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The mass spectra of a series of involatile $Rh(PPh_3)_2(CO)Y$ complexes (anion Y^- is F^-, Cl^-, I^-, $-NCO^-$, $-NCS^-$, $O_2CCH_3^-$, ONO_2^-, $O_2PF_2^-$, or $OSO_2CF_3^-$; $Rh(PPh_3)_2(CO)$ is shortened to RhL_2CO hereafter) were obtained using both laser desorption Fourier-transform ion cyclotron resonance (LDFTICR) and fast atom bombardment (FAB) techniques. The FAB positive ion spectra (sulfolane matrix) showed molecular ions for all complexes except $RhL_2COOSO_2CF_3$, which contained the most weakly-coordinating anion. These FAB spectra also exhibited fragment ions resulting from loss of CO and PPh_3. The sulfolane adduct of RhL_2CO^+ and a derivative were also observed for the series, especially prominent in spectra of complexes of the less tightly-bound anions. The LDFTICR positive-ion spectra were less consistent in fragmentation/rearrangement patterns over the range of anions Y^- than were their FAB counterparts; peak intensities of the former spectra were also highly variable due to difficulties in preparing consistent probe samples. Although the $[M + K]^+$ pseudomolecular
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ion was detected for every complex except $RhL_2^{\square}COOSO_2^{\square}CF_3^{\square}$, only several of the molecular ions were observed; otherwise, fragmentation patterns similar to those of the FAB experiments were seen. No molecular ions were seen for any $RhL_2^{\square}COY$ in the LDFTICR negative ion spectra; however, $Rh(CO)Y_2^-$, $Rh(PPh_3^{\square})(CO)Y_2^-$, and $Rh_2(CO)_2^{\square}Y_2^-$ were characteristically observed, with peak intensities again quite variable. Several tetrarhodium species, $Rh_4(CO)_xY_2^-$ (x = 2-4), were detected as well.

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Contribution from the Departments of Chemistry, University of South Alabama, Mobile , Alabama 36688, and University of Florida, Gainesville, Florida 32611, and the Mass Spectrometry Facility, College of Chemistry, University of California, Berkeley 94720

A Comparison of Laser Desorption and Fast Atom Bombardment Mass Spectra of a Series of $Rh(PPh_3)_2(CO)Y$ Complexes

Daniel M. Branan,[†] Norris W. Hoffman,[*,†] E. Andrew McElroy,[†] David L. Ramage,[†] Martha J. Robbins,[†] John. R. Eyler,[*,‡] Clifford H. Watson,[‡] Paul deFur,[§] and Julie A. Leary[*,§]

Abstract: The mass spectra of a series of involatile $Rh(PPh_3)_2(CO)Y$ complexes (anion Y^- is F^-, Cl^-, I^-, $-NCO^-$, $-NCS^-$, $O_2CCH_3^-$, ONO_2^-, $O_2PF_2^-$, or $OSO_2CF_3^-$; $Rh(PPh_3)_2(CO)$ is shortened to $RhL_2(CO)$ hereafter) were obtained using both laser desorption Fourier-transform ion cyclotron resonance (LDFTICR) and fast atom bombardment (FAB) techniques. The FAB positive-ion spectra (sulfolane matrix) showed molecular ions for all complexes except $RhL_2(CO)OSO_2CF_3$, the species containing the most weakly-coordinating anion. Thesc FAB spectra also exhibited fragment ions resulting from loss of CO and PPh_3. The sulfolane adduct of $RhL_2(CO)^+$ and a derivative were also observed for the series, especially prominent in spectra of complexes of the less tightly-bound anions. The LDFTICR positive-ion spectra were less consistent in fragmentation/rearrangement patterns over the range of anions Y^- than were their FAB counterparts; peak intensities of the former spectra were also highly variable due to difficulties in preparing consistent probe samples. Although the $[M + K]^+$ pseudomolecular ion was detected for every complex except $RhL_2(CO)OSO_2CF_3$, only several molecular ions were observed in the series; otherwise, fragmentation patterns similar to those of the FAB experiments were seen. No molecular ions were seen for any $RhL_2(CO)Y$ in the LDFTICR negative-ion spectra; however, $Rh(CO)Y^-$, $Rh(PPh_3)(CO)Y^-$, and $Rh_2(CO)_2Y_2^-$ were characteristically observed, with peak intensities again quite variable. Several tetrarhodium species, $Rh_4(CO)_xY_2^-$ (x = 2-4), were detected as well.

Introduction

New techniques in mass spectrometry are being applied with increasing frequency in inorganic chemistry for characterizing involatile compounds and studying their chemical properties. Newer techniques used to produce gaseous ions from transition-metal complexes include fast atom bombardment (FAB),[1,2] laser-desorption Fourier-transform ion cyclotron resonance (LDFTICR),[3-5] field desorption (FD),[2f,6] thermospray,[2f] fast-heating chemical ionization,[2f] and liquid secondary-ion mass spectrometry (LSIMS).[7] One of our groups had earlier determined relative anion affinities in solution for a wide series of $Rh(PPh_3)_2(CO)Y$ complexes;[8] thus we were interested in comparing mass spectrometric properties of the species therein obtained by two of the softer ionization techniques, FAB and LDFTICR, and possibly correlating those properties with the nature of the anion Y^-. We report here results of those mass spectrometric studies (Y^- = F^-, Cl^-, I^-, $-NCO^-$, $-NCS^-$, $O_2CCH_3^-$, ONO_2^-, $O_2PF_2^-$, $OSO_2CF_3^-$) for both positive and negative ions. To the best of our knowledge, this study represents the first comparison of FAB and LDFTICR mass spectrometry of a broad series of low-valent transition-metal complexes in which only the anion is varied.

Experimental Section

Compound Preparation. The Rh(I) complexes were prepared and characterized as previously described.[8,9] The degree of interaction with sulfolane was studied by preparing 2 mM

solutions in 1:1 (volume) sulfolane/CH_2Cl_2 (Aldrich, 99%, and Sargent-Welch reagent, respectively) and recording their spectra in a CaF_2 cell on a Perkin-Elmer 1430 IR spectrophotometer.

Fast Atom Bombardment Mass Spectrometry. Low- and high-resolution FAB spectra were obtained on a VG ZAB2-EQ hybrid mass spectrometer (using the 11-250J data system) equipped with a cesium ion gun operated at 20 kV above ground. Resolution was measured at 1:1,000 with an 8 kV accelerating potential and data accumulated at a scan speed of 10 s/decade for the low-resolution acquisition. High-resolution measurements were obtained at 1:10,000 resolution and data acquired using polyethylene glycol as an internal standard. 1-2 μL samples of $RhL_2(CO)Y$/sulfolane or $RhL_2(CO)Y$/m-nitrobenzyl alcohol mixtures were loaded onto stainless-steel probe tips. Single-scan data were collected for all $RhL_2(CO)Y$.

Laser-Desorption Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry. Laser-desorption experiments were performed using a Nicolet FTMS/1000 Fourier-transform ion cyclotron resonance mass spectrometer. The instrumentation and methodology have been described previously.[10] Ions were desorbed and trapped in a 2.54 cm cubic cell located in the uniform field region of a 3.0 tesla super-conducting magnet. The ions were excited by the standard frequency chirp excitation method and 16K time-domain points were acquired during broadband detection (medium-resolution spectra). High-resolution spectra of the molecular-ion region were collected using heterodyne detection, digitizing 64K data points. Typically, averaging the signal produced by

three laser shots provided mass spectra of high signal-to-noise ratio; however, strong variability in peak intensities still resulted in the averaged spectra (*vide infra*). Spectra have been converted to stick plots herein for simplicity of presentation unless otherwise stated.

The output from a Lumonics TE 860 pulsed carbon dioxide laser was focused through a 7.63 cm focal length, 1.27 cm diameter ZnSe lens onto the end of a solids probe on which the analyte had been deposited. The laser produced a pulse of 1 s duration having an average energy of 1.5 joules/pulse. The laser beam had a rectangular cross-section of 2 x 3 cm collimated by a 4 m radius-of-curvature mirror prior to entering the vacuum chamber. The laser power density impinging upon the solids probe was estimated to be 1×10^8 W/cm^2. Three laser pulses were fired at the probe in its initial position; then it was rotated manually to provide a fresh surface for the next three pulses.

Sample preparation involved dissolving the solid Rh(I) complex in dichloromethane and depositing the resulting solution on a stainless steel solids probe tip with a micropipette. [The solutions are unchanged by exposure to the atmosphere.] Solvent was allowed to evaporate and the probe was inserted into the vacuum chamber. The mass spectrometer was then evacuated to a pressure of $2\text{-}5 \times 10^{-8}$ torr. Detection of the ions occurred after a 1s delay following the laser pulse to allow time for desorbed neutrals to be pumped away. No significant difference was observed in the appearance of the mass spectra when the delay between desorption and detection was varied from 250 ms to 5 s.

The LDFTICR negative-ion spectra were evaluated for the presence of signals corresponding to monoanions of formula $Rh_w(PPh_3)_x(CO)_yY_z^-$ using a program LDRHLCOY (not including isotope distributions) written in Microsoft® QUICKBASIC.

Results and Discussion

The positive-ion FAB mass spectra showed molecular ions with expected isotope patterns for all the $Rh(PPh_3)_2(CO)Y$ complexes (abbreviated as $RhL_2(CO)Y$ hereafter) except $RhL_2(CO)OSO_2CF_3$. Even $RhL_2(CO)OSO_2CF_3$, however, exhibited a signal for $RhL_2OSO_2CF_3^+$ (at m/z 776 of medium-weak intensity relative to that for $RhL_2(CO)^+$), an ion most likely formed via CO loss from the molecular ion. IR analysis of solutions of the $RhL_2(CO)Y$ set in 1:1 sulfolane/CH_2Cl_2 showed only the triflate complex to interact strongly with sulfolane (affording carbonyl bands at 2015 and 1990 cm^{-1} versus a single band at 1998 cm^{-1} in pure CH_2Cl_2). Sulfolane was much poorer at displacing anions Y- from $Rh(PPh_3)_2(CO)Y$ than the neutral nitrogen ligand pyridine.[9] The weakly-coordinating triflate ion is apparently easily displaced by the sulfolane matrix to afford ions at m/z 775 and 759; these correspond respectively to the sulfolane complex $[RhL_2(CO)(sulfolane)]^+$ and its derivative $[RhL_2(CO)(sulfolane) - O]^+$. Fragment ions observed at m/z 279 assigned to Ph_3POH^+ suggest that an oxygen atom is lost from sulfolane and transferred to PPh_3.[11] These ions were more prominent in the spectra of complexes of the more weakly-coordinating anions (i.e., $RhL_2(CO)OSO_2CF_3$, $RhL_2(CO)OPOF_2$, and $RhL_2(CO)ONO_2$[9]), but

they also appeared to lesser extents in spectra of the other complexes.[12] High-resolution mass measurements were conducted to verify the elemental composition of the sulfolane complex and its derivative; the results are shown in Table I.

Insert Table I

Transfer of oxygen from the sulfolane matrix (in FAB-MS) to organometallic compounds has been observed in one of our laboratories; however, this phenomenon has not been an analytical problem since the molecular ion itself has also always been seen.[14,15] For handling hygroscopic compounds, sulfolane has become our (Berkeley) FAB matrix of choice due to its aprotic nature and ease of use in inert atmospheres. Despite its relatively high volatility, two or three spectra can be recorded easily for a sample, each with the correct corresponding isotope pattern.[16] Although m-nitrobenzyl alcohol (NBA) is often used for FAB mass spectra of organometallic and inorganic compounds,[2c] the latter matrix gave no molecular-ion information for seven of the nine $RhL_2(CO)Y$ analyzed but did produce many ions heavier than the molecular ions (e.g., m/z 794, 944, and 972). These high-mass ions were not observed in the sulfolane spectra, nor do they appear to be NBA matrix-complex analogs of those observed for sulfolane.

Relative intensities of the molecular ions failed to parallel solution anion affinities for the series. In addition to the molecular ion and the sulfolane complex and derivative ion discussed above, fragment ions corresponding to various ligand

losses were also seen for most of the complexes analyzed; they are listed in Table II. In addition to the molecular ions produced in the sulfolane FAB spectra, fragments corresponding to loss of CO and PPh_3 were usually observed in relatively high abundance.

The FAB positive-ion spectrum for $RhL_2(CO)I$ (Figure 1) is characteristic of the set of $RhL_2(CO)Y$ (note that it does not display the occasionally-observed sulfolane adducts). The spectrum for $RhL_2(CO)NCO$ (Figure 2) is also representative, except that it contains a signal at m/z 698 for $[M + H]^+$ in addition to that at 697 for $[M]^+$; a similar pattern was noted in the $RhL_2(CO)NCS$ spectrum. Often observed when analyzing iridium complexes[17] are both the protonated molecular ion and the radical cation, a phenomenon we attribute to the overall basicity of the molecule. Here N-coordination of the NCO^- and NCS^- ligands to Rh(I) might be expected to enhance Bronsted basicity of the respective Group 16 atoms.

Insert Table II

Insert Figures 1 and 2

Unlike the positive-ion spectra, negative-ion FAB-MS gave no useful information. These spectra showed only ions derived from the sulfolane matrix.

The LDFTICR positive-ion spectra were less consistent in fragmentation/rearrangement over the range of anions Y^- than were their FAB analogs. Signal intensities varied considerably for

each laser pulse; results discussed here pertain to averages of signals produced from three individual laser pulses. Even those averaged spectra provided only qualitative data; strong peaks in one averaged spectral set became weak signals in another, and vice-versa - peak height reproducibility was about 50% on average.[18] The irregular surface composition stemming from the probe-coating technique affords variable inputs of internal energy for the $RhL_2(CO)Y$ molecules. The molecular composition in the selvedge region also changes considerably over the three-pulse series for different locations on the sample probe.

Only for $RhL_2(CO)Cl$, $RhL_2(CO)I$, and $RhL_2(CO)NCO$ were molecular ions observed (very intense signal for $RhL_2(CO)Cl$ and weak signals for $RhL_2(CO)I$ and $RhL_2(CO)NCO$); however, similar to the FAB positive-ion spectra, the $RhL_2(CO)YK^+$ adduct,[19] $[M + K]^+$, was detected for every complex except $RhL_2(CO)OSO_2CF_3$. The signals common to all complexes were those for $[M - Y]^+$, $[M - CO - Y]^+$, $[M - PPh_3 - Y - Ph + H]^+$, and $[M - PPh_3 + K]^+$. Observed commonly but not for every complex were signals for $[M + K - CO]^+$; seen less frequently were peaks due to species generated by simple loss of CO. A sample spectrum, that of $RhL_2(CO)NCO$, is displayed in Figure 3. Results are summarized in Table II. As for the FAB data, little correlation between mass spectrometric behavior and Rh(I) anion affinity holds. The $RhL_2(CO)OSO_2CF_3$ spectrum exhibited a signal at m/z 671, assigned to $Rh(PPh_3)_2(CO)(O)^+$ formed by net oxygen-atom abstraction by Rh(I) from the triflate ligand. Similar behavior was noted for complexes of the other weakly-coordinating anions in the series,

$RhL_2(CO)ONO_2$ and $RhL_2(CO)OPOF_2$, and even the much stronger-bound acetate ligand fragmented to a minor degree via oxygen-atom transfer to rhodium.

Insert Figure 3

Although all of the LDFTICR negative-ion spectra for our Rh(I) set failed to display molecular-ion signals, they did exhibit some interesting ion-molecule chemistry. Anions which would be formed via loss from the molecular ion of only CO or only Y were not observed; however, two examples of $Rh(PPh_3)Y^-$ did appear. Prominent signals were found for $Rh(PPh_3)(CO)Y^-$, (one PPh_3 lost) and $Rh(CO)Y^-$ (two PPh_3 lost). The former species were identified by observing the $^{12}C/^{13}C$ isotope patterns expected for one PPh_3 present, since $Rh(PPh_3)(CO)Y^-$ and $Rh_3(CO)_3Y^-$ (the latter possibly formed via ion-molecule reactions) have the same mass but different isotope ratios. Also seen for all except the $RhL_2(CO)OSO_2CF_3$ complex was the dirhodium anion, $Rh_2(CO)_2Y_2^-$. Observed in some negative-ion spectra were the tetrarhodium clusters of formula $Rh_4(CO)_xY_2^-$, where x may be 2, 3, or 4; two or three values of x were usually observed in these particular cluster series (e.g., for $RhL_2(CO)NCO$ in Figure 3). Free anions Y^- were also seen in the spectra of $RhL_2(CO)Cl$, $RhL_2(CO)I$, $RhL_2(CO)NCS$, $RhL_2(CO)OPOF_2$, and $RhL_2(CO)OSO_2CF_3$. Characteristic negative ions generated by laser desorption are presented in Table II.

The LDFTICR negative-ion spectrum for $RhL_2(CO)ONO_2$ displayed several additional interesting features. One of its ion-molecule

reaction products, $Rh_2(CO)_2(ONO_2)_2^-$ (m/z 386), showed oxygen-atom loss similar to that described previously; signals were also observed at m/z 370, 358, and 342 corresponding to $Rh_2(CO)_2(ONO_2)(NO_2)^-$, $Rh_2(CO)(ONO_2)_2^-$, and $Rh_2(CO)(ONO_2)(NO_2)^-$, respectively.

Fragmentation patterns and ion-molecule reactions for both the FAB and LDFTICR positive-ion and the LDFTICR negative-ion spectra can be rationalized in terms of well-understood bonding schemes and electron density on the central rhodium.[20] For the positive-ion spectra, energy input allows dissociation of anion Y^- to form $Rh(PPh_3)_2(CO)^+$. This anion removal lowers electron density at the rhodium; the resulting decreased π back-bonding into the CO π^* orbitals promotes CO dissociation to form $Rh(PPh_3)_2^+$. Less favorable ligand loss from $Rh(PPh_3)_2(CO)^+$ is that of PPh_3 (since it is a much weaker π-acid than CO[20]) to form $Rh(PPh_3)(CO)^+$, observed to a smaller extent in the FAB and not at all in the LDFTICR spectra. The LDFTICR spectra did, however, show a strong peak (and the FAB spectra a weaker one) at m/z 317 assigned to $Rh(PPh_2H)(CO)^+$, which might be formed via $Rh(PPh_3)(CO)^+$; loss of a phenyl group from coordinated PPh_3 has ample precedent in the solution chemistry[21] of organometallic compounds. Lewis acid adducts $RhL_2(CO)YK^+$ (and $RhL_2(CO)YH^+$ for $RhL_2(CO)NCO$ and $RhL_2(CO)NCS$ by FAB) are not unexpected, for the lone pairs on atoms of coordinated Y^- still have some Lewis basicity, especially in the absence of solvation effects;[22] that $RhL_2(CO)OSO_2CF_3$ failed to display such an adduct is reasonable, given the weakness with which it coordinates to t ansition

metals. K^+ might also be expected to form adducts with the complexes which have lost a PPh_3 ligand. Such adducts were observed in every $RhL_2(CO)Y$ spectrum (including that of $RhL_2(CO)OSO_2CF_3$; why its K^+ adduct is seen for [M - PPh_3] but not M cannot be readily explained in electronic terms, so the phenomenon may be steric in nature). For the negative-ion spectra, consecutive loss of PPh_3 from $Rh(PPh_3)_2(CO)Y^-$ to form $Rh(PPh_3)(CO)Y^-$ and $Rh(CO)Y^-$ should be facile. Excess electron density due to the negative charge is decreased upon removal of each PPh_3 donor ligand; alternatively, for d^9 $Rh(PPh_3)_2(CO)Y^-$, presumably square-planar, the "extra" electron will occupy the $d_{x^2-y^2}$ orbital, antibonding with respect to Rh/PPh_3, so PPh_3 dissociation should be facile. The absence of signals for $Rh(PPh_3)_2Y^-$ (hypothetically formed via CO loss) is easily explained, for the negative charge on the molecular ion provides additional electron density on rhodium for stronger π back-bonding into the CO π^* orbitals to retard CO dissociation. The formation of $Rh_2(CO)_2Y_2^-$ is not unlikely, for the neutral dimers $Rh_2(CO)_2Y_2$ have been prepared for many anions.[23] The smaller quantities of the tetrarhodium clusters, $Rh_4(CO)_xY_2^-$ (x = 2-4), observed likely come from two sequential ion/molecule reactions of the dirhodium anion with monorhodium neutrals in the selvedge region. The absence of clearly identifiable trirhodium species in the spectra suggests significantly lower stability for such clusters, which apparently either find a monorhodium species to proceed to the tetrarhodium clusters or decompose into mono- and dirhodium anions.

A recent study[3] comparing FAB and LDFTICR mass spectra of the ferric haloporphyrin complexes Fe(tpp)X found the two techniques comparable for generating molecular ions. A similar comparison for low-volatility pharmaceuticals[24] showed LDFTICR to be superior in producing molecular or pseudomolecular ions. LD, FAB, and SIMS provided similarly useful desorption ionization methods for mass spectra of pyrilium ions.[15] [LDFTICR was not included in a mass spectrometric study of Tc(III) complexes which compared FAB, FD, thermospray, and fast-heating chemical ionization.[2f]] Our study shows FAB produces positive molecular ions for all the Rh(I) series here except the complex of the very weakly-coordinating $OSO_2CF_3^-$, with only moderate variability in ion signal intensities. Because LDFTICR generates a much lower percentage of positive molecular ions for the series and detects pseudomolecular ions $[M + K]^+$ with only moderate reproducibility, it appears analytically somewhat less useful than the FAB molecular ion method. The LDFTICR negative-ion spectra, however, provide useful data for anionic ligand characterization via the strong $Rh(CO)Y^-$ signals.

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Table I. High-Resolution FAB-MS Mass Measurements[a]

Elemental Composition	Measured Mass (mu)	Theoretical Mass (mu)	Difference (mmu)
$C_{41}H_{38}P_2O_3SRh$	775.1099	775.1072	-2.7
$C_{41}H_{38}P_2O_2SRh$	759.1107	759.1123	+1.6

[a] mu for mass units; mmu for milli mass units

Table II. Characteristic Ions Observed for $Rh(PPh_3)_2(CO)Y$ by FAB and LDFTICR Mass Spectrometry[a,b]

FAB(+)	LDFTICR(+)	LDFTICR(-)
M^+/P(8)	M^+/P(3)	M^-/P(0)
$[M-CO]^+$/P-28(9)	$[M-CO]^+$/P-28(5)	$[M-CO]^-$/P-28(0)
$[M-Y]^+$/655(9)	$[M-Y]^+$/655(9)	$[M-Y]^-$/655(0)
$[M-CO-Y]^+$/627(9)	$[M-CO-Y]^+$/627(9)	$[M-CO-Y]^-$/627(0)
$[M-PPh_3-Y]^+$/393(9)	$[M-PPh_3-Y]^+$/393(9)	$[M-PPh_3-Y]^-$/393(9)
$[M-PPh_3-Y-Ph+H]^+$/317(9)	$[M-PPh_3-Y-Ph+H]^+$/317(9)	$[M-PPh_3-Y-Ph+H]^-$/317(9)
	$[M+K]^+$/P+39(8)	$[M-2PPh_3]^-$/P-524(9)
	$[M+K-CO]^+$/P+11(6)	$Rh_2(CO)_2Y_2^-$/262+2Y(8)
	$[M+K-PPh_3]^+$/P+11(6)	$Rh_4(CO)_xY_2^-$/412+28x+2Y(4)[c]

[a] Format is ion/mass(number of set of 9 species displaying signal)

[b] P is mass of molecular ion M^+

[c] x = 2-4

Figure Captions

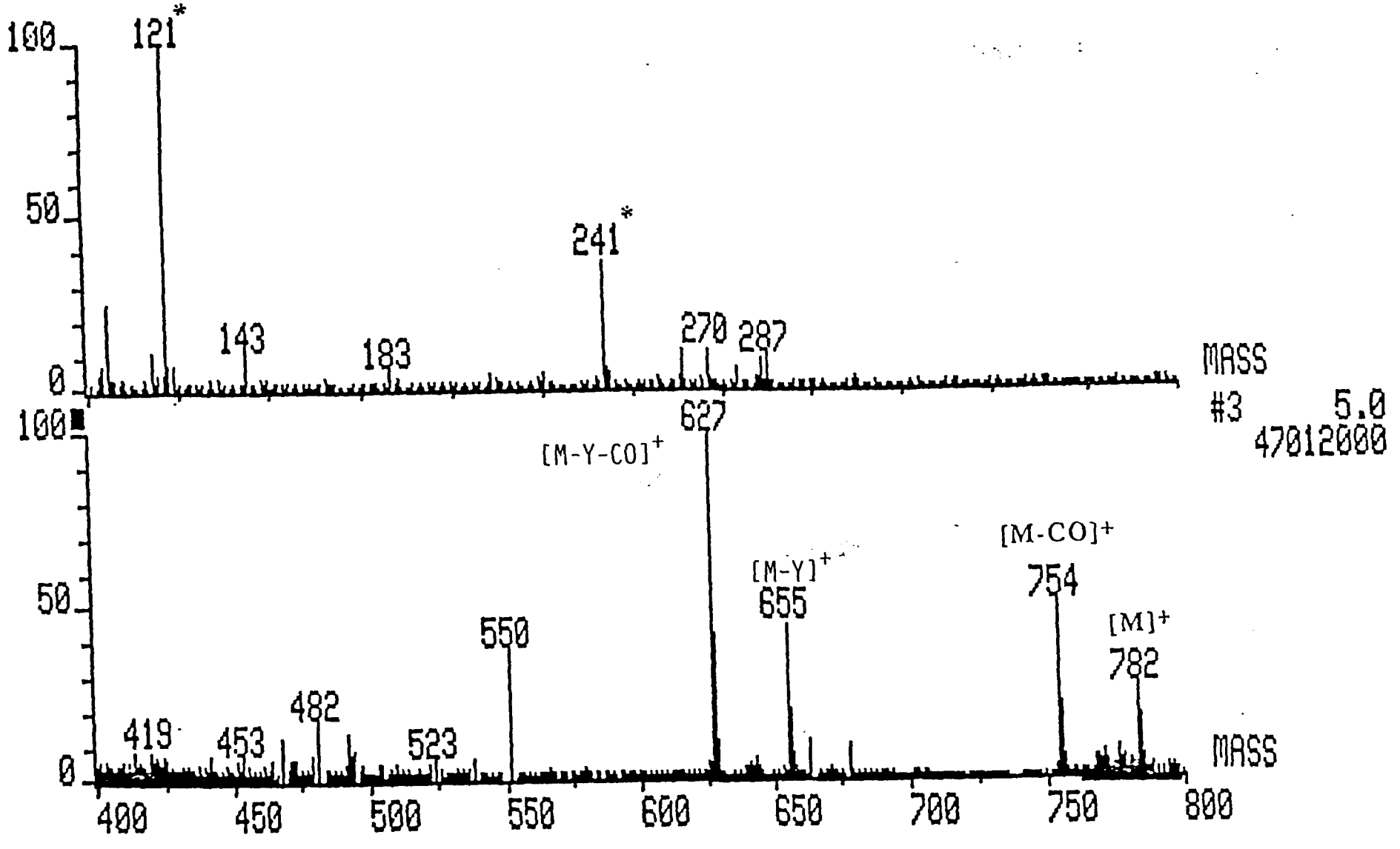
Fig. 1: FAB-MS Positive-Ion Spectrum of $Rh(PPh_3)_2(CO)I$

Fig. 2: FAB-MS Positive-Ion Spectrum of $Rh(PPh_3)_2(CO)NCO$

Fig. 3: LDFTICR-MS Positive-Ion Spectrum of $Rh(PPh_3)_2(CO)NCO$

Fig. 4: LDFTICR-MS Negative-Ion Spectrum of $Rh(PPh_3)_2(CO)NCO$

Fig. 1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50
0
121*
143
183
241*
270
287
MASS
#3
5.0
47012000
100
50
0
627
[M-Y-CO]+
[M-Y]+
655
[M-CO]+
754
[M]+
782
550
482
419
453
523
MASS
400
450
500
550
600
650
700
750
800

Fig.2

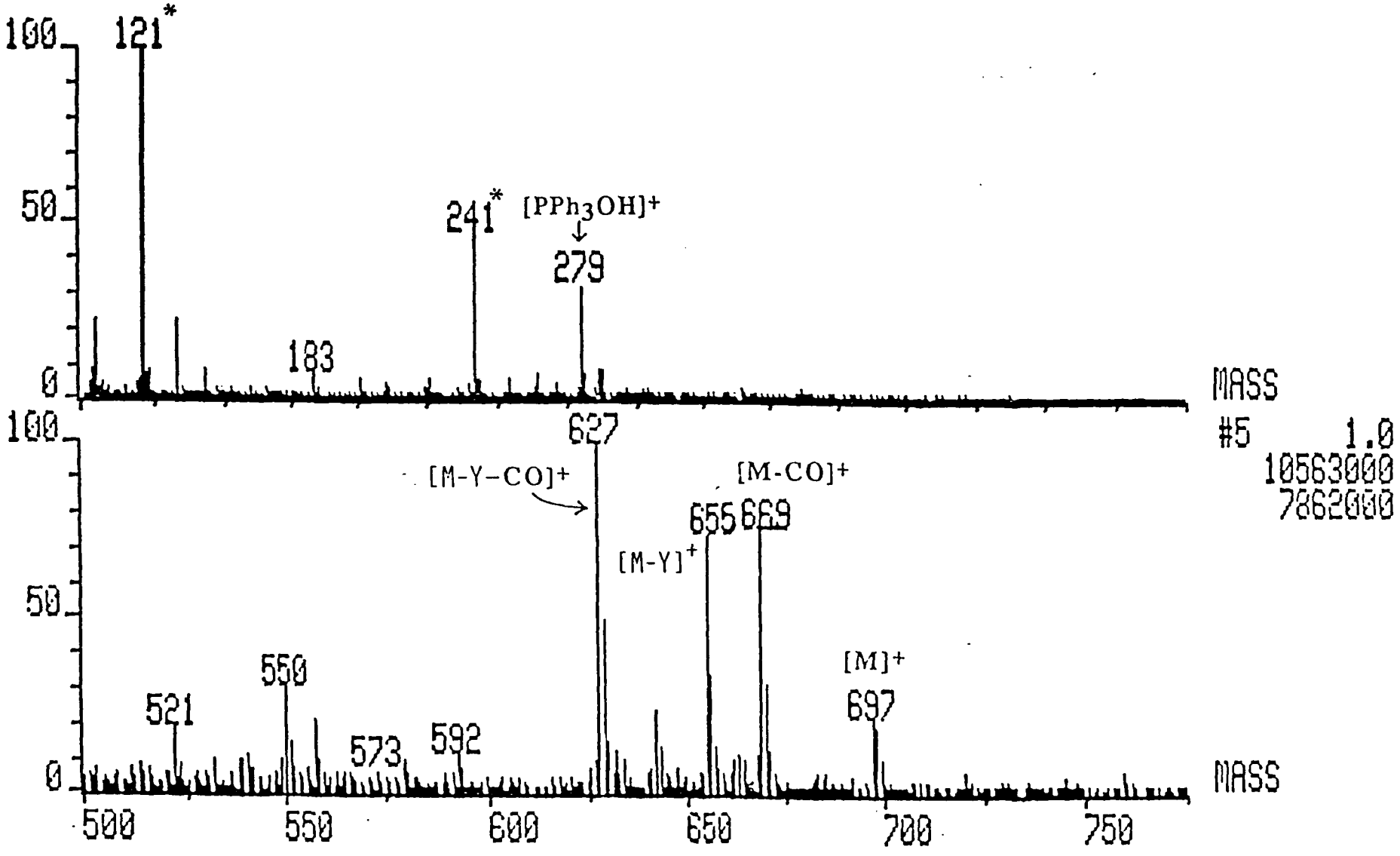

100
121*
50
241*
[PPh3OH]+
279
183
0
MASS
#5 1.0
10563000
7862000
627
[M-Y-CO]+
[M-CO]+
655
669
[M-Y]+
50
550
[M]+
521
697
573
592
0
MASS
500
550
600
650
700
750

Fig. 3

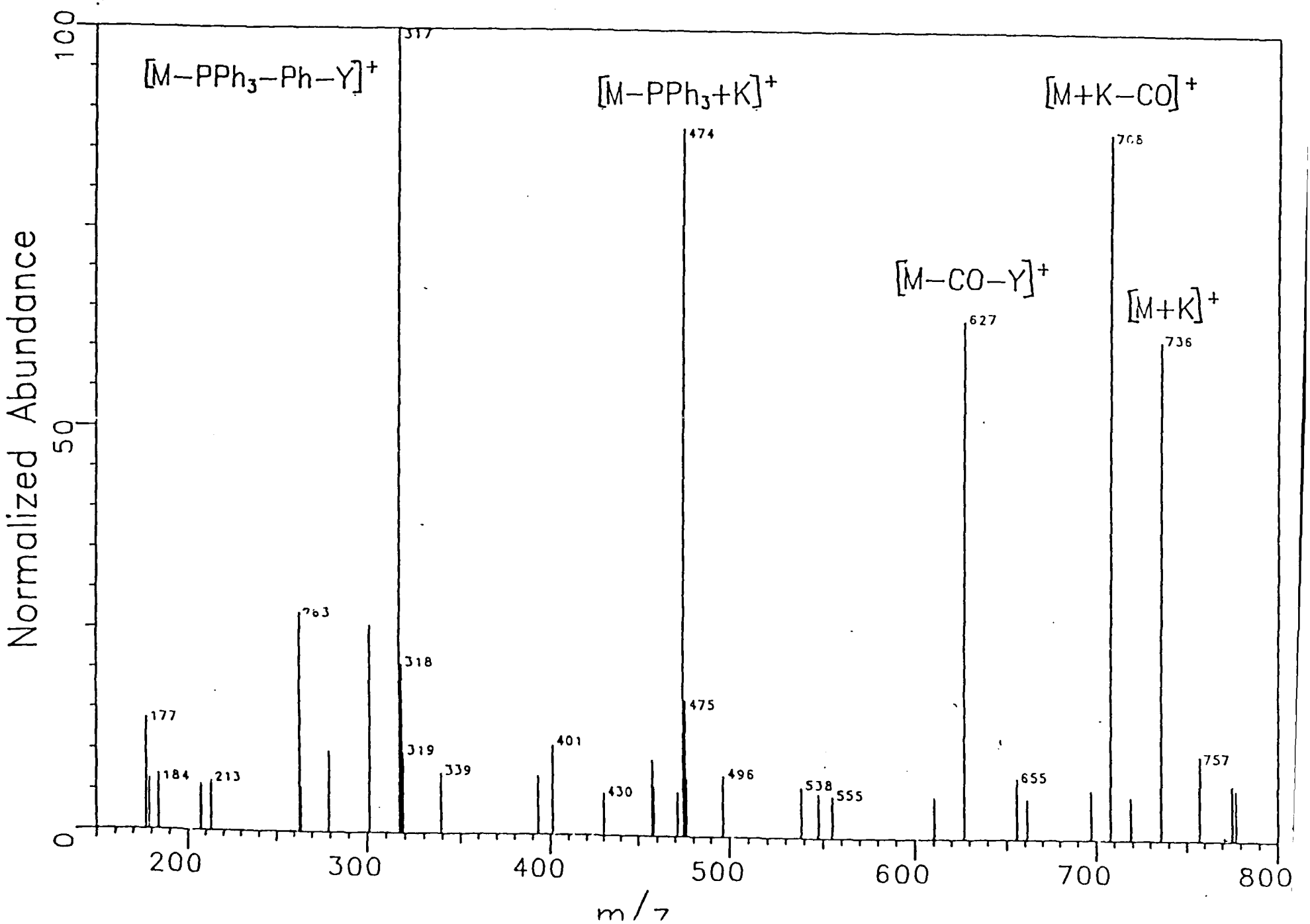
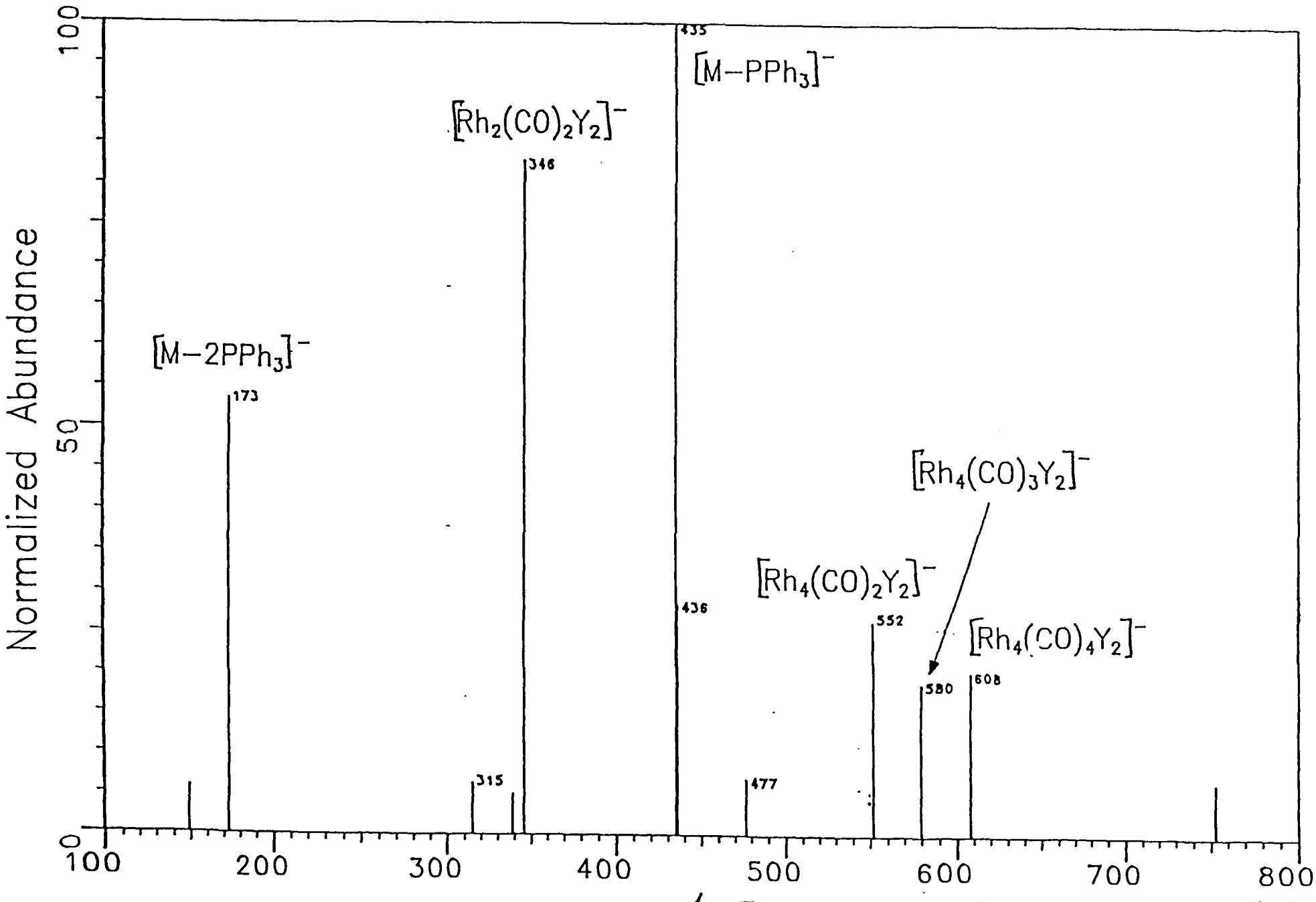

[M−PPh3−Ph−Y]+
[M−PPh3+K]+
[M+K−CO]+
[M−CO−Y]+
[M+K]+
317
474
708
627
736
763
318
475
177
319
401
184
213
339
430
496
538
555
655
757
Normalized Abundance
100
50
0
200
300
400
500
600
700
800
m/z

Fig. 4


Normalized Abundance
100
50
0
100
200
300
400
500
600
700
800
[M−2PPh3]−
173
[Rh2(CO)2Y2]−
346
315
[M−PPh3]−
435
436
477
[Rh4(CO)3Y2]−
[Rh4(CO)2Y2]−
552
[Rh4(CO)4Y2]−
580
608

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