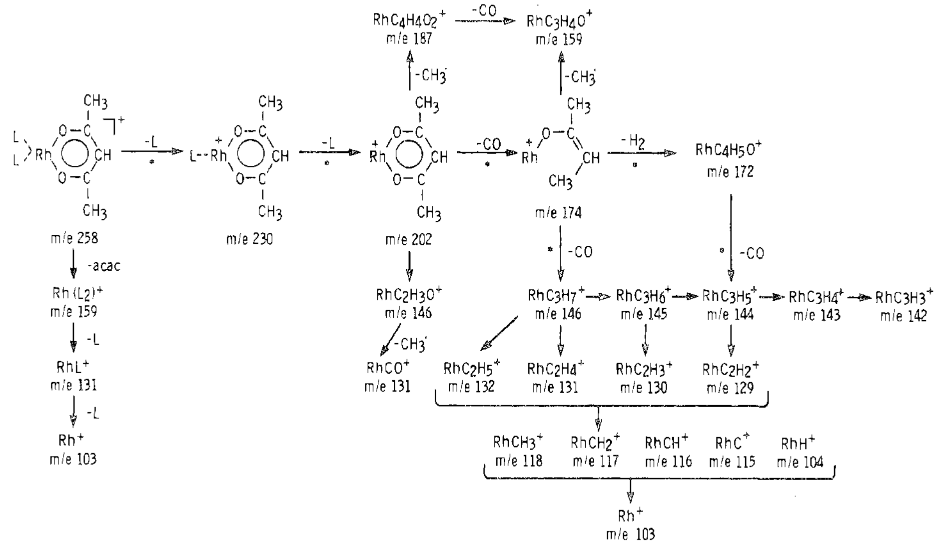


Figure 1. EI mass spectrum of dicyclopentadienerhodium(I) 3-trifluoroacetylcamphorate, compound 4c.

Scheme I



photoplate by means of a microdensitometer-linear comparator system.[15] The data were collected by a PDP 8/I computer and transmitted to an IBM 360/50 computer for data processing.[16]

The computer program TPEAKS was used in this study for data analysis. TPEAKS calculates exact masses and relative abundances of mass spectral peaks when given an elemental composition and isotopic distributions.[16]

Results and Discussion

Complexes 1a and 1b. The mass spectra of complexes **1a** and **1b** were investigated by low-resolution and high-resolution mass spectrometry. The fragmentation pattern and the relative intensities of rhodium-containing ions are given in Scheme I and Table I, respectively. Both complexes give an abundant molecular ion peak, *m/e* 258, and have identical fragmentation patterns. However, the relative intensities of the various ions are markedly different. The mass spectrum of **1a** was also the subject of a recent investigation.[5,6] By comparison of the relative intensities of the molecular ions and the ions $(M - 2L)^+$, it is clear that **1a** is more stable than **1b**, which corroborates well with the fact that **1a** may be obtained by exchange of ethylene with CO from **1b**,[12] albeit a relative stabilization of the L-Rh bond can be expected for **1b**, since the oxidation number of Rh can be formally regarded as +2 upon electron impact and C_2H_4 is a better σ donor than CO.

In addition to the stepwise elimination of two monodentate ligands L, two CO molecules are cleaved from the β-diketonate ring (see Scheme I). These fragmentations were confirmed by the observation of appropriate metastables (for the transition 202 → 174: calcd, 149.9; found, 150.0; for the transition 174 → 146: calcd, 122.5; found, 122.5. Elimination of CO from the β-diketonate ring is necessarily accompanied by rearrangement (migration of $CH_3\cdot$); *cf. m/e* 174, Scheme I. Loss of a second CO thus produces the ion $Rh(C_3H_7)^+$, *m/e* 146 (rhodium-σ-isopropyl ion). This ion may lose H_2 to give $Rh(C_3H_5)^+$. This step can be rationalized in view of the known stability of rhodium-allyl complexes.[17-19] Further loss of H_2 affords the ion $Rh(C_3H_3)^+$ which might be represented as a cyclopropenylrhodium ion.

In close similarity to results obtained for trivalent metal acetylacetonates,[20,21] a loss of one methyl group from the β-diketonate ring is insignificant (see Table I), and elimination of two methyl groups, *e.g.*, $(M - 2L - 2CH_3\cdot)^+$ (calcd for RhO_2C_3H 171.9022), an assignment made for the ion *m/e* 172 in ref 6, does not occur. Accurate mass measurements confirm that this abundant ion corresponds to $(M - 2L - CO - H_2)^+$ (calcd for $RhOC_4H_5$ 171.9386; found for **1a** 171.9386 and for **1b** 171.9394). The same argument applies

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Table I. EI Mass Spectra of Compounds **1a** and **1b**[a]

	Rel intens		
m/e	**1a**	**1b**	Ion assignment
258	100	52	M^+
230	84	75	$(M - L)^+$
202	64	100	$(M - 2L)^+$
187	7	3	$[M - (2L + CH_3)]^+$
174	22	23	$[M - (2L + CO)]^+$
172	65	55	$[M - (2L + CO + H_2)]^+$
159	8 (96)	10 (87)	$[M - (2L + CH_3 + CO)]^+$
	(4)	(13)	$[M - (acac)]^+ = Rh(L)_2{}^+$
146	46 (39)	46 (47)	$[M - (2L + 2CO)]^+ = RhC_3H_7{}^+$
	(61)	(53)	$[M - (2L + CH_3COCH)]^+ = RhOC_2H_3{}^+$
145	4	6	$RhC_3H_6{}^+$
144	50	45	$RhC_3H_5{}^+$
143	5	9	$RhC_3H_4{}^+$
142	8	14	$RhC_3H_3{}^+$
132	6 (100)	9 (50)	$RhOCH^+$
	(0)	(50)	$RhC_2H_5{}^+$
131	39 (46)	53 (69)	$RhC_2H_4{}^+$
	(54)	(31)	$Rh(CO)^+$
130	16	31	$RhC_2H_3{}^+$
129	14	34	$RhC_2H_2{}^+$
118	6	9	$RhCH_3{}^+$
117	7	10	$RhCH_2{}^+$
116	6	6	$RhCH^+$
115	14	8	RhC^+
104	3	6	RhH^+
103	28	53	Rh^+
100	10	3	$Hacac^+$
85	16	7	$[Hacac - CH_3]^+$

[a] In this and other tables the value in parentheses for a particular *m/e* value is the percentage contribution to that *m/e* value as calculated from high-resolution mass spectral data for each indicated ion species. All relative intensities equal to or less than 5% are excluded, except for those ions in the molecular ion region in each table and some significant ions in Table IV.

Table II. EI Mass Spectra of Compounds **2a** and **2b**

	Rel intens		
m/e	**2a**	**2b**	Ion structure
406	100	61	M^+
387	1	1	$(M - F)^+$
378	95 (68)	100	$(M - C_2H_4)^+$
	(32)		$(M - L)^+$
359	1	1	$[M - (F + L)]^+$
350	23 (47)	14	$[M - (L + C_2H_4)]^+$
	(53)		$(M - 2L)^+$
348	19	12	$[M - (2L + H_2)]^+$
331	1	2	$[M - (F + 2L)]^+$
322	25 (59)	33 (92)	$[M - (2L + CO)]^+$
	(41)	(8)	$[M - (2L + C_2H_4)]^+$
320	15	32	$[M - (2L + CO + H_2)]^+$
304	10	25	$[M - (F + 2L + C_2H_3)]^+$
294	29	2	$[M - (2L + CO + C_2H_4)]^+$
292	3	3	$[M - (2L + CO + C_2H_4 + H_2)]^+$
248	40	7	$H - tfaCam^+$
233	20	5	$(H - tfaCam - CH_3)^+$
220	23 (20)	7 (30)	$(H - tfaCam - C_2H_4)^+$
	(80)	(70)	$RhC_9H_9{}^+$
209	3	7	$RhC_8H_{10}{}^+$
208	5	8	$RhC_8H_9{}^+$
206	7	3	$RhC_8H_7{}^+$
205	18	8	$RhC_8H_6{}^+$
196	7	9	$RhC_7H_9{}^+$
195	7	10	$RhC_7H_8{}^+$
185	6	6	$RhC_6H_{10}{}^+$
184	7	8	$RhC_6H_9{}^+$
182	8	9	$RhC_6H_7{}^+$
181	7	9	$RhC_6H_6{}^+$
172	5	10	$RhC_5H_9{}^+$
168	6	7	$RhC_5H_5{}^+$
159	9 (0)	10 (100)	$RhC_4H_8{}^+$
	(100)	(0)	$Rh(CO)_2{}^+$
157	4	6	$RhC_4H_6{}^+$
144	9	9	$RhC_3H_5{}^+$
142	4	6	$RhC_3H_3{}^+$
131	16 (17)	40 (87)	$RhC_2H_4{}^+$
	(83)	(13)	$RhCO^+$
130	2	6	$RhC_2H_3{}^+$
129	3	13	$RhC_2H_2{}^+$
103	18	24	Rh^+

to the ion at *m/e* 144, which is mainly represented by the ion $(M - 2L - 2CO - H_2)^+$ (calcd for $RhC_3H_5{}^+$ 143.9437) rather than $(M - 2L - CO - 2CH_3)^+$ (calcd for $RhOC_2H$ 143.9073; found for **1a** 143.9435 (96%)[22] and 143.9068 (4%); found for **1b** 143.9444 (87%) and 143.9083 (13%)). These elemental compositions also reflect the fact that ion energetics would favor the loss of molecular species (CO, H_2) as opposed to the loss of two consecutive methyl radicals.

The fragmentation of complexes **1a** and **1b** is characterized by a stepwise loss of four groups, where each group weighs 28 amu. High-resolution mass spectrometry permits differentiation of the 28 mass units for CO (27.9949) and C_2H_4 (28.0313). Thus, the molecular ion of **1b** loses at first the two monodentate C_2H_4 ligands followed by the stepwise loss of two CO molecules from the β-diketonate ring. This order of elimination does hold for complex **1a** as well. The importance of accurate mass measurements for the determination of elemental composition and thus ion identification is also illustrated in the evaluation of the peaks at *m/e* 131, *i.e.*, $Rh(CO)^+$ and $Rh(C_2H_4)^+$. According to Table I, intense peaks for these ions occur in both spectra. The occurrence of the ion $Rh(CO)^+$ in the mass spectrum of **1b** is particularly interesting. It originates from the β-diketonate bond, whereby RhOC → RhCO rearrangement is assumed to take place. If this reasoning is also valid for **1a**, the ion $Rh(CO)^+$ (which contributes 54% to the ion current of *m/e* 131) may arise from two different sources, *viz.*, from monodentate carbonyl-rhodium bonds and from carbonyl of the chelate. However, an exact differentiation would be possible only by the mass spectrum of a complex such as $(^{13}CO)_2Rh(acac)$. Interesting is the high abundance of the ion $Rh(C_2H_4)^+$ in the spectrum of **1a** which contributes the remaining 46% to *m/e* 131. Its origin is assumed to arise from the ions $Rh(C_3H_n)^+$ where $n = 3$-7. Here again it is reasoned that the ion $Rh(C_2H_4)^+$ in the spectrum of **1b** is the result of two contributions, namely, from monodentate ethylene and from ethylene obtained from the chelate ring.

Cleavage from the molecular ion of the β-diketonate ring to give $(RhL_2)^+$ is not a major process. Only in the spectrum of **1b** does the process $(M - Hacac)^+$ occur to a minor extent, whereby the hydrogen is possibly abstracted from monodentate ethylene. Noteworthy is the occurrence of rhodium acetylide (128.9201), hydride (103.9148), and carbide (114.9052) ions, together with $Rh(CH_n)^+$ moieties for $n =$ 1-3. The three accurate masses given were found values and agree to within ±3 mmu with theoretical values. The acetylacetonyl ion ($acac^+$) is not present, but the acetylacetone ion ($Hacac^+$) does occur.

Complexes 2a and 2b. In close analogy to the results obtained with compounds **1a** and **1b**, the mass spectra of **2a** and **2b** are characterized by the stepwise loss of the two monodentate ligands L of mass 28. However, the peak *m/e* 378, $(M - L)^+$, is obscured by the competing loss of ethylene, $(M - C_2H_4)^+$, from the 3-trifluoroacetylcamphorate ligand. Thus, high-resolution mass spectrometry of **2a** clearly shows that the peak $(M - 28)^+$ can resolve the contributions $(M - CO)^+$ (32%) and $(M - C_2H_4)^+$ (68%). Obviously, the loss of ethylene from the β-diketonate ligand must be of com-

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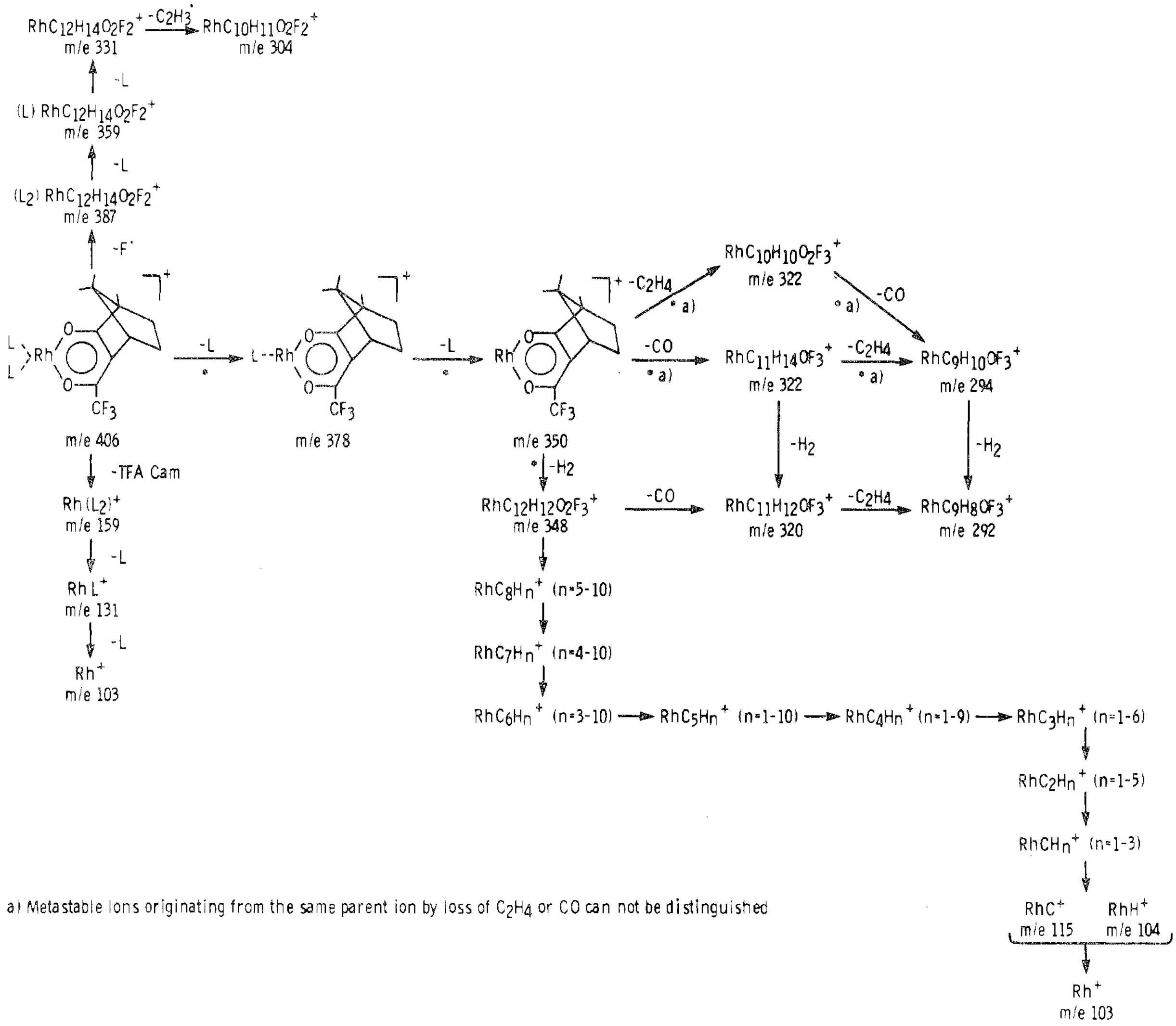
(22) See footnote *a* in Table I.

Scheme II



a) Metastable ions originating from the same parent ion by loss of C_2H_4 or CO can not be distinguished

parable low energy to compete favorably with the loss of monodentate CO from the molecular ion. It is believed that the ethylene originates from C_5 and C_6 of camphor giving rise to the formation of a trimethylcyclopentadienyl entity still attached to the six-membered metal-β-diketonate ring. Previously no loss of ethylene has been observed[23,24] from camphor itself. However, a small contribution of that process gives rise to the ion at *m/e* 220 for tfacCam, which itself occurs at *m/e* 248 in the mass spectra of **2a** and **2b**.

The further fragmentation of the chelate is summarized in Scheme II. Because of the presence of the more complicated camphor group, no attempts have been made to assign abundant ions to definite structures. It should be noted that only one CO molecule is lost from the metal-β-diketonate ring. The second one is probably cleaved as the trifluoroacetyl moiety, $COCF_3$.

Even though the relative intensities of the ion at *m/e* 387 in Table II are quite small, this ion is still interesting. It is due to the loss of a fluorine radical from M^+, a process which may be interpreted as benzylic cleavage.

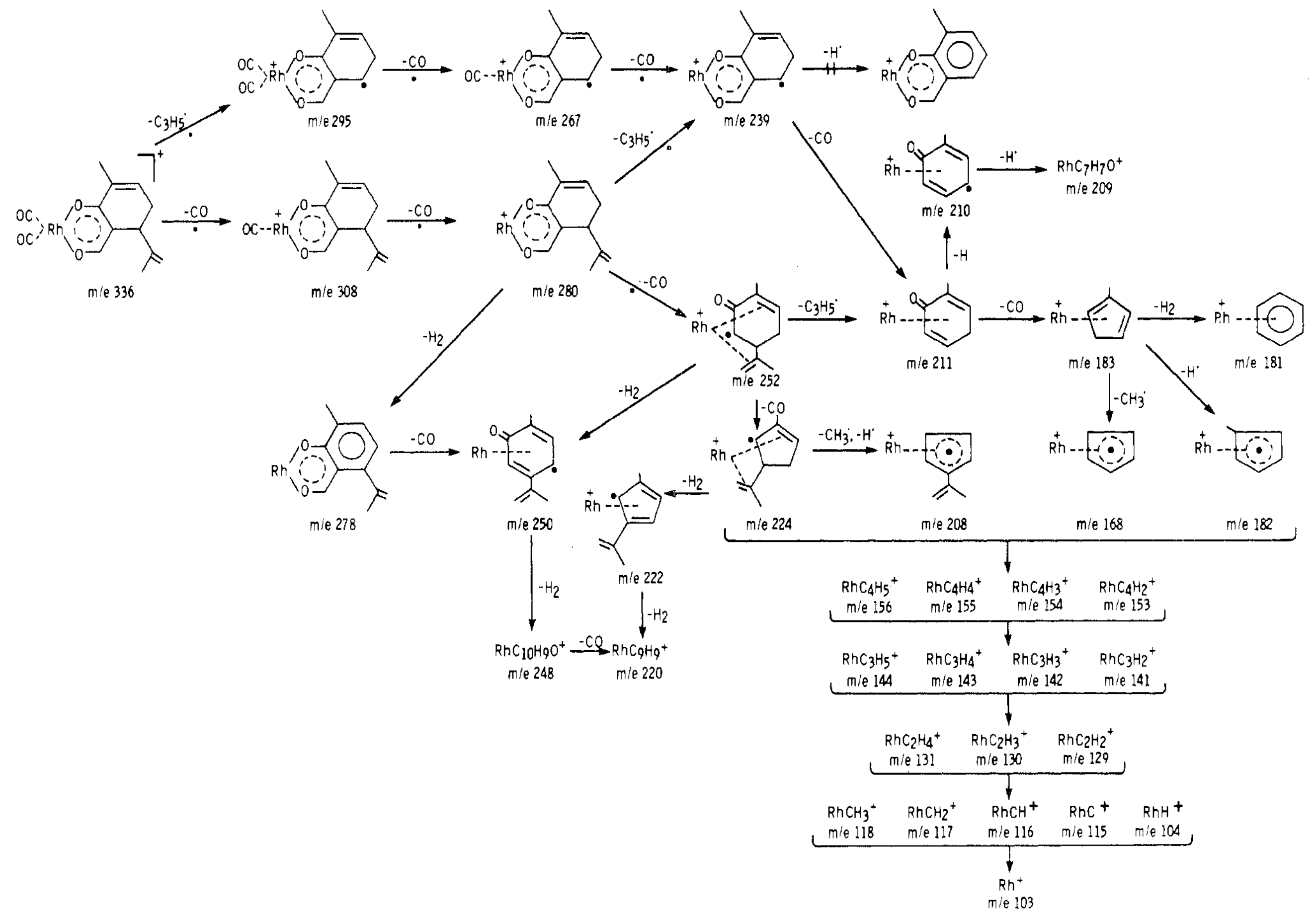
Complex 3. In the mass spectrum of 3 (containing 3-formylcarvone[13] as chelating ligand) (see Table III) four molecules of CO are successively expelled from the molecular ion. In addition, the isopropenyl group is easily eliminated from the molecular ion and consecutive fragments. All peaks of the high-resolution mass spectrum were assigned and the structures proposed for the observed ions are given in Scheme III. The fragmentation pattern may be divided into two pathways. In the first one the isopropenyl group remains attached to the fragments formed by fragmentation of the molecule upon electron impact. Thus, the molecular ion loses two monodentate CO molecules to yield the abundant

Table III. EI Mass Spectrum of Compound 3

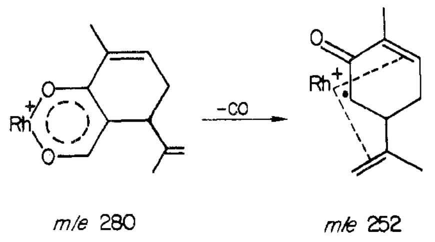
m/e	Rel intens	Ion structure	*m/e*	Rel intens	Ion structure
336	100	M^+	196	10	$RhC_7H_9^+$
308	85	$(M - CO)^+$	194	8	$RhC_7H_7^+$
295	53	$(M - C_3H_5)^+$	192	6	$RhC_7H_5^+$
280	28	$(M - 2CO)^+$	183	12	$RhC_6H_8^+$
278	19	$[M - (2CO + H_2)]^+$	182	57	$RhC_6H_7^+$
267	43	$[M - (C_3H_5 + CO)]^+$	181	41	$RhC_6H_6^+$
252	22	$(M - 3CO)^+$	180	28	$RhC_6H_5^+$
250	88	$[M - (3CO + H_2)]^+$	156	8	$RhC_5H_4^+$
248	24	$M - (3CO + 2H_2)]^+$	155	12	$RhC_5H_3^+$
239	33	$[M - (C_3H_5 + 2CO)]^+$	154	14	$RhC_5H_2^+$
224	8	$RhC_9H_{13}^+$	144	14	$RhC_3H_5^+$
222	65	$RhC_9H_{11}^+$	143	6	$RhC_3H_4^+$
220	12	$RhC_9H_9^+$	142	18	$RhC_3H_3^+$
219	6	$RhC_9H_8^+$	141	6	$RhC_3H_2^+$
218	26	$RhC_9H_7^+$	131	20	$RhCO^+$
211	28	$[M - (C_3H_5 + 3CO)]^+$	130	6	$RhC_2H_3^+$
210	26	$[M - (C_3H_5 + 3CO + H)]^+$	129	8	$RhC_2H_2^+$
209	10	$[M - (C_3H_5 + 3CO + 2H)]^+$	115	10	RhC^+
208	12	$RhC_8H_8^+$	103	53	Rh^+

[23] D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, 31, 115 (1966).
[24] D. R. Dimmel and J. Wolinsky, *J. Org. Chem.*, 32, 410 (1967).

Scheme III



rhodium β-diektonate ion of *m/e* 280, which may lose H_2 to give a fragment with a fully aromatic C_6 system (a rhodium-salicylaldehyde derivative). This formulation is supported by the existence of stable rhodium-salicylaldimine complexes.[25] Another abundant ion is formed by elimination of CO from the ion of *m/e* 280 accompanied by opening of the metal-β-diketonate ring to form *m/e* 252. It has been proposed[5] that the positive charge generated upon electron impact of the metal atom is delocalized within the π-electron system of the "quasiaromatic" metal-β-diketonate ring under participation of an atomic d orbital of the metal. Destruction of this structure by the loss of a CO molecule is therefore assumed to be energetically unfavorable and should take place only if a new energetically stable entity is formed. It is proposed that the fragmentation step 280 → 252 is accompanied by a rearrangement, leading to formation of a diolefinic σ-π type rhodium complex from the former rhodium β-diketonate, including hydrogen transfer, *viz.*



This formulation is supported by the known stability of complexes of transition metals with diolefinic ligands such as dipentene, *e.g.*, (dipentene)$PtCl_2$,[26] and by the isolation of of carvonerhodium(I) complexes;[27] *cf.* compound **4d**. Since the isopropenyl group does participate in the bonding with the metal, it is not cleaved from the C_6 ring at this stage of fragmentation of the molecule. Elimination of CO from the ion at *m/e* 252 leads first to diolefinic five-membered ring systems which eventually collapse to a number of stable substituted cyclopentadienylrhodium ions (*m/e* 208, 182, 168). Loss of the cyclopentadienyl substituents from *m/e* 208 and 182 is energetically unfavorable.

The second pathway in which the isopropenyl group has already been lost from the molecular ion by competition with the monodentate CO molecules involves rearrangement of the rhodium atom from a β-diketonate bond to a diolefinic bond of the type of a cyclohexadienonerhodium ion after loss of CO, *i.e.*, *m/e* 239 → 211. The ion at *m/e* 210 may be formulated as an aroxyl(methylphenoxy)rhodium radical ion. Loss of CO from *m/e* 211 leads to a methyl-π-cyclopentadienerhodium ion at *m/e* 183, which loses the methyl group to give the cyclopentadienylrhodium ion at *m/e* 168.

The cyclopentadienylrhodium ions may lose acetylene to give cyclopropenylrhodium ions. This fragmentation is an established trend in the mass spectrometry of metallocenes.[28] Adopting the concept of the possibility of changes in the valency of the metal,[28,29] the ion $(C_5H_5)Rh^+$ (*m/e* 168) may

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[25] R. Ugo, G. La Monica, S. Cenini, and F. Bonati, *J. Organometal. Chem.*, 11, 159 (1968).

[26] N. C. Baenziger, R. C. Medrud, and J. R. Doyle, *Acta Crystallogr.*, 18, 237 (1965).

[27] V. Schurig, submitted for publication.

[28] E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, 47, 1525 (1964).

[29] M. J. Lacey and J. S. Shannon, *Org. Mass Spectrom.*, 6, 931 (1972).

be formally regarded as π-h^5-cyclopentadienylrhodium d^7 ion and $(C_3H_3)Rh^+$ (*m/e* 142) as π-h^3-cyclopropenyliumrhodium d^9 ion, respectively. The same argument should apply to the loss of C_2H_2 from *m/e* 182 to give a methylcyclopropenyliumrhodium ion, *m/e* 156. Further fragmentation affords abundant ions such as $Rh(CO)^+$, RhC^+, $Rh(C_2H_2)^+$, and $Rh(C_2H_4)^+$. Interestingly, no aromatization of the C_6 ring is observed in the second pathway: elimination of a hydrogen radical from the *m/e* 239 ion does not occur.

The mass spectrum of **3** clearly shows the strong influence of the rhodium atom on the fragmentation pattern of the organic moiety. Only such stable fragments are formed in which the positive charge of the metal can delocalize with appropriate orbitals of pertinent ligands. Although assignments of ions in mass spectrometry are often rather speculative, the trend proposed in Scheme III seems plausible as it is compatible with the organometallic chemistry of rhodium.

Complexes 4a-d. The mass spectra of the volatile complexes **4a-d** with two crowded bidentate ligands show quite unexpectedly very simple fragmentation patterns (see Figure 1). Relative intensities of abundant ions together with other fragments of interest are listed in Table IV. The abundance of the molecular ions and the fragments $Rh(diolefin)^+$ indicate the marked stability of the diolefin-rhodium bonds. A similar observation has been made[27] recently on a number of rhodium(I)-β-diketonate complexes with 1,6-Cl_2COD as the stable diolefinic ligand. By contrast, the rhodium-β-diketonate bond is less stable and the 3-trifluoroacetylcamphorate ligand is thus easily lost from the molecular ion. The free β-diketonate ligand itself formed by hydrogen abstraction appears in the mass spectrum as an ion of low abundance at *m/e* 248.

The fragmentation patterns of the ions $Rh(diolefin)^+$ are similar to those observed previously on related complexes.[2] Noteworthy is the occurrence of ions such as $Rh(C_nH_n)^+$ where $n = 1$-7, for all complexes regardless of the nature of the diolefin. This again illustrates the importance of the presence of the metal atom for the course of fragmentation of the ligands. The formation of stable cyclopentadienylrhodium ions, *m/e* 168, with **4a** and **4c** can be explained by a retro-Diels-Alder type fragmentation[8] followed by hydrogen loss. Loss of the bridging CH_2 entity in **4a** is insignificant despite the fact that Dewar benzene-rhodium complexes have been found to be stable.[30] Obviously, retro-Diels-Alder type fragmentation (loss of ethylene, followed by loss of hydrogen) is favored. The mass spectrum of **4d** with carvone as the diolefinic ligand closely resembles that of **3**. This is in agreement with the proposed occurrence of a carvonerhodium ion through rearrangement from the rhodium formylcarvonate ion (*vide infra*), after the loss of CO from the ion at *m/e* 280 in Scheme III.[31] In **4d** both bidentate ligands are chiral and two diastereoisomers,[27] (+)-carvonerhodium 3-trifluoroacetyl-*d*-camphorate and (−)-carvonerhodium 3-trifluoroacetyl-*d*-camphorate, have been measured by high-resolution mass spectrometry. Although only a subtle difference in the intensities of the fragment ions of the β-diketonate was expected, no such diastereoisomeric effect was noticed. The free energy difference between the two diastereoisomers is obviously too small to be distinguished by mass spectrometry.

Table IV. EI Mass Spectra of Compounds 4a-d

	Rel intens			
Ion structure	4a	4b	4c	4d
M^+	100	100	45	100
$(M-CH_3)^+$	9	5		1
$(M-C_2H_4)^+$	47	45	1	6
$(M-C_3H_6)^+$	8	5	1	1
$(M-C_3H_7)^+$	20	8	2	10
$(M-C_5H_7)^+$			67	
$Rh(diolefin)^+$	40	45	17	38
−H	50	30	55	10
−2H	13	9	100	7
−3H	9	21	10	1
−4H	2	24	6	2
−5H	1	10	5	1
−6H		15	3	
$Rh(C_6H_6)^+$	3	21	4	10
$Rh(C_6H_5)^+$	1	6	2	4
$Rh(C_5H_6)^+$	37	7	15	3
$Rh(C_5H_5)^+$	41	14	35	5
$Rh(C_4H_6)^+$	1	17	1	3
$Rh(C_4H_4)^+$	2	7	1	3
$Rh(C_3H_4)^+$	2	3	2	3
$Rh(C_3H_3)^+$	5	4	4	3
$Rh(C_2H_4)^+$	1 (55)		1 (63)	1 (75)
$Rh(CO)^+$	(45)		(37)	(25)
$Rh(C_2H_2)^+$	1	3	1	1
RhC^+	8	1	2	1
Rh^+	9	11	9	6
$Rh(tfaCam)^+$				1
$HtfaCam^+$	1	1	1	2
$(diolefin)^+$	1	1	1	1
$(diolefin-H)^+$	7	3	3	1

Chemical Ionization Mass Spectra of 1a, 1b, 2a, and 2b. Chemical ionization (CI) mass spectrometry involves a reagent gas at a relatively high pressure (~1 Torr) in the ion source.[32] Ionization of the gas by an electron beam of a few hundred electron volts[33,34] results in a series of extremely fast ion-molecule reactions. The stable products of these reactions then undergo many collisions with the reagent gas so that ions near thermal energy are produced. These ions then interact with the compound of interest.

For example, with methane as a reagent gas, CH_5^+, $C_2H_5^+$, and $C_3H_5^+$ account for approximately 47, 41, and 6% of the plasma, respectively.[35] Due to the strong Bronsted acid character of the CH_5^+ ion, protonation of the compound of interest will usually occur. CI mass spectrometry may therefore be a sensitive probe for metal complex basicity. In addition, adduct ions may be observed with $C_2H_5^+$ and $C_3H_5^+$. Because of the very low energy content of the ion-molecule reaction products, the number of fragmentations is usually minimized.

Table V contains the CI mass spectra of compounds **1a** and **1b**, and Table VI, the spectra of **2a** and **2b** using methane as the reagent gas.

A major peak in the spectra is the protonated molecule $(M + H)^+$ at *m/e* 259 for compounds **1a** and **1b**. An interesting group of ions occurs at *m/e* 101, 129, and 141 and corresponds to the adduct ions of the acetylacetone molecule. Therefore, even though CI processes transfer lower

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(30) H. C. Volger and M. M. P. Gaasbeck, *Recl. Trav. Chim. Pays-Bas*, 87, 211 (1968).

(31) Accordingly, preliminary investigations on the carvone-rhodium(I) cyclopentadienide complex[27] showed an ion at *m/e* 246.9994 (69% relative abundance; accurate mass calculated for $C_{11}H_{12}Rh = 246.9984$) in the EI spectrum due to "monomethylrhodiocene."

(32) F. H. Field, *Accounts Chem. Res.*, 1, 42 (1971).

(33) J. H. Futrell and L. H. Wojcik, *Rev. Sci. Instrum.*, 42, 244 (1971).

(34) I. Dzidic, D. M. Desiderio, M. S. Wilson, P. F. Crain, and J. A. McCloskey, *Anal. Chem.*, 43, 1877 (1971).

(35) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, 88, 2621 (1966).

Table V. CI Mass Spectral Data of Compounds **1a** and **1b** with CH_4 at a Source Pressure of 0.6 Torr at 90°

Ion	m/e	Rel intens	
		1a	**1b**
$(MH + Hacac)^+$	359	2	2
$[(MH + Hacac) - L]^+$	331	3	4
$[(MH + Hacac) - 2L - 2H]^+$	301	1	1
$(M + C_2H_5)^+$	287	6	1
MH^+	259	96	100
$(MH - L)^+$	231	10	84
$(MH - 2L - 2H)^+$	201	9	1
$(Hacac + C_3H_5)^+$	141	8	2
$(Hacac + C_2H_5)^+$	129	21	7
$(HacacH)^+$	101	100	43

Table VI. CI Mass Spectral Data of Compounds 2a and **2b** with CH_4 at a Source Pressure of 0.6 Torr at 110°

Ion	m/e	Rel intens	
		2a	**2b**
$(M + C_2H_5)^+$	435	12	8
MH^+	407	100	100
$(MH - HF)^+$	387	17	22
$(tfaCam + C_2H_5)^+$	277	9	6
$(tfaCamH)^+$	249	38	22
$(tfaCamH - HF)^+$	229	5	3

levels of energy to the molecule, the production of $(Hacac + H)^+$ ions is still energetically favorable for **1a** and **1b**. Because the acetylacetone species exists in such abundance, adduct ions occur at M + 101, which are due to the [di(ligand)rhodium acetylacetonate + acetylacetone + H]$^+$ species (see *m/e* 359). The losses of CO and then H_2CO occur from both *m/e* 359 and *m/e* 259 $(M + H)^+$ species.

It was stated above that compound **1a** is more stable than **1b**. The data in Table V corroborate this fact. Again, by comparing the relative intensities of $(M + H)^+$ and $(M + H - 28)^+$, we see that 28 amu is lost quite readily from **1b**.

This observation of ions at *m/e* 101 but not at *m/e* 100 involves a very interesting mechanism. Initially, the protonated molecular ion $[L_2Rh(acac)]H^+$ forms at *m/e* 259. Because of the high proton affinity of the acac moiety and the resonance stability of the Hacac molecule, Hacac cleaves from the molecular ion. The neutral molecule Hacac is then protonated to give rise to the abundant $(Hacac + H)^+$ ion at *m/e* 101. The positive ion $(RhL_2)^+$ is not found due to chemical instability but rather fragments to form the ligand (L^+) at *m/e* 28, which cannot be readily resolved from the abundant CI plasma ions.

The CI mass spectra of **2a** and **2b** are quite simple. $(M + 1)^+$ and $(M + 29)^+$ ions for camphor occur at *m/e* 249 and 277, respectively. A very interesting peak occurs in both spectra at *m/e* 387 and is due to the loss of HF. This is a very favorable process in regard to the energetical aspects: first the molecule is protonated and then the much more stable HF bond is formed (bond strength: C-F, 61.4 kcal/mol; H-F, 135 kcal/mol). By comparison of the relative intensity of the protonated molecular ion peak with the protonated β-diketone peak (internal standard), it follows qualitatively that the ethylene complexes **1b** and **2b** exhibit a greater proton affinity than the carbonyl complexes. This is a consequence of the better π-acceptor properties of the carbonyl group with respect to the ethylene group.

Conclusions

High-resolution mass spectrometry has provided accurate mass measurements of square-planar rhodium(I)-β-diketonate complexes. The elemental compositions derived from these accurate masses have enabled us to propose detailed fragmentation schemes for the complexes. In some cases, hypothetical ion structures previously reported by other authors had to be revised in accordance with elemental compositions and basic ion energetic considerations.

Many elemental compositions indicate that extensive molecular rearrangements must occur in the organic portions of the molecule. As the ionization potential of rhodium is low and an ionization energy of 70 eV has been employed, most of the excess energy can go into fragmentation of the organic moieties. The presence of rhodium plays a most important role in the fragmentation of the ligands observed. Differences in the EI spectra of diastereoisomeric rhodium complexes were not observed.

CI mass spectrometry can play a useful role in the structural elucidation of these complexes. The spectra are simplified and only the most energetically favorable processes occur. Corroboration was obtained in the comparison of the stabilities of some of the complexes. As CI has a wide variety of gases available of varying acid-base characteristics, much interesting work will be done in this area. It is proposed to use CI as a probe for metal complex basicity.

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Registry No. **1a**, 14874-82-9; **1b**, 12082-47-2; **2a**, 36654-16-7; **2b**, 36484-13-6; **3**, 51391-41-4; **4a**, 36484-16-9; **4b**, 36484-14-7; **4c**, 36484-15-8; **4d**, 51391-42-5.