Fourier Transform Mass Spectrometry of Several Organometallic Complexes: Laser Desorption versus Electron Impact Ionization

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This study compares laser desorption (LD) and electron impact (EI) ionization Fourier transform mass spectrometry (FTMS) for the characterization of the $Ph_2SbOSbPh_2$-bridged nickel dicarbonyl dimer $Ni_2(CO)_4(\mu_2\text{-}Ph_2SbOSbPh_2)_2$ (1), the metal (pentamethylcyclopentadienyl)cyclopentaphosphido sandwich complex $Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_5)$ (2), and two diphosphido-bridged metal pentamethylcyclopentadienyl dimers, $Fe_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}P_2)_2$ (3) and $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}P_2)_2$ (4). Results presented herein strikingly illustrate that LD/FTMS (in contrast to EI/FTMS) can furnish valuable spectral data for organometallic compounds that have negligible vapor pressure and are thermally unstable. It is further shown that both positive- and negative-ion mass spectra often yield complementary information and that MS/MS spectra obtained by collision-activated dissociation (CAD) of the molecular ion may greatly aid in the spectral analysis. Although EI/FT mass spectra of the low-volatility 1 gave no useful information, LD/FT mass spectra provided proof of the compound's composition, which had been tentatively formulated from a prior X-ray crystallographic investigation. In the case of the relatively volatile 2, both EI and LD spectra exhibited the molecular ion peak as well as similar fragment ion patterns. Although the entire structure of the cobalt dimer (4) was elucidated from an X-ray structural determination, the number and the connectivities of the bridging phosphorus atoms in the corresponding iron dimer (3) could not be unambiguously established because of a crystal disorder. While room-temperature EI/FT mass spectra could not be obtained for either 3 or 4, LD/FT mass spectra revealed molecular ion peaks and fragment ion patterns entirely consistent with each dimer possessing two bridging P_2 ligands.

Introduction

The method of laser desorption Fourier transform mass spectrometry (LD/FTMS), alternatively denoted as laser desorption Fourier transform ion cyclotron resonance (LD/FT/ICR) mass spectrometry,[1] has now been used extensively for the characterization of compounds of low volatility. Since the inital report[2] describing the pulsed desorption technique with a CO_2 laser, many classes of compounds including polymers,[3-6] peptides,[3,7-9] oligosaccharides,[10-14] drugs,[15,16] and a variety of other biomolecules and organic compounds[17,18] have been investigated by use of a LD ionization source. Recent reviews[19-23] give a more complete account of the range of applications of LD/FTMS. Direct comparative analyses of LD/FT and fast-atom bombardment (FAB) mass spectra of several low-volatility drugs,[15,16] of a series of polymers,[5] and of alkyltriphenylphosphonium salts[24] revealed, in general, that significantly less ion fragmentation occurred and high-mass and pseudomolecular ions were much more readily detected via the LD ionization source relative to the FAB ionization source.

Despite the successes obtained with LD/FTMS in the analytical examinations of organic and bioorganic compounds, relatively little effort appears to have been made to explore the utility of this particular method for the analysis of low-volatility inorganic and organometallic

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complexes.[25] Wilkins and co-workers[3,26–29] have obtained LD/FTMS spectra for several metalloporphyrins, including chlorophyll a and b. Hein and Cody[17] and Marshall and co-workers[15,18,19,30] have reported laser desorption mass spectra of a few metal complexes, and the latter group[31] has also carried out a comprehensive investigation of the formation and reactivities of gas-phase triosmium carbonyl oligomers from $H_2Os_3(CO)_{10}$ via EI/FTMS.

This paper emphasizes the tremendous potential of LD/FTMS for the characterization of low-volatility inorganic–organometallic complexes by making a direct comparison between laser desorption (LD) and electron impact (EI) spectrometry for four organometallics that possess markedly different room-temperature vapor pressures. Mass spectral measurements of the particular compounds clearly point to the inherent limitation of EI ionization for low-volatility compounds that are thermally labile. Of special interest and importance is that the LD/FT mass spectral analyses provided vital information that enabled the stoichiometries to be ascertained for the antimony–nickel complex (**1**) and the iron dimer (**3**). In other words, the mass spectral analyses reported herein were performed to solve "real-world" problems, viz., to establish the identities of two new organoantimony and organoiron complexes.

Experimental Section

Mass spectra were obtained with a Nicolet FTMS-2000 Fourier transform mass spectrometer equipped with a 3.0-T superconducting magnet, a Nicolet laser desorption interface, and a Tachisto 215G pulsed infrared CO_2 laser operated as an aperture-controlled stable resonator. All sample preparations of air- and/or moisture-sensitive compounds were carried out under nitrogen in a glovebag. A few tens to hundreds of micrograms of each sample were dissolved in a suitable solvent, usually dichloromethane, and the solution was allowed to evaporate on the stainless steel tip of the direct insertion probe of the mass spectrometer. The sample could also be deposited directly onto the probe tip if sensitivity to solvents and/or solvent impurities were of concern. The thickness of the sample layer appears not to be critical, although an excessively thick sample layer may have detrimental effects on spectral quality due to a high-pressure burst accompanying a given laser/sample interaction. An ultrathin sample layer tends to result in excessive ion fragmentation along with suppression or even loss of the molecular ion signal.

The laser was focused onto the probe tip to give an estimated spot size of ca. 100 μm with an estimated output energy of approximately 0.01–0.05 J/pulse. The probe was rotated a few degrees after each laser shot so that the laser always struck a fresh spot on the sample layer. A time delay of 0.5–5 s between the laser pulse and ion detection was used to reduce any detrimental effects on spectral quality produced by the pressure burst accompanying laser desorption. During each delay, the ions produced in the desorption process were stored in the cell of the FTMS. Room-temperature EI spectra of samples obtained by the same preparation techniques were acquired on the same instrument. The background pressure in the mass spectrometer was well below 10^{-8} Torr for all measurements.

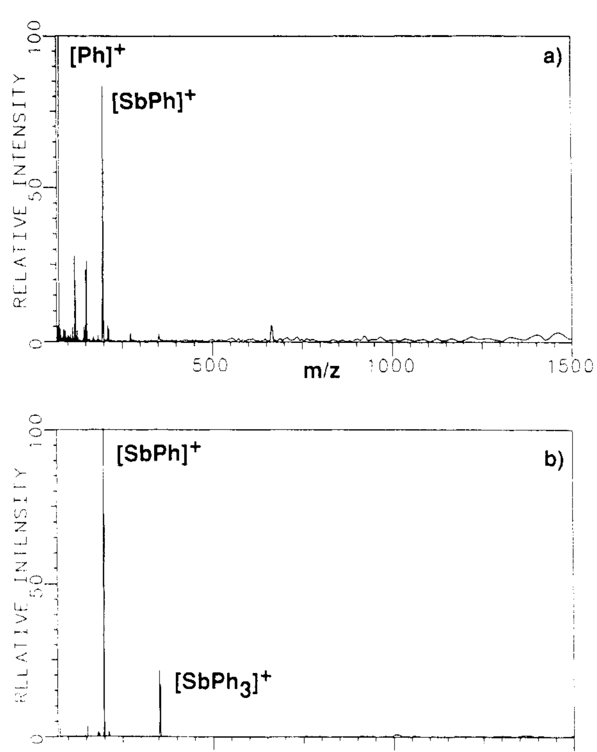

Figure 1. $Ni_2(CO)_4(\mu_2\text{-}Ph_2SbOSbPh_2)$ (1): (a) 70-eV positive-ion EI/FT mass spectrum at room temperature; (b) 10-eV positive-ion EI/FT mass spectrum obtained at room temperature.

Both positive- and negative-ion mass spectra were obtained for each sample. Normally, 32–64K data-point transients were collected in the broad-band mode,[32] for which the high-frequency cutoff varied from 250 to 1000 kHz. Accurate mass determinations and isotope distribution patterns aided in the spectral analysis. Mass calibration was based on a LD/FTMS spectrum of KBr-doped poly(ethylene glycol) (PEG-600) with an average molecular weight of 600.

Results and Discussion

$Ni_2(CO)_4(\mu_2\text{-}Ph_2SbOSbPh_2)$ (1). This nickel–antimony complex was obtained as a side product from the room-temperature reaction of the $[Ni_6(CO)_{12}]^{2-}$ dianion[33] with Ph_2SbCl in THF solution, from which the $[Ni_{12}(SbPh)_2(CO)_{18}]^{2-}$ dianion containing a noncentered icosahedral $Ni_{10}Sb_2$ core was isolated as the main product.[34] An X-ray diffraction study[34] of 1 revealed a molecular geometry (structure I) of crystallographic C_i-$\bar{1}$ symmetry consisting

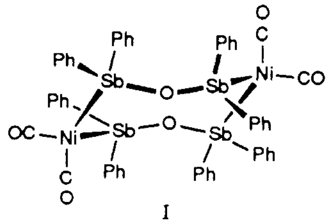

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Table I. Assignment of Major Peaks in the Positive- and Negative-Ion LD/FTMS Spectra of $Ni_2(CO)_4(\mu_2\text{-}Ph_2SbOSbPh_2)_2$ Complex

m/z	assignt
	Positive Ions
214.5/215.5	$SbPh_4^{2+}$
275/277	$SbPh_2^+$
313.5/314.5/315.5	$Sb_2Ph_5^{2+}$
352/354	$SbPh_3^+$
429/431	$SbPh_4^+$
473/475/477	$Sb_2Ph_3^+$
550/552/554	$Sb_2Ph_4^+$
~568[a]	$(Sb_2Ph_4O - H)^+$
627/629/631	$Sb_2Ph_5^+$
643/645/647	$Sb_2Ph_5O^+$
~673[a]	$Sb_3Ph_4^+$
~688[a]	$(Sb_3Ph_4O - H)^+$
~749[a]	$(Sb_3Ph_5 - H)^+$
~765[a]	$(Sb_3Ph_5O - H)^+$ and $(Sb_3Ph_5O)^+$
~827[a]	$Sb_3Ph_6^+$
~843[a]	$Sb_3Ph_6O^+$
	Negative Ions
291/293	$SbPh_2O^-$
377/379/381	$SbPh_2ONi(CO)^-$
438/440/442	$SbPh_3Ni(CO)^-$

[a] ~*xxx* designates that the cluster center or the most intense peak of the isotopic mass clusters was at *xxx*.

of two $Ni(CO)_2$ moieties connected by Ni–Sb bonds with two bridging $Ph_2SbOSbPh_2$ ligands. The electron-density peak connecting the two antimony atoms was initially assigned as an oxygen atom from structural–electronic considerations. Strong crystallographic evidence for this assignment was provided from anisotropic least-squares refinements, which gave a physically meaningful equivalent isotropic thermal parameter only when this ring atom was designated as an oxygen atom. Nevertheless, the purpose of the mass spectral analysis was to establish independently and unequivocally the existence of an antimony-connecting oxygen atom within each of the two centrosymmetrically related $Ph_2SbOSbPh_2$ ligands.

The slight volatility of this compound in the high-vacuum system of the FTMS-2000 spectrometer allowed the acquisition of EI spectra with a high signal-to-noise ratio. Figure 1, parts a and b, displays the 70- and 10-eV positive-ion EI/FT mass spectra, respectively. Unfortunately, the information obtained from these spectra was of limited value because only low-mass ion peaks were detected. Prominent ion peaks observed in the 70-eV positive-ion EI spectrum correspond to $[SbPh]^+$ at *m/z* 198/200, Sb^+ at *m/z* 121/123, and Ph^+ at *m/z* 77. No ion peaks of a higher mass were observed. Positive-ion spectra at 20, 10, and 7 eV show an additional ion peak at *m/z* 352/354 identified as $[SbPh_3]^+$. Both negative-ion EI spectra and spectra obtained after reaction delay times between ion formation and detection to facilitate self-chemical ionization (self-CI) did not provide any additional information.

The major peaks and their assignments obtained in the positive- and negative-ion LD/FTMS spectra of 1 are given in Table I. Molecular or pseudomolecular ions that would yield the formula weight were not detected. However, the observed ion fragment peaks are completely compatible with the existence of an oxygen atom within each bridging $Ph_2SbOSbPh_2$ ligand. A positive-ion LD/FT spectrum is shown in Figure 2a, and an expansion of its high-mass region is displayed in Figure 2b. As can be seen in Table I, several monooxygen–antimony–phenyl ion fragments were detected in the positive-ion LD/FT mass spectrum. A negative-ion LD/FT mass spectrum of 1 also gave ion peaks (Table I) corresponding to monooxygen–antimony–phenyl ion fragments. Most important was the observation of the $[SbPh_2O]^-$ ion at *m/z* 291/293 and the $[SbPh_2ONi(CO)]^-$ ion at *m/z* 377/379/381. These ion fragments cleave naturally from the molecule without rearrangements and thereby provide convincing evidence for the linkage of the two Ph_2Sb moieties within a ligand by an oxygen atom.

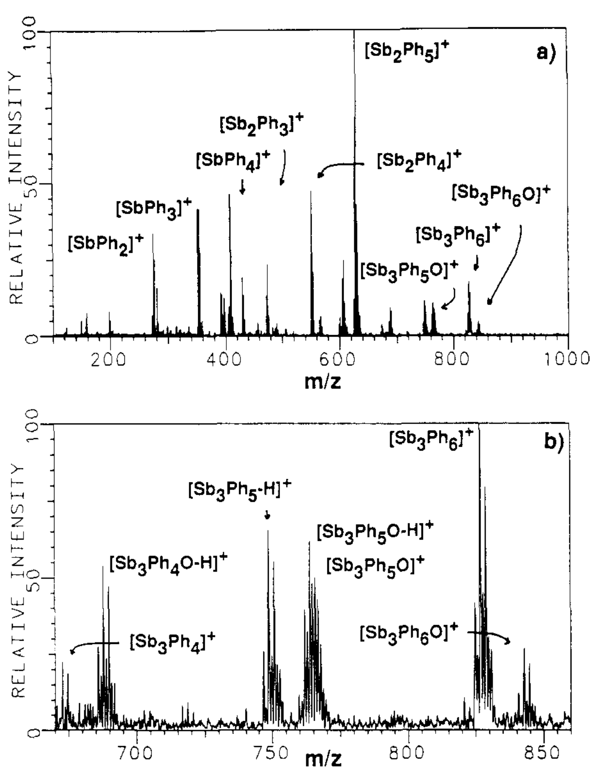

Figure 2. $Ni_2(CO)_4(\mu_2\text{-}Ph_2SbOSbPh_2)$ (1): (a) positive-ion LD/FT mass spectrum; (b) expansion of its high-mass region.

The possibility that the oxygen-containing ions may be formed via ion/molecule reactions during the delay between the laser pulse and ion detection was a concern in determining the composition of 1. If such reactions were to occur, the oxygen could come from two possible sources: either from oxygen contamination within the background pressure of the instrument or from the carbonyl groups in the sample. The latter possibility is highly unlikely in view of the stability of the carbonyl entity, as demonstrated experimentally from mass spectral analyses of many metal carbonyl clusters.[25,31] The partial pressure of oxygen and oxygen-containing molecules is only a small fraction of the total background pressure of 10^{-8} Torr found in the instrument, and the ions produced in the EI spectra did not react to produce oxygen-containing ions, even with delay times of several seconds. Thus, it is assumed that the significant ion/molecule reactions occur only between laser desorbed ions and laser desorbed neutrals. Further support for these conclusions is the fact that the $[SbPh_2O]^-$ ion, detected in negative-ion LD/FT mass spectra, at *m/z* 291/293 was observed in high abundance at both the shortest and longest delay times; it follows that this ion must be formed predominantly in the desorption process rather than in subsequent ion/molecule reactions during the resulting pressure burst.

This compound (1) is the first example of a metal dimer formed from bis(diphenylstibine) oxide, which itself exists as a molecular compound.[35] The origin of this bridging ligand can be readily attributed to the partial hydrolysis

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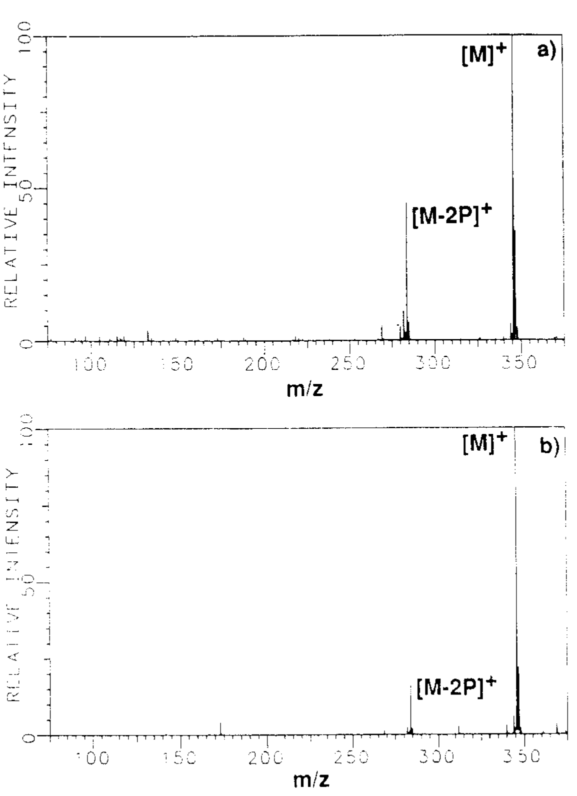


Figure 3. $Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_5)$ (2): (a) 70-eV positive-ion EI/FT mass spectrum at room temperature; (b) positive-ion LD/FT mass spectrum.

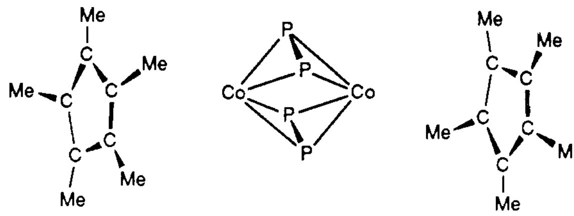
of the Ph_2SbCl reagent with adventitious water (presumably from "wet" solvent). This collective information from both positive- and negative-ion LD/FTMS illustrates that even in cases where EI spectra are obtainable, LD/FT mass spectra may still be of much greater usefulness.

$Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_5)$ (2). This molecular sandwich compound, which is an electronic and structural analogue of decamethylferrocene, was analyzed in order to discern differences between EI/FT and LD/FT mass spectra. Its synthesis by the refluxing of $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2]_2$ with P_4 in xylene was recently reported by Scherer and Bruck,[36] who characterized it from multinuclear NMR spectra and from an EI (70 eV) mass spectrum. This green compound was independently isolated in our laboratory from the photochemical reaction of $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2]_2$ with P_4 in toluene.[37] Chromatographic separation on silica gel of a hexane extract of the resultant solid mixture obtained by removal of toluene from the photolyzed brown solution gave (in a typical reaction) a green band (2), which was crystallized in a 10% yield.[37]

Both positive- and negative-ion EI/FT and LD/FT mass spectra of 2 gave similar results, which were also analogous to those reported by Scherer and Bruck.[36] Positive-ion EI/FT and LD/FT mass spectra for this compound are shown in Figure 3, parts a and b, respectively. The most intense peak corresponds to the molecular ion, $[M]^+$, of 2, while the second strongest peak is readily assigned to the $[M - 2P]^+$ ion. It is apparent that this mononuclear iron sandwich complex is sufficiently volatile as well as thermally stable such that its mass spectra are essentially independent of the mode of ionization.

$Fe_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}P_2)_2$ (3) and $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}P_2)_2$ (4). The iron dimer was obtained in our laboratory as a yellow-brown solid from the above-mentioned photochemical reaction by extraction of the resultant solid mixture with a hexane/toluene solution (1:1) followed by crystallization (4% yield).[37] The cobalt dimer was similarly synthesized in our laboratory from the photolysis of $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ and P_4 in toluene. The toluene was removed from the resultant reddish brown solution, and the residue chromatographed on a silica gel column. Elution with hexane gave unreacted $Co(\eta^5\text{-}C_5Me_5)(CO)_2$ followed by the bluish purple 4 (7% yield after crystallization) and $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$.[37] Thermal chemical preparations and structural characterizations of the tetramethylethylcyclopentadienyl cobalt and rhodium derivatives of 4 have recently been communicated by Scherer and co-workers.[38]

The determined molecular configuration (structure II) of the cobalt dimer (4), which contains two 14-electron $Co(\eta^5\text{-}C_5Me_5)$ fragments linked by two four-electron-donating η^2-coordinated P_2 ligands at a nonbonding Co···Co distance of 3.100 (2) Å, was unambiguously determined from our X-ray crystallographic study.[37] Its molecular configuration is analogous to those of the electronically equivalent $Rh_2(\eta^5\text{-}C_5Me_4Et)_2(\mu_2\text{-}P_2)_2$ molecule and one of the two crystallographically independent $Co_2(\eta^5\text{-}C_5Me_4Et)_2(\mu_2\text{-}P_4)$ molecules reported by Scherer et al.[38-40]



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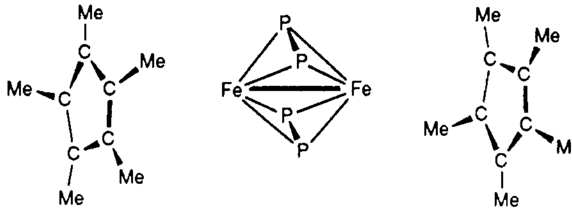
The molecular architecture (structure III) of the corresponding 34-electron iron dimer (3) was found from an X-ray crystallographic study[37] to be closely related to that (structure II) of the 36-electron cobalt dimer (4) except for a significantly shorter metal–metal distance of 2.59 (1) Å characteristic of an Fe–Fe single bond (which also allows each iron atom to attain a "closed shell" electronic configuration). However, a crystallographic disorder of the bridging phosphorus atoms in 3 prevented a definitive determination of the number and bonding modes of the phosphorus atoms. Convincing evidence that the stoichiometry and connectivities of the bridging phosphorus atoms in 3 are identical with those in 4 was provided by



III

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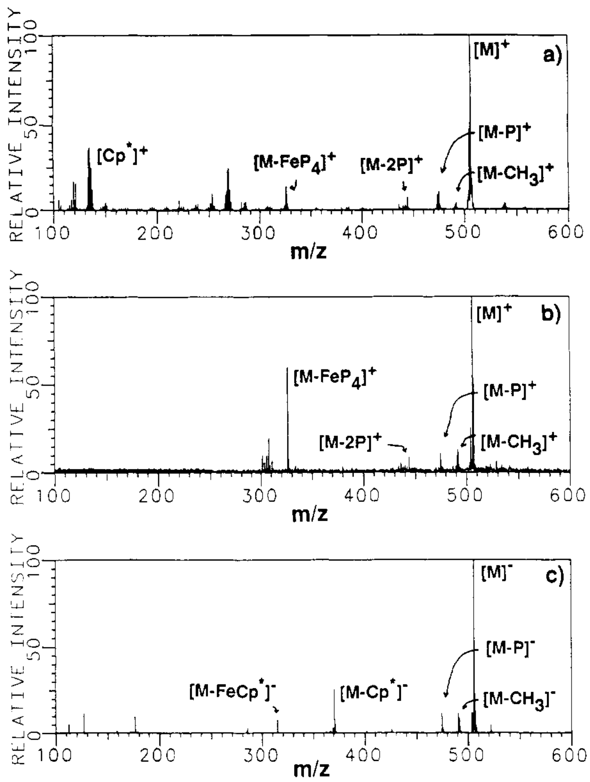

Figure 4. $Fe_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}P_2)_2$ (**3**): (a) positive-ion LD/FT mass spectrum; (b) positive-ion LD/FT-MS/MS spectrum of the collision-activated dissociation (CAD) of the molecular ion, $[M]^+$, obtained after isolation and excitation of $[M]^+$ to 35 eV with Kr as the collision gas; (c) negative-ion LD/FT mass spectrum.

the comparative mass spectral analysis presented below.

The fact that neither positive- nor negative-ion EI/FT mass spectra could be obtained for either **3** or **4** is presumably due to their negligible vapor pressure at room temperature. Positive-ion LD/FT spectra for **3** and **4** are shown in Figures 4a and 5a, respectively. Figure 5b shows an expanded section of the high-mass region of the LD/FT spectrum of the cobalt dimer. The peaks in these spectra are well resolved with high signal-to-noise ratios. An abundant molecular ion signal is observed at *m/z* 506 and 512 for the iron and cobalt dimers, respectively. The detection of these parent ions provided indisputable evidence that four phosphorus atoms are also present in the iron dimer (**3**). The observation that Figure 4a,b reveals a much larger parent ion peak and relatively smaller fragment ion peaks for **3** compared to those for **4** is *not inconsistent* with the existence of direct metal–metal bonding only in the iron dimer. A MS/MS spectrum (Figure 4b), obtained by collison-activated dissociation (CAD)[41] of the molecular ion of the iron dimer, displayed daughter ion peaks analogous to the fragment ion peaks observed in the LD/FT spectrum of the cobalt dimer. The corresponding iron/cobalt fragment ion peaks for the most abundant ions observed in their positive-ion spectra are $[M]^+$ at *m/z* 506/512, $[M - Me]^+$ at *m/z* 491/497, $[M - P]^+$ at *m/z* 475/481, $[M - 2P]^+$ at *m/z* 444/450, and $[M - FeP_4]^+/[M - CoP_4]^+$ at *m/z* 326/329 (where M denotes the neutral parent molecule). A negative-ion LD/FTMS spectrum (Figure 4c) of the iron dimer also contains several informative ion peaks, viz., $[M]^-$ at *m/z* 506, $[M - Me]^-$ at *m/z* 491, $[M - P]^-$ at *m/z* 475, $[M - C_5Me_5]^-$ at *m/z* 371, and $[M - Fe(C_5Me_5)]^-$ at *m/z* 315. The close similarity of these two fragment ion patterns detected in the positive-ion spectra of **3** and **4** is completely consistent with the iron dimer (**3**) being structurally analogous to the crystallographically proven cobalt dimer (**4**), which possesses four bridging phosphorus atoms with connectivities corresponding to two discrete P_2 ligands.

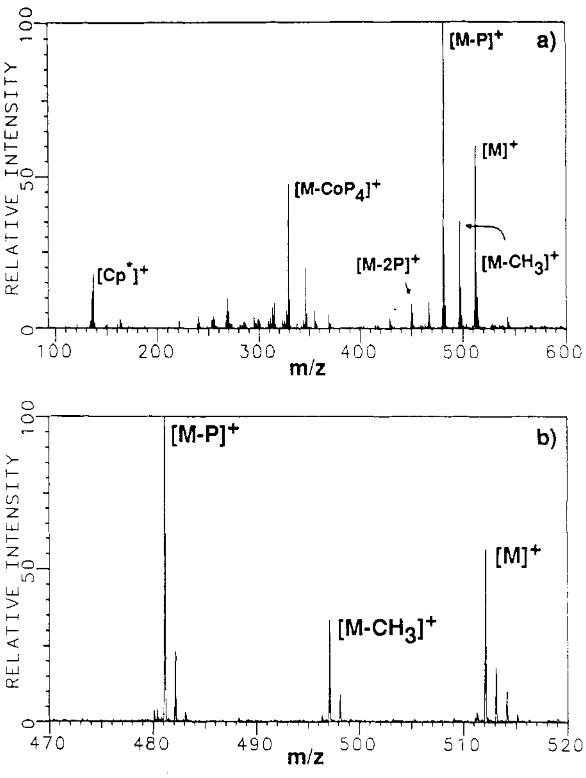

Figure 5. $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}P_2)_2$ (**4**): (a) positive-ion LD/FT mass spectrum; (b) an expansion of its high-mass region.

Conclusions. The examples discussed above illustrate that LD/FTMS can be a powerful tool in mass spectral analyses of low-volatility organometallic complexes, especially those that are thermally unstable. A direct comparative analysis of EI/FT and LD/FT mass spectra of four organometallic complexes with varied room-temperature vapor pressures revealed that laser desorption ionization gave (1) either similar or much superior information for the two compounds for which both EI and LD spectra were observed and (2) highly useful information for the other two compounds for which only LD spectra could be detected.

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[41] Cody, R. B., Jr. *Anal. Chem.* **1988**, *60*, 917, and references therein.