tered-glass shaker with a NaCl solution (0.5 M, 50 °C, 60 mL, 10 × 5 min), DMF (room temperature 60 mL, 10 × 5 min), and H_2O (room temperature, 60 mL, 10 × 5 min). Following the three-step washing sequence, the resin was shaken in NaCl solution (0.5 M, room temperature, 60 mL) for 1 h and an aliquot was filtered and counted to monitor the rate of bleed. The washing procedure was repeated (5–10 cycles) until the bleed rate fell below 1000 cpm/100 mg per hour (this value is based on a specific activity of 10^7 cpm/100 mg). Finally, the resin was rinsed with CH_2Cl_2 (60 mL, 3 × 5 min) and the solvent is removed under high vacuum overnight. Note that it is important that the bulk of the unattached glycine be removed by washing before the resin is dried for storage. Otherwise, it takes considerably longer for the rate of bleed to reach a constant (base-line) level upon reswelling the dried beads.

Synthesis and Washing of the Polyamide Resin Derivatized with Unlabeled Tetrapeptide. The cold tetrapeptide was synthesized on the resin by using the same procedure as for the radiolabeled tetrapeptide, except that cold glycine was used in place of the [2-^{14}C]glycine (−5 °C, 36 h). Before warming of the mixture to room temperature, 50 μCi of labeled glycine was added to the resin derivatized with the cold tetrapeptide. The resin mixture was warmed to room temperature and shaken for 24 h. The resin was then washed and the radioactivity monitored as described for the radiolabeled tetrapeptide.

General Procedure for Measuring Rates of Hydrolysis. A sample of polyamide resin derivatized with labeled tetrapeptide **4** (100 mg) was put in a 1-dram vial. The appropriate buffer (4 mL) was added and the vial was shaken for 24 h on a Milligen Model 504 shaker. The vial was centrifuged for 1 min (1000 rpm, IEC Clinical Centifuge), and two 1-mL aliquoits were carefully withdrawn from the top and filtered through a cotton plug into glass scintillation vials. Hionic-fluor (9 mL, Packard) was added, the vials were shaken by hand, and the radioactivity was counted (Packard Tri Carb Model 1500 scintillation counter).

Fresh buffer (2 mL) was added to the 1-dram vial containing the resin. After shaking of the mixture for 24 h, two 1-mL samples were withdrawn and counted as before. This procedure was repeated 12 more times (14 total), and the number of new counts produced every 24 h was calculated by using the following formula:[18]

$$2 \times [2\ (\text{counts}/1\ \text{mL of sample after 24 h}) - (\text{counts}/1\ \text{mL of sample as start})] = \text{total new counts produced in 24 h}$$

The data for the last 72 h was averaged and the mean value was used to calculate a rate constant by using the following formulae:

$$k = V/[\mathrm{S}]$$

$$V = [\text{av number of new counts}/24\ \text{h (for 100 mg of resin)}] \times [24\ \text{h}/86400\ \text{s}]\ [1\ \mu\text{Ci}/2.2 \times 10^6\ \text{counts}] \times [1\ \mu\text{mol}/50\ \mu\text{Ci}]$$

$$[\mathrm{S}] = [3 \times 10^7\ \text{counts (for 100 mg of resin)}] \times [1 \mu\text{mol}/50\ \mu\text{Ci}] \times [1\ \mu\text{Ci}/2.2 \times 10^6\ \text{counts}]$$

Communications to the Editor

CO_2-Laser Desorption and Multiphoton Ionization of Tris(2,2′-bipyridyl)ruthenium

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Elucidation of the spectroscopy of metal coordination compounds is an important ingredient in arriving at an understanding of their photophysical and photochemical properties. However, in solution and the condensed phase, most metal complexes and organometallic compounds display electronic spectra that are environmentally broadened and are therefore relatively uninformative, and the low volatility of these species usually precludes gas-phase studies.[4,5] Ideally, it would be desirable to measure spectra of metal coordination compounds under molecular beam conditions where the cooling and rarefaction afforded by expansion would assist in reducing thermal congestion in the electronic spectrum.[6] The spectroscopy of ruthenium polypyridyl complexes is of particular interest, because of their relevance as photosensitizers for solar energy conversion schemes.[7] However, to our knowledge there have been no successful attempts to introduce such molecules into the gas phase for measurement of their spectroscopy.

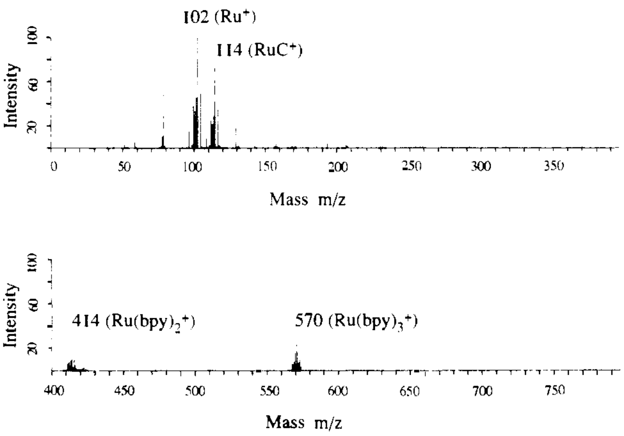

Figure 1. Resonance enhanced multiphoton ionization time-of-flight mass spectrum following CO_2-laser desorption of $[Ru(bpy)_3](CH_3COO)_2$.

We have succeeded in producing a seeded molecular beam expansion of the tris(2,2′-bipyridyl)ruthenium moiety by using a pulsed CO_2-laser desorption technique[8-10] that has been employed successfully to introduce many other involatile species into molecular beam expansions for analytical[11] purposes.

Details of the CO_2-laser desorption and multiphoton ionization technique have been described elsewhere.[8-10] In the present ap-

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plication, tris(2,2′-bipyridyl)ruthenium(II) acetate is encased in a polyethylene tablet mixed with finely divided metal powder (gold or silver, 1 μm diameter). The use of such composite materials to aid desorption will be fully described in a future publication. This method of sample preparation has been found to minimize fragmentation during the desorption process. The CO_2 TEA low-pressure laser (bimodal pulse, initial spike FWHM = 1 μs, tail FWHM = 10 μs, 10 mJ pulse energy) is weakly focussed on the sample probe which is located 2–3 mm below the axis of the expansion orifice. The desorbed compound is carried downstream to the ionization region (differentially pumped) where two-photon ionization is effected by a focussed frequency doubled pulsed dye laser tuned to 290 nm. At this wavelength, the photon energy is sufficient to resonantly ionize the bipyridyl ligands via the first excited electronic state. Ions are detected with a Bruker TOF-1 reflectron time-of-flight mass spectrometer.

Figure 1 displays the multiphoton ionization mass spectrum of the tris(2,2′-bipyridyl)ruthenium complex following CO_2-laser desorption. Clearly evident is the cluster of peaks around m/z = 570 amu. This almost certainly corresponds to the $[\text{Ru(bpy)}_3]^+$ ion since there is little likelihood that clustering would lead to a doubly charged dimer ion. Indirect confirmation of this assignment is obtained from the isotopic splitting pattern (due to the seven Ru and the ^{13}C and ^{15}N isotopes in natural abundance) and from the observation of the $[\text{Ru(bpy)}_2]^+$ fragment (m/z = 414 for the most abundant Ru isotope). Ru^+ and RuC^+ fragments (m/z = 102, 114 for the most abundant ^{102}Ru isotope) are also observed. There is also evidence for some pyridine derived fragments (C_5H_4N, m/z = 78). Obviously absent from the spectrum displayed in Figure 1 are $[\text{Ru(bpy)}]^+$, (m/z = 258), $[\text{Ru(bpy)}_3]^{2+}$, (m/z = 285), and bipyridyl$^+$ (m/z = 156).

It is a little surprising at first glance, given that the original sample is a salt of the Ru(II) complex, that the $[\text{Ru(bpy)}_3]$ complex appears in the mass spectrum only as a *singly* charged cation. (Both the acetate and trifluoromethanesulfonate salts yielded the same results). In the following analysis of the mass spectrum we suggest possible reasons as to why this may be the case.

The assignment of the cluster of peaks at m/z = 570 as the $[\text{Ru(bpy)}_3]^+$ complex does not appear to be in any doubt. Because of the instrumental configuration (positively charged repeller grid), only a neutral $[\text{Ru(bpy)}_3]$ complex could enter the ionizing region. The laser photon energy (4.3 eV) is sufficient to two-photon ionize one of the bpy ligands, thus we observe $[\text{Ru(bpy)}_3]^+$ cation. The neutral $[\text{Ru(bpy)}_3]$ complex is probably formed during the desorption process as a consequence of progressive electron attachment to the $[\text{Ru}^{\text{II}}\text{(bpy)}_3]^{2+}$ cation, leading to $[\text{Ru(bpy)}_3]^+$, $[\text{Ru(bpy)}_3]^0$, and possibly $[\text{Ru(bpy)}_3]^-$. (Only the neutral species will enter the ionizing region.) Support for this mechanism comes from electrochemical and spectral studies of the reduction of $[\text{Ru}^{\text{II}}\text{(bpy)}_3]^{2+}$ in solution where sequential addition of electrons occurs, the added electrons remaining somewhat localized on the separate ligands.[12]

Other species found in the mass spectrum ($[\text{Ru(bpy)}_2]^+$, Ru^+, $C_5H_4N^+$) could appear either as a result of dissociation of the $[\text{Ru(bpy)}_3]^+$ cation during ionization or if they are formed as dissociation products during the desorption process. We favor the latter explanation since there is no evidence in the mass spectrum for the bipyridyl ligand that would be released on dissociation of $[\text{Ru(bpy)}_3]^+$. Ionization of bipyridyl, if present, would be possible with the available photon energy. During desorption, bipyridyl released due to dissociation of $[\text{Ru(bpy)}_3]^+$ presumably attaches an electron and is therefore not transmitted through the ionization region. The small yield of C_5H_4N is probably due to the dissociation $\text{bpy}^- \rightarrow C_5H_4N^- + C_5H_4N$, with the neutral fragment being transmitted and ionized via near-resonant multiphoton ionization.

This demonstration that tris(2,2′-bipyridyl)ruthenium may be introduced into a molecular beam offers immense promise for the application of laser spectroscopy to metal coordination compounds in general. We are proceeding toward applying this combination of laser desorption with resonance enhanced multiphoton ionization spectroscopy to measure the electronic spectrum of $[\text{Ru(bpy)}_3]$ under cold molecular beam conditions.

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Photooxidation of $(\eta^5\text{-C}_5\text{H}_5)[\text{P(OMe)}_3]_2\text{Mo}{\equiv}\text{CPh}$ in $CHCl_3$. Intermediacy of a 17-Electron Cationic Metal Carbyne

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The photochemistry of metal carbyne complexes has recently been shown to lead to several interesting reaction types, including coupling with ancillary carbonyl ligands to give ketenyl complexes,[1,2] protonation of the carbyne carbon,[3] insertion into a C–H bond,[4] and addition of the carbyne carbon to an alkyne to produce a cyclopropenyl complex.[5] Spectroscopic studies of metal carbynes[6] have demonstrated the presence of low-lying metal-to-ligand charge-transfer (MLCT) excited states, and the observed modes of reactivity have been attributed to these states. We have now observed yet another class of reaction for excited state metal carbynes. Upon photolysis in $CHCl_3$ or CH_2Cl_2 in the presence of PMe_3, the carbyne $(\eta^5\text{-C}_5\text{H}_5)[\text{P(OMe)}_3]_2\text{Mo}{\equiv}\text{CPh}$ (**1**) undergoes an electron-transfer reaction and subsequent ligand exchange to yield $[(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2(\text{Cl})\text{Mo}{\equiv}\text{CPh}]^+\text{Cl}^-$ (**2**) via highly unusual 17-electron metal carbyne intermediates.[7]

Carbyne complex **1**[8] does not undergo thermal reaction with $CHCl_3$ or CH_2Cl_2 nor can its phosphite ligands be photochemically exchanged for phosphines in tetrahydrofuran. However, photolysis of **1** in $CHCl_3$ solution in the presence of PMe_3 results in rapid disappearance of the starting material and formation of **2**,[10] 2 equiv of free $P(OMe)_3$ and 2 equiv of an unidentified product that contains PMe_3.[11] NMR experiments show **2** to be formed in

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(8) **1** is synthesized by reaction of sodium cyclopentadienide with $\text{Cl[P(OMe)}_3]_4\text{Mo}{\equiv}\text{CPh}$.[9] For **1**: ^{1}H NMR (C_6D_6) 3.49 (filled in doublet, 18 H), 5.34 (s, 5 H), 6.97 (m, 1 H), 7.05 (t, 2 H), 7.51 (d, 2 H) ppm; ^{31}P NMR (C_6D_6) 213 ppm; ^{13}C NMR (C_6D_6) 51.1, 89.8, 125.7, 128.5, 149.9, 286.3 (t, J_{CP} = 26.5 Hz) ppm; UV (THF) 324 (ϵ = 2000) 500 (ϵ = 50) nm.

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(10) For **2**: ^{1}H NMR ($CDCl_3$) 1.78 (filled in doublet, 18 H), 6.18 (d, J_{CP} = 2 Hz, 5 H), 7.25 (m, 2 H), 7.43 (m, 3 H) ppm; ^{13}C NMR ($CDCl_3$) 17.8 (t, J_{CP} = 17.5 Hz) 101.5, 128.9, 129.5, 132.4, 144.2, 354.6 (t, J_{CP} = 33 Hz) ppm; MS (FAB) M^+ 439. Isotope abundance for the molecular ion matched simulation for $MoC_{18}H_{28}P_2Cl$. Anal. ($C_{18}H_{28}Cl_2MoP_2$) C, H, Cl.

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