

Wavelength-Dependent Photofragmentation of a Mixed-Ligand Cyclometalated Platinum(II) Coordination Compound in a Molecular Beam

Franklin P. Ow,[†] Peter I. Djurovich,[‡] Mark E. Thompson,[‡] and Jeffrey I. Zink^{*,†}

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, and Department of Chemistry, University of Southern California, Los Angeles, California 90089

Received July 11, 2007

The photofragmentation of (3-Me-4',6'-dfppy)Pt(dpm) (dfppy = difluorophenylpyridinato; dpm = dipivaloylmethyl or 2,2,6,6-tetramethyl-3,5-heptanedionato-*O,O*) in a molecular beam is reported. Time-of-flight mass spectra (TOF-MS) and resonance-enhanced multiphoton ionization (REMPI) data are presented and discussed. The dissociation patterns are strongly wavelength-dependent. With 355 nm excitation, the heaviest mass platinum-containing fragments are Pt⁺ and diatomic PtC⁺. The formation of PtC⁺ is the result of an intramolecular rearrangement on the ligand. During irradiation with 410–500 nm light, the fragmentation pattern changes such that the parent ion and platinum-containing fragments of the parent are formed in abundant yield. The (3-Me-4',6'-dfppy) ligand remains intact and coordinated to platinum, but coordinated (dpm) successively breaks apart. A spin-forbidden charge-transfer absorption band centered at around 460 nm plays an important role in the gas-phase photoexcitation of the parent molecule; it is observed in the REMPI spectrum of the parent ion.

Introduction

The photochemistry of transition-metal compounds in solution is a mature field; both the experimental results and underlying concepts are described extensively in books and reviews. In contrast, the gas-phase photochemistry of transition-metal compounds is not well studied or understood, in part because of the absence of benchtop methods of identifying the reaction products. Mass spectrometry provides a powerful technique for characterization of both the primary and secondary reaction products. Gas-phase photochemistry of volatile metal-containing compounds is of interest for several reasons. Photochemical reactions unencumbered by solvation can be studied. Wavelength-dependent reactions and multiphoton reactions are common and can provide a powerful method of controlling the reactivity once the principles are understood. Understanding of the reactivities is important in applications such as photoassisted chemical

vapor deposition, and measurements of the reactions provide detailed data for comparison with predictions from electronic structure calculations.

The pioneering work on gas-phase photochemistry of metal-containing compounds monitored by mass spectrometry focused on metal-carbonyls^{1–7} and metallocenes.^{8–14} The results of these studies are generalized by cleavage of relatively weak metal–ligand bonds to produce the bare metal atom in dominant yield. It had been generally established and accepted on the basis of results from these organometallic compounds that formation of the parent ion and heavy metal-containing photofragments is uncommon.¹⁵

Recent results on metal-containing compounds suggest that gas-phase photochemical reactions are much richer and more complicated than once previously thought.^{16–24} For example, in the case of chromocene²⁵ and the mixed-ligand cyclopentadienyl cyclooctadiene cobalt compound²⁴ where photooxidation (ionization) was an important reaction pathway, the parent ion was observed at all excitation wavelengths

* E-mail: zink@chem.ucla.edu. Phone: (310)-825-8651. Fax: (310)-206-4038.

[†] University of California, Los Angeles.

[‡] University of Southern California.

(1) Ashfold, M. N. R.; Howe, J. D. *Annu. Rev. Phys. Chem.* **1994**, *45*, 57–82.

(2) Boesl, U.; Neusser, H. J.; Schlag, E. W. *Chem. Phys. Lett.* **1982**, *87*, 1–5.

(3) Johnson, P. M. *Acc. Chem. Res.* **1980**, *13*, 20–26.

and the relative amount of parent ion formed was strongly wavelength-dependent. At certain wavelengths, the parent ion could be generated in greater yield than the bare metal ion itself and was the most dominant ion signal observed. Other peaks from ions with masses greater than that of the metal ion were also detected, resulting from partial ligand loss or from ligand fragments that remain coordinated to the metal. These results were unexpected because coordinate covalent metal–ligand bonds tend to be weaker than covalent ligand-centered bonds and dissociation of intact ligands was expected. In the case of the mixed-ligand coordination compound *trans*-bis(trifluoroacetato)bis(*N,N'*-dimethylethylenediamine)nickel(II) (Ni(dmen)₂(tfa)₂),²² dmen lost hydrogen atoms and methyl groups to readily form mono- and diimine species, both as free ligands and while remaining attached to nickel. Photochemical reactions of transition-metal compounds in solution typically involve intact ligand loss.^{26–28}

In other recent work, it was found that irradiation of lanthanide^{20,21,29} and transition-metal β -diketonates^{30,31} could

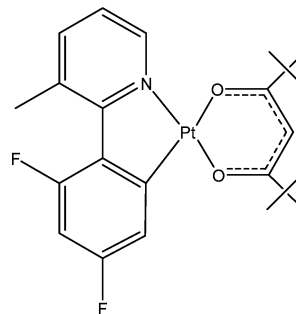


Figure 1. Structure of the parent molecule, (3-Me-4',6'-dfppy)Pt(dpm), where dfppy = difluorophenylpyridine and dpm = dipivaloylmethane (see ref 32).

result in the formation of very stable diatomic metal species, such as metal oxides, carbides, and fluorides. In these studies, diatomic MO⁺ arose from ligands where oxygen and nitrogen were bonded to the metal, but MC⁺ and MF⁺ ions were formed after intramolecular rearrangement of the β -diketonate ring, resulting in either carbon or fluorine abstraction by the metal. The existence of metal heteroatoms has important implications for photodeposition applications. While metal oxides and nitrides (i.e., II–VI, III–V materials) may be desirable products, metal fluorides are detrimental to the usage of the thin metal film in microelectronic applications.

In this work, we report on the photofragmentation of a mixed-ligand coordination complex, platinum(II) (2-(4',6'-difluorophenyl)-3-methylpyridinato-*N,C'*')(2,2,6,6,-tetramethyl-3,5-heptanedionato-*O,O'*), (3-Me-4',6'-dfppy)Pt(dpm),³² in the gas phase (Figure 1).

This compound combines a bidentate ligand, dpm, that is commonly used to provide volatility to coordination compounds, with a cyclometalating ligand that gives rise to metal-to-ligand charge-transfer bands in the visible region of the spectrum. Photoexcitation at visible wavelengths produces the parent ion with the largest intensity. The parent ion successively loses substituents resulting in a series of metal-containing peaks consisting of small fragments of the coordinated ligand. The two different ligands behave very differently; intact (3-Me-4',6'-dfppy) dissociates, but (dpm) undergoes unique photochemical reactions, including an intramolecular rearrangement resulting in the formation of diatomic platinum carbide. The ligand photolabilization reactions are wavelength-dependent and are explained in terms of the accessibility of known metal-to-ligand charge-transfer transitions.

Experimental Section

Materials. (3-Me-4',6'-dfppy)Pt(dpm) was prepared by the reported procedure.³² All reagents were commercially available from Aldrich and used without further purification.

Spectroscopy. Photoionization mass spectra were measured at 355 nm (20–65 mJ/pulse, $\sim 10^8$ – 10^9 W/cm²) and in the range of 410–610 nm (~ 20 mJ/pulse, $\sim 10^8$ W/cm²). The time-of-flight

- (4) Jackson, R. L. *Acc. Chem. Res.* **1992**, *25*, 581–586.
- (5) Schlag, E. W.; Neusser, H. J. *Acc. Chem. Res.* **1983**, *16*, 355–360.
- (6) Karny, Z.; Naaman, R.; Zare, R. N. *Chem. Phys. Lett.* **1978**, *59*, 33–37.
- (7) Dietz, T. G.; Duncan, M. A.; Liverman, M. G.; Smalley, R. E. *J. Chem. Phys.* **1980**, *73*, 4816–4821.
- (8) Smalley, R. E.; Wharton, L.; Levy, D. H. *Acc. Chem. Res.* **1977**, *10*, 139–145.
- (9) Ketkov, S. Y.; Selzle, H. L.; Heinrich, L.; Schlag, E. W. *Isr. J. Chem.* **2004**, *44*, 65–69.
- (10) Ketkov, S. Y.; Selzle, H. L.; Heinrich, L.; Schlag, E. W. *Mol. Phys.* **2004**, *102*, 1749–1757.
- (11) Ketkov, S. Y.; Selzle, H. L.; Heinrich, L.; Schlag, E. W. *J. Chem. Phys.* **2004**, *121*, 149–156.
- (12) Ketkov, S. Y.; Selzle, H. L.; Heinrich, L.; Schlag, E. W.; Titova, S. N. *Chem. Phys.* **2003**, *293*, 91–97.
- (13) Ketkov, S. Y.; Selzle, H. L.; Heinrich, L.; Schlag, E. W.; Domrachev, G. A. *Chem. Phys. Lett.* **2003**, *373*, 486–491.
- (14) Ketkov, S. Y.; Selzle, H. L.; Heinrich, L.; Schlag, E. W.; Domrachev, G. A. *Inorg. Chem. Commun.* **2002**, *5*, 909–912.
- (15) Gedanken, A.; Robin, M. B.; Kuebler, N. A. *J. Phys. Chem.* **1982**, *86*, 4096–4107.
- (16) Muraoka, P.; Byun, D.; Zink, J. I. *J. Am. Chem. Soc.* **2000**, *122*, 1227–1228.
- (17) Muraoka, P.; Byun, D.; Zink, J. I. *Coord. Chem. Rev.* **2000**, *208*, 193–211.
- (18) Jaeger, T. D.; Duncan, M. A. *J. Phys. Chem. A* **2004**, *108*, 11296–11301.
- (19) Jaeger, T. D.; Duncan, M. A. *Int. J. Mass Spectrom.* **2005**, *241*, 165–171.
- (20) Ow, F. P.; Berry, M. T.; May, P. S.; Zink, J. I. *J. Phys. Chem. A* **2006**, *110*, 7751–7754.
- (21) Ow, F. P.; Berry, M. T.; May, P. S.; Zink, J. I. *J. Phys. Chem. A* **2007**, *111*, 4144–4149.
- (22) Ow, F. P.; Henderson, B.; Zink, J. I. *Inorg. Chem.* **2007**, *46*, 2243–2248.
- (23) Muraoka, P.; Byun, D.; Zink, J. I. *J. Phys. Chem. A* **2001**, *105*, 8665–8671.
- (24) Byun, D.; Zink, J. I. *Inorg. Chem.* **2003**, *42*, 4308–4315.
- (25) Muraoka, P. T.; Byun, D. S.; Zink, J. I. *J. Am. Chem. Soc.* **2000**, *122*, 5670.
- (26) Sykora, J.; Sima, J. *Photochemistry of Coordination Compounds*; Elsevier: Amsterdam, 1990.
- (27) (a) Zink, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8039–8046. (b) Zink, J. I. *Inorg. Chem.* **1973**, *12*, 1957–1959. (c) Incorvia, M. J.; Zink, J. I. *Inorg. Chem.* **1974**, *13*, 2489–2494.
- (28) Zink, J. I. *Coord. Chem. Rev.* **2001**, *211*, 69–96.
- (29) Nelson, B. N.; Caster, A. G.; Berry, M. T. *Chem. Phys. Lett.* **2004**, *396*, 256–260.
- (30) Talaga, D. S.; Hanna, S. D.; Zink, J. I. *Inorg. Chem.* **1998**, *37*, 2880–2887.
- (31) Talaga, D. S.; Zink, J. I. *Inorg. Chem.* **1996**, *35*, 5050.

(32) Brooks, J.; Babayan, Y.; Sergey, L.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055–3066.

(33) Wiley, W. C.; McLaren, I. H. *Rev. Sci. Instrum.* **1955**, *26*, 1150–1157.

Table 1. Significant Ions Formed during Photofragmentation of (3-Me-4',6'-dfppy)Pt(dpm) with Various Excitation Wavelengths in the UV and Visible^a

(+) ion	excitation wavelength (nm)		
	355	430	460
H	27	trace	trace
C	100	100	100
CH ₃	26	98	95
C ₂	40	99	96
C ₃	20	117	140
CH ₃ CHO	21	trace	trace
OC ₃	49	trace	trace
<i>t</i> -butyl	26	407	402
O ₂ C ₃	21	176	117
dpm - <i>t</i> -butyl	21	trace	trace
Pt	22	186	137
PtC	trace	unknown	unknown
ppy	0	274	189
Pt(ppy)	0	306	169
(ppy)Pt(CH)	0	287	156
(ppy)Pt(OC) ₂	0	154	109
P-2 <i>t</i> -butyl	0	267	150
P- <i>t</i> -butyl	0	277	152
P	0	403	230

^a All ions are listed with their intensities relative to that of carbon, arbitrarily set to 100. For the cases where peak assignment is difficult, the relative intensity is marked "unknown." When the assignment is definite but the signal-to-noise is low, "trace" is used.

(TOF) mass spectrometer was constructed based on a design in the literature.³³ Photoionization occurs in a stainless steel cube (30 cm edges) equipped with quartz windows and evacuated to less than 10⁻⁶ Torr by a 6 in. diffusion pump fitted with a water-cooled baffle. (3-Me-4',6'-dfppy)Pt(dpm) is sublimed at 145 °C before it is seeded in He with a backing pressure of about 10³ Torr and is admitted to the high-vacuum chamber via a pulsed nozzle. The high-speed solenoid valve (General Valve series-9, 0.5 mm orifice) sends a 0.2 ms pulse of the sublimed sample (entrained in He) to intersect the ionization laser beam at 90°. An OPOTEK optical parametric oscillator (410–680 nm, 6 ns pulse width, ~20 mJ/pulse, 10–20 cm⁻¹ bandwidth) pumped by the third harmonic of a Quantel Brilliant Nd:YAG laser is used for excitation. An optional KV-389 filter is used to eliminate residual pump (355 nm) from the visible laser beam. The fragment ions are accelerated through a 1 m flight tube kept at 10⁻⁶ Torr using a Varian V300HT 6 in. air-cooled turbomolecular pump. Accelerator voltages are 3000 V, 2100 V, and ground, respectively, in order from farthest to nearest the detector. Ions are detected using a 40 mm diameter triple microchannel plate detector assembly (R.M. Jordan, Inc.). The ion signal is processed using a Tektronix TDS2022 200 MHz dual channel digital oscilloscope interfaced to a PC.

Results and Discussion

Mass spectra resulting from the irradiation of gaseous (3-Me-4',6'-dfppy)Pt(dpm) in the UV at 355 nm and in the visible from 410 to 500 nm were obtained. All significant peaks are listed in Table 1 with their intensities relative to that of carbon.

The platinum cation is always observed, but its relative intensity is highly wavelength-dependent. Diatomic PtC⁺ is sometimes observed, and the mechanism for its formation can be deduced from the TOF mass spectrum. The formation of the parent ion and heavy metal-containing peaks are observed with excitation within the 410–500 nm visible wavelength region. Their relative intensities also exhibit

unique wavelength dependencies. The dpm moiety is never found to remain intact coordinated to the metal center nor is observed as an intact cation. Only smaller dpm fragments are found. The (3-Me-4',6'-dfppy) ligand, labeled as ppy, exhibits the opposite photochemical behavior. It always is intact when coordinated and is observed as the intact cation.

The gas-phase photodissociation reactions of many metal-organic compounds have been studied.^{2–25} In most cases, irradiation caused fragmentation of the parent molecule into neutral species followed by ionization of the bare metal atom. Not only was the metal cation the dominant species formed but it was also usually the heaviest fragment observed in the mass spectra.^{1–15} Observation of the intact parent ion and heavy metal-containing fragments was rare in the reported studies. Recent studies from our laboratory have shown that this is not as uncommon as previously thought; the excitation wavelength can significantly alter the photofragmentation routes, and the intensity of the parent ion peak can dominate that of the metal cation.^{16,17,20–25}

The mixed-ligand cyclometalated complex, (3-Me-4',6'-dfppy)Pt(dpm), has an unusual photofragmentation pattern. (In all spectra, (3-Me-4',6'-dfppy) will be labeled as ppy.) First, the parent ion can be the dominant species, with an intensity 3 times more than those of the metal cation and light organic fragments. Second, the photochemical behavior of the (3-Me-4',6'-dfppy) ligand versus that of dpm is different. While (3-Me-4',6'-dfppy) either stays attached to platinum or is dissociated completely, dpm exhibits unique internal fragmentation reactivity while remaining bound to the metal. Third, the excitation wavelength drastically alters the reaction pathways. Only within a small excitation wavelength region is the parent ion observed. Fourth, the intensity of dissociated (3-Me-4',6'-dfppy) to bound (3-Me-4',6'-dfppy) changes within a specific wavelength region which can be explained in terms of accessibility of a known triplet absorption transition. Finally, diatomic platinum carbide is the result of an intramolecular rearrangement from the bound β -diketonate moiety and does not originate from the existing platinum–carbon bond in the starting material (i.e., not from (3-Me-4',6'-dfppy)).

1. Primary Photochemical Reactions. The primary photochemical reactions are photo-oxidation (photoionization) and C–C bond-breaking resulting in dissociation of *t*-butyl groups. The mass spectrum resulting from photodissociation in the 410–500 nm range (Figure 2) does not follow the conventional pathway of organometallics where fragmentation of the parent molecule precedes photoionization.

If the absorption rate is slower than the photochemical relaxation rate across the ionization continuum, the parent molecule preferentially ionizes before any photochemical dissociation reactions occur.¹⁵ The parent ion (P⁺, 583 *m/z*) is the heaviest and most dominant ion signal detected. Smaller fragments of the parent ion are also detected in significant yield at 526 and 469 *m/z* (Figure 2), resulting from dissociation of one and two *t*-butyl groups from the β -diketonate moiety, respectively (Figures 3 and 4).

With the exception of the parent ion, the dpm ligand is never observed intact while coordinated to platinum; only

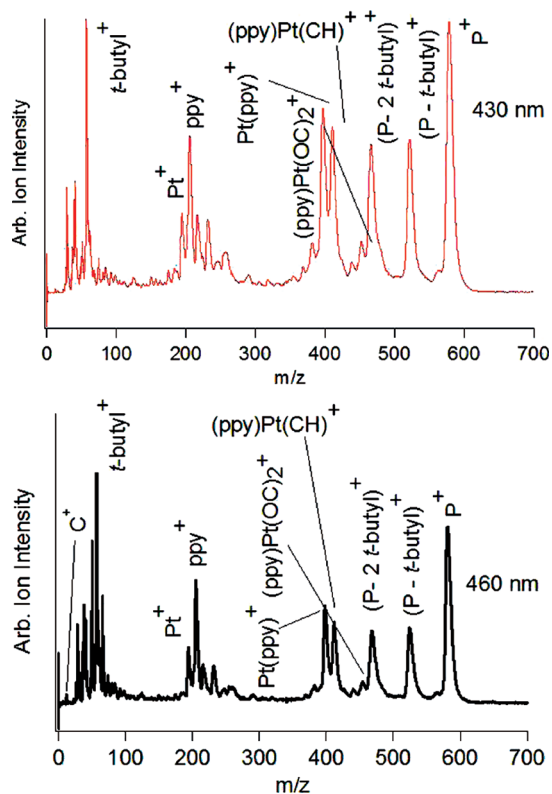


Figure 2. Mass spectra resulting from the photofragmentation of (3-Me-4',6'-dfppy)Pt(dpm) with visible excitation at 430 and 460 nm. The parent ion is the heaviest fragment formed and is the dominant species with 430 nm excitation. PtC^+ is not detected. The ppy ligand remains intact when coordinated to platinum and as the free cation. The ratio of $\text{ppy}^+:\text{Pt}(\text{ppy})^+$ is sensitive to excitation wavelength and increases as the wavelength increases from 430 to 460 nm.

smaller fragments of the ligand are found coordinated to the metal: (3-Me-4',6'-dfppy)Pt(OC) $_2^+$, 455 *m/z* and (3-Me-4',6'-dfppy)Pt(CH) $^+$, 412 *m/z*. It is notable that the (3-Me-4',6'-dfppy) ligand remains completely intact and coordinated to the metal center while dpm breaks apart.

The successive loss of *t*-butyl groups from the coordinated dpm ligand is not unprecedented; our photodissociation studies on a series of Ln(dpm) $_3$ (Ln = Eu, Gd, Tb) have also shown that the C–C bonds between the *t*-butyl groups and dpm ring are the first to be cleaved.^{20,21} It is interesting that the relative intensity ratios of (P-2*t*-butyl) $^+:(P-t$ -butyl) $^+:\text{P}^+$ are the same in both the lanthanide study and the current work, independent of the visible excitation wavelength between 410 and 450 nm.

2. Photochemical Behavior of Coordinated Ligands.

Fragments of the dpm ligand remain coordinated to platinum: (3-Me-4',6'-dfppy)Pt(CH) $^+$ and (3-Me-4',6'-dfppy)Pt(OC) $_2^+$ are bound (Figure 5).

Conversely, the lanthanide study showed that the dpm ring broke off completely from the metal after losing both *t*-butyl groups. The dpm photochemical behavior in the platinum compound studied here has not been previously observed for metal β -diketonate systems and was unexpected. The bond dissociation energies of coordinate-covalent transition-

metal–ligand bonds (e.g., $D(\text{Pt}–\text{C}) = 71$ kcal/mol)³⁴ are usually less than those of covalent ligand-centered bonds²⁶ (e.g., $D(\text{C}=\text{O}) = 191$ kcal/mol).³⁵ Hence, the breakup of the dpm ring would be expected to occur after the ligand is photolabilized from the metal center. The aforementioned heavy mass peaks are all broad in the mass spectra due to various degrees of deprotonation, masking platinum isotope resolution.

3. Metal–Ligand Photodissociation. While both the (3-Me-4',6'-dfppy) and dpm ligands are bidentate, they undergo very different photochemical reactions (Figure 6).

The (3-Me-4',6'-dfppy) group is observed as an intact ligand bound to platinum ($\text{Pt}(3\text{-Me-4',6'-dfppy})^+$, 399 *m/z*) and also as a free stable cation (ppy^+ , 204 *m/z*). The amount of free (3-Me-4',6'-dfppy) $^+$ is greater than that bound to the metal center as the excitation wavelength changes from 430 to 460 nm (i.e., the ratio of (3-Me-4',6'-dfppy) $^+:\text{Pt}(3\text{-Me-4',6'-dfppy})^+$ increases). At 460 nm, no other mass peak is more intense than that of (3-Me-4',6'-dfppy) $^+$ except the parent ion, where the ratio of (3-Me-4',6'-dfppy) $^+:\text{P}^+$ also increases.

4. Products from Multiple Photofragmentation Steps. The TOF mass spectra at 355 nm (Figure 7) show several mass peaks resulting from fragmentation of free dpm ligand: {dpm-*t*-butyl} $^+$, O_2C_3^+ , *t*-butyl, OC_3^+ , and CH_3CHO^+ .

Both the (3-Me-4',6'-dfppy) and dpm ligands can contribute to C_3^+ , C_2^+ , CH_3^+ , C^+ , and H^+ . However, C_3^+ , C_2^+ , and C^+ can easily originate from O_2C_3^+ and OC_3^+ . It is notable that no distinct mass peak assignments can be attributed to (3-Me-4',6'-dfppy) fragmentation. It is possible that after intact (3-Me-4',6'-dfppy) dissociates from platinum, it does not absorb photons. Any small organic fragments from (3-Me-4',6'-dfppy) then exist only as neutral species and are thus undetectable via TOF mass spectrometry. However, dpm continues to efficiently photofragment after dissociation from the metal.

This ligand behavior is also characteristic of the TOF mass spectra taken at 410–500 nm (Figure 2). After losing both *t*-butyl groups, dpm can follow multiple photodissociation routes. It may remain attached to platinum, while the majority of the ring falls apart, yielding (3-Me-4',6'-dfppy)Pt(CH) $^+$ and (3-Me-4',6'-dfppy)Pt(OC) $_2^+$. The alternative route is for dpm to leave the metal with its core intact, yielding {dpm-*t*-butyl} $^+$ and the series of organic fragments observed with UV excitation discussed in the preceding paragraph. The intensities of these small organic fragments (see Table 1) are now much greater than those caused by UV irradiation. The (3-Me-4',6'-dfppy) ligand, however, undergoes no such photochemical reactivity. It remains intact and coordinated to platinum, yielding (3-Me-4',6'-dfppy)Pt(CH) $^+$, (3-Me-4',6'-dfppy)Pt(OC) $_2^+$, and (3-Me-4',6'-dfppy)Pt $^+$. When the (3-Me-4',6'-dfppy) ligand dissociates intact from platinum, it is stable enough to efficiently ionize, yielding the free ligand cation.

The data suggest that dpm dissociates from platinum before (3-Me-4',6'-dfppy) does. No ion signals are observed

(34) Lewis, F. D.; Miller, A. M.; Salvi, G. D. *Inorg. Chem.* **1995**, *34*, 3173.

(35) Douglas, A. E. *J. Phys. Chem.* **1955**, *59*, 109–110.

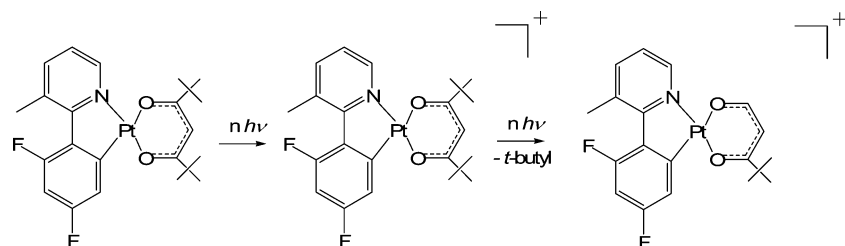


Figure 3. Primary photochemical reactions with visible excitation. Photo-oxidation produces the parent ion, the most intense metal-containing species in the mass spectrum. Dissociation of a *t*-butyl group also occurs.

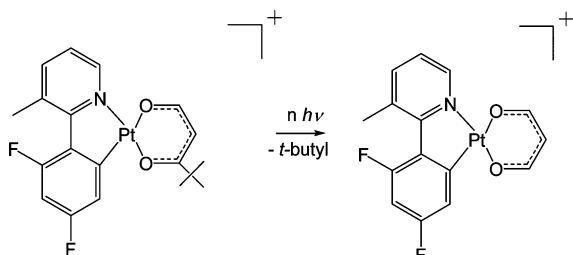


Figure 4. Successive photodissociation of *t*-butyl groups.

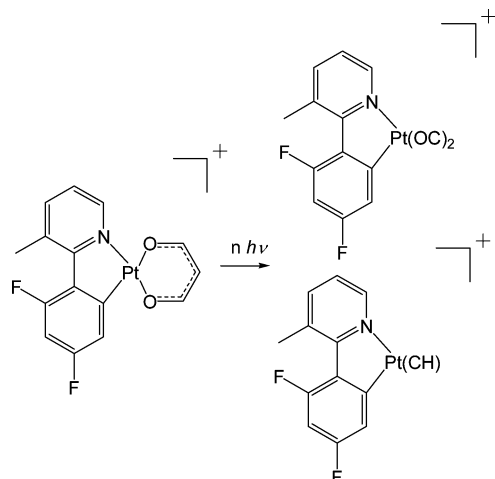


Figure 5. The ppy ligand remains attached to the metal and intact while the dpm ligand photofragments.

that contain dpm without coordinated (3-Me-4',6'-dfppy). On the other hand, (3-Me-4',6'-dfppy)Pt(CH)⁺ and (3-Me-4',6'-dfppy)Pt⁺ are prominent peaks. This may be a consequence of stronger metal–ligand bonds for (3-Me-4',6'-dfppy) than those of dpm.

The heaviest mass peaks observed with 355 nm excitation (Figure 7) were the naturally occurring isotopes of platinum (192, 194, 195, 196, and 198 *m/z*) and diatomic platinum carbide, PtC⁺ (207 *m/z*). Pt⁺ was produced with the highest ion yield in the heavy mass region above 100 *m/z*. Both the intact (3-Me-4',6'-dfppy) and dpm ligands were never observed, either as free cations or while coordinated to the metal center. The dpm with a *t*-butyl group dissociated was observed at 127 *m/z*.

The region below 100 *m/z* consists of peaks of small organic molecules arising from dissociation of the dpm ligand. The free *t*-butyl group is detected at 57 *m/z*, along with various amounts of hydrogen atom loss (51–56 *m/z*). The intact dpm core, O₂C₃⁺, is observed at 60 *m/z*, having

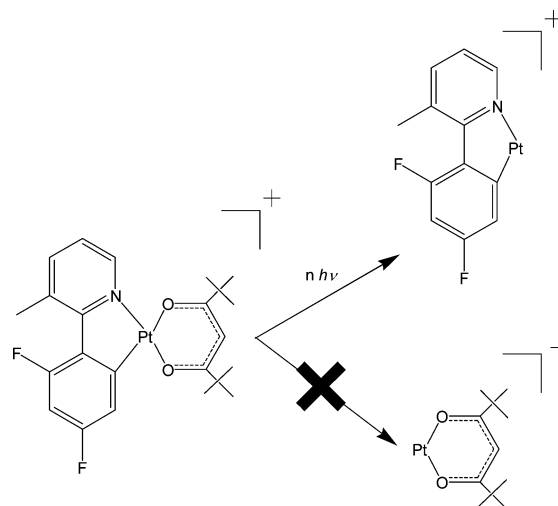


Figure 6. Metal–ligand dissociation. The Pt(ppy) fragment is formed in high yield, but Pt(dpm) is never observed.

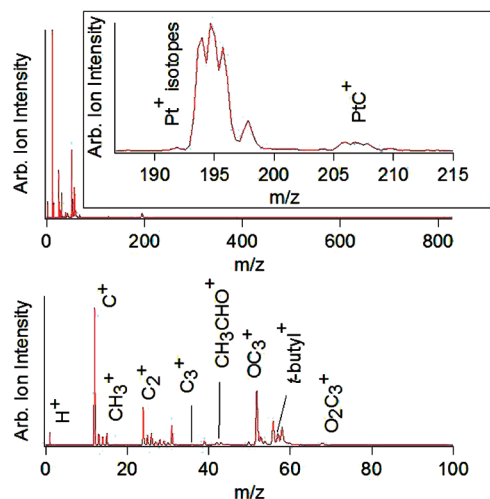


Figure 7. Mass spectra resulting from multiphoton fragmentation and ionization of (3-Me-4',6'-dfppy)Pt(dpm) with 355 nm excitation. Pt⁺ and PtC⁺ are readily formed (inset). Extensive photodissociation of the dpm ligand produces low mass ligand fragments.

lost both *t*-butyl groups. This fragment of the dpm ligand breaks apart atom by atom, losing an oxygen atom (OC₃⁺, 48 *m/z*), losing the second oxygen (C₃⁺, 36 *m/z*), and then losing successive carbons (C₂⁺, 24 *m/z*) until atomic carbon is produced as the most dominant ion formed at 355 nm excitation. An alternate fragmentation route is suggested from the observation of different dpm fragments where the O₂C₃ core is no longer intact: CH₃CHO⁺ with successive hydrogen

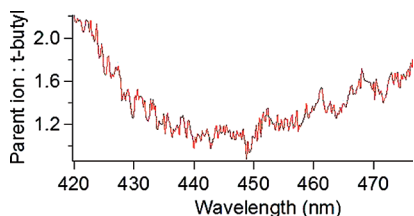


Figure 8. REMPI action spectrum of the ratio of the parent ion to *t*-butyl⁺ from 420 to 480 nm.

loss (41–44 *m/z*). Its relevance to the formation of diatomic PtC⁺ will be discussed later.

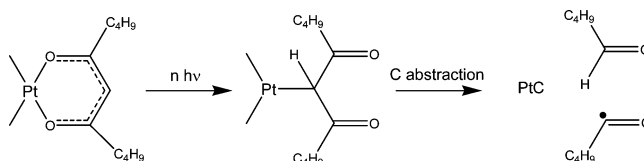
5. Wavelength-Dependent Photoionization of the Parent Molecule. The photochemical behavior of the neutral parent molecule is sensitive to the excitation wavelength. With 355 nm light, the parent ion and heavy metal-containing peaks are never observed. The heaviest mass peaks involving the metal are Pt⁺ and PtC⁺. (In the mass region above 100 *m/z*, the β -diketonate ligand minus a *t*-butyl group at 127 *m/z* is the major species.) Under 410–500 nm irradiation, the parent ion is the heaviest peak observed and is generally the most dominant ion signal. In order to rule out any power effects, TOF mass spectra were taken with 355 nm irradiation at the same fluences that were used for 410–500 nm excitation ($\sim 10^8$ W/cm²). The parent ion and heavy mass peaks were still never detected.

Two pathways are evident. With 355 nm light, the parent molecule absorbs photons and dissociates into fragments before it is ionized. The ionized parent molecule is not present in the mass spectrum. This process is the classic fragmentation before the ionization mechanism of multiphoton ionization.^{5,15} With visible excitation between 410 and 500 nm, the parent molecule absorbs photons and preferentially ionizes before any metal–ligand bonds are cleaved. The subsequent fragments formed can in turn absorb additional photons, resulting in a series of heavy metal-containing peaks until eventually platinum is produced. This sequence is the classic ionization before fragmentation mechanism.^{5,15}

In order to further study the wavelength dependencies, ion intensities of the platinum ion and the parent ion were monitored as a function of excitation wavelength in the 410–500 nm region. Figure 8 shows the relative intensity of the parent ion to *t*-butyl⁺ as a function of excitation wavelength.

The intensity of *t*-butyl⁺ exhibited no wavelength dependence; plotting the relative intensity eliminates baseline contributions from OPO shot-to-shot fluctuations. In general, it is expected that the REMPI spectrum of the gaseous parent ion would yield a vibronically structured action spectrum that is slightly blue-shifted relative to the parent molecule's solution-phase absorption spectrum. In Figure 8, the observed onset of the excitation spectrum at 450 nm occurs at about the same energy as that observed in the solution-phase absorption spectrum at 460 nm.³² This trend suggests that absorption of the first photon in the gas phase in this region involves the same excited state as that involved in the solution-phase absorption. The intensity slowly increases as the wavelength increases from 450 to 500 nm. The molecule does not absorb in this wavelength region, and the ionization

Scheme 1. Proposed Mechanism for the Formation of PtC⁺ from Irradiation of (3-Me-4',6'-dfppy)Pt(dpm) with UV and Visible Irradiation



may be the result of multiphoton processes where the first photon is not in resonance with an excited state.

6. Wavelength Dependence of the Photolabilization of (3-Me-4',6'-dfppy). Figure 2 shows the TOF mass spectra taken with 430 and 460 nm irradiation. As the excitation energy decreases, the peak intensity ratio of (3-Me-4',6'-dfppy)⁺:Pt(3-Me-4',6'-dfppy)⁺ increases. In addition, the relative amount of (3-Me-4',6'-dfppy)⁺ to the parent ion also increases. The data suggest that the Pt–N and Pt–C bonds are weakened to a greater extent as the excitation wavelength approaches 460 nm. This wavelength is in resonance with the reported lowest energy triplet absorption band centered at around 460 nm ($\epsilon = 40$ M⁻¹ cm⁻¹).³² This charge-transfer band has been characterized as a mixture of metal to ligand and ppy-centered orbitals. Thus, ppy is labilized to a greater extent in this region.

7. Formation of Diatomic Platinum Carbide and the Absence of Platinum Fluoride. Previous photofragmentation studies on gaseous metal-containing β -diketonates^{30,31} detected diatomic metal compounds such as MO⁺, MC⁺, and MF⁺. In several cases, the heteroatom came from the initial metal–atom bond in the starting material. In other cases, an intramolecular ligand rearrangement resulted in atom abstraction by the metal. Our TOF data suggest that such a rearrangement is occurring.

With 355 excitation, PtC⁺ is efficiently formed. The (3-Me-4',6'-dfppy) ligand would be the likely origin of the carbon due to the existence of the Pt–C bond in the starting material. However, previous work³⁶ has shown that carbon can be abstracted by platinum (Scheme 1) from the β -diketonate ligand after an intramolecular rearrangement. Diatomic metal fluorides and/or carbides were formed in a series of homoleptic transition-metal β -diketonate systems (M(hfac)₂; M = Cr(III), Ni(II), Cu(II), Pd(II), Pt(II))³⁶ and in the mixed-ligand coordination compound *trans*-bis(trifluoroacetato) bis(*N,N'*-dimethylethylenediamine)nickel(II).²² The proposed mechanism involved excitation of the π – π^* system on the hfac ring, cleaving an M–O bond, and leading to rotation about the C–C bond bringing the CF₃ group into proximity with the metal. This is followed by fluorine abstraction by the metal. Alternatively, with multiphoton absorption, an intramolecular rearrangement could enable the β -carbon to bind to the metal. Such M–C bonds are known for Pd and Pt complexes.³⁴ Interestingly, carbon abstraction only occurred in Pd(hfac)₂ and Pt(hfac)₂.³⁶ In the proposed scheme, one of the organic byproducts was an aldehyde, CH₃CHO. Figure 7 clearly shows this ion to be present in our mass

(36) Cheon, J.; Kang, H.-K.; Zink, J. I. *Coord. Chem. Rev.* **2000**, 200–202, 1009–1032.

spectra and does not fit with the dominant dp fragmentation pattern (e.g., $O_2C_3^+$, OC_3^+ , C_3^+ , C_2^+). The abstraction mechanism is further supported by the data in Figure 2, where $(ppy)Pt(CH)^+$ is a major peak.

Since fluorine abstraction by transition metals is known to readily occur in the gas phase, the mass region where PtF^+ would occur was scrutinized (Figure 7 inset). No ion signal was detected at any of the wavelengths studied. Fluorine abstraction from the (3-Me-4',6'-dfppy) ligand does not occur, perhaps due to the structural rigidity of the macrocyclic system. The intramolecular rearrangement required for abstraction to occur appears to be unique to mono- and bidentate β -diketonate ligands.

Summary

The photodissociation routes of gaseous (3-Me-4',6'-dfppy)Pt(dpm) have been characterized via TOF-MS and REMPI. A strong wavelength dependence is clear, revealing a rich amount of unique photochemistry. Under UV irradiation, the platinum cation and PtC^+ are the heaviest mass peaks observed, while with violet-blue light the parent ion is both the dominant and heaviest peak detected. Diatomic PtC^+ is the result of an intramolecular rearrangement of dpm and does not come from the initial Pt–C bond in the starting

material. The ligands follow strikingly different photofragmentation pathways. The macrocyclic ligand either stays intact while attached to the metal center or falls off completely, but the β -diketonate moiety is always observed as a fragment (never intact) when it is coordinated or dissociated. In addition, dpm dissociates first with violet-blue excitation. Finally, a spin-forbidden charge-transfer absorption band centered at around 460 nm seems to play a very important role in the gas-phase photoexcitation of the parent molecule, as this transition is observed in the parent ion TOF-REMPI.

(3-Me-4',6'-dfppy)Pt(dpm) can be added to the growing list of metal-containing coordination compounds where ionization of the parent molecule can precede ligand fragmentation. Depending on excitation wavelength, the parent ion and metal-containing mass peaks can be generated in dominant yield, even more so than the metal cation. This wavelength-selected mechanism is much more common than previously once thought.

Acknowledgment. This work was made possible by a grant from the National Science Foundation (CHE-0507929).

IC701383Y