plication, tris(2,2′-bipyridyl)ruthenium(II) acetate is encased in a polyethylene tablet mixed with finely divided metal powder (gold or silver, 1 $\mu$m 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 $\mu$s, tail FWHM = 10 $\mu$s, 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 $[Ru(bpy)_3]^+$ 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 $[Ru(bpy)_2]^+$ 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 $[Ru(bpy)]^+$, ($m/z$ = 258), $[Ru(bpy)_3]^{2+}$, ($m/z$ = 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 $[Ru(bpy)_3]$ 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 $[Ru(bpy)_3]^+$ complex does not appear to be in any doubt. Because of the instrumental configuration (positively charged repeller grid), only a neutral $[Ru(bpy)_3]$ 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 $[Ru(bpy)_3]^+$ cation. The neutral $[Ru(bpy)_3]$ complex is probably formed during the desorption process as a consequence of progressive electron attachment to the $[Ru^{II}(bpy)_3]^{2+}$ cation, leading to $[Ru(bpy)_3]^+$, $[Ru(bpy)_3]^0$, and possibly $[Ru(bpy)_3]^-$. (Only the neutral species will enter the ionizing region.) Support for this mechanism comes from electrochemical and spectral studies of the reduction of $[Ru^{II}(bpy)_3]^{2+}$ 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 ($[Ru(bpy)_2]^+$, $Ru^+$, $C_5H_4N^+$) could appear either as a result of dissociation of the $[Ru(bpy)_3]^+$ 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 $[Ru(bpy)_3]^+$. Ionization of bipyridyl, if present, would be possible with the available photon energy. During desorption, bipyridyl released due to dissociation of $[Ru(bpy)_3]^+$ 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 $bpy^- \rightarrow C_5H_4N^- + C_5H_4N$, 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 $[Ru(bpy)_3]$ under cold molecular beam conditions.

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## Photooxidation of $(\eta^5\text{-}C_5H_5)[P(OMe)_3]_2Mo{\equiv}CPh$ 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 $(\eta^5\text{-}C_5H_5)[P(OMe)_3]_2Mo{\equiv}CPh$ (**1**) undergoes an electron-transfer reaction and subsequent ligand exchange to yield $[(\eta^5\text{-}C_5H_5)(PMe_3)_2(Cl)Mo{\equiv}CPh]^+Cl^-$ (**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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(7) To our knowledge, the only other report of a 17-electron metal carbyne involves the oxidative conversion of $Cl(PMe_3)_4W{\equiv}CH$ to $[W_2(CPMe_3)_2(PMe_3)_4Cl_4]$ by $C_2Cl_6$ and $AlCl_3$. Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476–484.

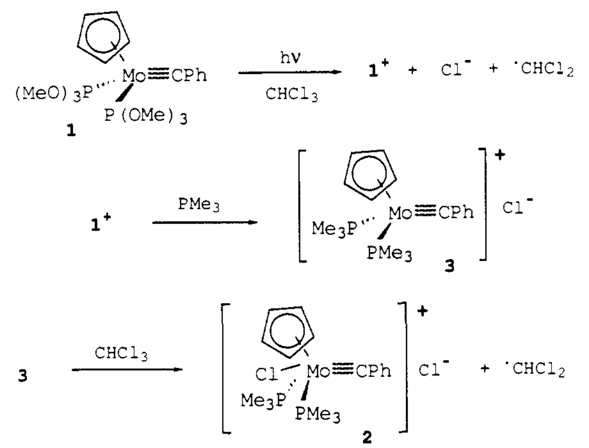
(8) **1** is synthesized by reaction of sodium cyclopentadienide with $Cl[P(OMe)_3]_4Mo{\equiv}CPh$.[9] For **1**: $^1H$ NMR ($C_6D_6$) 3.49 (filled in doublet, 18 H), 5.34 (s, 5 H), 6.97 (m, 1 H), 7.05 (t, 2 H), 7.51 (d, 2 H) ppm; $^{31}P$ NMR ($C_6D_6$) 213 ppm; $^{13}C$ NMR ($C_6D_6$) 51.1, 89.8, 125.7, 128.5, 149.9, 286.3 (t, $J_{CP}$ = 26.5 Hz) ppm; UV (THF) 324 ($\epsilon$ = 2000) 500 ($\epsilon$ = 50) nm.

(9) Mayr, A.; Dorries, A. M.; McDermott, G. A.; Van Engen, D. *Organometallics* **1986**, *5*, 1504–1506.

(10) For **2**: $^1H$ 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.

0002-7863/88/1510-7535$01.50/0

**Scheme I**



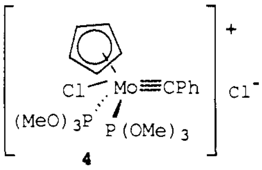
quantitative yield. Irradiation of **1** in $CHCl_3$ in the absence of phosphine does not lead to identifiable products even upon subsequent addition of $PMe_3$ to the reaction mixture. Cyclic voltammetry of **1** in the absence of additional ligands shows an irreversible oxidation at 0.35 V versus $Ag/Ag^+$. No evidence of a return wave could be seen at scan rates up to 1 V/s, consistent with decomposition of the cation. Attempts at electrochemistry in the presence of $PMe_3$ resulted only in phosphine oxidation.

The mechanism shown in Scheme I is consistent with these observations. Electron transfer from excited state **1** to chloroform gives the 17-electron cationic complex $\mathbf{1}^+$, chloride ion, and $^{\bullet}CHCl_2$.[12] The organic radical is then scavenged by the excess phosphine.[13] Ligand exchange of phosphines for phosphites occurs from the 17-electron species $\mathbf{1}^+$ to give **3**. Abstraction of a chlorine atom from the solvent yields the final product **2** and another $^{\bullet}CHCl_2$ radical. The overall reaction sequence thus produces 2 equiv of $^{\bullet}CHCl_2$ radical for each equivalent of **1** consumed, consistent with the assignment of the unidentified phosphine-containing product as the result of radical trapping.

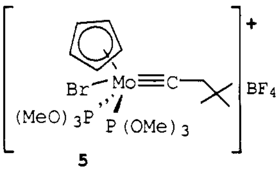
Electron transfer from the MLCT states of metal complexes to halocarbons has previously been observed in the photooxidation of $M(CNPh)_6$ (M = Mo, W) in $CHCl_3$ to give the seven-coordinate product $[M(CNPh)_6Cl]^+Cl^-$.[14] Photochemical reduction of halocarbons by metal complexes has also been observed upon excitation of charge transfer to solvent (CTTS) transitions.[15] However, comparison of the UV-vis spectra of **1** in $CHCl_3$, $CH_2Cl_2$, and THF reveals no transition in the region 300–550 nm that could be attributed to CTTS. Involvement of CTTS states can thus be ruled out in the photooxidation of **1**. In addition, reaction occurs upon irradiation of the lowest energy transition of **1** ($\lambda > 520$ nm), an absorption that is unchanged in solvents such as THF which are poor electron acceptors.

The irreversibility of the electrochemical oxidation of **1** suggests that $\mathbf{1}^+$ undergoes rapid chemical reaction. In addition, the substitutional lability of organometallic complexes is known to be greatly increased upon oxidation to 17-electron cationic species.[16] Given the $\pi$-acidity of the phosphite ligands, it is reasonable that dissociation of $P(OMe)_3$ from $\mathbf{1}^+$ should be facile and exchange for phosphines should be favorable. Conversion from the resulting metal radical **3** to the final product **2** requires abstraction of $Cl^{\bullet}$ from solvent. Such halogen abstractions are well known for metal radicals.[17,18]

Reversing the order of the ligand exchange and atom abstraction steps would result in intermediacy of the 18-electron cationic complex **4**, which would then exchange its $P(OMe)_3$ ligands for



**4**



**5**

phosphines. We believe this to be less likely as the analogous complex **5** and its hydride analogue have been described as stable.[19] As we see no intermediates in the conversion of **1** to **2**, the ligand exchange process must be fairly rapid. Although no information on the reactivity of **5** with phosphines is available, its reported properties do not suggest that the phosphites are labile enough for the conversion of **4** to **2** to occur without detectable intermediates.

Photooxidation of metal carbyne **1** adds electron transfer to the photoprocesses that have been observed for these complexes. The resulting odd electron species undergoes ligand exchange and halogen abstraction. However, no reaction occurs at the metal–carbon triple bond despite the presence of both metal and organic radicals. Further studies on this reaction are in progress.

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(11) This unstable $PMe_3$-containing product has a single $^1H$ NMR signal at 1.87 ppm (d, $J_{CP} = 12$ Hz). The proton–phosphorus coupling constant suggests that the phosphine is not metal bound, but its lability prevented isolation and further characterization. We believe this compound to result from trapping of radicals by excess phosphine.

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# Atom-Transfer Annulations in Heterocycle Synthesis. An Efficient Synthesis of (−)-Trachelanthamidine and Related Ring Systems

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Annulation sequences which involve free-radical intermediates have achieved increasing importance for the synthesis of bioactive substances. Among the various methods for effecting radical annulations, those which involve an atom-transfer propagation step would appear optimum for cases in which premature chain termination via hydrogen atom transfer is problematic.[1,2] In this communication we will describe the first examples of $\gamma$-butyrolactam-forming atom-transfer annulations of allylic $\alpha$-iodoacetamides as well as the application of this new method in an en-

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