Scheme I

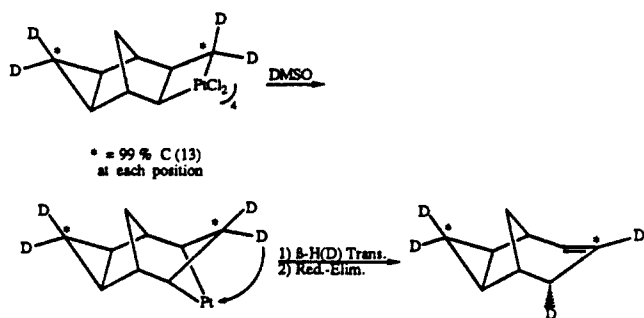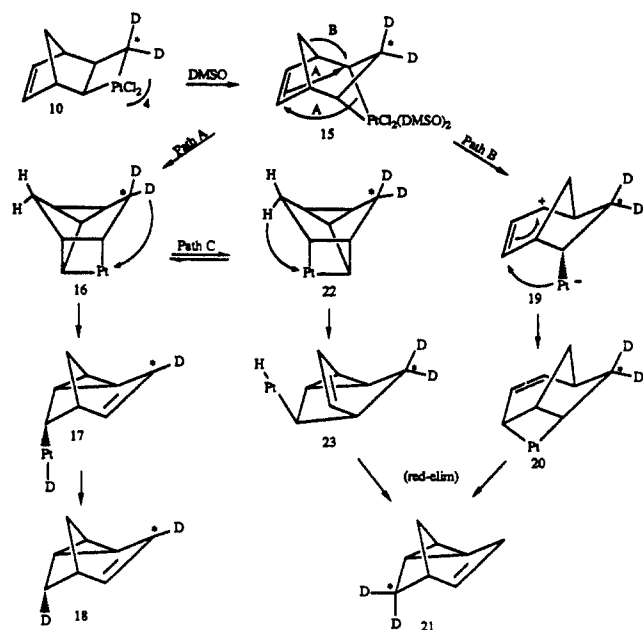* = 99 % C(13)
at each position

1) β-H(D) Trans.
2) Red.-Elim.

Scheme II

at the exo position of carbon b (eq 4). To distinguish between these two pathways, compound **12** was prepared.[12,13] Path B would *not* be adversely affected by this substitution, and path C would be *entirely precluded* since the β-hydrogen elimination is blocked by the phenyl substituent. The results are shown as eq 5. Both *pathways* (B and C) would have given ^{13}C label at carbon (b) (compare eq 5 to paths B and C in **21** Scheme II). Since the only label observed was at carbon (a), it must be concluded that path C was blocked by the phenyl substituent in **12** and B is not followed at all. Hence, it appears that path A is responsible for 66% of the product and C is responsible for 33% of the product in the Pt(II)-catalyzed transformation of **2** via the *platina(IV)-cyclobutane intermediate* which is shown as structure **10**.

Supplementary Material Available: Spectroscopic data for **3, 5, 8, 11**(D), **11**(^{13}C), and **14** (4 pages). Ordering information is given on any current masthead page.

(12) Prepared with diazomethane (99% [13]C), Pd(OAc)$_2$, and 7-phenyl-norbornadiene (Frinton).

(13) Dissolution of **13** in pyridine and CDCl$_3$ gave the stable platina-(IV)cyclobutane monomer: ^{13}C NMR (CDCl$_3$) –2.5 (t, J_{PtC} = 375 Hz), 10.7 (d, J_{PtC} = 406 Hz), 41.7 (d), 41.9 (d, J_{PtC} = 22 Hz), 52.1 (d, J_{PtC} = 84 Hz), 56.8 (d), 131.0 (d, J_{PtC} = 28 Hz), 132.8 (d) (142.4, 128.8, 127.3, 124.8; phenyl carbons).

Electrospray Ionization: A New Tool for the Analysis of Ionic Transition-Metal Complexes

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Ionic transition-metal complexes have been difficult to analyze by mass spectrometry because of their low volatility, high thermal lability, and their tendency to undergo reduction during the ionization process.[1–6] We have succeeded in generating, by electrospray ionization, intense beams of intact gas-phase cations from ionic transition-metal complexes, such as [Ru^{II}(bpy)$_3$]Cl$_2$ (where bpy = 2,2'-bipyridyl) (I) and [Ru^{II}(phen)$_3$]Cl$_2$ (where phen = 1,10-phenanthroline) (II). In contrast to infrared laser desorption multiphoton ionization,[2] fast atom bombardment,[3,6] and field desorption,[6] the cations observed from these complexes with electrospray ionization do not undergo reduction by electron or hydrogen transfer.

Electrospray ionization is a gentle ionization technique that can produce multiply charged ions from organic molecules in solution. Several workers[7–9] have interfaced atmospheric pressure electrospray ionization sources to quadrupole mass analyzers and have obtained mass spectra from a variety of compounds including dyes, polymers, peptides, and proteins. Recently, we have designed a novel electrospray ionization source for use with a single quadrupole mass analyzer.[10] In this source, the charged droplets, produced by electrospray at atmospheric pressure, are focused and transported through a 203-mm-long stainless steel capillary tube into a region maintained at a pressure of 1–10 Torr. Controlled heating of the capillary tube assists in the evaporation of solvent from these droplets and in the desolvation of solvated analyte ions. Because complete desolvation of the analyte ions is not always achieved by heat alone, the ions exiting the capillary tube may remain partially solvated. Application of an electrostatic field in the low-pressure region between the capillary exit and a coaxial skimmer causes collisional activation of these solvated analyte ions.[10,11] This electrostatic field can be easily varied and provides a fine control over the amount of collisional activation. At low levels of activation, complete desolvation of the cations can be effected without causing fragmentation. At higher levels of activation, the desolvated cations can be induced to undergo dissociation to give structurally informative fragment ions.

The potential of the technique is evident from the electrospray ionization mass spectra (Figure 1) of [Ru^{II}(bpy)$_3$]Cl$_2$ (M_r = 641), obtained by electrospraying a 15 pmol/μL solution in acetonitrile. When the level of collisional activation is low (Figure 1a), the most intense peak in the spectrum corresponds to the Ru(bpy)$_3^{2+}$ ion at m/z 285.[12] The spectrum also exhibits a series of lower

(1) Chan, K. W. S.; Cook, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 5031–4.

(2) Beavis, R.; Lindner, J.; Grotemeyer, J., Atkinson, I. M.; Keene, F. R.; Knight, A. E. W. *J. Am. Chem. Soc.* **1988**, *110*, 7534–5.

(3) Callahan, J. H.; Hool, K.; Reynolds, J. D.; Cook, K. D. *Anal. Chem.* **1988**, *60*, 714–9.

(4) Miller, J. M.; Balasanmugam, K.; Nye, J.; Deacon, G. B.; Thomas, N. C. *Inorg. Chem.* **1987**, *26*, 560–2.

(5) Cetini, G.; Operti, L.; Vaglio, G. A.; Bandini, A. L.; Banditelli, G.; Minghetti, G. *Org. Mass Spectrom.* **1989**, *24*, 479–84.

(6) Cerny, R. L.; Sullivan, B. P.; Bursey, M. M.; Meyer, T. J. *Anal. Chem.* **1983**, *55*, 1954–8.

(7) Whitehouse, C. M.; Dreyer, R. N.; Yamashita, M.; Fenn, J. B. *Anal. Chem.* **1985**, *57*, 675. Fenn, J. B.; Mann, M.; Meng, C. K.; Wong, S. F.; Whitehouse, C. M. *Science* **1989**, *246*, 64.

(8) Loo, J. A.; Udseth, H. R.; Smith, R. D. *Anal. Biochem.* **1989**, *179*, 404.

(9) Covey, T. R.; Bonner, R. F.; Shushan, B. I.; Henion, J. D. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 249.

(10) Chowdhury, S. K.; Katta, V.; Chait, B. T. *Rapid Commun. Mass Spectrom.* **1990**, *3*, 81–7.

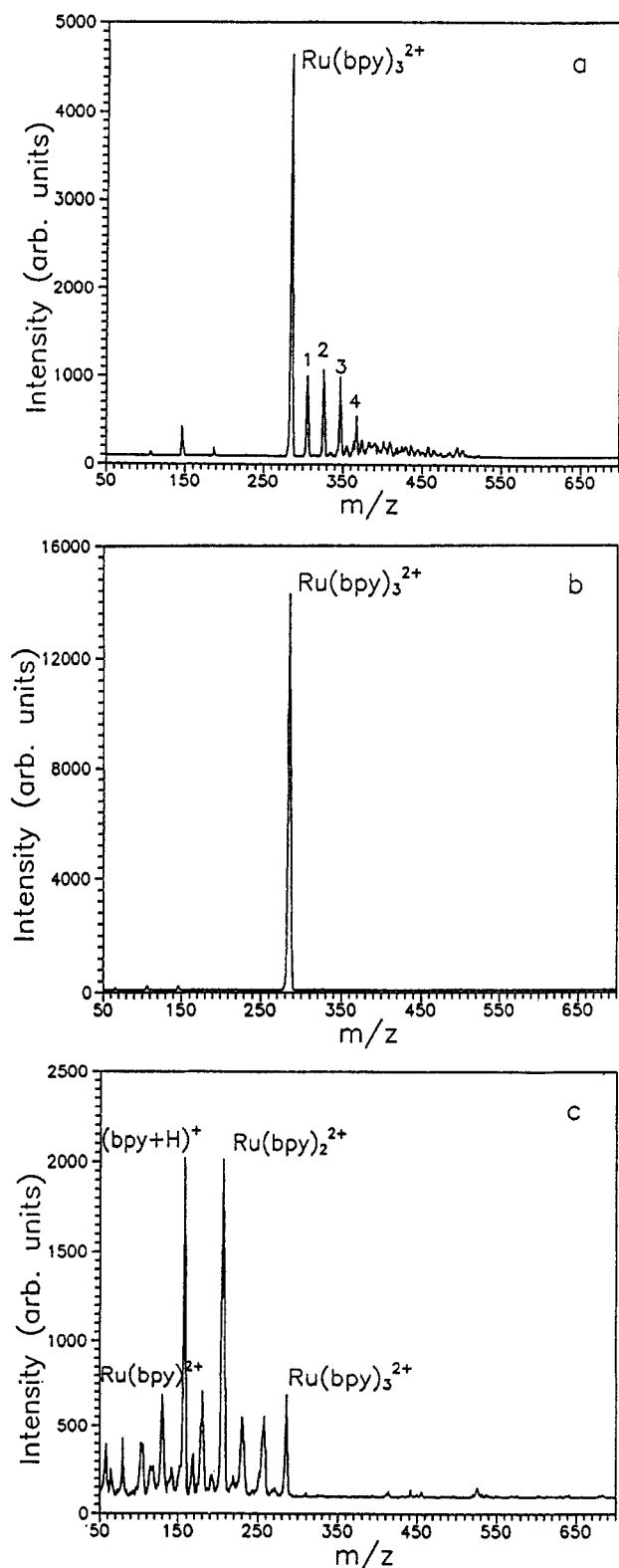(11) Loo, J. A.; Udseth, H. R.; Smith, R. D. *Rapid Commun. Mass Spectrom.* **1988**, *2*, 207.

Figure 1. Electrospray ionization mass spectra of [Ru^{II}(bpy)$_3$]Cl$_2$, obtained by electrospraying a 15 pmol/μL solution in acetonitrile at a rate of 2 μL/min. The total sample consumption per spectrum is less than 50 pmol. The spectra were obtained at three different collisional activation levels, indicated by the difference in potentials (ΔV) between the capillary exit and the skimmer. (a) At $\Delta V = 50$ V, the spectrum shows a peak from the Ru(bpy)$_3{}^{2+}$ ion at m/z 285 and peaks denoted as 1, 2, 3, and 4 are from attachment of one, two, three, and four acetonitrile molecules to the Ru(bpy)$_3{}^{2+}$ ion. The small peak at m/z 146 arises from an unidentified impurity. (b) At $\Delta V = 90$ V, the Ru(bpy)$_3{}^{2+}$ ion is completely desolvated. (c) At $\Delta V = 190$ V, the Ru(bpy)$_3{}^{2+}$ ion dissociates and fragment ions appear in the spectrum. Electron multiplier voltage = 2400 V.[13]
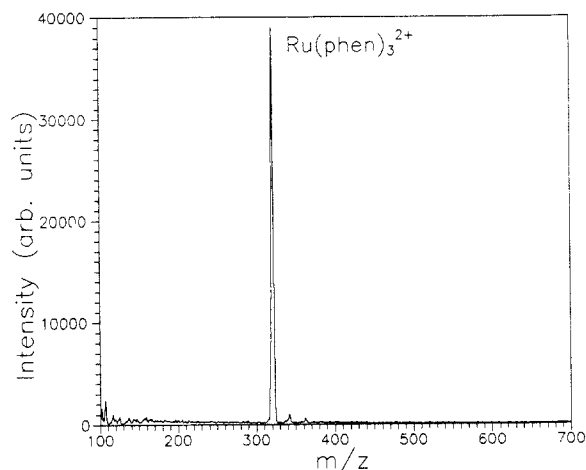

Figure 2. Electrospray ionization mass spectrum of [Ru^{II}(phen)$_3$]Cl$_2$, obtained by electrospraying a 2 pmol/μL solution (acetonitrile) at a rate of 2 μL/min. The total sample consumed in obtaining the spectrum was 9 pmol. The collisional activation ($\Delta V = 120$ V) is just sufficient for complete desolvation of the Ru(phen)$_3{}^{2+}$ ion (m/z 321). Electron multiplier voltage = 2600 V.[13]

intensity peaks resulting from the attachment of one, two, three, and four acetonitrile solvent molecules to the doubly charged ion. When the activation is just sufficient for complete desolvation (Figure 1b), the mass spectrum is completely dominated by a single intense peak of Ru(bpy)$_3{}^{2+}$ ions. There is no fragmentation or reduction. However, upon further increase of the activation (Figure 1c), the doubly charged ion dissociates and structurally informative fragment ions appear in the mass spectrum. The most intense of these correspond to Ru(bpy)$_2{}^{2+}$, Ru(bpy)$^{2+}$, and (bpy + H)$^+$ ions.

Results similar to those given above were obtained from I dissolved in neat methanol or neat acetone, demonstrating a considerable flexibility in the choice of solvent system. In contrast to electrohydrodynamic ionization,[1] nonvolatile solvents (e.g., glycerol) and added electrolytes are not required in the present technique.

Figure 2 shows the electrospray ionization mass spectrum of [Ru^{II}(phen)$_3$]Cl$_2$ ($M_r = 713$). Under the collisional activation conditions just sufficient for desolvation (Figure 2), the spectrum consists almost entirely of a single intense peak corresponding to the Ru(phen)$_3{}^{2+}$ ion at m/z 321.[12] There is no reduction or fragmentation of this doubly charged cation. The behavior of II at lower and higher activations is closely analogous to that observed for I (Figure 1).

The results presented above demonstrate that electrospray ionization is a powerful tool for the analysis of ionic transition-metal complexes. Both molecular weight and structural information can be obtained by controlling the degree to which the ionized molecules of interest are collisionally excited. The described electrospray ion source produces intense beams of transition-metal complex ions, that are either bare or solvated to a controllable extent. The ion fluxes appear to be sufficiently high for carrying out investigations of gas-phase ion–molecule reactions. Because the metal complex ions are produced in a supersonic jet expansion, it may also be possible to carry out photospectroscopic studies on these ions.

(12) The m/z values given for ions from both the complexes are for the component containing the most abundant of the seven naturally occurring isotopes of ruthenium, ^{102}Ru.

(13) Sensitivity for the complexes is sufficiently high that, to prevent saturation of the electronics, the electron multiplier was operated at reduced gains (lower applied voltages) than those normally used for protein measurements.[10]