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Field Desorption Mass Spectrometry of a Series of Various Metal Carbonyl 1,4-diazabutadiene Compounds

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It is shown that field desorption mass spectrometry is a useful method of characterizing the thermally labile and involatile organometallic complexes mentioned in the title. In most cases only molecular ions are generated, but in some cases also $(M-CO)^{+\cdot}$ *fragment ions are observed.*

Introduction

Various techniques are available for studying organometallic complexes. One of the most powerful methods of obtaining direct information about the molecular weight and the composition of the compounds is mass spectrometry. Moreover, this method is often used to elucidate the structure (apart from X-ray diffraction studies), especially when the number of nuclei to be detected with NMR techniques is too small.

Unfortunately, most of the routinely used techniques to generate ions in the mass spectrometer require that the complexes evaporate in high vacuum below their decomposition temperature. Furthermore, the complexes should be sufficiently stable to produce molecular ions when information about the molecular weight is required.

A relatively new and very valuable development is the method of field desorption mass spectrometry (FD-MS), which enables one to obtain mass spectra of thermally labile and non-volatile compounds [1]. This method has already been applied successfully to a variety of problems in organic, environmental and biochemistry [2]. The application of FD-MS has been extended recently to organometallic compounds [3–6] and it is expected to be a useful and good method of studying complexes, which are relatively unstable and/or non-volatile. FD mass spectra are obtained under mild conditions in comparison with the classical electron impact (EI) method. The generated ions, which in most cases are protonated or cationised molecules, but sometimes molecular ions, hardly contain any excess of internal energy so that fragmentation is usually not observed.

In the course of our work on the coordination and conversion of 1,4-diazabutadienes on bi- and polynuclear Fe, Ru and Os complexes, many intermediates with low thermal stability were isolated. Knowledge of the structure of these species appeared to be very important with respect to the understanding of the conversion of the diimine skeleton. The purpose of this paper is to show the application of FD-MS in the determination of the composition of these complexes. Some of the complexes have been studied in detail by X-ray diffraction. The available solid state structures provide unambiguously the composition of the complexes and thereby the justification of the preliminary conclusions about the composition drawn on the basis of FD-MS. This is of crucial importance for the more general application of FD-MS as an analytical tool in organometallic chemistry.

Experimental

The FD mass spectra were obtained with a Varian MAT 711 double focussing mass spectrometer equipped with a combined EI/FI/FD ion source and coupled to a spectro system MAT 100 data acquisition unit. FD emitters with an average length of 30 μm for the carbon microneedles were used. The samples were dissolved in chloroform and then loaded onto the emitters by the dipping technique. In all experiments emission-controlled FD [7] was used at a threshold of $3-5 \times 10^{-9}$ A measured between the field anode and the slotted cathode, 1.5 mm distance apart. See for the emitter currents, which were

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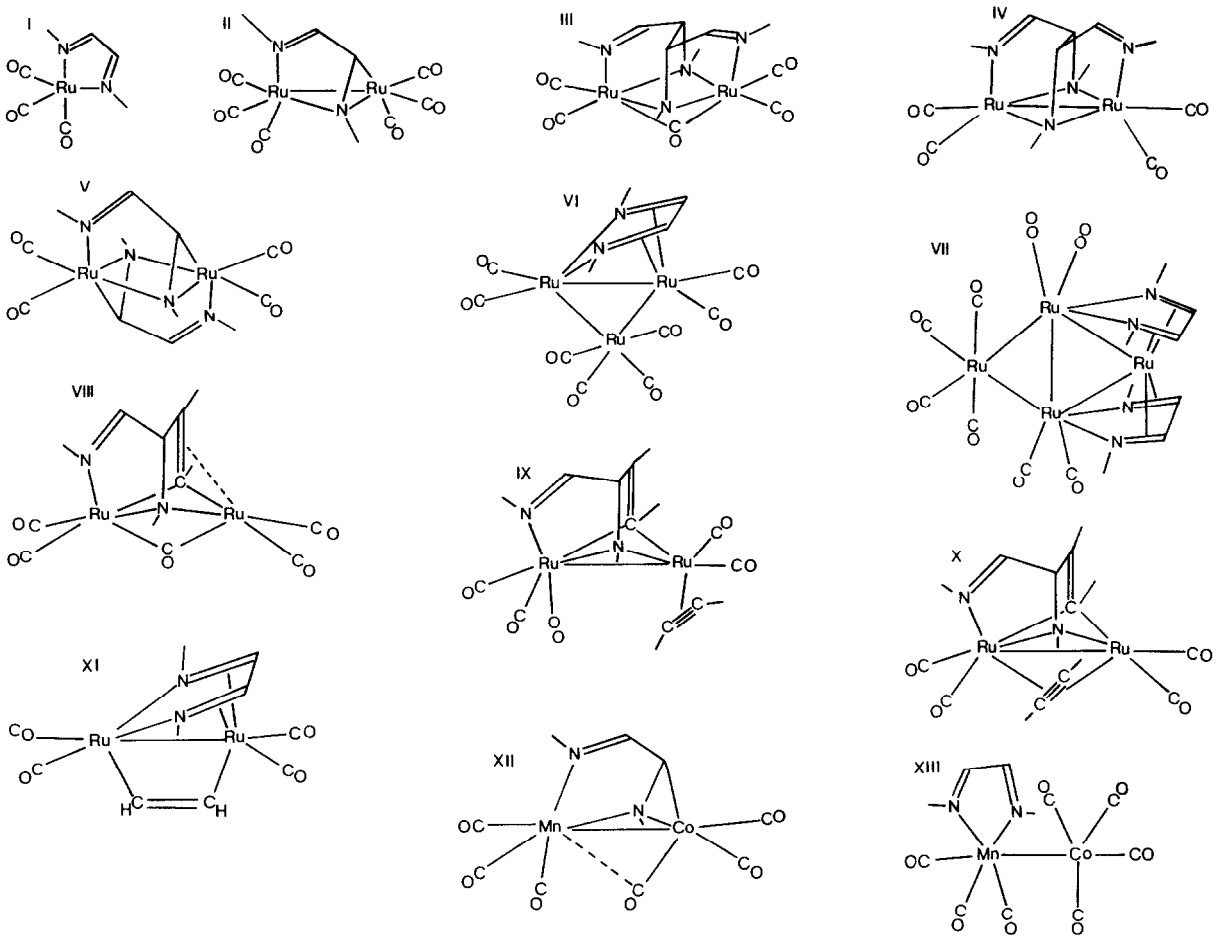

Fig. 1. Structure of the complexes under investigation.

used to desorb the samples, Table I. The source temperature was generally 50 °C.

The preparation of the complexes is or will be published elsewhere [8–12]. $Ru_3(CO)_{12}$ was obtained from Strem Chemicals, U.S.A.

Results

The structures of the complexes listed in Table I, are shown in Fig. 1 (I–XIII). In addition to FD-MS, the complexes have been characterized by ^{1}H-, ^{13}C-NMR, IR and UV-spectroscopy. Furthermore, the structures II, V, VII, VIII, XI and XII have been established by single crystal structure determinations, whereas the other structures have been proposed on the basis of analogy with the other known complexes. Structure VI is only tentative which will be determined by X-ray diffraction.

Table I lists m/z values and the relative intensities of a series of mono-, di-, tri- and tetranuclear metal carbonyl complexes which have in common the 1,4-diazabutadiene ligand or a derivative thereof.

All complexes give molecular ions with the exception of $MnCo(CO)\{c\text{-}C_3H_5\text{–}N{=}C(CH_3)\text{–}N{=}C(CH_3)\text{–}c\text{-}C_3H_5\}$ and $MnCo(CO)_6\{c\text{-}C_3H_5\text{–}N{=}C(CH_3)\text{–}C(CH_3)N\text{–}c\text{-}C_3H_5\}$ (type XII and XIII) which generate $[M\text{–}CO]^{+\bullet}$ as the fragment ions with highest mass at m/z = 446 and 418, respectively. All the $MM'(CO)_6$(DAB) complexes (M=M'=Ru, Os; M=Mn, Re and M'=CO; DAB = 1,4-diazabutadiene) give relatively abundant $[M\text{–}CO]^{+\bullet}$ ions and for some complexes these ions are even more abundant than the corresponding molecular ions. For $MnCo(CO)_6\{ipr\text{-}N{=}CH\text{–}CH{=}N\text{-}ipr\}$ (type XII complex) low abundant $[2M]^{+\bullet}$ and $[2M\text{–}CO]^{+\bullet}$ cluster ions are observed together with $[M]^{+\bullet}$ and $[M\text{–}CO]^{+\bullet}$ ions.

Discussion

Fragmentation is only scarcely observed in FD-MS so that in comparison with EI-MS valuable informa-

TABLE I. FD-MS Data of Metal Carbonyl 1,4-Diazabutadiene Complexes.[a]

Compound	M[b]	emitter current	m/z values of observed peaks (rel. int.)
Complex type I			
$Ru(CO)_3$-{mes-N=CH–CH=N-mes}	477	–	449(1.2) *450(1.7)* 473(4.2) 474(8.9) 475(4.20) 476(54.3) 477(67.9) *478(100)* 479(30.6) 480(61.7) 481(20.7)
Complexes type II			
$Ru_2(CO)_6$-{tbu-N=CH–CH=N-tbu}	538	0 mA	501(11.1) 502(6.9) 503(2.3) 504(4.6) 505(8.0) 506(7.6) 507(18.3) 508(13.7) *509(20.6)* 510(19.1) 511(17.9) 512(7.6) 513(19.8) 514(8.4) 529(7.6) 530(19.1) 531(22.5) 532(27.5) 533(44.3) 534(30.5) 535(51.5) 536(72.5) 537(78.0) 538(83.9) *539(100)* 540(58.8) 541(85.5) 542(15.3) 543(23.7) 544(7.6)
$Ru_2(CO)_6$-{ipr–N=CH–CH=N-ipr}	510	5 mA	474(0.4) 475(12.4) 476(8.2) 477(13.5) 478(29.8) 479(32.3) 480(64.9) 481(78.0) 482(77.3) *483(100)* 484(95.7) 485(46.1) 486(65.2) 487(10.6) 488(28.4) 489(7.4) 503(8.9) 504(13.5) 505(22.3) 506(32.6) 507(22.7) 508(58.2) 509(62.1) 510(63.8) *511(83.5)* 512(50.7) 513(40.4) 514(50.3) 515(13.8) 516(14.9)
$Ru_2(CO)_6$-{chex-N=CH–CH=N-chex}	590	5 mA	554(3.5) 555(11.8) 556(14.7) 557(18.5) 558(44.1) 559(42.4) 560(63.8) 561(75.3) 562(72.4) 563(98.8) *564(100)* 565(72.4) 566(78.5) 567(29.1) 568(35.0) 569(10.6) 583(3.5) 584(4.7) 585(5.3) 586(9.4) 587(7.1) 588(10.0) 589(10.6) 590(20.6) 591(20.0) *592(21.2)* 593(12.4) 594(15.3) 595(7.6) 596(5.9) 597(2.9)
$Ru_2(CO)_6$-{i-pr-N=CH–CCH_3=N-ipr}	524	0 mA	489(10.1) 490(7.5) 491(28.6) 492(21.1) 493(15.8) 494(28.6) 495(43.6) 496(39.8) 497(45.1) *498(54.9)* 499(33.1) 500(39.8) 501(15.0) 502(28.6) 503(6.0) 514(3.0) 515(3.8) 516(5.6) 517(13.5) 518(15.0) 519(25.6) 520(37.6) 521(31.6) 522(54.1) 523(69.9) 524(61.6) 525(99.2) *526(100)* 527(51.1) 528(72.2) 529(21.8) 530(21.1) 531(5.3)
$FeRu(CO)_6$-{tbu–N=CH–CH=N-tbu}	493	0 mA	487(16.3) 488(11.6) 489(11.6) 490(40.3) 491(54.3) 492(46.5) *493(100)* 494(32.6) 495(56.6) 496(16.3) 497(5.4)
$Os_2(CO)_6$-{tbu-N=CH–CH=N-tbu}	715	mA	708(9.5) 709(6.3) 710(16.7) 711(34.7) 712(26.3) 713(63.2) 714(65.3) 715(84.2) *716(100)* 717(97.9) 718(63.2) 719(70.5) 720(18.9) 721(25.3) 722(8.4)
$Os_2(CO)_6$-{ipr-N=CH–CH=N-ipr}	688	3 mA	659(2.4) 660(2.6) 661(4.7) 662(5.3) 663(6.6) *664(5.3)* 665(1.6) 666(3.9) 682(7.9) 683(7.9) 684(10.5) 685(15.8) 686(26.3) 687(57.9) *688(100)* 689(76.3) 690(78.9) 691(26.3) 692(68.4) 693(15.8) 694(7.9)
Type III complexes			
$Ru_2(CO)_5$-{tbu-N=CH–CH–N-tbu)$_2$}	678	10 mA	671(4.8) 672(12.0) 673(13.3) 674(31.1) 675(26.5) 676(47.0) 677(78.3) 678(84.3) *679(100)* 680(98.8) 681(50.6) 682(82.5) 683(19.3) 684(24.1) 685(4.2)

(continued overleaf)

TABLE I. *(continued)*

Compound	M[b]	emitter current	m/z values of observed peaks (rel. int.)
Type IV complexes			
$Ru_2(CO)_4$-{(ipr-N=CH–CH-N-ipr)$_2$}	594	10 mA	586(4.9) 587(11.3) 588(14.8) 589(22.2) 590(37.3) 591(42.3) 592(51.4) 593(73.2) 594(76.8) 595(89.4) *596(100)* 597(54.2) 598(64.0) 599(27.5) 600(27.6) 601(6.3)
$Ru_2(CO)_4$-{(chex-N=CH–CH–N-chex)$_2$}	754	20 mA	747(8.1) 748(16.2) 749(21.6) 750(59.5) 751(43.2) 752(70.3) 753(78.4) 754(86.5) *755(100)* 756(89.2) 757(64.9) 758(73.0) 759(29.7) 760(27.0) 761(13.5)
Type V complexes			
$Ru_2(CO)_4$-{ipr-N=CH–CH=N-ipr}$_2$	594	10 mA	587(5.8) 588(14.4) 589(18.3) 590(28.8) 591(32.7) 592(30.8) 593(61.5) 594(84.6) 595(71.2) *596(100)* 597(94.2) 598(67.3) 599(69.2) 600(21.2) 601(31.7) 602(11.5)
$Ru_2(CO)_4$-{chex-N=CH–CH=N-chex}$_2$	754	–	722(32.1) 723(46.4) 724(53.6) 725(64.3) 726(89.3) *727(100)* 728(82.1) 729(50.0) 730(71.4) 731(28.6) 732(41.1) 751(32.1) 752(25.0) 753(39.3) 754(57.1) *755(60.7)* 756(50) *757(60.7)* 758(46.4) 759(42.8) 760(25.0) 761(21.4) 762(17.9)
$Ru_2(CO)_4$-{ptol-N=CH–CH=N-ptol}$_2$	786	5 mA	780(15.0) 781(14.8) 782(28.4) 783(22.5) 784(30.2) 785(64.8) 786(67.5) *787(100)* 788(63.8) 789(42.6) 790(52.4) 791(20.0) 792(14.7)
Type VI complexes			
$Ru_3(CO)_8$-{isobut-N=CH–CH=N-isobut}	695	0 mA	684(3.4) 685(4.7) 686(7.6) 687(16.9) 688(20.3) 689(24.6) 690(27.1) 691(44.9) 692(56.8) 693(61.9) 694(70.0) *695(100)* 696(74.6) 697(14.1) *698(100)* 699(84.7) 700(73.7) 701(39.0) 702(38.1) 703(12.7) 704(14.4) 705(5.1)
$Ru_3(CO)_8$-{neop-N=CH–CH=N-neop}	723	5 mA	711(3.0) 712(6.0) 713(7.4) 714(10.4) 715(16.3) 716(20.7) 717(25.2) 718(34.1) 719(51.8) 720(53.3) *721(100)* 722(88.9) 723(74.1) 725(83.0) 726(51.1) 727(48.9) 728(13.0) 729(24.4) 730(6.7) 731(11.9)
Type VII complexes			
$Ru_4(CO)_8$-{ipr-N=CH–CH=N-ipr}$_2$	908	–	900(11.8) 901(35.3) 901(29.4) 903(41.2) 904(44.1) 905(55.9) 906(64.7) 907(67.6) *908(100)* 909(67.6) 910(50.0) 911(23.5) 912(47.1) 913(50.0) 914(17.6) 915(23.5) 916(8.8)
$Ru_4(CO)_8$-{chex-N=CH–CH=N-chex}$_2$	1068	20 mA	1055(20.3) 1056(29.0) 1057(26.1) 1058(20.3) 1059(52.2) 1060(46.4) 1061(49.3) 1062(57.9) 1063(60.0) 1064(75.4) 1065(75.4) *1066(100)* 1067(58.0) 1068(49.3) 1069(55.1) 1070(59.6) 1071(20.3) 1072(27.5) 1073(15.9)
$Ru_4(CO)_8$-{isobut-N=CH–CH=N-isobut}$_2$	964	5 mA	952(6.7) 953(8.6) 954(7.7) 955(14.4) 956(14.8) 957(23.0) 958(24.4) 959(39.2) 960(47.4) 961(54.5) 962(64.1) 963(60.3) 964(93.8) 965(95.7) 966(99.5) *967(100)* 968(65.1) 969(75.6) 970(46.9) 971(33.5) 972(33.5) 973(12.4) 974(15.3) 975(6.6) 976(6.7)
$Ru_4(CO)_8$-{neop-N=CH–CH=N-neop}$_2$	1020	–	1013(23.4) 1014(31.2) 1015(43.8) 1016(21.9) 1017(37.5) 1018(50.8) 1019(59.4) 1020(82.8) 1021(89.1) 1022(81.3)

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TABLE I. *(continued)*

Compound	M[b]	emitter current	m/z values of observed peaks (rel. int.)
			1023(98.4) *1024(100)* 1025(91.4) 1026(71.9) 1027(50.0) 1028(31.3) 1029(29.7) 1030(10.9) 1031(10.9)
Type VIII complexes			
$Ru_2(CO)_5$-{tbu-N=CH–CH(N-tbu)(phenyl)(C=CH}	612	5 mA	605(12.8) 606(1.6) 607(35.2) 608(49.5) 609(43.2) 610(52.8) 611(65.6) 612(68.8) *613(100)* 614(81.6) 615(95.2) 616(46.5) 617(65.6) 618(20.8) 619(20.8) 620(6.4) 621(4.8)
$Ru_2(CO)_5$-{tbu-N=CH–CH(N-tbu)(tbu)C=CH}	592	6 mA	585(21.7) 586(14.5) 587(24.6) 588(34.2) 589(31.9) 590(60.9) 591(79.7) 592(78.3) 593(94.2) *594(100)* 595(68.1) 596(81.1) 597(24.6) 598(27.5) 599(10.1)
$Ru_2(CO)_5$-{tbu-N=CH–CH(N-tbu)-($CH_3OC(=O)$–C=CH)}	594	5 mA	590(21.0) 591(37.1) 592(53.2) 593(80.6) 594(64.5) 595(75.8) *596(100)* 597(53.2) 598(71.0) 599(34.7) 600(41.3) 601(16.1)
$Ru_2(CO)_5$-{tbu-N=CH–CH(N-tbu)-($CH_3OC(=O)$–C=C–$C(=O)OCH_3$)}	652	5 mA	644(10) 645(22) 646(12) 647(26) 648(33) 649(36) 650(54) 651(68) 652(77) 653(82) *654(100)* 655(56) 656(54) 657(21) 658(34) 659(18)
$Ru_2(CO)_5$-{ipr-N=CH–CH(N-ipr)-($CH_3OC(=O)$–C=C–$C(=O)OCH_3$)}	624	5 mA	619(22.5) 620(36.0) 621(44.0) 622(42.7) 623(65.2) 624(70.8) 625(82.0) 626(97.8) *627(100)* 628(58.4) 629(91.0) 630(34.8) 631(49.4) 632(13.5)
$Ru_2(CO)_5$-{ipr-N=CH–CCH_3(N-ipr)-(ptol)–C=CH}	598		591(14) 592(22) 593(31) 594(79) 595(37) 596(38) 597(54) 598(75) 599(65) *600(100)* 601(49) 602(42) 603(10)
Type IX complexes			
$Ru_2(CO)_5$-[{tbu-N=CH–CH–(N-tbu)-($CH_3OC(=O)$–C=C–$C(=O)OCH_3$)}-{$CH_3OC(=O)$–C≡C–$C(=O)OCH_3$}]	794	2 mA	787(21.2) 788(19.5) 789(28.2) 790(51.1) 791(43.1) 792(67.8) 793(93.1) 794(90.8) *795(100)* 796(98) 797(83.3) 798(73.6) 799(38.5) 800(50.6) 801(20.7)
$Ru_2(CO)_5$[{ipr-N=CH–CH–(N-ipr)–($CH_3OC(=O)$–C=C–$C(=O)OCH_3$)}{$CH_3OC(=O)$–C≡C–$C(=O)OCH_3$}]	766	10 mA	760(23.8) 761(22.9) 762(39.6) 763(397) 764(64.3) 765(74.0) 766(75.8) 767(79.3) *768(100)* 769(67.0) 770(81.1) 771(29.1) 772(34.4) 773(21.1) 774(11.5)
$Ru_2(CO)_5$[{chex-N=CH–CH(N-chex)–($CH_3OC(=O)$–C=C–$C(=O)OCH_3$}{$CH_3OC(=O)$–C≡C–$C(=O)OCH_3$}]	846	11 mA	840(17.6) 841(22.5) 842(33.2) 843(36.9) 844(56.7) 845(73.3) 846(77.5) 847(89.3) *848(100)* 849(79.7) 850(71.7) 851(38.0) 852(28.3) 853(23.0) 854(11.2)
Type X complexes			
$Ru_2(CO)_4$[{tbu-N=CH–CH–(N-tbu)–($CH_3OC(=O)$–C=C–$C(=O)$–CH_3}{$CH_3OC(=O)$–C≡C–$C(=O)OCH_3$}]	766	10 mA	760(8.9) 761(11.6) 762(17.9) 763(31.3) 764(31.7) 765(53.6) 766(86.6) 767(80.4) 768(97) *769(100)* *769(100)* 770(65.2) 771(89.3) 772(24.1) 773(29.5) 774(80.4)
$Ru_2(CO)_4$[{tbu-N=CH–CH–(N-tbu)–(phen)C=CH}-{$CH_3OC(=O)$–C≡C–$C(=O)OCH_3$}]	726	10 mA	720(12.2) 721(12.1) 722(20.9) 723(23.5) 724(39.1) 725(49.6) 726(60.9) 727(65.2) *728(100)* 729(38.3) 730(66.1) 731(17.4) 732(31.3)

(continued overleaf)

TABLE I. *(continued)*

Compound	M[b]	emitter current	m/z values of observed peaks (rel. int.)
Type XI complexes			
$Ru_2(CO)_4$-{ipr-N=CH–CH=N-ipr}(HC≡CH)}	480	3 mA	472(4.2) 473(13.4) 474(16.8) 475(21.8) 476(45.4) 477(33.6) 478(64.7) 479(81.5) 480(75.6) *481(100)* 482(91.6) 483(51.3) 484(69.7) 485(17.6) 486(25.1) 487(6.7)
$Ru_2(CO)_4$-{chex-N=CH–CH=N-chex}-(HC≡CH)}	560	3 mA	552(8.9) 553(8.9) 554(13.9) 555(41.8) 556(30.4) 557(59.5) 558(74.4) 559(75.9) 560(88.6) *561(100)* 562(50.6) 563(69.6) 564(19.0) 656(24.1) 566(7.6) 567(2.5)
Type XII complexes			
$MnCo(CO)_6$-{ipr-N=CH–CH=N-ipr}	422	10 mA	*394(81)* 395(10.5) *422(100)* 423(12.9) *816(1.1)* 817(0.2) *844.(1.4)* 845(0.2)
$MnCo(CO)_6$-{tbu-N=CH–CH=N-tbu}	450	0 mA	*450(100)* 451(22.2) 452(3)
$Mn(Co(CO)_6$-{chex-N=CH–CH=N-chex}	502	2 mA	*474(100)* 475(28.6) 476(4.8) *502(62.7)* 503(12.8) 504(3.2)
$MnCo(CO)_6$-{cpr-N=CH–CH=N-cpr}	418	0 mA	*390(100)* *418(74.3)*
$MnCo(CO)_6$-{ipr-N=CH–CCH_3=N-ipr}	436	0 mA	*408(38.1)* *436(100)* 437(30.2)
$MnCo(CO)_6$-{cpr-N=CCH_3–CCH_3=N-cpr}	446	10 mA	*418(100)* 419(56.7)
$ReCo(CO)_6$-{tbu-N=CH-CH=N-tbu}	581	0 mA	580(68.0) 581(16.9) *582(100)* 583(20.3)
$ReCo(CO)_6$-{chex-N=CH–CH=N-chex}	633	10 mA	605(4.8) *606(7.1)* 633(49.0) *634(100)*
Type XIII complexes			
$ReCo(CO)_7$-{cpr-N=CCH_3–CCH_3=N-cpr}	605	0 mA	576(93.4) 577(25) *578(100)* 579(26.3) *604(72.0)* 606(59.9)
$MnCo(CO)_7$-{cpr-N=CCH_3–CCH_3=N-cpr}	474	0 mA	*418(100)* 419(15.7) 446(62.6) 447(21.7)

[a]Abbreviations: tbu = tertair-butyl; ipr = isopropyl; chex = cyclohexyl; cpr = cyclopropyl; isobut = isobutyl; neop = neopentyl; mes = mesityl. [b]M is based upon ^{101}Ru.

tion about the molecular structure is not obtained. However, sometimes this problem can be overcome to some extent by measuring a series of complexes which have different substituents attached to the ligands.

Information about the number of metal atoms in the complex, can be obtained from the isotopic pattern when the element has more than one stable isotope. Figure 2 shows the observed and calculated isotopic pattern of $Ru_2(CO)_6${chex-N=CH–CH=N-chex} (type II complex), which are in perfect agreement with each other. The calculated pattern has been corrected for naturally occurring ^2H, ^{13}C, ^{15}N and ^{18}O.

Sometimes the absence of fragmentation is a great advantage, for example when mixtures of products have to be analysed. Fragmentation might cause overlap of the isotopic pattern of the different components. Furthermore, in binuclear complexes or clusters of ruthenium, loss of small fragments such as methyl, would also lead to overlap of isotopic distributions, thereby preventing a meaningful interpretation of the spectra. An example of the simplification of a mass spectrum by application of FD technique is shown in Fig. 3, which gives the relevant regions of the EI and FD spectra of $Ru_3(CO)_{12}$.

It is important to note that the molecular weights and compositions of the complexes II, V, VII, VIII,

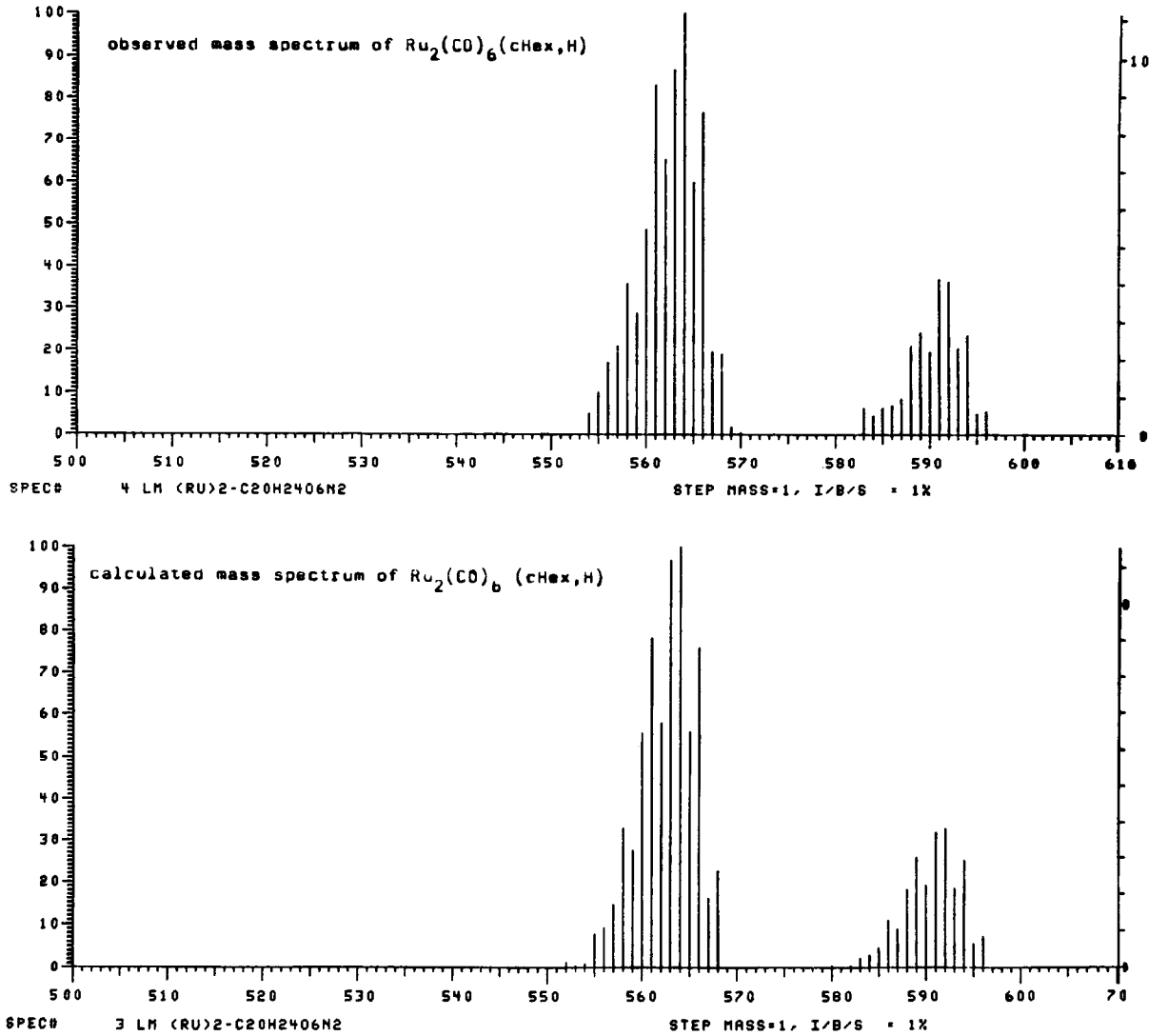

Fig. 2. Observed and calculated FD-MS spectra of $Ru_2(CO)_6$(cHex, H).

XI and XII as indicated by their FD spectra are in agreement with the solid state structures. This indicates that molecular ions are released indeed from the emitter.

In some cases (I, II, VIII, XII, XIII) the fragmentation reaction $M^{+\bullet} \rightarrow [M-CO]^{+\bullet} + CO$ is observed. This parallels the thermal stability of these complexes as observed in solution. $Ru_2(CO)_6(DAB)$ releases carbon monoxide to dimerize according to eqn. 1.

$$\underset{\text{II}}{Ru_2(CO)_6(DAB)} \xrightarrow[\text{n-heptane}]{\text{toluene}} 2CO + \tfrac{1}{2}\underset{\text{VII}}{Ru_4(CO)_8(DAB)_2} \qquad (1)$$

For the loss of one carbonyl group from the molecular ions of the $MCo(CO)_6(DAB)$ complexes (XII), the corresponding metastable peaks are sometimes observed. They provide evidence that the fragmentation to give $[M-CO]^{+\bullet}$ is not only due to pyrolysis on the emitter, if any.

$MCo(CO)_7(DAB)$ complexes (M = Mn, Re; XIII) have been isolated as extremely unstable reaction intermediates in the formation of $MCo(CO)_6(DAB)$ which easily release carbon monoxide according to eqn. 2.

$$\underset{\text{XIII}}{MCo(CO)_7(DAB)} \xrightarrow{\text{n-heptane}} CO + \underset{\text{XII}}{MCo(CO)_6(DAB)} \qquad (2)$$

This reaction occurs very rapidly at modest temperatures (20–50 °C) and therefore $MnCo(CO)_7\{c\text{-}C_3H_5\text{–}N{=}C(CH_3)\text{–}C(CH_3){=}N\text{–}c\text{-}C_3H_5\}$ produces $[M-CO]^+$ ions without any formation of the corresponding molecular ions. However, a low abun-

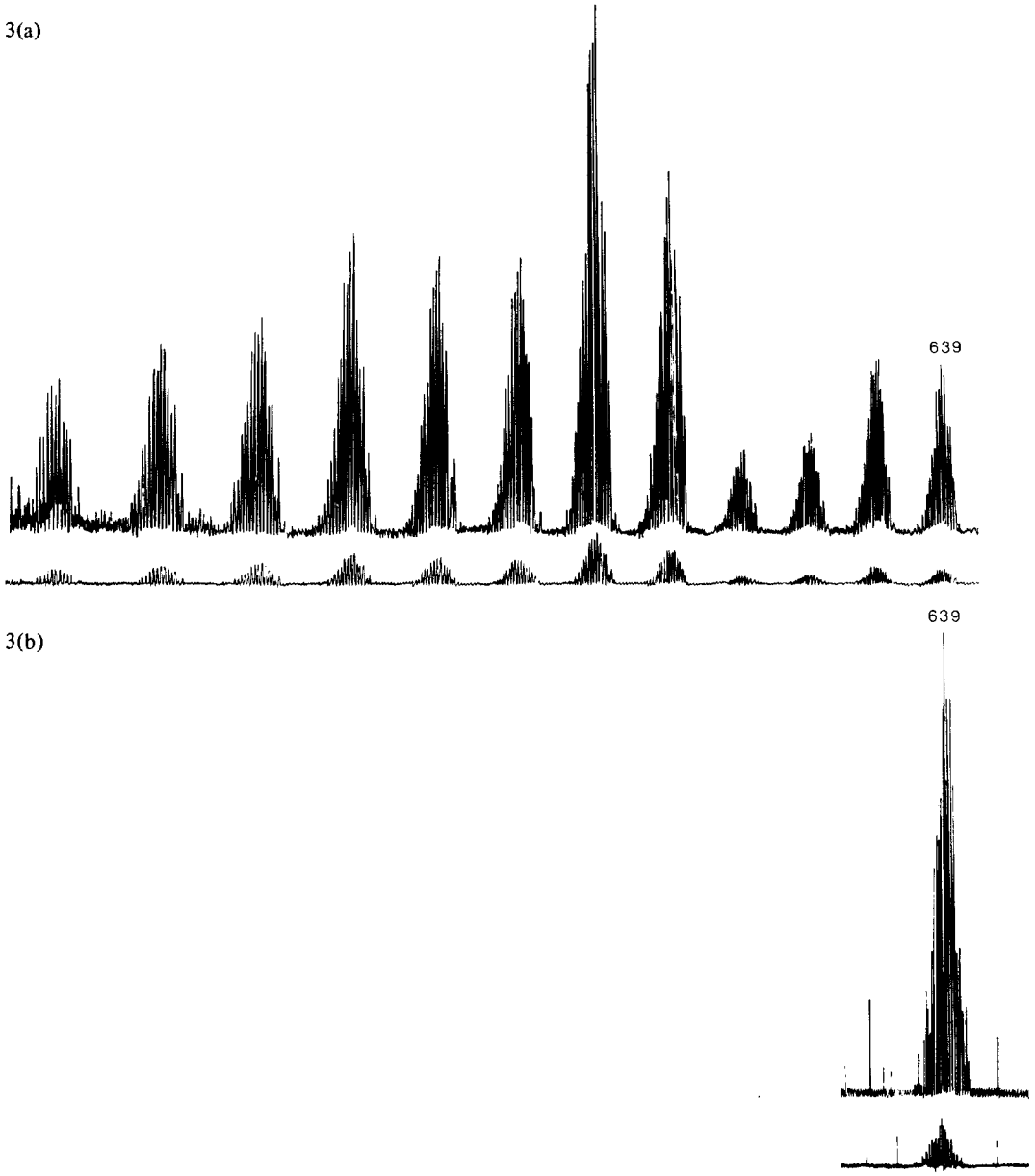

Fig. 3. EI-MS (3a) and FD-MS (3b) spectra of $Ru_3(CO)_{12}$ showing the absence of fragmentation in the latter case.

dant $[M]^{+\bullet}$ ion is observed for $ReCo(CO)_7\{c\text{-}C_3H_5\text{–}N{=}CCH_3\text{–}CCH_3{=}N\text{–}c\text{-}C_3H_5\}$ (XIII).

Sometimes peaks due to cluster ions appear in the FD-mass spectra such as in those of $MnCo(CO)_6$ {ipr-N=CH–CH=N-ipr} (complex typ XII), where peaks due to $[2M]^{+\bullet}$ and $[2M\text{–}CO]^{+\bullet}$ ions are observed in addition to the peaks due to the $[M]^{+\bullet}$ and $[M\text{–}CO]^{+\bullet}$ ions. Note that the term 'cluster ions' is not meant to indicate clusters in the sense of chemical entities, such as for example $Ru_4(CO)_8(DAB)_2$ (complexes type VII). The $[2M]^{+\bullet}$ ions are considered to be dimers, which are held together by Van der Waals interactions. This is another indication that the ions are generated indeed without an excess of internal energy.

It will now be obvious that FD-MS is a useful analytical method. However, problems may arise to determine the elemental composition of a complex by high resolution mass measurements due to the absence of suitable reference compounds and to a relatively low signal to noise ratio. This will be true especially for high molecular weight compounds and for complexes with complicated isotopic patterns.

Furthermore, even for binuclear ruthenium and osmium complexes the low resolution spectra have

to be simulated taking into account the natural isotopic contributions of ^{2}H, ^{13}C, ^{15}N and ^{18}O, in order to fit the isotopic patterns unambiguously with the molecular weight. Measurements of a series of complexes can help to solve this problem also.

Conclusion

FD-MS is a very valuable method for obtaining detailed information about the composition and the molecular weight of unstable organometallic complexes. It is hoped therefore that it will be applied more generally to such kind of chemical problems. Finally, it should be noted that information about the complexes presented in this paper has been confirmed by other techniques, such as X-ray diffraction and elemental analyses.

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