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FAST ATOM BOMBARDMENT MASS SPECTRA OF [(diars)Fe(CO)$_2$(C(O)Me)(P-donor)]$^+$ BF_4^- SALTS *

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Summary

Characteristic fast atom bombardment (FAB) mass spectra (8 keV, argon, glycerol matrix) have been obtained for an isostructural series of organometallic cations of the form *cis,trans*-[(diars)Fe(CO)$_2$(C(O)Me)L]$^+$ BF_4^- (L = phosphorus donor). The fast atom bombardment mass spectra (FABMS) obtained show relatively abundant fragments corresponding to the cationic portion of the complex [C^+]. Extensive fragmentation also occurs via successive CO loss, phosphorus donor ligand cleavage, and ligand decomposition. Evidence for a rearrangement fragmentation corresponding to the process [Fe–(C(O)Me)]$^+$ → [Fe–Me]$^+$ + CO is presented.

Introduction

Fast atom bombardment mass spectrometry (FABMS) represents a relatively new desorption ionization (DI) technique with unique potential applications in the structure elucidation of nonvolatile, thermally fragile organometallics [1–7]. As with other DI methods, FABMS circumvents thermolysis problems associated with the requirement of gas phase electron impact (EI) ionization by desorption of analyte directly from condensed states. Further, FABMS offers several practical advantages relating to ease of sample preparation and spectral reproducibility compared to field desorption mass spectrometry (FDMS) as well as secondary ion mass spectrometry (SIMS). This paper reports the FAB mass spectra of a series of closely related non-volatile, isostructural, organometallic salts with the general composition *cis,trans*-[(diars)Fe(CO)$_2$(C(O)Me)(P-donor)]$^+$ BF_4^- which did not afford useful mass spectra using the standard EI techniques. Significantly, the FABMS technique

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produces abundant ions corresponding to the cationic portion of the complex, C^+, as well as a rich array of structurally diagnostic, high m/z fragments. The results obtained established a framework for future organometallic applications of the FABMS technique.

Experimental

General

Nuclear magnetic resonance (NMR) spectra (^1H and $^{13}C\{^1H\}$) were recorded on a Bruker WP-80 spectrometer. Chemical shifts are reported in ppm relative to internal tetramethylsilane. Infrared spectra were obtained as mineral oil mulls or in methylene chloride solution (0.1 mm KBr cells) and were recorded using a Perkin–Elmer model 283 spectrometer; band positions are reported in cm^{-1} (± 2). All preparative work was carried out under an atmosphere of dry, prepurified nitrogen using the general techniques described by Shriver [8]. 4-Ethyl-2,6,7-trioxa-1-bicyclo[2.2.2]octane (ETPB) was purchased from Strem Chemicals and used as received. The acyl complexes [(diars)$Fe(CO)_2(C(O)Me)$(P-donor)]BF_4 (P-donor = $P(OMe)_3$, $PhP(OMe)_2$, $Ph_2P(OMe)$, PMe_3, $PhPMe_2$, Ph_2PMe) were prepared from *fac*-[(diars)$Fe(CO)_3Me]BF_4$ [9] following the procedure described previously [10].

Mass spectra were recorded on a VG Instruments 7070HS mass spectrometer equipped with a VG 2035 data system. Electron impact spectra were obtained at 70 eV with a source temperature of 426 K; samples were introduced via a direct probe inlet. Fast atom bombardment (FAB) spectra were obtained using a standard VG argon atom source operating at 8 keV which was oriented to give a 70° angle of incidence with respect to the directed secondary ion beam. A portion of a glycerol mull of analyte prepared from ca. 2 mg analyte/drop glycerol was positioned on the FAB probe at ambient temperature. FAB mass spectra were calibrated using an electron impact perfluorokerosene (PFK) mass calibration file which was checked against the [n(glycerol) + H^+] background ion series of neat glycerol. Spectra were recorded over a mass range up to 800 with a resolving power of ca. 1000. In general, ion currents were found to be persistent over a period of several minutes and multiple spectra (ca. 20–30 scans) were recorded for each sample. The data presented are either an average over several scans or a single representative spectrum chosen by visual inspection.

Preparation of cis,trans-[(diars)$Fe(CO)_2(C(O)Me)$(ETPB)]BF_4

Following the procedure described previously [10], 200 mg (0.379 mmol) of *fac*-[(diars)$Fe(CO)_3Me]BF_4$ [9] in 10 ml of methylene chloride was treated with a two-fold excess of ETPB at 273 K. After stirring for 3 h, the solvent was removed in vacuum. The crude product was triturated with several fresh (5 ml) portions of ether to remove residual ETPB. The resulting pale yellow, sticky residue was chromatographed on a short (0.8 cm × 2.0 cm) bed of Florisil with methylene chloride elution. Two recrystallizations from methylene chloride/ether gave the title acyl complex as pale yellow prisms, m.p. 167 °C (dec.). Analysis, Found: C, 34.67; H, 4.55. $C_{20}H_{30}As_2FeO_6PBF_4$ calcd.: C, 34.82; H, 4.38%. IR (CH_2Cl_2): ν(CO) 1998(s), 2038(s); acyl, 1650; BF_4, 1055(br) cm^{-1}. ^1H NMR (ppm, $CDCl_3$, 304 K): AsMe, 1.74 (s,6H), 1.88 (s,6H); C(O)Me, 2.61 (d, $J(^{31}P^1H)$ 0.6 Hz, 3H); $C_6H_4As_2$, 7.78 (s, 4H); ETPB, OCH_2, 4.28 (d, $J(^{31}P^1H)$ 4.4 Hz, 6H); ETPB, Me, 0.78 (m, 3H); ETPB,

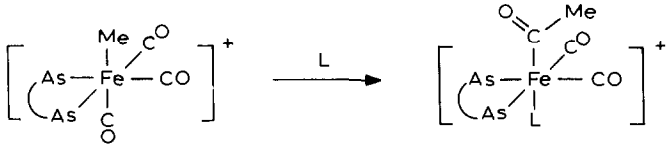
CH_2, 1.26 (m, 2H). ^{13}C NMR (ppm, $CDCl_3$, 305 K): AsMe, 14.66 (d, $J(^{31}P^{13}C)$ 4.82 Hz), 15.38 (d, $J(^{31}P^{13}C)$ 4.82 Hz); C(O)Me, 51.62 (d, $J(^{31}P^{13}C)$ 25.7 Hz); $C_6H_4As_2$, (*meta*) 130.65, (*ortho*) 132.73, (*ipso*) 136.97; FeCO, 209.32, (d, $J(^{31}P^{13}C)$ 17.7 Hz); C(O)Me, 258.63(d, $J(^{31}P^{13}C)$ 43.4 Hz); ETPB, OCH_2, 75.20 (d, $J(^{31}P^{13}C)$ 6.4 Hz), C, 35.63 (d, $J(^{31}P^{13}C)$ 32.1 Hz), CH_2, 22.85, Me, 6.87.

Preparation of [(diars)Fe(CO)$_2$(Me)(ETPB)]BF$_4$

100 mg (0.145 mmol) of *cis,trans*-[(diars)Fe(CO)$_2$(C(O)Me)(ETPB)]BF_4 was decarbonylated by heating at 100 °C, 0.1 torr for 24 h. The resulting yellow oil was purified by florisil chromatography in methylene chloride followed by two recrystallizations from methylene chloride/ether to give the title methyl complex as pale yellow prisms, m.p. 110 °C (dec.). Analysis, Found: C, 34.61, H, 4.56. $C_{19}H_{30}As_2FeO_5PBF_4$ calcd.: C, 34.48; H, 4.57%. IR (CH_2Cl_2): ν(CO) 1998(s), 2044(s); BF_4, 1050(br., s) cm^{-1}. ^1H NMR (ppm, CD_2Cl_2, 304 K): FeMe, −0.48 (d, $J(^{31}P^1H)$ 6.5 Hz, 3H); AsMe, 1.79 (m, 12H); $C_6H_4As_2$, 7.80 (m, 4H); ETPB, OCH_2, 4.48 (d, $J(^{31}P^{13}C)$ 5.0 Hz, 6H); ETPB, Me, 0.89 (m, 3H), CH_2, 1.87 (m, 2H). ^{13}C NMR (ppm, $CDCl_3$, 306 K): FeMe, −14.34 (d, $J(^{31}P^{13}C)$ 22.4 Hz); AsMe, 8.44, 8.86, 14.85, 15.27; $C_6H_4As_2$, (*ortho, meta*) 130.49, 132.29, (i) 136.47 (d, $J(^{31}P^{13}C)$ 3.5 Hz), 137.72 (d, $J(^{31}P^{13}C)$ 5.2 Hz); FeCO, 203.83 (d, $J(^{31}P^{13}C)$ 24.1 Hz), 210.45 (d, $J(^{31}P^{13}C)$ 36.1 Hz); ETPB, OCH_2, 75.87 (d, $J(^{31}P^{13}C)$ 6.9 Hz), C, 35.49 (d, $J(^{31}P^{13}C)$ 32.7 Hz), CH_2, 22.37, Me, 6.73.

Results and discussion

Previously [10] we reported the synthesis (eq. 1) and spectroscopic characterization of a series of octahedral acyl complexes which were prepared in conjunction with our mechanistic studies on migratory carbonyl insertion. The structure and stereochemistry was established spectroscopically and, in one instance (**2g**), on the basis of a single crystal X-ray study [11].



(1) (2) (1)

(As⌒As = o-phenylenebis(dimethylarsine), L = $P(OMe)_3$ (a), $PhP(OMe)_2$ (b), Ph_2POMe (c), PMe_3 (d), $PhPMe_2$ (e), Ph_2PMe (f), ETPB (g))

Attempts to characterize the cationic acyl complexes by mass spectroscopy were frustrated by the common problems of extremely low volatility coupled with low thermal stability. Figure 1A shows a typical result obtained for this series using 70 eV electron impact ionization. The EI spectrum clearly has limited potential for structure characterization since it is devoid of structurally relevant, high m/z fragments. The largest fragment for complex **2g**, observed as a low intensity peak at $m/z = 357$, is presumably a thermolysis product. Although the 357 peak can be formulated as $[(diars)FeMe]^+$, no information regarding the fragmentation pattern giving rise to it can be determined. The inapplicability of EI mass spectrometry as a

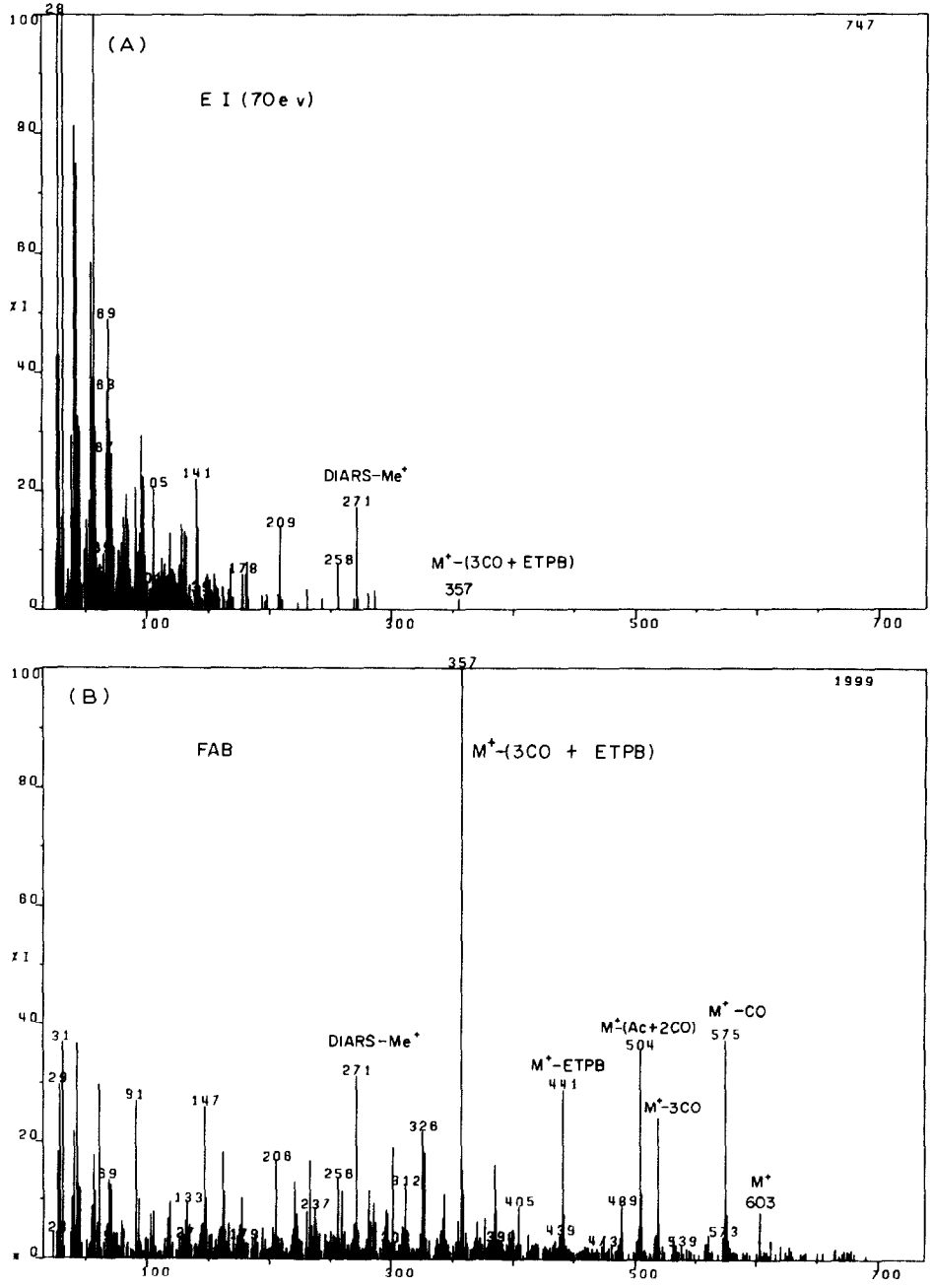


Fig. 1. (A) 70 eV electron impact mass spectrum of **2g**. (B) 8 keV fast atom bombardment mass spectrum of **2g**.

structural tool in the present case is further emphasized by the potential presence of the $[(diars)FeMe]^+$ fragment in all the acyl complexes examined in this study.

Figure 1B shows the result obtained for the same complex (**2g**) using an argon

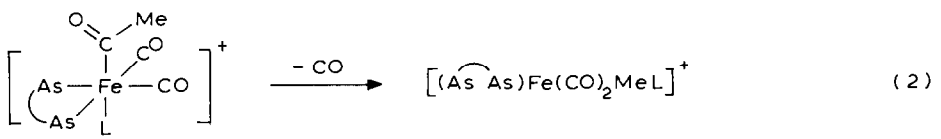
fast atom bombardment source operating at 8 keV. A strikingly different spectrum results. The $[(diars)FeMe]^+$ ($m/z = 357$) fragment becomes the base peak and a series of structurally relevant ions at higher m/z values as well as the parent cation are evident. The fragmentation apparent in Fig. 1B suggests that FABMS may be a significantly "harder" ionization technique than field desorption mass spectrometry (FDMS) which, except in isolated cases [12], tends to give a parent cation with little or no major fragmentation for organometallic salts [12–15]. The extent of fragmentation observed is reminiscent of that found for the secondary ion mass spectrometry (SIMS) technique [16–19] and lends support to the generalization [1] that the physical processes involved in particle induced desorption/ionization are less important than the chemical processes. Unlike the SIMS technique, however, the FABMS ion currents were persistent over a period of several minutes without the restriction of reduced particle flux ("static SIMS condition").

Table 1 presents a summary of the fast atom bombardment mass spectra obtained for the acyl complexes **2a–2g**. The spectra presented are corrected for background glycerol peaks corresponding to the series $[n(glycerol) + H]^+$. The glycerol background was, however, significantly repressed in the presence of the organometallic salts examined in this study and in some cases no correction was necessary. An overview of the results presented in the table shows that all the complexes except **2c** exhibit prominent $[C^+]$ ions corresponding to the cationic portion of the complex. Thus the intact, even electron cations are desorbed and provide a means for rapid identification of the salt. In each case the base peak appears to be $[(diars)FeMe]^+$ at m/z 357. Considerable arsenical ligand fragmentation, which has also been observed in the EI mass spectra of related volatile diars complexes [9,20,21], was found for all complexes examined.

A number of common fragments occur for the series **2a–2g**. Several fragmentation series, presumably originating from $m/z = 441$ $[(diars)MeFe(CO)_3]^+$ and from ligand, $m/z = 286$ $[(diars)]^+$ ·], were assigned (cf. Table 1).

The heavier fragments are, of course, more characteristic of the individual structures and therefore represent a critical test for the application of FABMS as a structure elucidation tool for carbonyl complexes. Table 2 compares a number of important fragments for the series **2a–2g**. Clearly, the major fragmentations observed are systematic and follow the empirical trends established on the basis of conventional mass spectra obtained from volatile organometallics with related mixed carbonyl/Group VA ligand spheres [22,23]. Stepwise carbon monoxide loss and competing phosphine ligand cleavage dominate the observed fragmentation patterns.

Fragments corresponding to the loss of one and three CO equivalents from the cation peak C^+ are abundant, however a $C^+ - 2CO$ fragment was systematically absent or appeared only weakly (ca. 1% relative abundance). While the occurrence of simultaneous loss of two CO groups which results in gaps in the CO cleavage sequence $[L_mM(CO)_n]^+$ ($m = n, n-1, n-2, \ldots, 0$) is unusual [22], it is not without precedence [24,25]. We interpret these results on the assumption that the initial CO



(2) (3) (2)

(Continued on p. 82)

TABLE 1

FAST ATOM BOMBARDMENT MASS SPECTRA OF THE ACYL COMPLEXES **2a–2g** AND THE METHYL COMPLEXES **1**, **3g** [b]

m/z	Assignment [a]	Relative abundance (%)									Mean S D	
		2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**3g**	**1**		
641							5				5	0
631	[C$^+$ (**2f**)]			6							6	0
630				19							19	0
629				66							66	0
628	[C$^+$ (**2c**) – CO]			9			5				7	2
627				6							6	0
614							20				20	0
613	[641 – CO]						45				45	0
611	[C$^+$ (**2b**)]		8*				6				7	1
603	[C$^+$ (**2f**)]							8			8	0
584			22								22	0
583	[611 – CO]		69								69	0
581			6								6	0
579						6					6	0
577	[C$^+$ (**2e**)]								7		7	0
576								7	17		12	5
575	[603 – CO]							37*	84		42	32
574				11							11	0
573	[629 – 2CO]			31					5		18	13
565	[C$^+$ (**2a**)]	21									21	0
559				10							10	0
558				32*			11				21	10
557	[629 – 2CO + Me]			6			32				19	13
552						33					33	0
551	[579 – CO]					97					97	0
542	[641 – 3CO – Me]						42				42	0
537	[565 – CO]	73									73	0
536						9					9	0
535	[579 – CO – Me]	7									7	0
533									5		5	0
532	[560 – CO]								6		6	0
528			14								14	0
527	[611 – 3CO]		40								40	0
520								6	14		10	4
519	[603 – 3CO]							24*	45		35	10
518									6		6	0
517	[C$^+$ (**2d**)]				7						7	0
513			5								5	0
512	[611 – 3CO – Me]		45*	5							25	20
511			7								7	0
508						7					7	0
506	[579 – 2CO – Me							5			5	0
505								11	9		10	1
504								35*	50		43	7
503	[603 – 3CO – Me]							5			5	0
496						11					11	0
495	[579 – 3CO]					50					50	0
494		9*				5					7	2
493	[537 – 2CO + Me]					5					5	0
490					16						16	0

TABLE 1 (continued)

m/z	Assignment [a]	Relative abundance (%)									Mean	S.D.
		2a	2b	2c	2d	2e	2f	2g	3g	1		
489					98*			9	11		40	42
487	[517 − CO]				6						6	0
482		7									7	0
481	[565 − 3CO]	33				8					21	12
480	[579 − 3CO − Me]					39					39	0
475					6						6	0
474					7						7	0
467		11									11	0
466	[517 − CO − Me]	40									40	0
464						6					6	0
447					5						5	0
446					11						11	0
443	[517 − 2CO − Me]				7		5				6	1
442		14	15		7	5	6	7		7	9	4
441		66	38	9	18	17	23	29		60	33	19
437	[Cl]						11				11	0
434					14						14	0
433	[517 − 3CO]				69						69	0
418					44						44	0
385		24	16	10	15	10	15	16		21	16	4
375						13					13	0
373	[Cl − 2CO]	10	23	36	6	5					16	12
359		6	8	14	9	12	8	11	9	12	10	2
358		16	16	14	22	12	18	15	21	13	16	3
357	[C2]	100	100	100	100	100	100	100	100	81	98	6
327	[C2 − 2Me]	9	9		15	10	13	18	17	8	12	4
326		18	14	12	16	16	19	22	23	18	18	3
313	[C2 − CH_2 − 2Me]				14			5			10	5
301	[diars + Me]	7	5	17	14	17	38	19	10	57	20	16
287				15				6		8	10	4
282		11	8	13	12	20	15	12	12	11	13	3
271	[C2 − 5Me]	12	17	34	21	25	27	31	24	24	24	6
259								12			12	0
256	[C3 − Me]		5	10	6	7	19	14	10	8	10	4
242				13							13	0
241	[C3 − 2Me]		20	6							13	7
237		11	10	11	11	10	11	8	10	7	10	1
236					13						13	0
233				5				17	12	5	10	5
221		11	11	13	18	13	12	13	14	14	13	2
206	[342 − $AsMe_2$]	14	12	15	17	14	16	22	19	17	16	3
197										10	10	0
196			11								11	0
195		35	5					5			15	14
183				12			7				10	3
177		7	9	6	12	15	12	10	13	10	10	3
162		13	14	17	11	26	20	18	15	25	18	5
153	[HFeAsMe_2]					12					12	0
148		10	6	14	13	15	14	10	10	11	11	3
147		14	19	23	50	28	31	26	28	26	27	9
139	[162 − Me]		13	7		22					14	6
133			7	11	9	15	10	9	8	9	10	2

(continued)

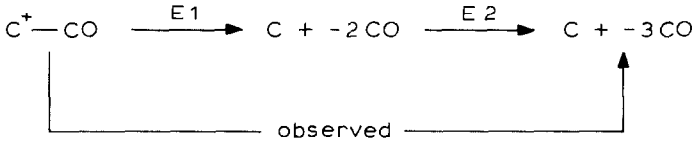
TABLE 1 (continued)

m/z	Assignment [a]	Relative abundance (%)									Mean	S.D.
		2a	2b	2c	2d	2e	2f	2g	3g	1		
91	[HAsMe]	9	13	14	17	20	17	30	16	17	17	5
77	[HAsMe]			7	16						11	5
75	[As]				10	18	5	6		22	12	7
73	[As]									19	19	0
71	[FeMe]	7	6	6	14	15	8	13	10	10	10	3
69	[FeMe]							14	8		11	3
61	[FeMe]	10	8	10	30	6	13	30	8	34	17	11
57	[FeH]			6		23	6	13	15	43	18	13
56	[Fe]	15	16	20	21	16	18	18	25	61	23	14

[a] Assignments: C^+ = cationic portion of complex, C1 = $[(diars)Fe(CO)_3Me]^+$ [441], C2 = $[(diars)FeMe]^+$ [357], C3 = $[diars]^+$ [286]; * denotes assigned peak; for peaks $m/z > 441$, minimum mean reported intensity = 5; for peaks < 441, minimum mean reported intensity = 10. [b] L = $P(OMe)_3$ (**a**), $PhP(OMe)_2$ (**b**), Ph_2POMe (**c**), PMe_3 (**d**), $PhPMe_2$ (**e**), Ph_2PMe (**f**), ETPB (**g**).

loss occurs with rearrangement as has been demonstrated with other acyl-transition metal complexes [26] (cf. eq. 2).

Decarbonylation with carbon monoxide extrusion [27,28] preserves an $18e^-$ environment to give the coordinatively saturated and correspondingly energetically more stable six-coordinate fragment **3**. Thus the initial CO loss is highly favoured and the C^+–CO fragment is abundant across the series **2a**–**2g**. Subsequent simultaneous loss of two terminal CO groups from **3** is apparently a favourable process and gives a high concentration of the $C^+ - 3CO$ fragment [24,25]. Observation of the appropriate metastable is necessary to establish this point since the results are subject to an alternate interpretation which assumes that the energy required for the second step (E2) is considerably less than that required for the first step (E1), cf. eq. 3.



(3)

The propensity for simultaneous loss of two CO groups recurs in the ion series derived from the 441 fragment, $[(diars)Fe(CO)_3Me^+]$ which is formed by phosphine cleavage from C^+ and appears in all the complexes studied. Subsequent stepwise CO loss is interrupted and fragmentation proceeds directly to give a relatively intense $C^+ - (L + 2CO)$ peak at $m/z = 385$. The peak corresponding to $C^+ - (L + CO)$ appears, but only very weakly (ca. 1–4%). Support for the rearrangement fragmentation 2 → 3 derives from the direct synthesis and isolation of the proposed daughter ion **3g** by thermal decarbonylation at 100 °C according to eq. 2. The reaction is nearly quantitative and no other products were detected (viz. NMR). Interestingly, only one of the four possible isomers was isolated. The presence of four non-equivalent As-methyl groups requires the absence of symmetry planes bisecting and

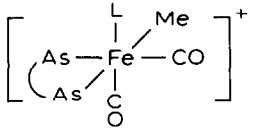
TABLE 2

COMPARISON OF MAJOR IONS FOR THE ACYL COMPLEXES **2a–2g** [a]

Fragment	Relative abundance (%)						
	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**
C^+	21	8	2	7	6	5	8
$C^+ - CO$	72	69	66	98	97	45	37
$C^+ - 3CO$	33	40	30	69	50	32	24
$C^+ - 3CO - Me$	40	45	31	44	39	42	35
$C^+ - L$	66	38	9	18	17	23	29
$C^+ - L - 2CO$	23	16	10	16	10	15	16
$C^+ - L - 3CO$	100	100	100	100	100	100	100

[a] L = $P(OMe)_3$ (**a**), $PhP(OMe)_2$ (**b**), Ph_2POMe (**c**), PMe_3 (**d**), $PhPMe_2$ (**e**), Ph_2PMe (**f**), ETPB (**g**).

containing the diars group and hence defines an all *cis* geometry, **4** or **5** *. Structure **5** (L = PMe_3) has been confirmed by a single crystal X-ray analysis [29].



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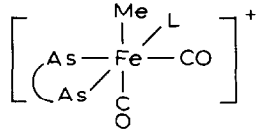


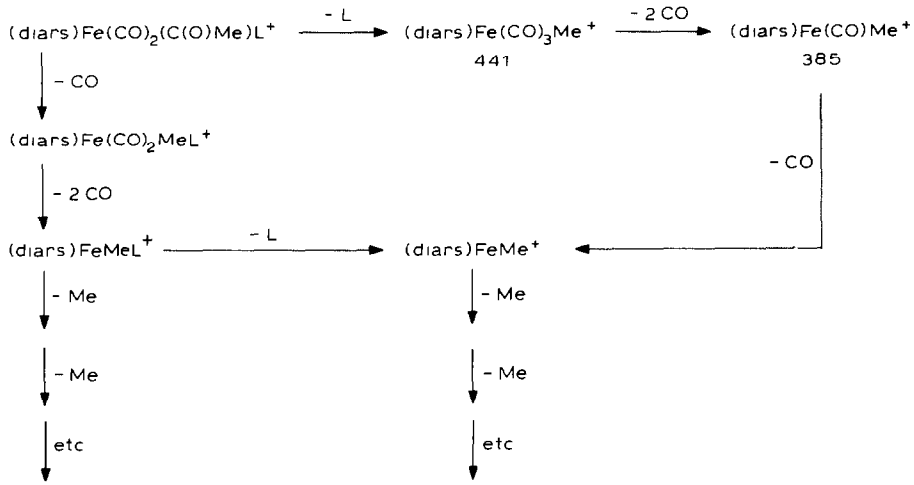
(5)

The FAB mass spectrum of the decarbonylation product, **3g**, is presented in Table 1. In keeping with its mode of preparation, complex **3g**, which does not decarbonylate readily under preparative conditions, displays a more intense cation peak C^+, ($m/z = 575$, relative abundance 84%) than does the acyl complex **2g** ($m/z = 603$, relative abundance 8%). Further comparison of the data reveals many major common fragments for **2g** and **3g** with similar abundancies (based on equivalent concentrations of $m/z = 575$) and provides additional corroboration for the structural assignment. Significantly, the C^+ ion of **3g** ($m/z = 575$), like the $C^+ - CO$ daughter from **2g**, prefers the simultaneous loss of two CO groups and shows a prominent peak at $m/z = 519$ (45%) with only an extremely weak peak corresponding to $C^+ - CO$ ($m/z = 547$, 1%), Mueller [22] has addressed the question of sequencing of metal–ligand bond cleavages in complexes with mixed ligand spheres. In general, Group V donor ligands are more difficultly cleaved than is carbon monoxide. However, both the donor/acceptor strength of the ligand, as determined by its substituents, and the electron density on the central metal are important factors which can alter the established order. Previous results establish [22] that Group V donor ligand cleavage becomes less competitive as the donor/acceptor ratio increases. Intuitively, an increase in formal positive charge on the central metal can be expected to augment the effect. For the series **2a–2g** the relative ordering of ligand cleavage, given (cf. Table 2) by the ratio $(C^+ - CO)/(C^+ - L)$ is: **2c** (L = $Ph_2P(OMe)$, 7.3) > **2d** (L = PMe_3, 6.1) > **2e** (L = $PhPMe_2$, 5.7) > **2f** (L = Ph_2PMe,

* The mechanism and scope of this reaction are currently under investigation: the results will be reported elsewhere [29].

2) > **2b** (L = $PhP(OMe)_2$, 1.8) > **2g** (L = ETPB, 1.3) > **2a** (L = $P(OMe)_3$, 1.1). For this isostructural series the donor/acceptor ratio is conveniently given by Tolman's Electronic Parameter, ν [30] which defines the order: **d** (PMe_3, 2064.1) > **e** ($PhPMe_2$, 2065.3) > **f** (Ph_2PMe, 2067.0) > **c** ($Ph_2P(OMe)$, 2072.0) > **b** ($PhP(OMe)_2$, ca. 2073) > **a** ($P(OMe)_3$, 2079.5) > **g** (ETPB, 2086.8). The correspondence of the overall trends is, with the exception of **2c**, quite good and confirms the applicability of the FABMS technique to structural problems of this nature. Scheme 1 presents a possible general fragmentation pattern for the acyl series which incorporates the above discussion.

SCHEME 1



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References

1 K.L. Busch and R.G. Cooks, Science, 218 (1982) 247
2 K.L. Rinehart Jr., Science, 218 (1982) 254.
3 J.M. Miller, J. Organomet. Chem., 249 (1983) 299.
4 M. Barber, R.S. Bordoli, G.J. Elliot, R.D Sedgwick and A.N. Tyler, Anal. Chem., 54 (1982) 645A.
5 M. Barber, R.S. Bordoli, R.D. Sedgwick and A.N. Tyler, Nature, 293 (1981) 270.
6 R. Davis, I.F. Groves, J.A. Durrant, P. Brooks, and I. Lewis, J. Organomet. Chem., 241 (1983) C27.
7 A.I. Cohen, K.A. Glavan and J.F. Kronauge, Biomed. Mass. Spectrom., 10 (1983) 287.
8 D.F. Shriver, The Manipulation of Air Sensitive Compounds. McGraw-Hill, New York, 1969.
9 C.R. Jablonski, Inorg. Chem., 20 (1981) 3940.
10 C.R. Jablonski and Y.-P. Wang, Inorg. Chem., 21 (1982) 4037.
11 M. Makay and M.J. Newlands, Acta Cryst. C, submitted.
12 D.E. Games, L.A.P. Kane-Maguire, and D.A. Sweigart, J. Organomet. Chem., 234 (1982) 323.
13 N.B.H. Henis, W. Lamanna, M.B. Humphrey, M.M. Bursey, and M.S. Brookhart, Inorg. Chim. Acta Lett., 76 (1982) L11.

14 C.N. McEwen and S.D. Ittel, Org. Mass. Spec., 15 (1980) 35.
15 N. Bild, E.R.F. Gesing, C. Quiquerez, and A. Wehrli, J. Organomet. Chem., 248 (1983) 85.
16 J. Pierce, K.L. Busch, R.A. Walton, and G. Cooks, J. Am. Chem. Soc., 103 (1981) 2583.
17 W. Ens, K.G. Standing, B.G. Chait, and F.H. Field, Anal. Chem., 53 (1981) 1241.
18 J.L. Pierce, K.L. Busch, R.G. Cooks, and R.A. Walton, Inorg. Chem. 21 (1982) 2597.
19 J.L. Pierce, D.E. Wigley, and R.A. Walton, Organometallics, 1 (1982) 1328.
20 W.R. Cullen and D.A. Harbourne, Can. J. Chem., 47 (1966) 3371.
21 R.D. Feltham and H.G. Metzger, J. Organomet. Chem., 33 (1971) 347.
22 J. Mueller, Ang. Chem. Int. Ed. Engl., 11 (1972) 653.
23 M.R. Litzow and T.R. Spalding, Mass Spectrometry of Inorganic and Organometallic Compounds, Elsevier, Amsterdam, 1973.
24 R.B. King, J. Am. Chem. Soc., 90 (1968) 1412.
25 J. Lewis, A.R. Manning, J.R. Miller, and J.M. Wilson, J. Chem. Soc. A, (1966) 1663.
26 M.J. Mays and R.N.F. Simpson, J. Chem. Soc. A, (1967) 1936.
27 E.J. Kuhlman and J.J. Alexander, Coord. Chem. Revs., 33 (1980) 195.
28 F. Calderazzo, Ang. Chem. Int. Ed. Engl., 16 (1977) 299.
29 C.R. Jablonski, Y.-P. Wang, and N. Taylor, unpublished results.
30 C.A. Tolman, Chem. Revs., 77 (1977) 313.