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Electron Impact Mass Spectra of Some Palladium(II) Chelates of Fluorinated β-Diketones

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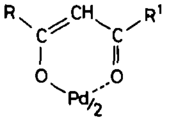
Introduction

The fragmentation pattern of metal β-diketonates in mass spectra are influenced by the nature of the metal. Some of the rearrangement reactions in the mass spectra of metal chelates of fluorinated β-diketones depend on whether the metal is class *a* or class *b* [1–3] and its redox properties [4]. Large number of β-diketonates of class *a* and intermediate type metals have been studied by mass spectrometry [5, 6]. Almost no mass spectral studies were reported on the class *b* metal complexes of fluorinated β-diketones. Kowalski *et al.* published the EI mass spectra of $Pd[(CH_3)_3CCOCHCOC_3F_7]_2$ [7]. However, few mass spectral studies of palladium and platinum (class *b* metal) complexes of fluorinated monothio-β-diketones were reported [8–10].



We have determined the mass spectra of palladium(II) chelates of β-diketones containing R^1 as CF_3, C_2F_5 and C_3F_7 groups. The main purpose of this investigation is to study the atom and group migration from the ligand to the metal and compare the spectra with those of the palladium chelates of related monothio-β-diketones ($RCSCH_2COR^1$). The mass spectrometry was used by Okeya *et al.* for the determination of the molecular weights of bis(β-diketonato)palladium(II) complexes [11].

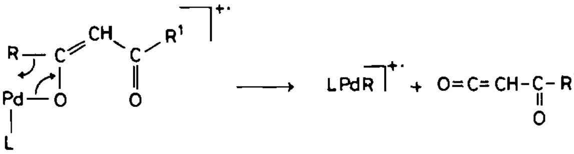
Experimental

The β-diketones ($RCOCH_2COCF_3$) with R as methyl, phenyl and 2-thienyl were obtained from the commercial sources. Others were prepared by Claisen condensation of the methyl ketone ($RCOCH_3$) and ethyl perfluorocarboxylate ($R^1COOC_2H_5$), catalyzed by sodium methoxide [12]. The method of preparation of the palladium(II) complexes was reported in a separate communication [13]. The EI mass spectra were obtained on an AEI MS-12 mass spectrometer at 70 eV and at a source temperature of 250 °C.

Results and Discussion

Palladium has several naturally occurring isotopes which give ion-cluster for each metal containing ion. This makes the identification of metal containing ions easier without any resort to high resolution mass spectrometry. The relative intensities of unipositive and dipositive metal containing ions are shown in Table I and Table II, respectively. The unipositive molecular ion is the base peak amongst the metal containing ions.

The mass spectra of palladium complexes of fluorinated β-diketones shows numerous R migration to the metal. In sharp contrast, such rearrangement is absent in the mass spectra of $Pd(RCSCHCOCF_3)_2$ [10]. This difference can be attributed to the class *b* character of the metal. The R migration to the metal in the mass spectra of metal β-diketonates can occur via a four or six-membered cyclic transition state [14]. The migration involves the simultaneous breaking of a palladium–oxygen bond as shown on the basis of four membered transition state.



The palladium–sulphur bond is stronger than palladium–oxygen bond due to the presence of some π bonding in the former. This is the reason for non-migration of R in the mass spectra of palladium complexes of monothio-β-diketones. The odd-electron RPdL ion can be formed either from even-electron $PdL_2{-}R^1$ or from odd-electron PdL_2 ion. But the formation of odd-electron ion from the even-electron ion are very rare. The metastable peak for the reaction, $PdL_2^{+\cdot} \rightarrow RPdL^{+\cdot}$, was observed (at 306.8) in a special mass spectral study of $Pd(RCOCHCOCF_3)_2$ with R = 2-thienyl. The strong class *b* character and the presence of d electrons in palladium(II) causes R migration which involves metal → R π bonding [15].

When R is a phenyl group the spectra shows the presence of HPdL and $PdL{-}R^1{-}H$ ions. The migration of hydrogem from the *ortho* position of the phenyl group to the metal was observed, and the

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TABLE I. Relative Intensities of Metal Containing Unipositive Ions in EI Mass Spectra of $Pd(RCOCHCOR^1)_2$.

Ions	R^1	CF_3				C_2F_5		C_3F_7	
	R	Methyl	Phenyl	2-Thienyl	2-Furyl	Phenyl	2-Thienyl	Phenyl	2-Thienyl
PdL_2		100	100	100	100	100	100	100	100
PdL_2-F		3.3	2.8	1.3	2.9	2.1	2.9		2.2
PdL_2-CO			2.4	1.3	2.9				
PdL_2-47				1.8		3.5	2.1		3.3
PdL_2-R^1		30	7.1	9.1	3.5	15.2	12.4	20.7	21.1
$RPdL$		14[a]	11.2[a]	21.8[a]	30[a]	9.6	15.3	7.8	18.3
$RPdL-CO$			23.7	2.8	0.5	15.2	20.6	14.5	3.9
$RPdL-R^1$		24.7	3.6	4.2	2	9		10.3	19
$RPdL-R^1-CO$						2.8			
$HPdL$			4			4.8		4.8	
PdL		53.3			3.1		5.9		6.7
$PdL-16$			3.8	50	66.7		64.7		88.9
$PdL-CO$			5		4.5	4.1		5.5	
$PdL-CO_2$					27.7				16.7
$PdL-R^1-H$			8.7			18		20	
$RPdCHR$			42.5	21.8	4.5	29	12.4		
$RCHPd$									24.4
RPd		47	46.2	29.5	24.1	49.6	47.1	41.4	61.1
Pd		18.7			16.6				
PdL_2-CH_3		4.7							
PdL_2-CH_3CO		36.7							
$PdL_2-R^1-CH_2CO$		2.4							
$PdL-R$		3.0							
$PdL-CH_2CO$		1.6							
$PdL-R^1$		8.7							

[a]When R^1 is CF_3, the PdL_2-138 ions can be written as RPdL or PdL_2-2CF_3. But the presence of RPdL in the case of complexes with R^1 as C_2F_5 and C_3F_7 indicate the same should hold true when $R^1 = CF_3$. Some m/e (based on ^{106}Pd) could not be identified: Compd. 2223(4), 211(2.4); Compd. 3271(7.6); Compd. 4321(1.5), 239(10); Compd. 8491(4.4%). Compound 2 also give PdL_2-2CO and the metastable peak was identified for its formation from PdL_2-CO.

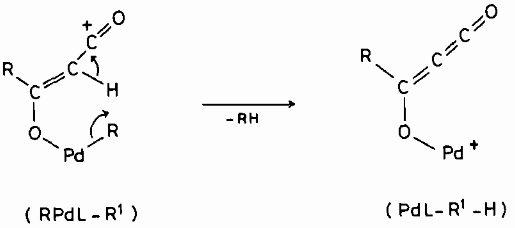
TABLE II. Relative Intensities[a] of Doubly Charged Ions in the Mass Spectra of $Pd(RCOCHCOR^1)_2$.

Ions	R^1	CF_3				C_2F_5		C_3F_7	
	R	CH_3	2-Furyl	Phenyl	2-Thienyl	Phenyl	2-Thienyl	Phenyl	2-Thienyl
PdL_2^{++}		1.0	4.21	1.6	3.2	2.73	3.46	2.5	5.7
$[PdL_2-R^1]^{++}$		1.66	2.0	0.56	1.37	1.4	1.8	1.0	3.33

[a]Calculated on the basis of singly charged molecular ion (PdL_2^+) as the base peak.

mechanism was discussed by Lacey *et al.* [14]. The $PdL-R^1-H$ ions are probably formed from $RPdL-R^1$ ions by the following mechanism.

The organometallics containing heavier metal (second and third transition series) can give rise to doubly charged ions in EI mass spectra [16]. Lacey *et al.* observed doubly charged L_2Th^{++} in the mass spectrum of $Th(PhCOCHCOPh)_4$. The positive charge is localised in the metal [14]. All the palladium(II) complexes in this study show the presence of dipositive, PdL_2^{++} and $[PdL_2-R^1]^{++}$, ions. In these ions the positive charge cannot be lodalised in the metal. When R is an aryl group the intensities of these ions vary as $PdL_2^{++} > [PdL_2-R^1]^{++}$ and the reverse is true



when R is a methyl group. The doubly charged molecular ions were identified on the basis of ^{105}Pd containing ions. With same R^1 the intensities of these dipositive ions vary as 2-thienyl > phenyl.

Loss of CO from the coordinated β-diketonate can occur in two ways. Most probably the CO adjacent to the fluorinated alkyl group (R^1) is eliminated due to weaker C–R^1 bond strength. A strong metastable peak was observed for the reaction, RPdL → RPdL–CO, in a special study of Pd(PhCOCHCOCF$_3$)$_2$.

As expected, due to strong class *b* character of palladium(II), no F migration was observed.

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