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Structural Characterization of Various Dirhodium Compounds Using Fast Atom Bombardment and Collision-Induced Dissociation Mass Spectrometry

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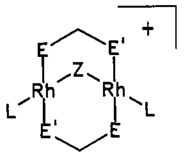
Fast atom bombardment (FAB) and collision-induced dissociation (CID) tandem mass spectra of a series of novel pyrazolato-bridged dirhodium A-frame compounds provide structure confirmation and useful information concerning the structural dependence of lability, based upon fragmentation pathways. CID mass spectra indicate that FAB matrix- and beam-induced *reduction* chemistry can alter the energy and/or the structure of the precursor molecules. However, it appears that FAB matrix- and beam-induced *oxidation* chemistry does not do so detectably.

Introduction

Structural characterization of inorganic and organometallic compounds by classical methods is often difficult.[1,2] Ultraviolet–visible (UV–vis) and electrochemical methods tend to yield limited structural insight, and in some instances even information from nuclear magnetic resonance and/or infrared spectroscopy is incomplete. While X-ray crystallographic analysis can provide detailed structural information for organometallic compounds, the technique is limited by the requirement that a crystal be isolated. Electron ionization mass spectrometry (MS) offers a powerful alternative structural tool, but volatility requirements have limited its application to inorganic and organometallic compounds of relatively low molecular mass (<500 Da).[1–3] Fast atom bombardment (FAB) MS[4] has proven viable for compounds of higher molecular mass,[1,5–9] but the presence of beam-induced chemical damage (*e.g.*, analyte reduction)[10–13] and the fact that fragmentation can be inefficient for high–mass molecules often limit the amount of structural information that can be gained from FAB mass spectra. Collision-induced dissociation (CID) MS[14,15] coupled with FAB ionization has proven useful in providing structural information for organic compounds like peptides[16] and small inorganic compounds (*e.g.*, $Fe(CO)_5$[17]). However, there have been relatively few reports of applications of CID MS to high mass inorganic and organometallic compounds.[1,9,18,19] This study assesses the feasibility of using FAB and CID MS to obtain structural information for a series of pyrazolato-bridged dirhodium A-frame compounds ($M(PF_6)_n$, where n = 1 or 2 and M represents structure **I** or **II**, respectively).[20,21] The compounds contain various apex pyrazolate anions (Z), central metal atoms (Rh) in varying oxidation states (1+ or 2+), various transoid bridging ligands (EE′), and various terminal ligands (L) (Table I). Structure **III** shows in more detail the spatial relationships among ligands in a representative complex, compound **2**. The series provides a means of assessing the extent to which stability and structural variations are reflected in CID fragmentation, as well as the effects of beam-induced chemical transformations.



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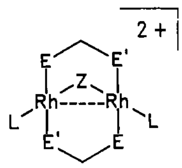

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Experimental Section

Mass Spectrometry. Mass spectra were obtained with a VG ZAB-EQ mass spectrometer operating at an accelerating potential of 8 kV. Research grade xenon (MG Industries) was used with an Ion Tech atom gun, operating at an emission current of 1.0 mA and a potential of 8.0 kV. In all cases, reported intensities represent the peak height of the most abundant ion in a given isotope cluster, normalized so the most intense ion in the spectrum = 100.

Standard MS Conditions. A thin film (5–10 μL) of a standard 10 mM solution of a complex in *m*-nitrobenzyl alcohol (NBA; Aldrich) was applied to a brass FAB probe tip.[10] NBA was used because it provides better sensitivity for organometallics[1,22] and reduced chemical damage,[10] compared with the more common glycerol matrix. Solutions were not degassed before analysis, but spectra were obtained only after emission had stabilized (typically after 1 min of bombardment). Spectra were then collected by summing data from 9 or 16 linear magnet scans (10

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(1) Miller, J. M. *Mass Spectrom. Rev.* **1990,** *9,* 319.

(2) Dang, Y.; Geise, H. J.; Claereboudt, J.; Van Den Heuvel, H.; Claeys, M. *Inorg. Chim. Acta* **1992,** *201,* 185.

(3) Budzikiewicz, H. *Mass Spectrom. Rev.* **1986,** *5,* 345.

(4) Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *J. Chem. Soc., Chem. Commun.* **1981,** 325.

(5) Bowen, R. D.; Danks, T. N.; Mitchell, D.; Thomas, S. E. *Org. Mass Spectrom.* **1988,** *23,* 674.

(6) Asker, K. A.; Greenway, A. M.; Seddon, K. R.; Shimran, A. A. *J. Organomet. Chem.* **1988,** *354,* 257.

(7) Boyd, R. K.; Embree, D. J.; McAlees, A. J.; Taylor, A. *Can. J. Chem.* **1991,** *69,* 257.

(8) Bignozzi, C. A.; Bortolini, O.; Traldi, P. *Rapid Commun. Mass Spectrom.* **1991,** *5,* 600.

(9) Didier, P.; Jacquet, L.; Kirsch-De Mesmaeker, A.; Hueber, R.; van Dorsselaer, A. *Inorg. Chem.* **1992,** *31,* 4803.

(10) Reynolds, J. D.; Cook, K. D.; Burn, J. L. E.; Woods, C. *J. Am. Soc. Mass Spectrom.* **1992,** *3,* 113.

(11) Shiea, J.; Sunner, J. *Org. Mass Spectrom.* **1991,** *26,* 38.

(12) Pelzer, G.; DePauw, E.; Dung, D. V.; Marien, J. *J. Phys. Chem.* **1984,** *88,* 5065.

(13) Kyranos, J. N.; Vorous, P. *Biomed. Environ. Mass Spectrom.* **1990,** *19,* 628.

(14) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry;* VCH: New York, 1988.

(15) Burlingame, A. L.; Maltby, D.; Russell, D. H.; Holland, P. T. *Anal. Chem.* **1988,** *60,* 294R.

(16) Sults, J. T. In *Biomedical Applications of Mass Spectrometry;* Suelter, C.H., Watson, J. T., Eds.; Wiley: New York, 1990; pp 145–201.

(17) Wysocki, V. H.; Kenttamaa, H. I.; Cooks, R. G. *J. Phys. Chem.* **1988,** *92,* 6465.

(18) Branan, D.; Hoffman, N.; McElroy, E. A.; Ramage, D.; Robbins, M.; Eyler, J.; Watson, C.; deFur, P.; Leary, J. *Inorg. Chem.* **1990,** *29,* 1915.

(19) Denti, G.; Serroni, S.; Sindona, G.; Uccella, N. *J. Am. Soc. Mass Spectrom.* **1993,** *4,* 306.

(20) Janke, C. J.; Tortorelli, L. J.; Burn, J. L. E.; Tucker, C. A.; Woods, C. *Inorg. Chem.* **1986,** *25,* 4597.

(21) Woods, C.; Tortorelli, L. J.; Rillema, D. P.; Burn, J. L. E.; DePriest, J. C. *Inorg. Chem.* **1989,** *28,* 1673.

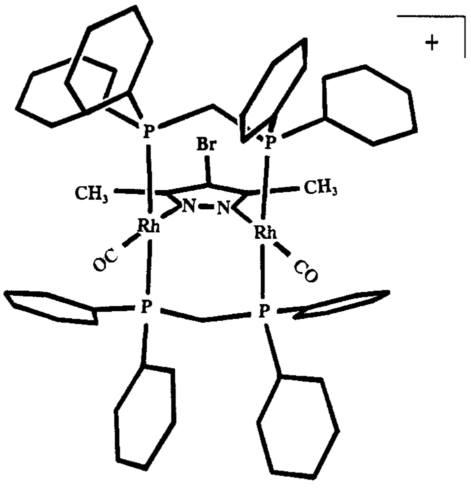
(22) Miller, J. M.; Balasanmugam, K.; Nye, J.; Deacon, G. B.; Thomas, N. C. *Inorg. Chem.* **1987,** *26,* 560.

0020-1669/93/1332-5517$04.00/0

Table I. Relative Intensities of Selected Ions in the FAB Mass Spectrum of Pyrazolato-Bridged Dirhodium Compounds of the General Formula $[Rh_2(X,Y)(EE')_2ZL_2](PF_6)_n$

						rel intens		
compd	(X,Y)[a]	EE′[b]	Z[c]	L[d]	n	$[MPF_6]^+$	$[M]^+$	$[M]^{2+}$
1	(I,I)	PP	4B35mpz	RNC	1	2	100	0
2	(I,I)	PP	4B35mpz	CO	1	8	100	0
3	(I,I)	PA	4B35mpz	RNC	1	3	100	0
4	(I,I)	PA	4B35mpz	CO	1	6	100	0
5	(I,I)	AA	4B35mpz	RNC	1	5	100	0
6	(I,I)	AA	4B35mpz	CO	1	6	100	0
7	(I,II)	PP	4B35mpz	RNC	2	6	100	4
8	(I,II)	PP	4B35mpz	CO	2	0	100	0
9	(I,II)	PA	4B35mpz	RNC	2	6	100	3
10	(I,II)	PA	4B35mpz	CO	2	0	100	0
11	(I,II)	AA	4B35mpz	RNC	2	14	100	7
12	(I,II)	PP	35mpz	RNC	2	31	100	6
13	(I,II)	PA	35mpz	RNC	2	7	100	4
14	(I,II)	AA	35mpz	RNC	2	6	100	3
15	(I,II)	PP	mtmpz	RNC	2	6	100	2
16	(I,II)	PA	mtmpz	RNC	2	6	100	2

[a] (X,Y) refers to the oxidation states of the central metal atoms. [b] PP = bis(diphenylphosphino)methane, PA = (diphenylphosphino)(diphenylarsino)methane, and AA = bis(diphenylarsino)methane. [c] 4B35mpz = 4-bromo-3,5-dimethylpyrazolate, 35mpz = 3,5-dimethylpyrazolate, and mtmpz = 3-methyl-5-(trifluoromethyl)pyrazolate. [d] RNC = *tert*-butyl isocyanide, and CO = carbon monoxide.



III

s/scan) over a period of 1–3 min. The reported results represent averages of at least three such spectra (27 or 48 total scans), each obtained with a fresh sample. Mass resolution was at least 2000 (10% valley).

High-Resolution MS Conditions. For high-resolution (>10 000; 10% valley) FAB MS, a crystal of the compound of interest was placed on the probe tip and then dissolved in 5–10 μL of a reference solution that contained 0.5 M poly(ethylene glycol) 1540 (Baker) and 0.05 M NaI (Aldrich) in NBA. Spectra were collected by summing data from 15 voltage scans over a period of 7–8 min, spanning a limited mass range (≈50 u) at 30 s/scan. When needed, the experiments were repeated with fresh sample in order to acquire data in a different 50-u mass window.

CID MS Conditions. For mass-analyzed ion kinetic energy spectroscopy (MIKES)[14] experiments, the ZAB magnet was tuned to transmit ions within a mass range of ±0.25 u, centered about the precursor ion of interest (low resolution). Helium was used as the collision gas, and the pressure was increased until the initial precursor ion intensity decreased by 50%. Spectra were then collected by summing data from 16 scans (10 s/scan) acquired over a period of 2–3 min. The hybrid scanning capabilities of the ZAB were not employed because low-energy CID was not efficient, and the ZAB does not effectively perform the linked E–Q scans necessary for high-energy CID with unit resolution of product ions over the relatively wide mass range needed.

Chemicals. The dirhodium compounds were synthesized, isolated, and purified by methods described elsewhere.[20,21] All other chemicals were reagent grade and were used as received.

Table II. Ions Detected in the FAB Mass Spectrum of Compound **7**

m/z[a]	rel intens	identification[b]	exptl m/z	diff (ppm)[c]
1460	6	$[MPF_6]^+$	1460.1468	10.9
1365	2	$[M + PF]^+$	1365.1576	−4.3
1331	4	$[M + O]^+$	1331.1682	−1.6
1315	100	$[M]^+$	1315.1692	1.9
1258	8	$[M - tBu]^+$	1258.0963	−8.6
1231	6	$[M + H - RNC]^+$	1231.0854	10.1
1147	4	$[M - 2RNC]^+$	1147.0343	4.8
1057	4	$[M - (RNC + Z)]^+$	1057.1457	−20.5
973	5	$[M - (2RNC + Z + H)]^+$	973.0611	19.1
896	4	?	896.0213	
658	4	$[M]^{2+}$		

[a] Nominal m/z of most abundant ion in each isotope cluster. [b] M refers to the molecular cation, ? refers to an unidentified ion, tBu refers to *tert*-butyl, RNC refers to *tert*-butyl isocyanide, and Z refers to 4-bromo-3,5-dimethylpyrazole. [c] $10^6[m/z(\text{exptl}) - m/z(\text{theoret})]/[m/z(\text{theoret})]$.

Results and Discussion

FAB MS. The FAB mass spectra of these 16 compounds were all rather simple; data for **7** (Figure 1 and Tables I and II) are representative. As would be expected, the doubly-charged molecular cation (M^{2+})[23] was only detected for those species in which the two Rh atoms were formally in different oxidation states (*i.e.*, Rh(I,II) compounds). In these cases, M^{2+} could be formed by complete dissociation of the molecular salt (*i.e.*, loss of both PF_6^- counterions). Double charge was confirmed by the half-integral separation of mass-to-charge ratios (m/z) for ions in the M^{2+} isotope clusters.

In contrast with M^{2+}, whose behavior was straightforward, the singly-charged molecular cation (M^+) was the base peak for all compounds, *regardless of the initial charge state* (M^+ or M^{2+}) of the cation in the salt. The underlying redox chemistry has been studied previously[10] and is attributable to a combination of matrix- and beam-induced reactions. Assignments were confirmed in part by the good match between measured and theoretical isotopic patterns (*e.g.*, for M^+ from **7**; Figure 2). Further confirmation was derived from high-resolution exact mass measurements (agreement with theoretical values was within 20 ppm, and generally well within that value; data for **7** in Table II are representative).

The ion-paired molecular cation MPF_6^+ was observed for the majority of compounds (Table I). For **7–16**, this cation can be formed by loss of one PF_6^- from the molecular salt. However, for **1–6**, formation of the ion-paired molecular cation must involve one-electron oxidation of the molecular salt. Again, both solvent- and beam-induced chemistry are involved.[10]

Fragment ions were of low intensity in all FAB spectra. While it is possible to rationalize those observed (*e.g.*, major pathways involve loss of one or both terminal ligands), the facts that few fragments were observed and none had high intensity would have limited their utility for providing structural insight, if the structures had been unknown. Furthermore, the beam-induced transformations outlined above would have complicated use of FAB for confirmation of ion mass. For a more thorough examination of ion structures and reactivity, tandem MS experiments were performed.

CID MS. At the outset of these experiments, we were particularly interested in acquiring and comparing CID spectra of analogous M^+ and M^{2+} ions, to ascertain the effect of charge state on CID behavior. Unfortunately, the intensity of doubly-charged precursors was low, as is typical of FAB.[1,22] Furthermore, singly-charged product ions in CID spectra of multiply-charged precursors may occur at higher m/z and require scanning to electrostatic analyzer (ESA) voltages higher than that for the

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[23] The term "molecular cation" (designated M^+ or M^{2+}) refers to the completely dissociated form of the $M(PF_6)_n$ salt, where $n = 1$ or 2 for M^+ or M^{2+}, respectively. The term "ion-paired molecular cation" refers to the singly charged $M(PF_6)^+$ species.

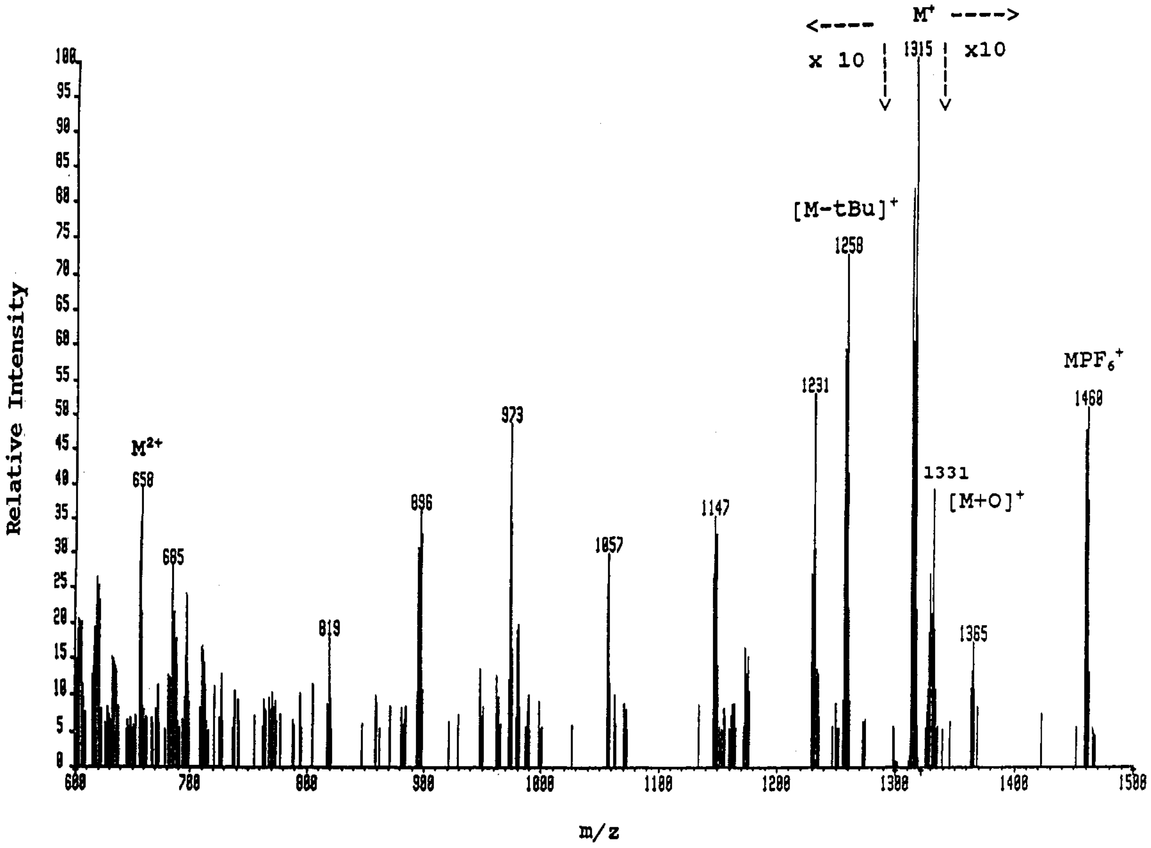

Figure 1. FAB mass spectrum of a 10 mM solution of compound 7 in NBA. Reprinted from ref 10 by permission of Elsevier Science Publishing Co. Copyright 1992 American Society for Mass Spectrometry.

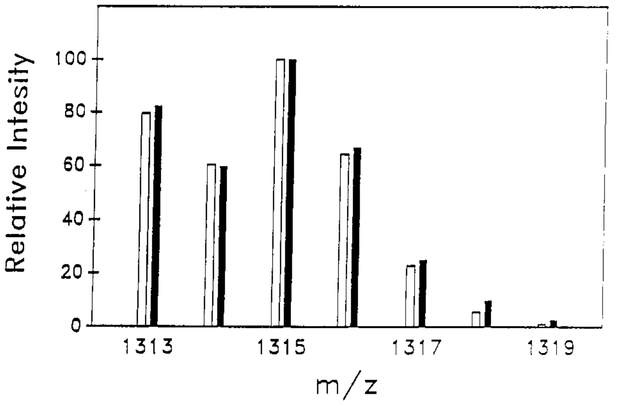

Figure 2. Comparison of measured intensities in the molecular cation region of the FAB mass spectrum of compound 7 with the expected natural isotopic distribution. Solid lines indicate the relative measured intensities; open lines indicate calculated distribution.

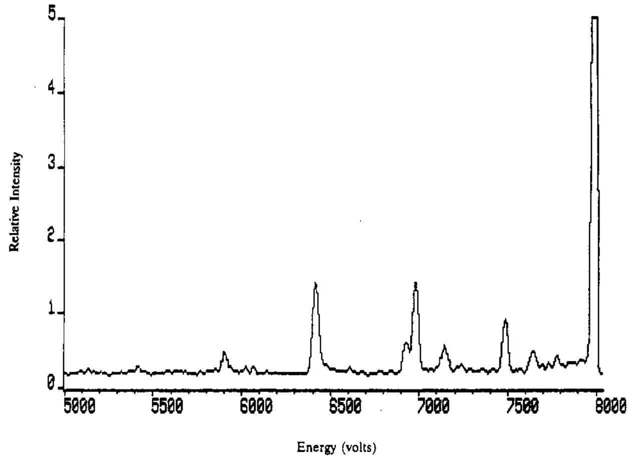

Figure 3. CID-MIKES mass spectrum of the *m/z* 1313 ion from compound 7.

precursor ion. The ZAB was not designed to accomplish such a scan, and attempts to acquire spectra under manual control were unsuccessful. Thus, informative CID spectra were obtained principally from M^+ and MPF_6^+ precursors.

CID of the Ion-Paired Molecular Cation. No prominent ions were detected in the CID mass spectra of MPF_6^+ ions from complexes lacking the RNC group, and there was only one prominent fragment when RNC was present. This ion corresponded to loss of a PF_6^- anion *plus* loss of a *tert*-butyl cation (tBu^+) from the RNC group. PF_6^- and tBu^+ may leave as an ion pair, or in the form of three neutrals: PF_5, HF, and isobutene. The latter process is not only entropically favored (three particles *versus* one), but it is enthalpically favored by about 21.5 kJ/mol (based upon gas-phase heats of formation[24-26]). Freas *et al.*[27] invoked a similar loss of PF_5 and HF from the ion-paired cation $[Ru(bdmt)(bpy)_2PF_6]^+$ (where bdmt = 3,3′:5,3″-bis(dimethylene)-2,2′:6,2″-terpyridine and bpy = 2,2′-bypyridine) under MIKES conditions. In the complexes studied here, the nitrogen atom of the RNC ligand has a formal positive charge and may be Coulombically restrained to reside near the PF_6^- anion, as it is in the X-ray structure of **12**.[28] This could favor the rearrangements necessary for concerted loss of multiple neutrals.

It is interesting to note that the CID mass spectra of MPF_6^+ cations formed from simple dissociation of compounds **7**, **9**, and

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(24) Gibson, N. A.; Weatherburn, D. C. *Anal. Chim. Acta* **1972**, *58*, 159.

(25) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, 17.

(26) Bartmess, J. E. Personal communication, University of Tennessee, Knoxville, TN.

(27) Liang, X.; Suwanrumpha, S.; Freas, R. B. *Inorg. Chem.* **1991**, *30*, 652.

(28) Tortorelli, L. J.; Woods, C.; Campana, C. F. *Acta Crystallogr.* **1992**, *C48*, 1311.

Table III. Ions Detected in the CID MIKES Spectrum of the Molecular Cation $[M]^+$ for Compounds **1** and **7** (Precursor *m/z* 1313)

	rel intens		
m/z	**1**	**7**	identification[a]
1256	31	27	$[M - tBu]^+$
1236	28	0	$[M - Ph]^+$
1230	61	62	$[M - RNC]^+$
1173	39	19	$[M - (tBu + RNC)]^+$
1147	100	100	$[M - (2RNC)]^+$
1138	49	34	$[M - Z]^+$
1055	89	100	$[M - (Z + RNC)]^+$
972	44	11	$[M - (Z + 2RNC)]^+$
895	44	0	$[M - (Z + 2RNC + Ph)]^+$

[a] Ph refers to phenyl (C_6H_5); all other assignments are as in Table II.

Table IV. Ions Detected in the CID MIKES Spectrum of the Molecular Cation $[M]^+$ for Compounds **2** and **8** (Precursor *m/z* 1205)

	rel intens		
m/z	**2**	**8**	identification[a]
1177	44	64	$[M - CO]^+$
1149	100	100	$[M - 2CO]^+$
1072	11	13	$[M - (2CO + Ph)]^+$
996	56	61	$[M - (Z + CO)]^+$
972	28	42	$[M - (Z + 2CO)]^+$
897	34	0	$[M - (Z + 2CO + Ph)]^+$

[a] Assignments are as in Tables II and III.

Table V. Ions Detected in the CID MIKES Spectrum of the Molecular Cation $[M]^+$ for Compounds **3** and **9** (Precursor *m/z* 1401), Compound **13** (Precursor *m/z* 1323), and Compound **16** (Precursor *m/z* 1377)

3		**9**		**13**		**16**		
m/z	intens	*m/z*	intens	*m/z*	intens	*m/z*	intens	identification[a]
1344	36	1344	23	1266	50	1320	26	$[M - tBu]^+$
1318	85	1318	100	1240	94	1294	100	$[M - RNC]^+$
1261	26	1261	26	1183	40	1237	13	$[M - (tBu + RNC)]^+$
1235	100	1235	87	1157	100	1211	67	$[M - 2RNC]^+$
1172	54	1172	76	1094	50	1148	36	$[M - Ph_2As]^+$
1158	23	1158	20	1080	28	1134	18	$[M - Ph_2AsCH_2]^+$
1115	15	1115	20	1037	22	1091	9	$[M - (Ph_2As + tBu)]^+$
1095	8							$[M - (Ph_2As + Ph)]^+$
1089	12	1089	17	1011	11	1065	13	$[M - (Ph_2As + RNC)]^+$
1032	15	1032	17	954	18	999	7	$[M - (Ph_2As + tBu + RNC)]^+$
1006	10	1006	19	928	7	982	16	$[M - (Ph_2As + 2RNC)]^+$
973	14	973	16	895	13	949	8	$[M - PA]^+$
896	8							$[M - (PA + Ph)]^+$

[a] Assignments are as in Tables I–III.

Table VI. Ions Detected in the CID MIKES Spectrum of the Molecular Cation $[M]^+$ for Compounds **5** and **11** (Precursor *m/z* 1489) and Compound **14** (Precursor *m/z* 1410)

5		**11**		**14**		
m/z	intens	*m/z*	intens	*m/z*	intens	identification[a]
1432	64	1432	71	1353	100	$[M - tBu]^+$
1406	34	1406	51	1327	50	$[M - RNC]^+$
				1270	8	$[M - (tBu + RNC)]^+$
1323	11	1323	28	1244	30	$[M - 2RNC]^+$
1260	80	1260	100	1181	70	$[M - Ph_2As]^+$
1246	24	1246	36	1167	44	$[M - Ph_2AsCH_2]^+$
1203	14			1124	8	$[M - (Ph_2As + tBu)]^+$
1163	20	1163	43	1098	21	$[M - (Ph_2As + RNC)]^+$
1080	8	1080	17	1015	40	$[M - (Ph_2As + 2RNC)]^+$
1017	47	1017	63	938	41	$[M - AA]^+$
934	65	934	14	855	42	$[M - (AA + RNC)]^+$
877	50	877	15	772	34	$[M - (AA + RNC + tBu)]^+$
851	100	851	23			$[M - (AA + 2RNC)]^+$
774	74					$[M - (AA + Ph_2AsCH_2)]^+$

[a] Assignments are as in Tables I–III.

Table VII. Ions Detected in the CID MIKES Spectrum of the Molecular Cation $[M]^+$ for Compounds **4** and **10** (Precursor *m/z* 1291) and Compound **6** (Precursor *m/z* 1379)

4		**6**		**10**		
m/z	intens	*m/z*	intens	*m/z*	intens	identification[a]
1263	26	1351	45	1263	12	$[M - CO]^+$
		1335	37			$[M - (CO + O)]^+$
1235	100	1323	100	1235	100	$[M - 2CO)]^+$
		1274	56			$[M - (CO + Ph)]^+$
1158	54	1246	54	1158	20	$[M - (2CO + Ph)]^+$
		1164	54			$[M - (2CO + 2Ph)]^+$
1062	33	1150	31	1062	10	$[M - Ph_2As]^+$
		1080	63			$[M - (Ph_2As + 2CO)]^+$
928	48					$[M - (Ph_2As + 2CO + Ph)]^+$

[a] Assignments are as in Tables I–III.

Table VIII. Ions Detected in the CID MIKES Spectrum of the Molecular Cation $[M]^+$ for Compound **12** (Precursor *m/z* 1235) and Compound **15** (Precursor *m/z* 1289)

12		**15**		
m/z	intens	*m/z*	intens	identification[a]
1178	25	1232	43	$[M - tBu]^+$
1152	61	1206	72	$[M - RNC]^+$
1095	35	1149	51	$[M - (tBu + RNC)]^+$
1069	69	1123	100	$[M - 2RNC]^+$
1060	100	1114	25	$[M - Z]^+$
977	50	1031	76	$[M - (Z + RNC)]^+$
894	37	948	37	$[M - (Z + 2RNC)]^+$

[a] Assignments are as in Tables I–III.

Table IX. Information Concerning Compounds **7**, **12**, and **15**

apex pyrazolate ligand[a]	gas-phase acidity[b]	compd	rel intens[c]	
			$[M - Z]^+$	sum
35mpz	81.05	**12**	145	271
4B35mpz	79.06	**7**	34	149
mtmpz	76.60	**15**	25	138

[a] See Table I for definitions. [b] Estimated enthalpy (kJ/mol) based upon AM1 semiempirical calculation for the following reaction: $HX(g) \rightarrow H^+(g) + X^-(g)$. [c] Intensity relative to $[M - 2RNC]^+$. Sum is the sum of the intensities for $[M - Z]^+$, $[M - (Z + RNC)]^+$, and $[M - (Z + 2RNC)]^+$.

11 are essentially identical to the CID spectra obtained when the corresponding precursor cations are generated by beam- or matrix-induced oxidation of compounds **1**, **3**, and **5**, respectively. This suggests that oxidation does not alter the structure and/or internal energy of MPF_6^+ cations sufficiently to affect CID fragmentation pathways.

CID of the Singly-Charged Molecular Cation. Compared with the FAB mass spectra, the CID MS results for the singly-charged molecular cations for these compounds are relatively complex and varied. However, several useful generalizations can be derived from careful comparison of the data. A representative MIKES spectrum (for compound **7**) is shown in Figure 3. Data for redox conjugate pairs (ions nominally differing only in the oxidation state of one Rh atom) are compared in Tables III–VIII. Table IX shows the effect of varying the apex pyrazolate ligand. Insofar as possible, the effects are described separately below.

(a) Beam- and Matrix-Induced Chemistry Effects. For each Rh(I,I)/Rh(I,II) redox conjugate pair, there are two sources of M^+: simple dissociation of the Rh(I,I) salt (*e.g.*, compound **1**) or reduction of the corresponding Rh(I,II) species (*e.g.*, from compound **7**). Unlike beam- and matrix-induced *oxidation* to form MPF_6^+ from Rh(I,I) salts, *reduction* reactions generate molecular cations with CID fragmentation pathways distinct from those observed for "native" Rh(I,I) cations (*e.g.*, compare data for compounds **1** and **7** in Table III). In general, CID of the reduced molecular cations (from compounds **7**–**11**) results in relatively less fragmentation than for the corresponding "native" ions (from compounds **1**–**5**, respectively), regardless of whether the reduction is beam-induced or results from matrix (equilibrium) electrochemistry. In particular, product ions arising from loss of a phenyl group from the transoid bridging ligands (PP, PA, and AA in Table I) are much more abundant in the CID mass spectra of the nonreduced molecular cations; they are missing altogether from M^+ CID spectra of the Rh(I,II) RNC-containing compounds (**7**, **9**, and **11**). The fact that CID mass spectra differ even when the reduction is matrix-induced (and presumably equilibrated prior to FAB MS sampling;[10] *e.g.*, compare spectral data for compounds **2** and **8** in Table IV) suggests that differences are structural rather than energetic. Isolation and structural characterization of matrix-reduced material could provide mechanistic insight concerning the reduction mechanism. Such work lies outside the scope of the current study.

(b) Transoid Bridging Ligand Effects. Variation of the transoid bridging ligand greatly affects the type and abundance of ions generated by CID. Only when the transoid bridging ligand is PP (compounds **1**, **2**, **7**, **8**, **12**, and **15**) are ions reflecting loss of the apex pyrazolate ligand (Z) detected. This may result from an inductive effect: the Rh–N(pyrazolate) bond may be weakened as electron density shifts to the stronger Rh–P (*versus* Rh-As) transoid bond. Alternatively, a steric effect may be responsible: pyrazolate binding may be weakened by the shortening of the Rh–Rh distance in complexes incorporating smaller (compared with As) phosphorus atoms.[29]

The greater relative strength of Rh–P interactions is also evident in the fact that *no* loss of the transoid bridging ligand (or fragments thereof) occurs when that ligand is PP, whereas such losses occur readily with PA or AA. Significantly, the loss of the intact PA bridging ligand is the only process observed which must result from the cleavage of a Rh–P bond; fragmentation of the PA ligand otherwise favors retention of phosphorus. Evidently, the CID process can impart sufficient energy to break one Rh–P bond, but not two. Crystallographic studies which show that the Rh–P and methylene C–P bonds are shorter than the corresponding Rh–As and methylene C–As bonds (for the dicarbonyl precursors to compounds **12** and **14**)[30] are consistent with stronger bonds to phosphorus.

The AA transoid bridging ligand is more labile (with regard to CID) than the PA ligand. For example, the relative abundance of the fragment ion arising from loss of the entire bridging ligand is greater for compound **11** than for compound **9**. Furthermore, **11** exhibits ions attributable to the loss of the bridging ligand *plus* some part of the terminal ligand, while compound **9** does not (Tables V and VI).

(c) Apex Ligand Effects. As noted above, CID losses involving the apex ligand (Z) are detected only when the transoid bridging ligand is PP. Among PP compounds, it would be expected that loss of Z should correlate with ligand basicity (*i.e.*, the least basic ligand should be least tightly bound). Basicities for the ligands studied here have not been tabulated, but one would expect the least basic ligand to be the one with the most electron-withdrawing substituents on the ring.[29] Thus, the relative basicity of the pyrazolate ligands should increase in the order mtmpz $<$ 4B35mpz $<$ 35mpz (in agreement with AM1 semiempirical calculations[31] of the gas-phase acidities for the conjugate acids; Table IX).

In using the set of compounds **7**, **12**, and **15** to test for correlation between basicity and Z loss, it is necessary to take account of the fact that CID of M^+ from each of these yields three product ions involving "pyrazolate" loss: $[M - Z]^+$, $[M - (Z + RNC)]^+$, and $[M - (Z + 2RNC)]^+$. It is noteworthy that the species lost is a neutral radical in each case, rather than the anionic pyrazolate; fragmentation is evidently accompanied by electron transfer. This can account for the fact that both the intensity at $[M - Z]^+$ and the sum of intensities of the three pyrazolate-free product ions follow the *reverse* of the projected trend based on ligand basicity (Table IX). For example, the most basic ligand (35mpz) shows the *most* extensive loss of the apex ligand. The more basic, electron-rich ligands are better able to give up an electron and leave as a neutral.

While changes in the transoid bridging ligand can affect the loss of the apex pyrazolate ligand (*i.e.*, only PP-containing compounds lose Z), the reverse is not true. None of the pyrazolate ligands promotes loss of the PP bridging ligand, and variation of Z has little effect on the other fragmentations of compounds with PA or AA bridges.

(d) Terminal Ligand Effects. When the terminal ligand is CO instead of RNC, the CID mass spectra are simpler, in part because there is little evidence of internal fragmentation of the CO ligand (only compound **6** shows such fragmentation). For compounds **4**, **6**, and **10**, only one or two ions are attributable to loss of parts of the transoid ligand (Table VII), far fewer than for the corresponding RNC analogs (compounds **3**, **5**, and **9**, respectively; Tables V and VI). Furthermore, the total intensity in these channels is relatively low for the CO-containing complexes; the transoid bridging ligand is evidently bound more tightly when CO rather than RNC is the terminal ligand. This is consistent with the enhanced back-bonding expected with the more electronegative oxygen atom (relative to the nitrogen atom in the RNC molecule).[29] The CO back-bonding removes electron density from the metal atoms, strengthening their interactions with the transoid bridging ligand by an inductive effect.

Conclusions

CID mitigates complications from beam- and matrix-induced artifacts and, for the relatively high-mass (>1000 Da) organometallic compounds studied here, yields more fragmentation (increased number and intensity) compared to FAB MS. Not only are CID spectra consistent with the expected structures for these compounds, but comparisons among them reveal valuable information concerning relative lability. Furthermore, such comparisons clearly establish the existence of structural differences between native and beam- or matrix-reduced materials, although it was not possible to definitively determine the nature of the differences.

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(29) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience: New York, 1972; pp 198–201.

(30) Woods, C. Unpublished results, University of Tennessee, Knoxville, TN.

(31) Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075.