and ν_{as}(Mo–O–Mo); together, they suggest that this species has a linear or nearly linear μ-oxo bridge. However, the large ^{18}O-isotope effect seen for ν_s(Mo–O–Mo) and the high intensity of the otherwise forbidden ν_{as}(Mo–O–Mo) seen at 805 cm^{-1} are unexpected for a linearly bridged M–O–M ion. Calculations on the distortional isomers **2a** and **2b** show that moving the bridging oxygen away from the symmetrical position is slightly *stabilizing* in both isomers.[31] Perhaps such a distortion is also operative in $[Mo_2O_3Cl_8]^{4-}$ to account for these effects.

A linearly bridged $Mo_2O_3^{4+}$ unit is expected to be diamagnetic, and in fact, all known examples of $Mo_2O_3^{4+}$ complexes, including **2a** and **2b**, are diamagnetic.[14,17] While paramagnetic Mo(V) species are very likely present in 6 M HCl solution, an earlier suggestion[2,35] that a "paramagnetic dimer" is responsible for the strong electronic absorption band at ~450 nm appears to warrant reinterpretation. A recent X-ray absorption study indicated the coexistence of significant fractions of the dinuclear $Mo_2O_4^{2+}$ and $Mo_2O_3^{4+}$ and the mononuclear MoO^{3+} species in 5 to 6 M HCl solutions.[36] This fact alone makes XAFS an ambiguous technique for the extraction of structural information. No information on the determination of phase shifts or multiple scattering was presented. Since second-shell distances are difficult to determine accurately and no authentic $Mo_2O_3^{4+}$ complexes were used as models for the XAFS analysis, the evaluation of a Mo–O–Mo angle of ~107° is open to question. Furthermore, this study does not independently establish the existence of a "paramagnetic μ-oxo dimer" of Mo(V).

Conclusions

Resonance Raman studies have clarified both the electronic and vibrational spectroscopic assignments associated with the linear μ-oxo bridge of the poly(pyrazolyl)borate $Mo_2O_3^{4+}$ dinuclear complexes **2a** and **2b**. The ~457-cm^{-1} band characteristic of $Mo_2O_3^{4+}$ has been definitively assigned as δ(Mo–O–Mo), and ν_s(Mo–O–Mo) has been found at ~380 cm^{-1} for **2a** and **2b**, as well as the 6 M HCl chloro complex $[Mo_2O_3Cl_8]^{4-}$. The intense 462-nm electronic transition, which is responsible for the resonance enhancement of the strong 380-cm^{-1} Raman-active vibration, is assigned as a CT band associated with the unique chromophore arising from the linear μ-oxo-bridged system.[34] Spectral studies reveal that limited hydrolysis of $HB(pz)_3MoOCl_2$ produces the linear μ-oxo species $[HB(pz)_3MoOCl]_2O$ (**2a**) and further hydrolysis converts **2a** to $Mo_2O_4[HB(pz)_3]_2$ (**3**) in a reversible pH-dependent reaction. For the Mo(V)/6 M HCl system, resonance Raman studies indicate that the intense ~450-nm electronic band is associated with a linear or nearly linear μ-oxo $[Mo_2O_3Cl_8]^{4-}$ species that is expected to be diamagnetic.

Acknowledgment. We thank Drs. Gilbert Haight, Stephen A. Koch, Gabriele Backes, and Joann Sanders-Loehr for their helpful comments and discussion during this research and the preparation of the manuscript. This work was supported by a faculty research award from the University of Portland (to S.E.L.) and a grant from the National Institutes of Health, GM 18865 (to T.M.L.). We are grateful for this financial support.

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(35) Hare, C. R.; Bernal, I.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 831.

(36) Yokoi, K.; Matsubayashi, N.; Miyanaga, T.; Watanabe, I.; Ikeda, S.; Murata, K. *Polyhedron* **1988**, *8*, 45.

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

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Received August 22, 1989

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 by 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. These 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 (SI) mass spectrometry.[7]

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(1) Bruce, M. I.; Liddell, M. J. *Appl. Organomet. Chem.* **1987**, *1*, 191.

(2) (a) Thomas, B. J.; Mitchell, J. F.; Theopold, K.-H.; Leary, J. A. *J. Organomet. Chem.* **1988**, *348*, 333. (b) Divisia-Blohorn, B.; Kyriakakou, G.; Ulrich, J. *Org. Mass Spectrom.* **1985**, *20*, 463. (c) Miller, J. M.; Balasanmugam, K.; Nye, J.; Deacon, G. B.; Thomas, N. C. *Inorg. Chem.* **1987**, *26*, 560. (d) Cohen, A. I.; Glavan, K. A.; Kronauge, J. F. *Biomed. Mass Spectrom.* **1983**, *10*, 287. (e) Unger, S. E. *Anal. Chem.* **1984**, *56*, 393. (f) Unger, S. E.; McCormick, T. J.; Treher, E. N.; Nunn, A. D. *Anal. Chem.* **1987**, *59*, 1145. (g) Barber, M.; Bordoll, R. S.; Sedgwick, R. D.; Tyler, A. N. *Nature (London)* **1981**, *293*, 270.

(3) Forest, E.; Marchon, J.-C.; Wilkins, C. L.; Yang, L.-C. *Org. Mass Spectrom.* **1989**, *24*, 197.

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 1:1000 with an 8-kV accelerating potential, and data were accumulated at a scan speed of 10 s/decade for the low-resolution acquisition. High-resolution measurements were obtained at a 1:10000 resolution, and data were acquired with polyethylene glycol as an internal standard. Samples (1–2 μL) of $Rh(PPh_3)_2(CO)Y$/sulfolane or $Rh(PPh_3)_2(CO)Y$/*m*-nitrobenzyl alcohol mixtures were loaded onto stainless steel probe tips. Single-scan data were collected for all $Rh(PPh_3)_2(CO)Y$.

Laser-Desorption Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry. Laser-desorption experiments were performed on 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-T superconducting magnet. The ions were excited by the standard frequency chirp excitation method, and 16K time-domain points were aquired during broad-band detection (medium-resolution spectra). High-resolution spectra of the molecular-ion region were collected by 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 J/pulse. The laser beam had a rectangular cross section of 2 × 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 micropipet. (The solutions were 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 (2–5) × 10^{-8} Torr. Detection of the ions occurred after a 1-s 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.

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

elemental compn	measd mass, mu	theoret mass, mu	diff, 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 mas units; mmu for millimass units

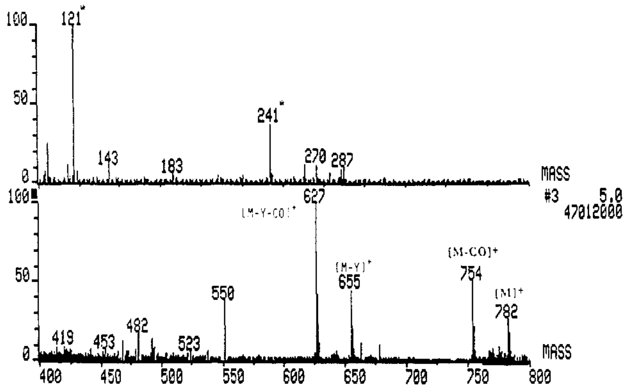

Figure 1. FAB positive-ion spectrum of $Rh(PPh_3)_2(CO)I$.

The LDFTICR negative-ion spectra were evaluated for the presence of signals corresponding to monoanions of formula $Rh_w(PPh_3)_x(CO)_yY_z^-$ by 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 $RhL_2(CO)Y$ 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.

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(4) Watson, C. H.; Baykut, G.; Eyler, J. R. *Anal. Chem.* **1987**, *59*, 1113.

(5) LD and a variety of other FTICR coordination chemistry studies have been reviewed: Sharpe, P.; Richardson, D. E. *Coord. Chem. Rev.* **1989**, *93*, 59.

(6) (a) Wilson, B. W.; Costello, C. E.; Biemann, K.; Orvig, C.; Davison, A.; Jones, A. G. *Anal. Lett.* **1979**, *12*, 303. (b) Farr, J. L.; Abrams, M. J.; Costello, C. E.; Davison, A.; Lippard, S. J.; Jones, A. G. *Organometallics* **1985**, *4*, 139. (c) Jones, A. G.; Davison, A.; LaTegoia, M. R.; Brodack, J. W.; Orvig, C.; Sohn, M.; Toothaker, A. K.; Lock, C. J. L.; Franklin, K. J.; Costello, C. E.; Carr, S. A.; Biemann, K.; Kaplan, M. L. *J. Nucl. Med.* **1982**, *23*, 801. (d) Unger, S. E. *Anal. Chem.* **1985**, *57*, 776.

(7) Tanaka, M.; Nagai, T.; Miki, E. *Inorg. Chem.* **1989**, *28*, 1704.

(8) Araghizadeh, F.; Branan, D. M.; Hoffman, N. W.; Jones, J. H.; McElroy, E. A.; Miller, N. C.; Ramage, D. L.; Salazar, A. B.; Young, S. H. *Inorg. Chem.* **1988**, *27*, 3752.

(9) Branan, D. M.; Hoffman, N. W.; McElroy, A. E.; Prokopuk, N. C.; Ramage, D. L.; Robbins, M. J.; Salazar, A. B.; Hill, W. E.; Webb, T. R. Submitted for publication in *Inorg. Chem.*

(10) Watson, C. H.; Baykut, G.; Mowafy, Z.; Katritzky, A. R.; Eyler, J. R. *Anal. Instrum.* (*N.Y.*) **1988**, *17*, 155.

(11) Such a process, sometimes called atom-transfer redox, is not uncommon for coordinated PPh_3: Horn, R. W.; Weissberger, E.; Collman, J. P. *Inorg. Chem.* **1970**, *9*, 2367.

(12) In the latter, intensities of $[RhL_2(CO)(sulfolane)]^+$ relative to RhL_2CO^+ were dependent upon their contact times with sulfolane prior to data collection, a phenomenon we cannot readily rationalize, given the rapidity with which these Rh(I) systems undergo ligand substitution reactions.[13]

(13) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1958; pp 420–1.

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 (3)
$[M - PPh_3 - Y]^+$/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 nine species displaying signal). [b] P is mass of molecular ion M^+. [c] x = 2–4.

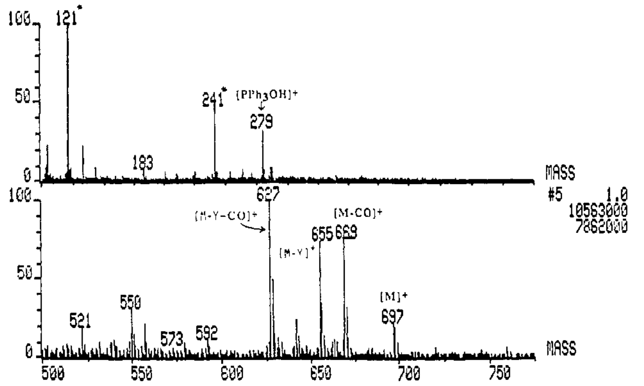

Figure 2. FAB positive-ion spectrum of $Rh(PPh_3)_2(CO)NCO$.

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 spectroscopy of organometallic and inorganic compounds,[2c] the latter matrix gave no molecular-ion information for seven of the nine $RhL_2(CO)Y$ compounds 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 analogues 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 *m/z* 697 for $[M]^+$; a similar pattern was noted in the $RhL_2(CO)NCS$ spectrum. Both the protonated molecular ion and the radical cation are often observed when iridium complexes are analyzed,[17] 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 Brønsted basicity of the respective group 16 atoms.

Unlike the positive-ion spectra, negative-ion FAB mass spectra 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 analogues. 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 case of 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, assisted 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 more strongly bound acetate ligand fragmented to a minor degree via oxygen atom transfer to rhodium.

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 $Rh_3(CO)_3Y^-$

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(14) Collman, J. P.; Garner, J. M.; Woo, L. K.; DeFur, P.; Leary, J. A. Unpublished results.

(15) Busch, K. L.; Hsu, B.-H.; Wood, K. V.; Cooks, R. G.; Schwarz, C. G.; Katritzky, A. R. *J. Org. Chem.* **1984**, *49*, 764. Sulfolane-solvated pyrilium cations (one or two sulfolanes per pyrilium) were observed along with sulfolane-free pyrilium cations in FAB mass spectra of pyrilium salts.

(16) Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141.

(17) Supplementary material for: Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719.

(18) A thorough study of the effect of sample preparation technique has been published for laser-desorption time-of-flight mass spectroscopy: Wilk, Z. A.; Viswanadham, S. K.; Sharkey, A. G.; Hercules, D. M. *Anal. Chem.* **1988**, *60*, 2338.

(19) The presence of very low levels of potassium within the FTICR often results in the appearance of pseudomolecular ions such as those described here.[4,5]

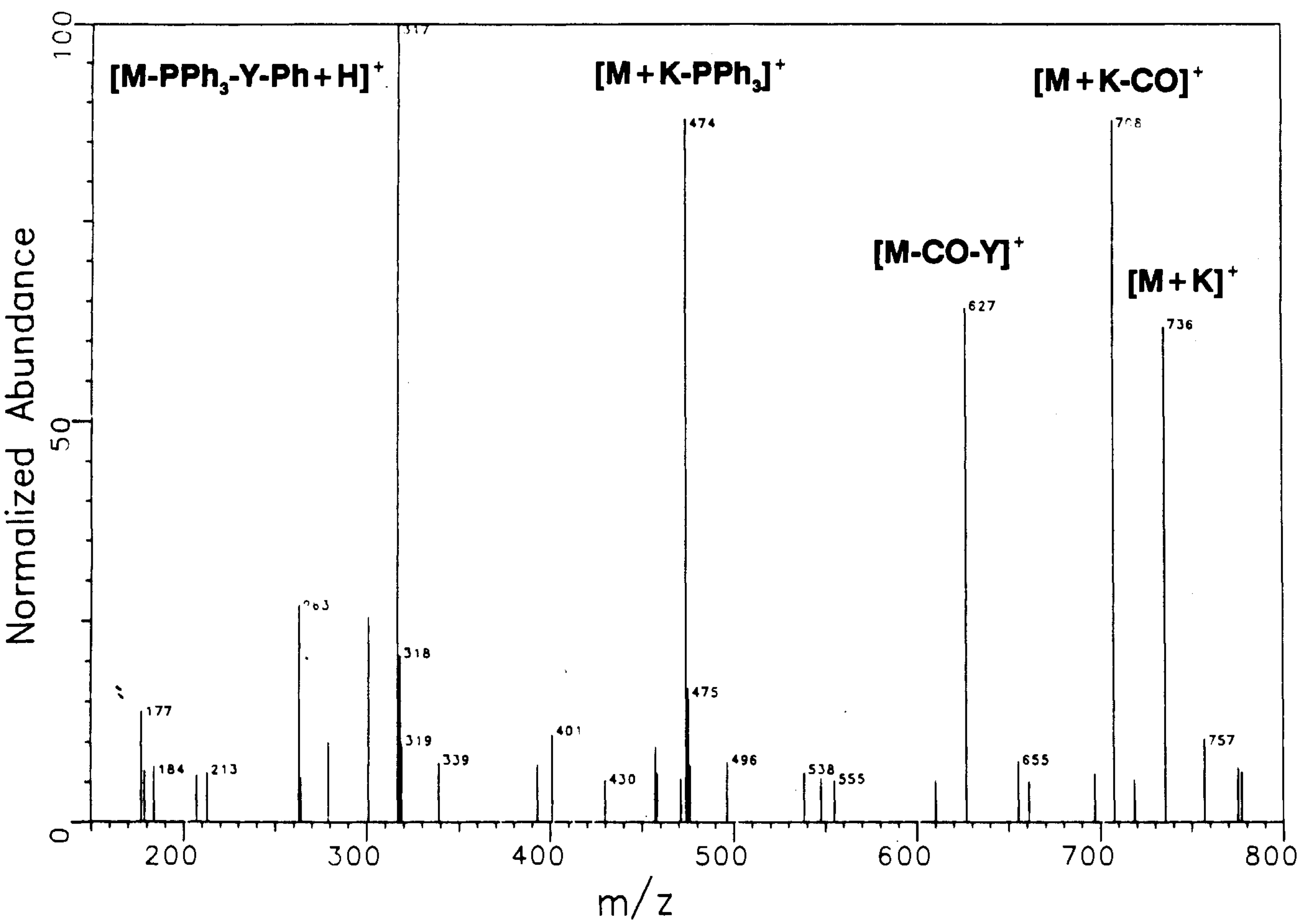

Figure 3. LDFTICR positive-ion spectrum of $Rh(PPh_3)_2(CO)NCO$.

(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 4). 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-MS) 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 transition metals. K^+ might also be expected to form adducts with the complexes that 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 $RhL_2(CO)Y^-$, 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

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(20) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(21) (a) Abatjoglou, A. G.; Billig, E.; Bryant, D. R. *Organometallics* **1984**, *3*, 932. (b) Garrou, P. *Chem. Rev.* **1985**, *85*, 171.

(22) Numerous examples of coordination of Lewis acids to halide and pseudohalide ligands of low-valent coordination compounds are known: (a) Scott, R. N.; Shriver, D. F.; Vaska, L. *J. Am. Chem. Soc.* **1968**, *90*, 1079. (b) Pankowski, M.; Bigorgne, M.; Chauvin, Y. *J. Organomet. Chem.* **1976**, *110*, 338. (c) Pankowski, M.; Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1972**, *35*, 155. (d) Kristoff, J. S.; Shriver, D. F. *Inorg. Chem.* **1973**, *12*, 1788.

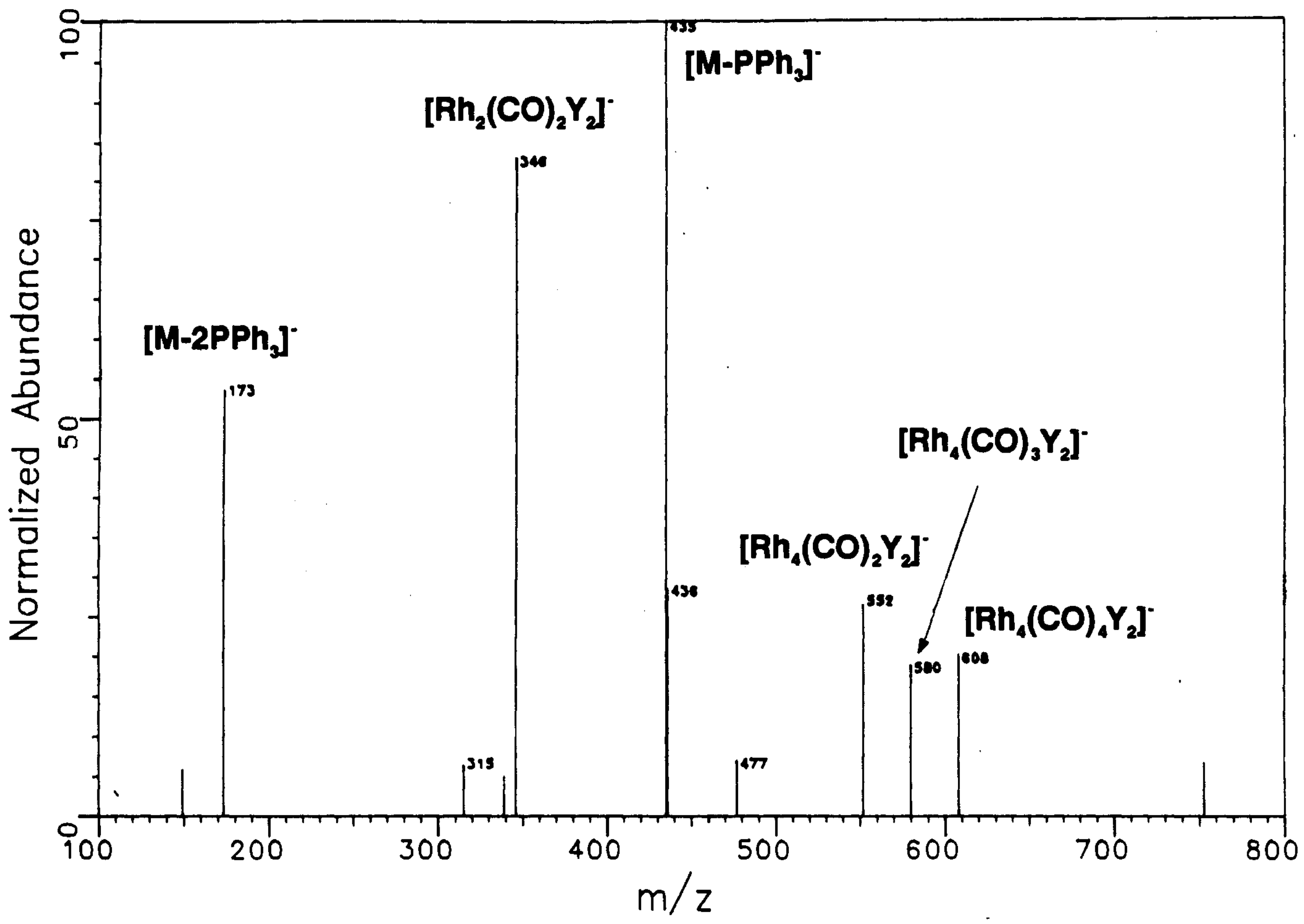

Figure 4. LDFTICR negative-ion spectrum of $Rh(PPh_3)_2(CO)NCO$.

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 liquid SI provided similarly useful desorption ionization methods for mass spectra of pyrilium ions.[15] (LDFTICR spectroscopy 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.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (N.W.H.), the Office of Naval Research and the National Science Foundation (CHE-8700765) (J.R.E.), and the College of Chemistry at the University of California at Berkeley for startup funds (J.A.L.) for support of this research.

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(23) Visi-Orosz, A.; Palyi, G.; Marko, L. *J. Organomet. Chem.* **1973**, *57*, 379 and references therein.

(24) Shomo, R. E.; Marshall, A. G.; Weisenberger, C. R. *Anal. Chem.* **1985**, *57*, 2940.