

Fast Atom Bombardment Tandem Mass Spectrometry of Organometallic Palladium Complexes Containing Terdentate Nitrogen Ligands

Kai A. N. Verkerk,^{†,‡} Chris G. de Koster,^{*,§,||} Bertus A. Markies,[‡] Jaap Boersma,[‡] Gerard van Koten,[‡] Wigger Heerma,^{||} and Johan Haverkamp^{||}

Bijvoet Center for Biomolecular Research, Mass Spectrometry, Utrecht University, P.O. Box 80083, 3508 TB Utrecht, The Netherlands, and The Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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Fast atom bombardment and collisional-induced dissociation tandem mass spectrometry were used to analyze 12 cationic organometallic palladium [Pd(L)(R)](OTf) complexes containing three different terdentate nitrogen ligands (L), an organic group (R) attached in the σ bonding mode, and a trifluoromethanesulfonate anion (OTf is CF_3SO_3^-) using *m*-nitrobenzyl alcohol as a matrix. FAB ionization gives abundant Pd(L)(R) cations and some fragment ions. Tandem mass spectrometry of collisionally activated monoisotopic $^{108}\text{Pd(L)(R)}$ cations affords additional information on fragmentation mechanisms and enables discrimination between isomeric complexes. The MS/MS experiments also provided evidence for the occurrence of an abundant gas-phase cyclopalladation reaction of the $^{108}\text{Pd(L)(R)}$ cations by activation of a sp^3 C–H bond according to an oxidative addition/reductive elimination or a multicentered pathway.

Introduction

The unique catalytic properties of many transition-metal complexes have led to an increased interest in the structures of the active species and prompted numerous studies concerning the influences of different ligand environments.^{1,2} In the past mass spectrometric techniques were of a limited value since many coordination complexes and organometallic compounds are prone to thermal decomposition, which hampered a detailed structural study. However, with the development of soft ionization techniques the possibility of analyzing involatile and thermally labile compounds was provided. Where other soft ionization techniques as field desorption (FD)^{3,4} and laser desorption⁵ (LD) have found application in this field, fast atom bombardment mass spectrometry (FAB-MS)^{6,7} has proven throughout the years to be a versatile and sensitive method for the

analysis of organometallics.⁸ With this technique parent ion molecular weight information as well as further structurally informative ions can be obtained. Together with the applicability of FAB mass spectrometry to organometallic compounds, new matrices for the (organometallic) samples were also investigated. In particular *m*-nitrobenzyl alcohol (NBA) gave good results for many compounds and has also successfully been applied in this study.^{8,9}

The recent availability of four sector instruments adds a new dimension to the analysis of organometallic compounds. In tandem mass spectrometry (MS/MS) the ion of interest is selected in the first mass spectrometer (MS-1) at unit resolution. The mass-selected ions collide with an inert gas such as helium in a collision cell located in the field-free region between MS-1 and the second mass spectrometer (MS-2). Upon collision, part of the translation energy of the ion (10 keV) is converted into internal energy. The internal energy acquired is sufficient to induce rapid fragmentations (10^{-13} – 10^{-5} s) of the collisionally activated ions. The product ions are analyzed at unit resolution in the second mass spectrometer.

An interesting advantage of studying reactions in the field-free region of the mass spectrometer by MS/MS techniques is that the selected ions are isolated species. Therefore, mass spectra obtained in such a way reflect the intrinsic properties of isolated reaction systems. The reactions are not affected by extraneous and variable phenomena such as participation of solvent molecules and/or counterions, which are superimposed upon factors determining the activation energy barrier, the stability of reactants, and the reaction products. Only unimolecular reaction product ions which are the result

* To whom correspondence should be addressed.

[†] Present address: Institut für Technische Chemie und Petrochemie der Rhein.-Westf. Technische Hochschule, Worringerweg 1, 52074 Aachen, Germany.

[‡] Debye Institute.

[§] Present address: FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands.

^{||} Bijvoet Center for Biomolecular Research, Mass Spectrometry Group.

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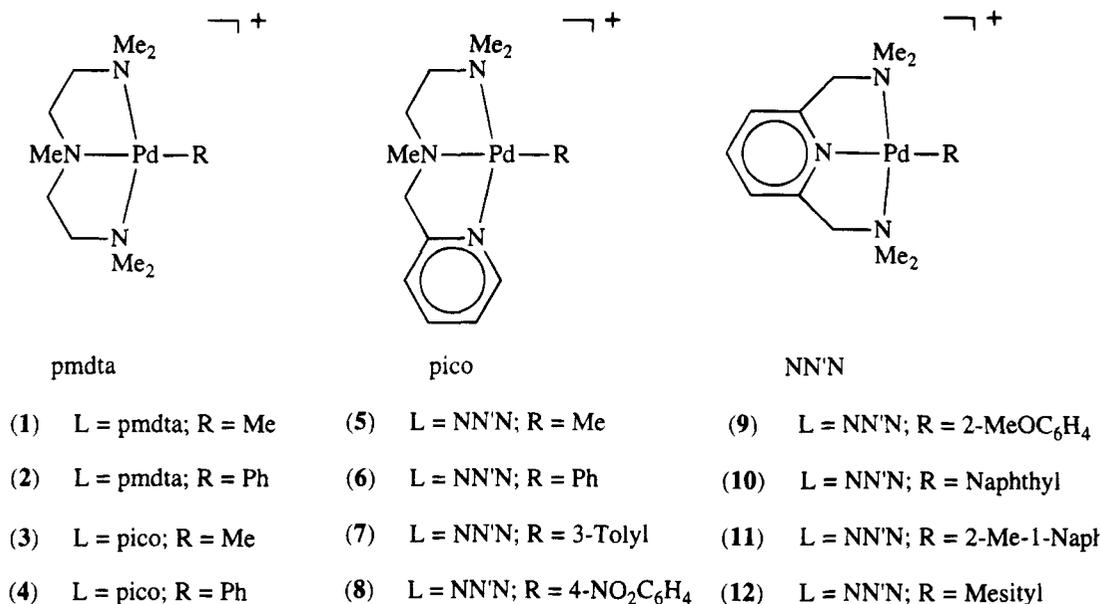


Figure 1. Structures of the complexes $[\text{Pd}(\text{L})(\text{R})]^+\text{OTf}^-$: pmdta = *N,N,N',N',N''*-pentamethyldiethylenetriamine; pico = *N,N,N'*-trimethyl-(2-picoyl)ethylenediamine; NN'N = 2,6-bis[(dimethylamino)methyl]pyridine; OTf = CF_3SO_3^- (trifluoromethanesulfonate); mesityl = 1,3,5-trimethylbenzene.¹⁰

of intramolecular isomerization and/or fragmentation in a solvent-free environment are collected on the detector of MS-2.

In this report the gas-phase ion chemistry of several organometallic palladium(II) complexes under FAB conditions is studied. Our results center around ionic complexes $[\text{Pd}(\text{L})(\text{R})\text{OTf}]^+$ where the cation consists of a neutral terdentate nitrogen ligand (L) coordinated to the dicationic palladium metal center with an anionic organic group (R) attached in the σ bonding mode. A noncoordinating triflate (OTf) is serving as anion.¹⁰ The used ligands (L) and organic groups (R) are depicted in Figure 1 with their adopted numbering. In addition to the structural information obtained by FAB-MS additional collision-induced dissociation MS/MS experiments have been carried out to enable unambiguous identification of the structures. A second subject of research is the applicability of MS/MS techniques as a tool to study the gas-phase chemistry of intramolecular C–H bond activation (cyclometalation) by transition-metal complexes.^{11–16} For this purpose the unimolecular loss of RH from mass-selected $[\text{Pd}(\text{L})(\text{R})]^+$ cations in the field-free region of the mass spectrometer is used as a model reaction.

Experimental Section

Positive FAB mass spectra and collisional-induced dissociation (CID) spectra were obtained with a JEOL JMS-SX102/102A four sector instrument of $B_1E_1-B_2E_2$ geometry (B = magnet, E = electrostatic analyzer). FAB mass spectra were obtained with MS-1. Tandem mass spectra were acquired by selecting the desired precursor ion with MS-1 and colliding

the selected ion at 10 keV translational energy in a collision cell operated at ground potential and located in the third field-free region of the instrument. The resulting fragment ions were determined by linked scanning of MS-2. The CID spectra were recorded at a main beam attenuation of 50% with helium as the collision gas. The resolution was 1000 (m/dm)_{10%} for MS-1 as well as for MS-2. Xenon was used as the FAB gas; the gun was operated at 6 kV and a 5 mA discharge current.

Samples were dissolved in methanol *pa* [Westburg] at a concentration of 0.1 mol·L⁻¹. Aliquots (1 μL) were transferred by syringe and mixed with 1 μL of *m*-nitrobenzyl alcohol (NBA) [Fluka] on the stainless steel FAB probe tip.

The details of the synthesis of the complexes including $[\text{Pd}(\text{NN}'\text{N})(\text{CD}_3)\text{OTf}]^+$ were described elsewhere in combination with the structural confirmation deduced by spectroscopic methods such as ¹H-NMR, ¹³C-NMR, IR, and elemental analysis. Several complexes were subjected to a crystallographic study.¹⁰

Results and Discussion

FAB Mass Spectra. The positive FAB mass spectra of the methyl compounds (R = CH₃) **1**, **3** and **5**¹⁰ are presented in Figure 2a–c, respectively. Partial positive ion FAB mass spectra of these and the other compounds are given in Table 1. $[\text{Pd}(\text{L})(\text{R})]^+$ cations form a cluster of very abundant peaks in the FAB mass spectra of all compounds. In all cases there is a good similarity between the calculated and observed isotope distribution (data not shown). Formation of $[\text{Pd}(\text{L})(\text{R})\text{OTf}]^+$ ions was not observed.

The fragmentation pattern was dominated by $[\text{Pd}(\text{L})(\text{R})-\text{RH}]^+$ cations yielding peaks at m/z 278 (¹⁰⁶Pd) for the pmdta complexes (**1**, **2**), whereas for the isomeric pico (**3**, **4**) and NN'N complexes (**5**–**12**) signals at m/z 300 (¹⁰⁶Pd) were found. The abundant loss of RH is the result of a cyclometalation reaction^{11–15} of the $[\text{Pd}(\text{L})(\text{R})]^+$ cation involving metal–carbon σ -bond formation by the ligand with concomitant loss of RH. The occurrence of cyclometalation reactions has also been observed for other FAB-ionized organometallics in the ion source of the mass spectrometer. For example,

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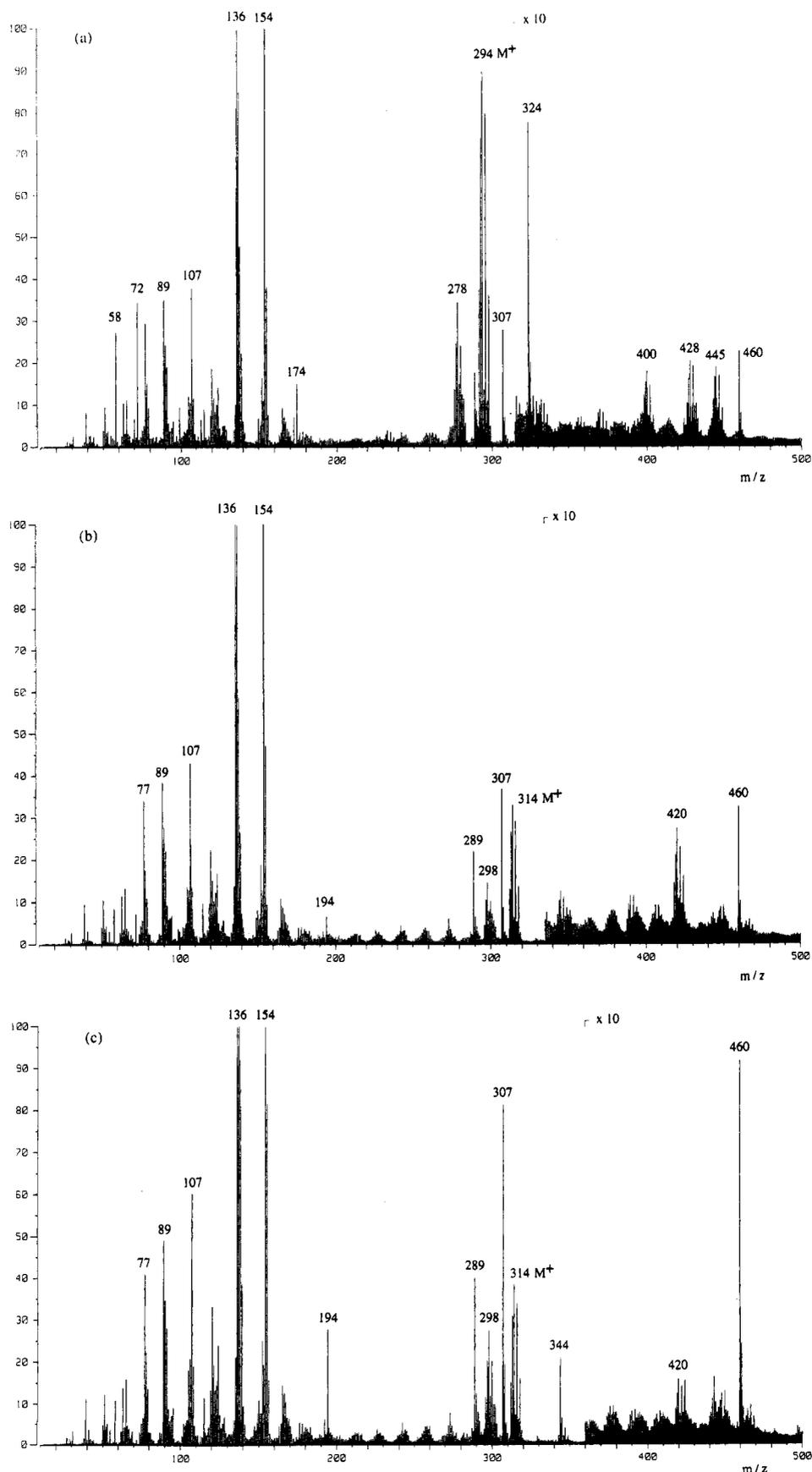


Figure 2. Positive ion FAB mass spectra of (a) Pd(pmdeta)(Me)OTf, (b) Pd(pico)(Me)OTf, and (c) Pd(NN'N)(Me)OTf.

Cerny et al. studied the fragmentations of bis(2,2'-bipyridyl) complexes of Ru(II) and Os(II) containing η^2 -alkene, carbonyl, and alkyl ligands by FAB-MS.¹⁷ They observed $[M(\text{bpy})_2 - \text{H}]^+$ ($M = \text{Os}, \text{Ru}$) fragments which

were ascribed to the formation of cyclometalated ions, in which one of the bipyridine ligands is bound to the metal center through a nitrogen and a carbon atom. So far similar ions have been reported to be present in the

Table 1. Abundant Ions in the FAB Mass Spectra of Complexes 1–12 (Relative Abundances in Parentheses)

| cation | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|--|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| [M + NBA] ⁺ | | 509 (7) | | 529 (10) | | 529 (14) | 543 (9) | 574 (19) | 559 (12) | | | 571 (13) |
| [M + NBA - H ₂] ⁺ | 445 (21) | | 465 (20) | | 465 (29) | | | | | | | |
| [M + Pd - H ₂] ⁺ | 400 (18) | | 420 (79) | 482 (21) | 420 (43) | 482 (12) | 496 (9) | 527 (12) | 512 (9) | | | |
| [M] ⁺ | 294 (1000) | 356 (1000) | 314 (1000) | 376 (1000) | 314 (1000) | 376 (1000) | 390 (1000) | 421 (1000) | 406 (1000) | 426 (1000) | 440 (1000) | 418 (1000) |
| [M - RH] ⁺ | 278 (302) | 278 (197) | 298 (351) | 298 (217) | 298 (678) | 298 (578) | 298 (651) | 298 (551) | 298 (581) | 298 (589) | 298 (546) | 298 (1076) |
| [L + H] ⁺ | 174 (185) | | 194 (219) | | | 194 (232) | 194 (172) | 194 (201) | | | | |
| [L - H] ⁺ | 172 (89) | | | | | 192 (142) | 192 (126) | 192 (150) | 192 (123) | 192 (243) | 192 (297) | 192 (203) |
| [M - RH + NBA - 3H] ⁺ | 428 (24) | | 448 (31) | 448 (14) | 448 (38) | 448 (21) | 448 (26) | 448 (26) | | | | |
| 344 | (101) | | | | (637) | (156) | (109) | (240) | (78) | (79) | (69) | |
| 72 | (433) | (298) | (248) | (141) | | | | | | | | |
| 58 | (342) | (250) | (335) | (161) | (320) | (211) | (273) | (171) | (199) | (207) | (363) | (290) |

^a *m/z* values based on ¹⁰⁶Pd. ^b M corresponds to Pd(L)(R).

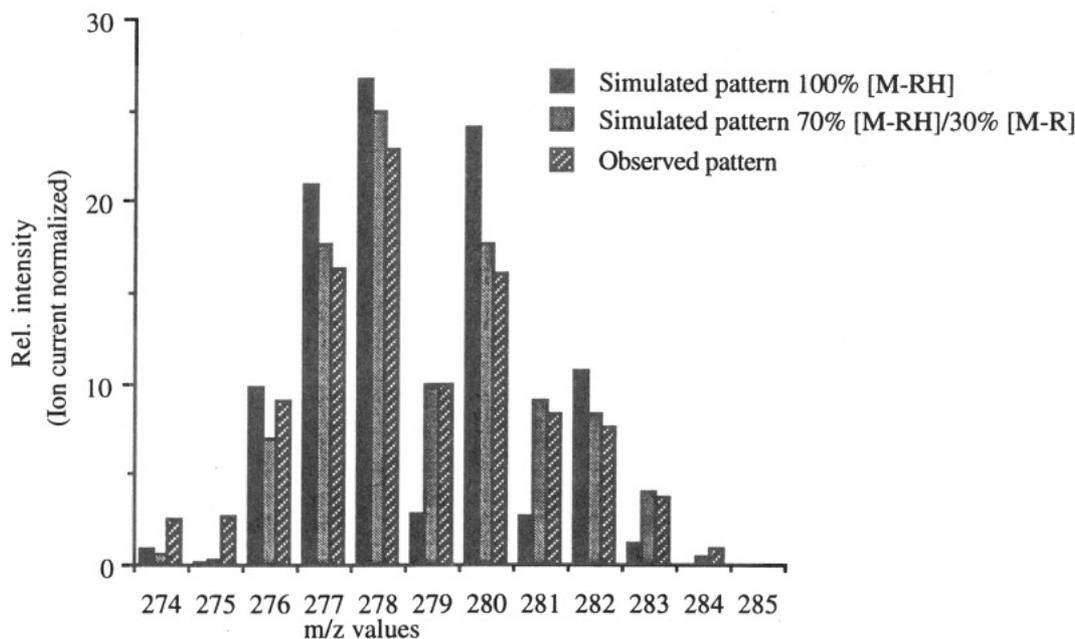


Figure 3. Comparison of the theoretical isotope distribution for formation of 100% [Pd(L)(R) - RH]⁺, 70% [Pd(L)(R) - RH]⁺/30% [Pd(L)(R) - R]⁺ cations and the observed isotope distribution; L = pmdeta, R = CH₃.

FAB mass spectra of several other organometallic complexes.^{18–24} However, these observations do not label cyclometalation as a common process; the structure of the ligand is of great influence,^{19,22,24,25} as was demonstrated by comparing several ligand systems. For example in the FAB mass spectra of neutral methanide and ionic carbene platinum(II) derivatives with dppe as a chelating ligand [Pt(dppe) - H]⁺ was found as the most abundant ion,¹⁹ whereas in contrast with this observation a study of platinum(II) and palladium(II) complexes containing dpmp and dpmp, respectively, as bi- and terdentate phosphine ligands, revealed that

cyclometalated species were totally absent in these cases.²⁵ [dppe = 1,2-bis(diphenylphosphino)ethane; dpmp = 1,1-bis(diphenylphosphino)methane; dpmp = bis(diphenylphosphinomethyl)phenylphosphine.]

A comparison between the theoretical and experimental isotope distribution (Figure 3) for the *m/z* 278 [Pd(L)(R) - RH]⁺ fragment ion of compound 1 indicates that homolytic dissociation of the Pd-R bond also occurred. The experimental values clearly show a deviating isotopic pattern compared with the cluster expected for 100% RH loss from the [Pd(pmdta)(CH₃)⁺ cation 1. Calculating the isotope pattern for the product ions of both fragmentations in a ratio of 70% [Pd(pmdta)(CH₃) - CH₄]⁺ and 30% [Pd(pmdta)(CH₃) - CH₃]⁺ results in a modeled isotope distribution which is quite consistent with the observed cluster (Figure 3). Formation of [Pd(L)]⁺ by loss of R[•] formally involves a reduction of Pd(II) to Pd(I). As demonstrated by this example, a decisive assignment of fragmentation reactions based on fitting calculated isotope distributions is rather elaborate.

Interactions between compound and matrix frequently occur,^{26,27} and these were also observed in the FAB mass spectra (Table 1) of the investigated palladium complexes, giving rise to small signals of ions corresponding to [Pd(L)(R) + (NBA)]⁺. Surprisingly, in

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Table 2. CID Spectra of the [Pd(L)(M)]⁺ Cations of Compounds 1–12. (Relative Abundances in Parentheses)

| | |
|--------------------|--|
| 1, <i>m/z</i> 296 | 281 (10), 280 (100), 278 (13), 266 (2), 264 (2), 249 (1), 235 (10), 223 (2), 178 (2), 165 (2), 141 (3), 139 (3), 127 (3), 72 (5), 58 (4) |
| 2, <i>m/z</i> 358 | 343 (1), 300 (1), 281 (14), 280 (100), 279 (2), 278 (10), 264 (3), 235 (10), 72 (5), 58 (3) |
| 3, <i>m/z</i> 316 | 315 (7), 301 (7), 300 (100), 299 (3), 298 (2), 285 (2), 257 (5), 256 (2), 243 (2), 242 (2), 229 (2), 228 (2), 200 (5), 149 (5), 135 (3), 121 (3), 91 (2), 72 (2), 58 (2) |
| 4, <i>m/z</i> 378 | 360 (2), 301 (15), 300 (100), 299 (4), 286 (2), 285 (2), 284 (2), 257 (5), 256 (4), 243 (2), 242 (2), 229 (3), 228 (2), 200 (5), 149 (5), 135 (4), 92 (2), 72 (2), 58 (2) |
| 5, <i>m/z</i> 316 | 301 (3), 300 (100), 299 (3), 298 (8), 284 (2), 268 (1), 258 (1), 255 (2), 241 (2), 214 (3), 149 (4), 147 (2), 58 (1) |
| 6, <i>m/z</i> 378 | 334 (1), 301 (32), 300 (100), 299 (7), 298 (8), 284 (5), 268 (2), 258 (3), 255 (2), 242 (2), 241 (25), 225 (2), 214 (3), 213 (1), 149 (5), 147 (3), 135 (1), 105 (1), 95 (2), 58 (2) |
| 7, <i>m/z</i> 392 | 377 (1), 374 (1), 348 (1), 305 (1), 301 (7), 300 (100), 299 (7), 298 (10), 284 (3), 268 (2), 258 (3), 255 (3), 242 (2), 241 (2), 214 (3), 192 (1), 149 (5), 147 (3), 135 (1), 105 (1), 95 (1), 91 (1), 58 (1) |
| 8, <i>m/z</i> 423 | 406 (1), 405 (1), 379 (1), 377 (1), 301 (10), 300 (100), 299 (8), 298 (13), 284 (7), 268 (3), 258 (4), 255 (4), 242 (3), 241 (4), 214 (5), 192 (13), 149 (6), 147 (4), 105 (3), 95 (2), 58 (1) |
| 9, <i>m/z</i> 408 | 393 (1), 390 (1), 364 (1), 301 (9), 300 (100), 299 (7), 298 (10), 284 (5), 268 (2), 258 (3), 255 (3), 242 (2), 241 (3), 214 (4), 192 (2), 185 (2), 149 (5), 147 (3), 134 (1), 105 (2), 95 (1), 58 (1) |
| 10, <i>m/z</i> 428 | 410 (1), 384 (1), 341 (1), 301 (7), 300 (100), 299 (9), 298 (11), 284 (6), 275 (4), 268 (2), 258 (4), 255 (3), 242 (2), 241 (3), 235 (2), 214 (4), 192 (1), 149 (6), 147 (3), 105 (2), 95 (1), 58 (1) |
| 11, <i>m/z</i> 442 | 424 (29), 301 (4), 300 (100), 299 (8), 298 (9), 289 (41), 288 (4), 287 (2), 284 (5), 271 (3), 268 (2), 258 (2), 255 (2), 242 (2), 241 (2), 214 (2), 192 (1), 154 (3), 149 (4), 147 (2), 140 (2), 105 (2), 90 (1), 89 (1), 58 (1) |
| 12, <i>m/z</i> 420 | 405 (2), 376 (1), 301 (4), 300 (100), 299 (7), 298 (8), 284 (5), 268 (3), 258 (3), 255 (3), 242 (2), 241 (3), 214 (4), 192 (1), 149 (4), 147 (2), 105 (1), 58 (1) |

all cases where R = Me this peak was found 2 *m/z* units lower pointing to a formal loss of H₂ from this [Pd(L)-(R) + (NBA)]⁺ complex. It is not clear whether these hydrogen atoms arise from NBA or the organopalladium complex, neither which mechanism accounts for the observed difference.

In the lower mass region(s) of the FAB mass spectra (Table 1) peaks were found at *m/z* 172 and 174 for the pmdta-containing derivatives and at *m/z* 192 and 194 for the pico- and NN'N-containing complexes. These peaks can be assigned to the intact ligands (L) and correspond to [L - H]⁺ and [L + H]⁺, respectively. Additionally, ligand fragment ion peaks were observed at *m/z* 58 and 72 which are assigned to the [(CH₂=NMe₂)⁺ and [CH₃CH=NMe₂]⁺ cations, respectively. The *m/z* 72 [CH₃CH=NMe₂]⁺ cation which is not observed in the spectra of NN'N-bound complexes (Table 1) in principle could allow discrimination between the isomeric pico and NN'N ligands because this structural fragment is not part of the NN'N ligand. However, the observation and assignment of peaks at *m/z* 58 and 72 in the FAB mass spectra is complicated by the fact that these ions are present in the lower mass range of the mass spectrum, which contains a lot of chemical background originating from matrix ions thus hampering conclusive discrimination of isomeric ligands.

Reduction processes occurring in the matrix can be held responsible for the presence of multiple metal ions of the composition [Pd(L)(R) + Pd - H₂]⁺. In other studies ions of this type were also found for [M(PPh₃)₄] (M = Pd,²⁶ Pt²⁹). In contrast with the earlier described

NBA-containing fragment ions, loss of H₂ was now found in all cases, the observed ions for **1a**, **2a**, and **3a** (R = CH₃) being more abundant than those of the other compounds. This could suggest that hydrogen dissociation is being favored by a small R group. However, within the limits of the present investigation this process could not be studied in further detail.

CID Spectra. The fragmentation patterns of complexes containing different ligands were compared by using CID to discriminate between the various ligand systems and to study the gas-phase ion chemistry of collisionally activated [Pd(L)(R)]⁺ cations. The CID spectra of the [Pd(L)(R)]⁺ cations were recorded by selecting the ¹⁰⁸Pd isotope. This isotope was chosen in order to prevent a ¹³C contribution from the preceding isotope. In each case the ligand structure was found to exert a significant influence on the obtained spectra. The relevant ions (abundance >1%) are summarized in Table 2. The spectra of the isomeric *m/z* 316 [Pd(pico)-(CH₃)]⁺ (**3**) and [Pd(NN'N)(CH₃)]⁺ (**5**) cations are presented in Figures 4 and 5, respectively.

The most important collisional-induced fragmentation of the [Pd(L)(R)]⁺ cations is loss of RH, producing peaks at *m/z* 280 (¹⁰⁸Pd) for the pmdta derivatives and at *m/z* 300 (¹⁰⁸Pd) for the pico- and NN'N-containing complexes. The abundant loss of RH is, as discussed above, the result of a cyclometalation reaction^{10–14} of the [Pd(L)-(R)]⁺ cation. In contrast with ion-source reactions, the occurrence of a cyclometalation reaction in the field-free region of the mass spectrometer offers the possibility of further mechanistic conclusions.

The mechanism of ion formation in the ion source under conditions of FAB has received considerable

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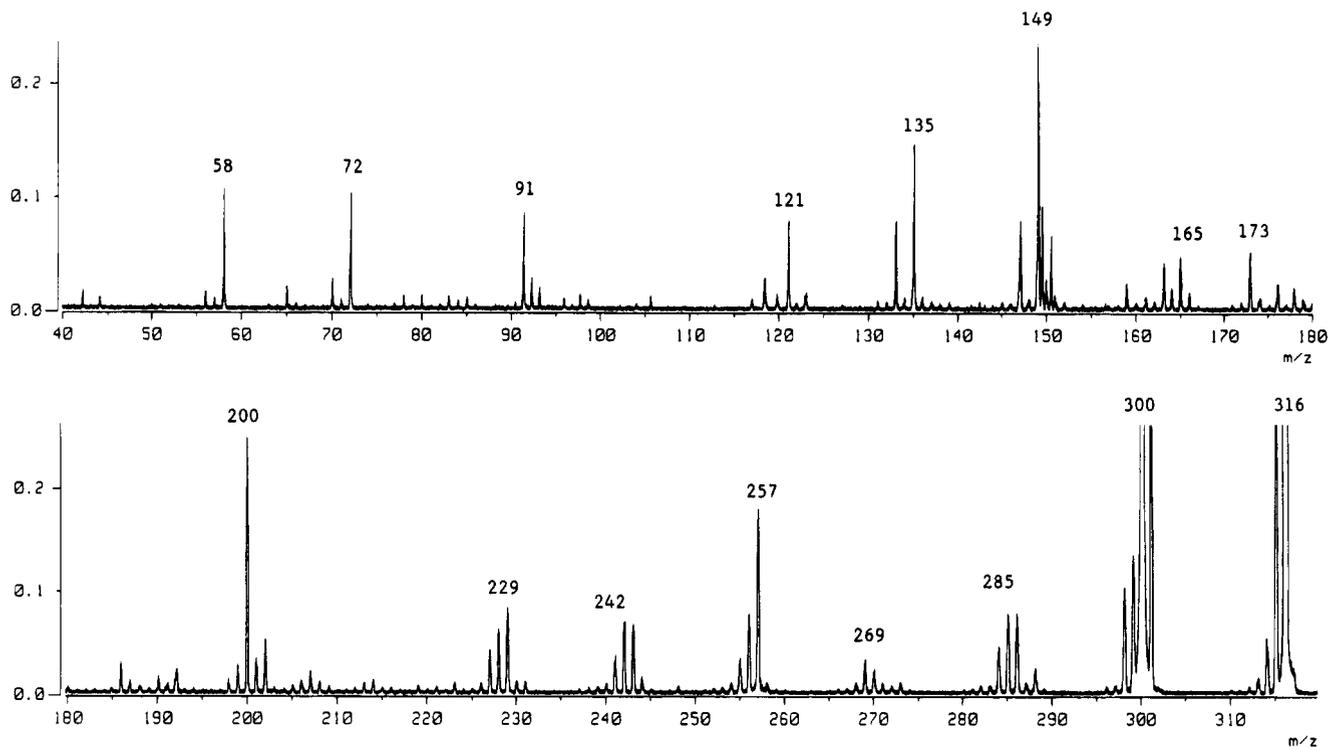


Figure 4. CID spectrum of the m/z 316 $[\text{Pd}(\text{L})(\text{R})]^+$ cation; L = pico, R = CH_3 .

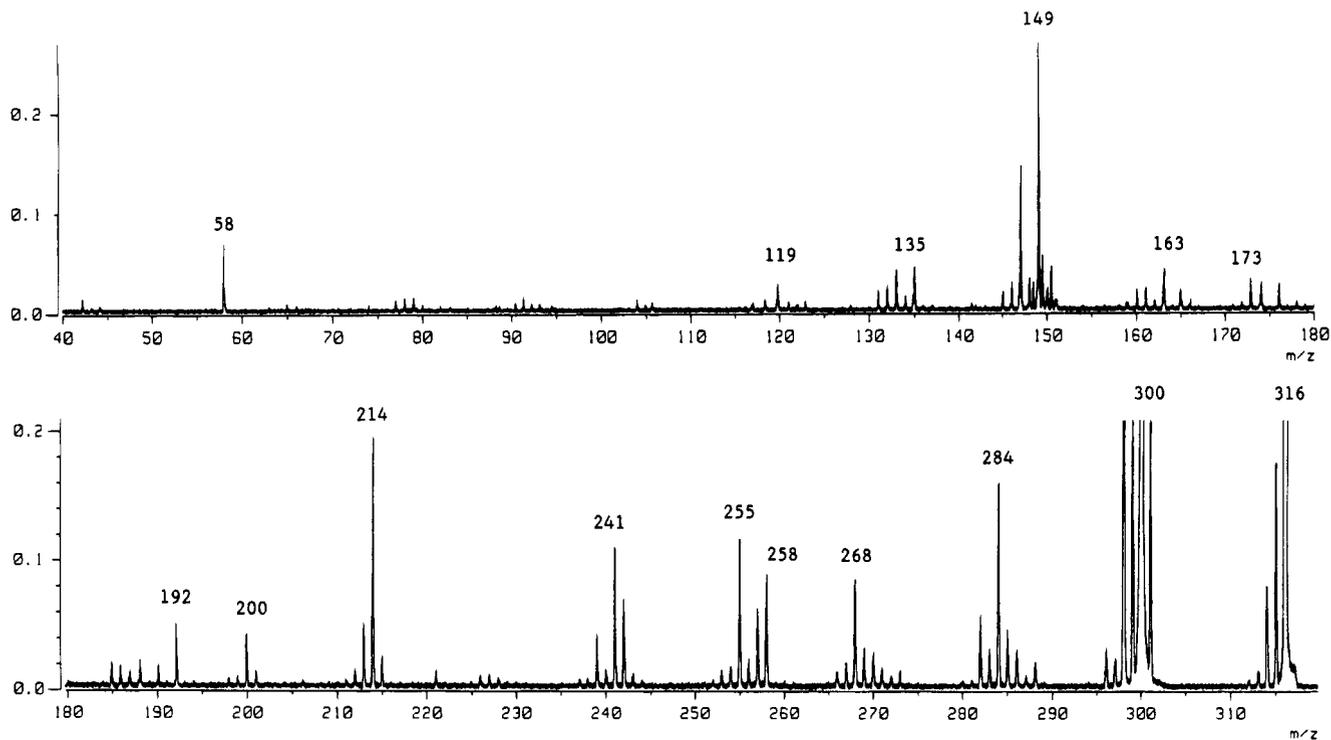


Figure 5. CID spectrum of the m/z 316 $[\text{Pd}(\text{L})(\text{R})]^+$ cation; L = NN'N, R = CH_3 .

attention.^{30,31} The ions detected in FAB mass spectra can be either preformed in solution before bombardment or produced during the energy dissipation process of the primary beam. The incoming atoms cause some ions to be formed in a collision cascade. As a result of the energy released, a cavity (selvedge region) is formed, filled with a high-pressure gas mainly consisting of

matrix molecules but also of matrix and analyte ions released as a result of the sputtering action of the primary beam. Under these chemical ionization-like conditions, reactive collisions governed by well-known gas-phase chemistry rules will occur.³²⁻³⁶ Therefore, the formation of $[\text{M} - \text{RH}]^+$ fragment ions by cyclo-

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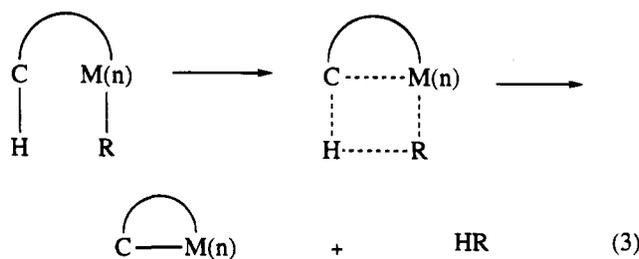
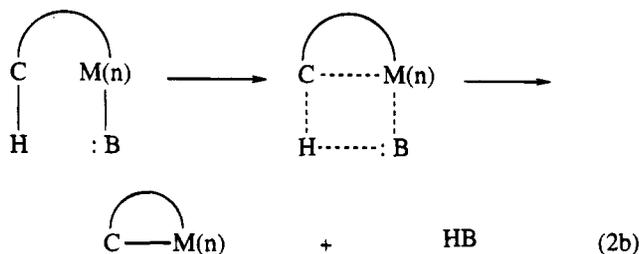
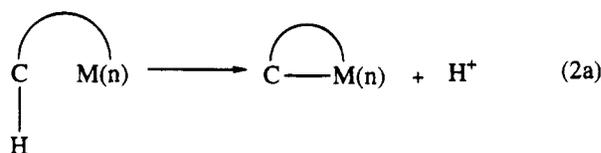
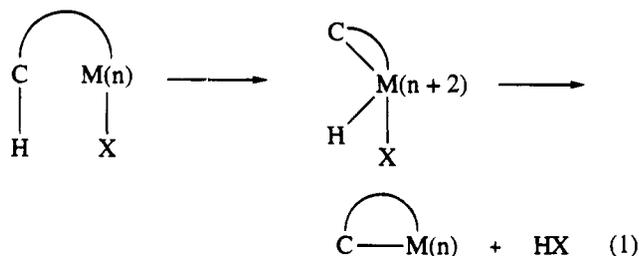
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metalation in the ion source of the mass spectrometer under conditions of FAB ionization precludes unambiguous, i.e. decisive, conclusions about the occurrence of solvent-assisted mechanisms.

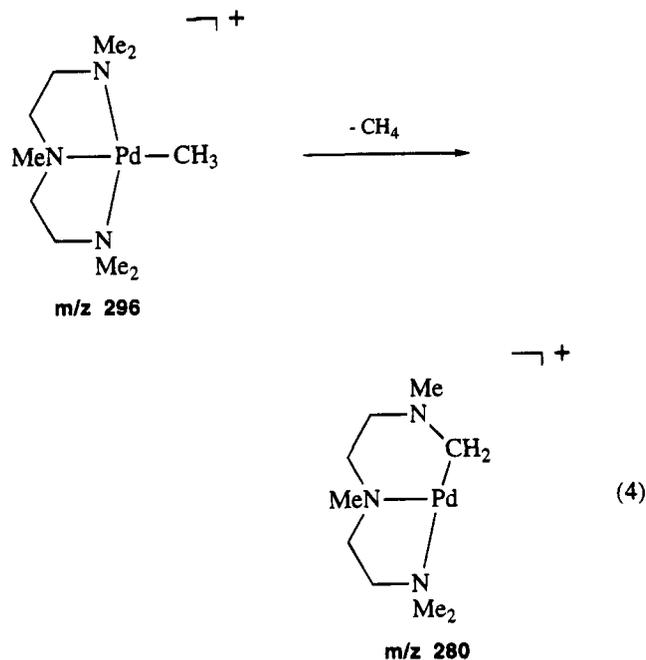
The unimolecular loss of RH from $[Pd(L)(R)]^+$ cations may be considered as a gas-phase analogue of a condensed-phase intramolecular cyclometalation reaction.¹⁰⁻¹⁴ In condensed phase chemistry cyclometalation reactions involving metal-carbon σ -bond formation occur for many reagents.¹³ There are three generally accepted mechanisms for C-H cleavage:¹⁵ oxidative addition (eq 1), electrophilic substitution (eq 2a,b), and



a multicentered pathway (eq 3). In an oxidative addition the C-H bond formally receives two electrons from the metal atom and the oxidation state of the metal $M(n)$ increases by two units ($M(n+2)$). In an oxidative addition the hydride remains in the coordination sphere. Subsequent reductive elimination of the hydride with a suitable ligand X is possible. In an electrophilic mechanism metal hydrides are not formed, the metal ion does not change its oxidation number, and the hydrogen dissociates as a free (eq 2a) or bound proton (eq 2b). Electrophilic reactions are often nucleophilically assisted by coordinated (eq 2b) or free bases which accept the leaving proton. The discrimination between the mechanistic pathways, oxidative addition/reductive elimination or electrophilic substitution, appears to be

complicated.^{15,37,38} A multicentered pathway (eq 3) may be formally considered as an electrophilic one which is nucleophilically assisted; i.e. the metal center is the electrophile which is assisted by the metal-bonded group R acting as a "base". The principal difference is that alkyl, benzyl, or phenyl groups (R) must be present instead of the base B (eq 3).

In condensed phase chemistry cyclopalladation reactions are well recognized. Electrophilic displacement mechanisms (eq 2a) and (eq 2b) are proposed to be operative in cyclopalladation chemistry. It has been shown for orthopalladation of ring-substituted *N,N*-dimethylbenzylamines that the kinetics of the cyclometalation reaction are solvent dependent.³⁹ The loss of RH in the field-free region of the mass spectrometer, however, can only be the result of an intramolecular isomerization reaction followed by a dissociation without the participation of the solvent or other reactants in the transition state. The amine methyl groups are the most likely sources of hydrogen in the $Pd(L)(R)$ cations. Additional support for this proposal is the observation that only CHD_3 neutrals are lost upon collisional activation of $[Pd(NN'N)(CD_3)]^+$ cations. It is assumed that the palladium-nitrogen bond is broken and a six-membered ring is formed *via* a carbon atom of the amine methyl group, as visualized for $Pd(pmdta)(CH_3)$ in eq 4. In condensed phase chemistry a five-membered ring



size of the cyclometalated species is reported to have the most ideal geometry.¹³ However, an X-ray structure of a six-membered ring in a Pd complex with relatively strain-free bond angles and lengths was described.⁴⁰ Another premise for an electrophilic mechanism like in eq 2b is the presence of base with an n-donor electron pair as a leaving group. In the model compounds

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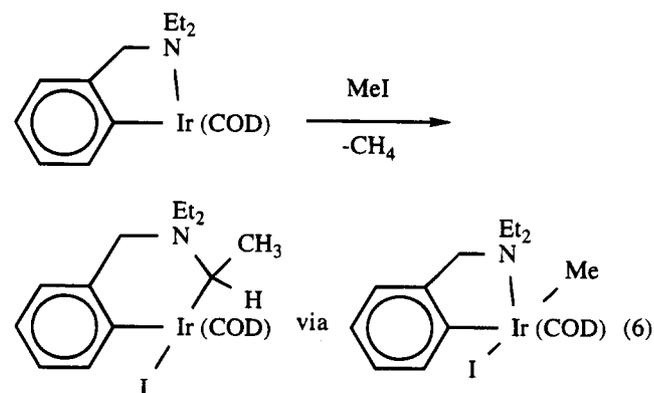
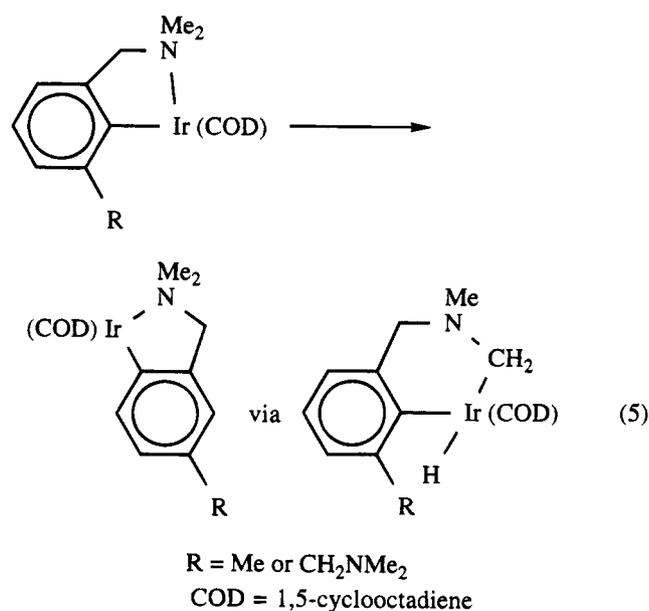
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(Figure 1) used in this study a covalent bonded R group is lost as RH. This result points in contrast with solution chemistry, to a cyclometalation mechanism (1) or (3) for the unimolecular loss of RH from collisionally activated Pd(L)(R)^+ cations. Furthermore, an interesting aspect in the case of $\text{Pd(pmdta)(CH}_3\text{)}$ is that a cyclopalladation reaction of a tertiary amine occurs by activation of an sp^3 C–H bond. Generally, in condensed phase chemistry of orthopalladated compounds, direct activation of C–H bonds by Pd(II) is the most feasible in the case of tertiary amines,⁴¹ whereas primary and secondary amines are usually not reactive toward such activation, and in cyclometalation sp^2 C–H bonds are more easily activated than sp^3 C–H bonds.^{42,43}

It must be noted that also in solution chemistry this unimolecular pathway is operative. An example where C–H bond cleavage and re-formation occurs is the quantitative skeletal rearrangement of $\text{Ir(C}_6\text{H}_3\text{CH}_2\text{-NMe}_2\text{-2-R-6)(COD)}$ ($\text{R} = \text{Me}$ or CH_2NMe_2) to $\text{Ir(C}_6\text{H}_3\text{-CH}_2\text{NMe}_2\text{-2-R-4)(COD)}$ shown in eq 5. The formation



of a coordinative unsaturated, three-coordinate Ir^{I} species through prior Ir–N bond dissociation is followed by intramolecular C–H bond cleavage and concomitant formation of an Ir^{III} intermediate. The latter intermedi-

ate reacts further by aryl C–H (forward reaction) or alkyl C–H (backward reaction) bond formation; cf. Scheme 1 in ref 44. The second example (eq 6) involves the generation of an Ir^{III} oxidative addition intermediate in the reaction of $\text{Ir(C}_6\text{H}_4\text{CH}_2\text{NET}_2\text{-2)(COD)}$ with MeI .⁴⁵ This intermediate reacts further under CH_4 elimination to form a six-membered ring compound comprising the N center and the Ir^{III} center. This structural motif is encountered in fragment ions m/z 300 (Schemes 1 and 2), which are both generated by unimolecular CH_4 loss. The reaction shown in eq 6 most likely involves a multicenter pathway (cf. eq 3) which so far is rare for C–H bond activation in late transition metal chemistry but recently has been shown to be operative for H–H bond activation.

Fragment ions $[\text{M} - \text{R}]^+$ caused by homolytic bond dissociation of Pd–R were also present, as the isotope clusters in the FAB mass spectra already indicated. The latter process where the σ -bound ligand is lost as a radical is a common fragmentation pathway for FAB-ionized organometallics. It represents a formal redox reaction involving reduction of Pd(II) to Pd(I). Kowalski²² found a similar behavior for $[(\text{PPh}_3)_3\text{PtR}]^+$ complexes ($\text{R} = \text{alkyl, vinyl}$), where fragment ions corresponding to $[\text{M} - \text{R}]^+$ were observed. Such observations reflect known solution properties: fragmentations taking place at the metal–ligand bonds and not within the ligands. Moreover, an analogous behavior is found for complexes bearing π -bound ligands where loss of the intact ligand occurs, as is predicted by their thermal displacement chemistry.^{17,23,46}

Abundant fragmentations of the pmdta derivatives 1 and 2 are losses of CH_4 and C_6H_6 . A fairly abundant signal is also found at m/z 278, which is assigned to the loss of H_2 from m/z 280. Subsequent elimination of azapropene ($\text{CH}_2=\text{N}-\text{CH}_3$) leads to the formation m/z 235 cations.

The CID spectra of the m/z 316 pico and NN'N cations (Table 2) show several collisional-induced fragmentation reactions of the nitrogen ligand, giving various peaks in the CID spectra. The isomeric pico and NN'N cations are easily differentiated by their CID spectra (Figures 4 and 5). The CID spectrum of m/z 316 Pd(pico)(CH_3) cations contains ions at m/z 72, 91, 200, and 229 whereas these ions are not present in the spectrum of m/z 316 Pd(NN'N)(CH_3) cations. The CID spectrum of m/z 316 NN'N cations shows ions at m/z 284, 258, 255, and 241 which are less abundant or absent in the spectrum of the m/z 316 pico cations. The fragmentation pathways leading to the generation of these ions are rationalized in Schemes 1 and 2. The mechanistic proposals are based on permutations of (consecutive/concerted) losses of H_2 , CH_4 , C_2H_4 , $\text{CH}_2=\text{N}-\text{CH}_3$, and CH_3N molecules and a CH_3^{\cdot} radical. It is plausible that several other pathways which are not depicted in Schemes 1 and 2 lead to similar product ions, as neutrals may be lost in different sequences.

The first collisional-induced fragmentation reaction step is loss of CH_4 or CH_3^{\cdot} ; yielding cations at m/z 300

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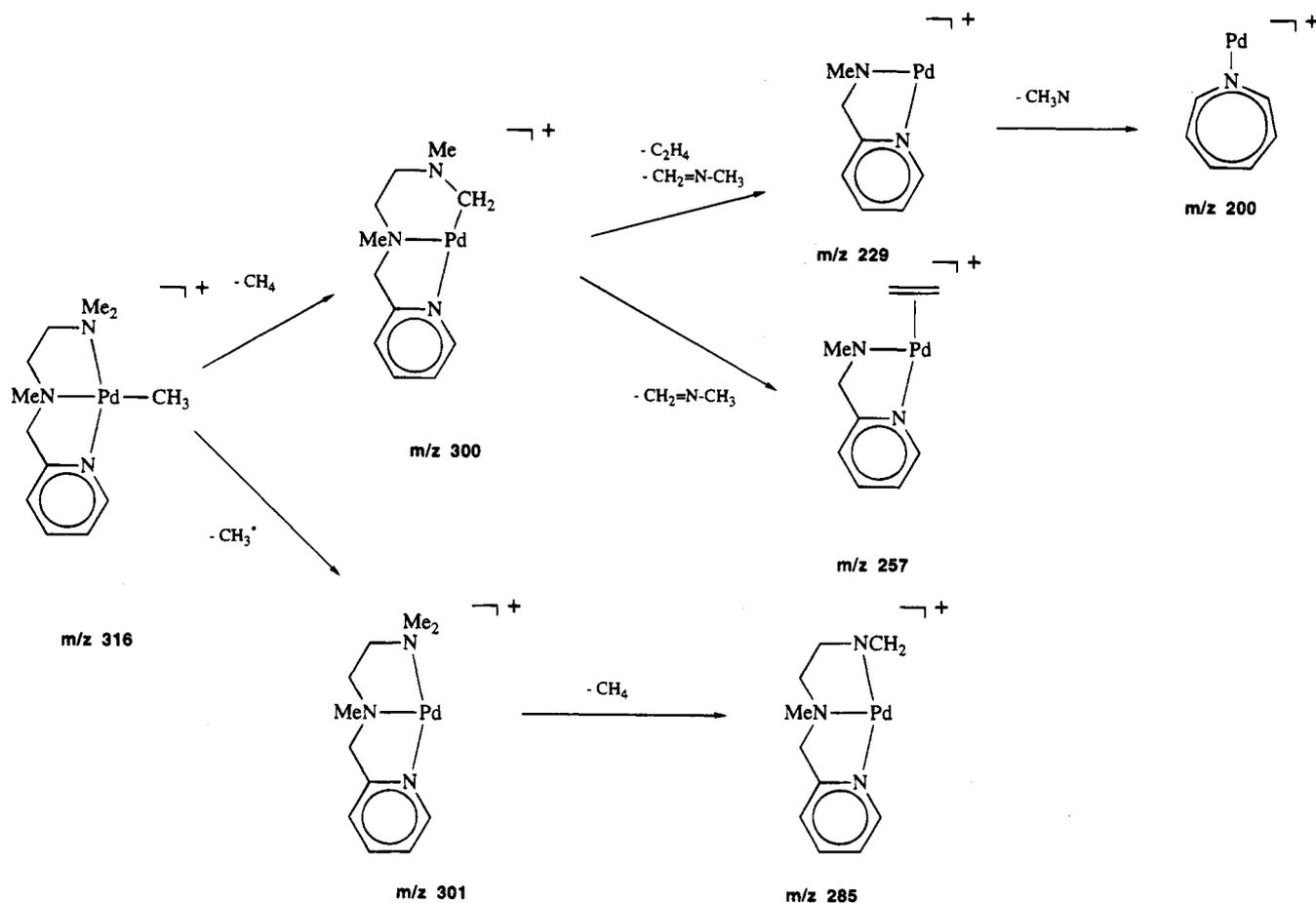
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Scheme 1



and 301, respectively. The second fragmentation of m/z 300 is elimination of H_2 , $\text{CH}_2=\text{N}-\text{CH}_3$, or CH_4 for the NN'N compounds and C_2H_4 or $\text{CH}_2=\text{N}-\text{CH}_3$ for the pico compounds. In the case of the pico ligand no abundant peak was found at m/z 298 corresponding to H_2 dissociating from the $[\text{M} - \text{RH}]^+$ cation. The pico ligand contains only one dimethylamino group, indicating that the hydrogen atoms involved in the initial CH_4 and subsequent H_2 loss from m/z 316 NN'N Pd(L)(R) cations are most likely originating from the dimethylamino group. The m/z 255 ion, resulting from expulsion of $\text{CH}_2=\text{N}-\text{CH}_3$ from m/z 298 pico cations is an azabenzyl cation (Pd(0)) which most likely ring-expands to a seven-membered ring with concomitant σ -bond formation between Pd and the azacycloheptatrienium N atom. In such a mechanism the oxidation state of Pd(II) remains unaltered. Ring expansion of azabenzyl cations to seven-membered ring azatropylium ions and methylpyridine molecular ions to azacycloheptatriene ions is a facile rearrangement reaction in gas-phase ion chemistry.⁴⁷ As H_2 loss of the m/z 300 cations is not a feasible process for the pico compounds, abundant formation of m/z 255 cations by subsequent loss of $\text{CH}_2=\text{N}-\text{CH}_3$ is not expected. The peak at m/z 255 present in Figure 5 is of minor importance in Figure 4. Formation of fragment ions at m/z 229 or 257 (present in Figure 4, absent in Figure 5) by loss of CH_4 , C_2H_4 , and $\text{CH}_2=\text{N}-\text{CH}_3$ or CH_4 and $\text{CH}_2=\text{N}-\text{CH}_3$, respec-

tively, requires a saturated six-membered ring intermediate which can only be formed by cyclometalation of the m/z 316 pico cations (Scheme 1). Another discriminating reaction channel of collisionally induced m/z 316 pico and NN'N cations is formation of m/z 284. This m/z 284 ion is the result of cyclometalation of m/z 316, yielding m/z 300, followed by loss of CH_4 . This process requires the presence of two dimethylamino groups. Loss of CH_4 from dimethylamino compounds is well recognized in the organic mass spectrometry of nitrogen compounds.^{48,49}

Conclusions

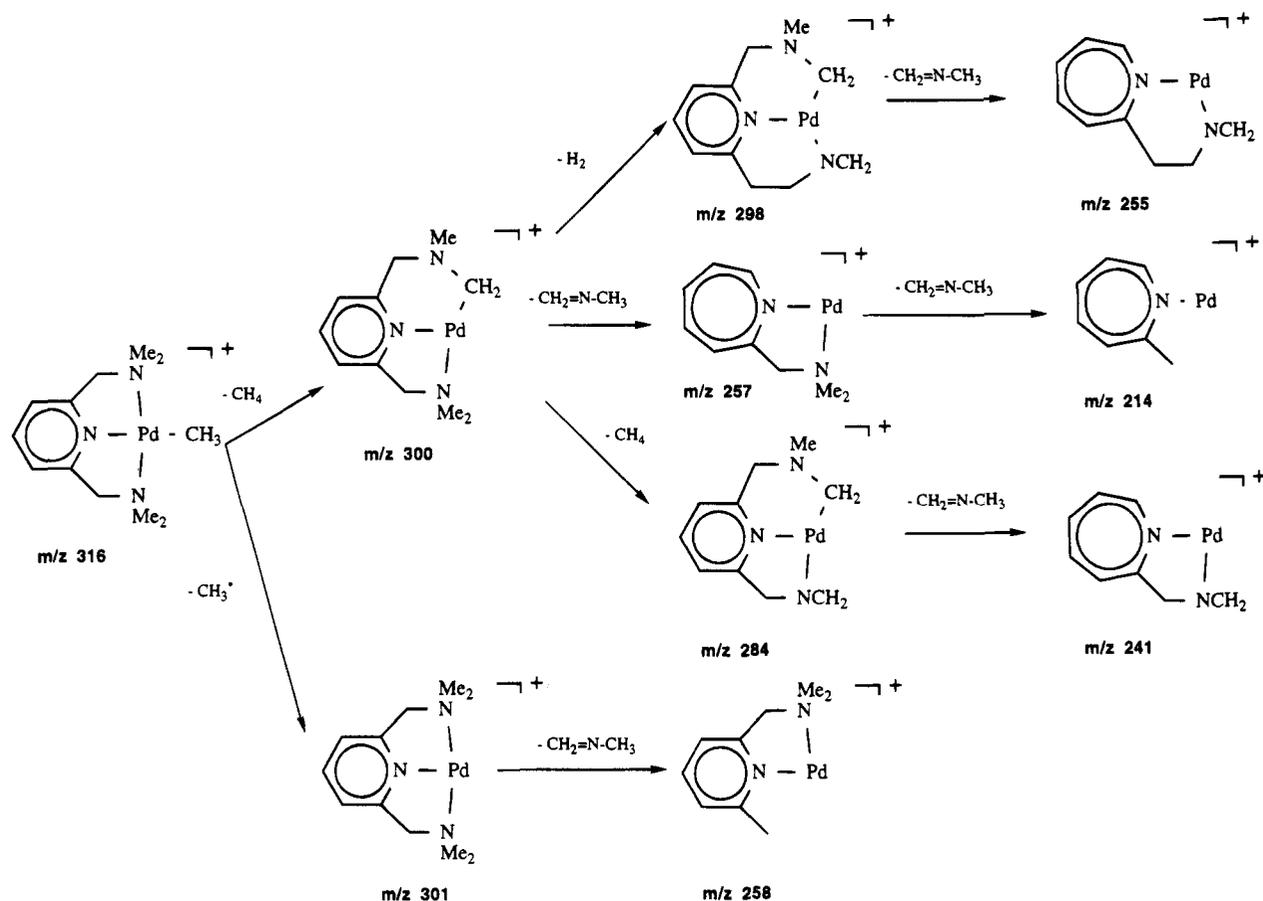
FAB-MS is a valuable technique for the structural characterization of organometallic palladium complexes containing terdentate nitrogen ligands. However, solely FAB-MS has its limitations. FAB ionization of the Pd(L)(R)(OTf) compounds with *m*-nitrobenzyl alcohol as a matrix gives abundant Pd(L)(R) cations. The Pd isotope distribution of their m/z values provides molecular mass information of the compounds. Structural information is present to a lesser extent in the FAB mass spectra, and correct assignment of a particular fragment ion, i.e. the identity of the neutral lost, is obscured by the interference of fragmentation reactions of higher and lower Pd isotopomers leading to isobaric fragment ions. Moreover, diagnostic fragment ions of

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Scheme 2



the ligand system are hidden in the chemical background originating from matrix ions.

FAB-MS/MS offers excellent possibilities to overcome such problems. In MS/MS experiments only the fragment ions from collisionally activated mass-selected monoisotopic ^{108}Pd cations are detected at unit mass resolution with MS-2. The MS/MS spectra contain a variety of ligand characteristic fragment ions, allowing discrimination of the isomeric terdentate pino and $\text{NN}'\text{N}$ nitrogen ligands. In addition to the structural analysis and elucidation of the fragmentation pathways of the $\text{Pd}(\text{L})(\text{R})$ cations to rationalize the formation of the structurally characteristic fragment ions, MS/MS was

also used to study cyclopalladation of the organopalladium compounds in a solvent-free system. Our MS/MS results clearly show, without the need of kinetic experiments with isotopically labeled molecules and/or solvents as required for condensed phase mechanistic studies, that a cyclopalladation reaction mode of the $\text{Pd}(\text{L})(\text{R})$ cations by activation of an sp^3 C-H bond is operative, which invokes an oxidative addition/reductive elimination or a multicentered pathway mechanism instead of a solvent or n -donor ligand assisted electrophilic substitution.

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