Mo$_3$O(O-*i*-Pr)$_{10}$ has been found to react separately with each of O$_2$ and MoO$_2$(O-*i*-Pr)$_2$ to form Mo$_6$O$_{10}$(O-*i*-Pr)$_{12}$ which has been structurally characterized and found to react further with O$_2$ to give [MoO$_2$(O-*i*-Pr)$_2$]$_n$. The details of this work will be the subject of a full paper. The thrust of this communication is to emphasize the potential of the generalized reaction 3 for syntheses of triangulo complexes of the type described here. A variety of X groups can be envisaged and conceivably this approach could be extended to include heterometallic systems.[9]

$$M{\equiv}M + M{\equiv}X \rightarrow M_3X \qquad (3)$$

---

(8) Preparation of MoO(O-*i*-Pr)$_4$. Mo$_2$(O-*i*-Pr)$_8$[6] (1.8 g) was dissolved in dry toluene (25 mL) in a 250-mL round-bottomed flask under a nitrogen atmosphere. The solution was frozen at −198 °C (liquid N$_2$), and the flask was evacuated and attached to a vacuum manifold. Dry molecular oxygen was added, and the solution was thawed and warmed to room temperature. The solution changed rapidly from blue to green to pale yellow and was stirred for 1 h at room temperature under 1 atm of O$_2$. The solvent was stripped, yielding a yellow viscous liquid MoO(O-*i*-Pr)$_4$. The compound was vacuum distilled (53 °C, 10^{-4} mmHg). Anal. Calcd for MoO(O-*i*-Pr)$_4$: C, 41.38; H, 8.10; N, 0.00. Found: C, 41.11; H, 7.90; N, 0.10. The ^{1}H NMR spectrum recorded in toluene-d_8 at 220 MHz, 16 °C, showed a septet at δ 4.77 and a doublet at δ 1.34 (δ in ppm relative to Me$_4$Si). The natural abundance ^{17}O NMR spectrum recorded at 30 °C in benzene showed a singlet at $\delta = 894$ with a peak width at half-height of 150 Hz (δ^{17}O relative to external H$_2{}^{17}$O). The narrow peak width is consistent with a terminal MoO group in a monomeric compound. A cryoscopic molecular weight determination in benzene also indicated that MoO(O-*i*-Pr)$_4$ is at least mostly monomeric in solution; $M_r = 410$ (calculated $M_r = 348$ for the monomer). Preparation of Mo$_3$O(O-*i*-Pr)$_{10}$. MoO(O-*i*-Pr)$_4$ (1.84 mmol) was dissolved in dry degassed toluene (25 mL) in a 50-mL round-bottomed flask fitted with a side arm and magnetic spin bar under a nitrogen atmosphere. Mo$_2$(O-*i*-Pr)$_6$ (1 g, 1.84 mmol) was added via the side-arm adaptor with stirring. The solution immediately turned from yellow to red and then to green. The solution was stirred for 1 h at room temperature and then the solvent was stripped and the green solids dissolved in CH$_2$Cl$_2$ (ca. 8 mL). The flask was placed in a refrigerator at ca. −15 °C for 12 h, during which time green crystals, Mo$_3$O(O-*i*-Pr)$_{10}$, formed which were collected by filtration and dried in vacuo; yield 1.5 g (ca. 80% based on Mo). Anal. Calcd for Mo$_3$O(O-*i*-Pr)$_{10}$: C, 40.27; H, 7.89; N, 0.00. Found: C, 40.17, H, 7.71; N, 0.07. The ^{1}H NMR spectrum recorded in toluene-d_8 at 220 MHz, 16 °C, showed septets at δ 5.67 (3 H), 5.42 (3 H), 4.64 (3 H), and 4.00 (1 H) and doublets at δ 1.64 (18 H), 1.57 (18 H), 1.19 (6 H), and 1.16 (18 H) with $J_{HH} = 7.0$ Hz; δ relative to Me$_4$Si. MoO(ONe)$_4$ and Mo$_3$O(ONe)$_{10}$ prepared in analogous reactions, are air-sensitive yellow and green crystalline solids, respectively. Both compounds gave satisfactory elemental analyses.

(9) We thank the Office of Naval Research for support. M.H.C. is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant and C.C.K. is the 1980–1981 Indiana University SOHIO Fellow.

Raman Spectroscopy of Excited Electronic States of Photoactive Metal Complexes. 1. Nitroprusside Ion

John W. Schindler and Jeffrey I. Zink*

Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

Received April 17, 1981

Knowledge of the structures and the bonding properties of electronic excited states is of primary importance in interpreting the photochemical reactions from these states. The current understanding of transition-metal photoreactions is based on predictions of both the bonding and the structural changes which occur after photoexcitation.[1-3] These predictions use ligand field and molecular orbital considerations. Experimental measures of these changes are rare. The primary experimental technique has been low-temperature electronic emission and/or absorption spectroscopic measurement of vibronic structure in concert with Franck–Condon calculations of the displacement along metal–ligand normal modes.[4-6] Optical spectra do not usually contain as detailed structural information as do vibrational spectra. Thus, an experimental measurement of the Raman spectra of metal complexes in their photoactive excited states could in principle provide direct measurements of the important bonding changes. The first such examples were recently obtained by using pulsed techniques.[7] We report here the first CW excited-state Raman spectrum of a photochemically active metal complex, that of the nitroprusside ion, Fe(CN)$_5$NO^{2-}.

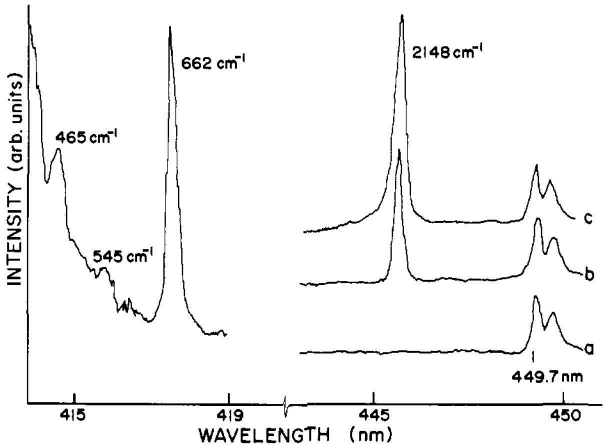


Figure 1. Raman spectra of aqueous K$_2$Fe(CN)$_5$NO. (a) Low laser power (or unfocused laser beam); (b) 0.1-W laser power, tightly focused; (c) 0.5-W laser power, tightly focused.

The 406.7-nm line of a krypton ion laser with maximum power of 0.5 W was used to excite the nitroprusside ion into its ^{1}A$_1$ electronic excited state. This transition corresponds to a metal d orbital (d_{xz}, d_{yz}) to nitrosyl π^*, metal-to-ligand charge-transfer transition.[8] The laser beam was tightly focused to a diameter of about 6 μm by using a 44 power microscope objective as the final focussing element. Plasma lines and the 413.1-nm line were removed (vide infra) by passing the beam through two dispersing prisms and an iris diaphragm. The *E* vector of the laser beam was adjusted to be either parallel or perpendicular to the line of the entrance optics. The Raman signals were collected by using an optical system containing a collecting lens, a right angle diaphragm, and a focusing lens and passed through a $^1/_2$-m monochrometer to a PAR optical multichannel analyzer. In a typical experiment, data were collected over 15-min interval using a delay time on the OMA of 15 s. A saturated solution of K$_2$Fe(CN)$_5$NO (ca. 1 M) was circulated by using a peristaltic pump through a 250-μm hyperdermic needle to produce a roughly 200-μm diameter jet stream of solution at the point of the laser focus. The calculated residence time in the focused laser beam ranged between 6 and 83 μs. The collecting optics allowed the tightly focused laser spot to be visually observed in the jet stream. All parts of the stream except that containing the most tightly focused spot were shuttered out. Under nearly optimum conditions of focus and laser power, the flux was about 1.02×10^{18} photons per second on an irradiated volume of 6.2×10^{-12} L. Given a calculated residence time per molecule for this situation of 77 μs, we estimate the photon-to-metal ratio to be 21 photons per molecule.

The metal–ligand and C–N stretching regions of the Raman spectrum obtained under tight focus and high power conditions are shown in Figure 1. The major peak of interest is the 2148 cm^{-1} peak arising from a C–N stretching mode.[9,10] The peak at

---

(1) Zink, J. I. *J. Am. Chem. Soc.* **1972**, 94, 8039; Inorg. Chem. **1973**, *12*, 1018; **1973**, *12*, 1957; *J. Am. Chem. Soc.* **1974**, *96*, 4464.

(2) (a) Wrighton, M.; Gray, H. B.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 165. (b) Geoffroy, G.; Wrighton, M. "Organometallic Photochemistry"; Wiley: New York, 1980.

(3) Van Quickenbourne, H. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208; **1978**, *100*, 475.

(4) Hipps, K. W.; Merrell, G.; Crosby, G. A. *J. Phys. Chem.* **1976**, *80*, 2232.

(5) Wilson, R. B.; Solomon, E. I. *Inorg.* Chem. **1978**, *17*, 1729.

(6) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951.

(7) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391; Dallinger, R. F.; Miskowski, V. M.; Gray, H. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1595.

(8) Monoharan, P. T.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3340.

(9) Khanna, R. K.; Brown, C. W.; Jones, L. H. *Inorg. Chem.* **1969**, *8*, 2195.

(10) Bates, J. B.; Khanna, R. K. *Inorg. Chem.* **1970**, *6*, 1376.

0002-7863/81/1503-5968$01.25/0 © 1981 American Chemical Society

449.7 nm is caused by internal scatter of the exciting laser line. It is present when the jet stream consists of distilled water but disappears when a 420-nm cutoff filter is placed in front of the entrance slit. The low-frequency peaks at 662 and 465 cm^{-1} are the M–C and M–N stretches, respectively.[9,10] The behavior of the 2148-cm^{-1} peak as a function of laser power is also shown in Figure 1. As the laser power decreases, the intensity of this peak decreases relative to that of the 449.7-nm scatter peak. A plot of the logarithm of the intensity of the Raman peak vs. the logarithm of the laser power gives a straight line with a slope of 2.3 ± 0.2, *proving that the 2148-cm^{-1} peak arises from an incoherent two-photon process.* The power dependences of the peaks in the metal–ligand stretching region could not be determined because of the background Raleigh scatter.[11]

The appearance of only one C–N mode in the excited-state Raman spectrum is probably a result of resonance enhancement of that mode in the excited state. In an attempt to observe other modes, both the 406- and 413-nm lines were used simultaneously with the goal of producing the excited state by absorption of the 406-nm line and observing resonance enhancement of other excited-state normal modes with the 413-nm line. The 2148-cm^{-1} C–N stretching mode was observed from both these laser lines, but no other normal modes were clearly detected. Apparently the 413-nm line is not different enough in frequency to provide resonance enhancement of any other modes. The technique of using several lines simultaneously is of great potential utility and is being explored further.

The C–N stretching frequency observed from the excited state of the complex is in the same region as those observed from the ground-state complex.[9-10] In order to assign the excited-state Raman peak, two orthogonal polarization direction were used. No readily distinguishable qualitative differences in the intensities were observed. These results must be interpreted with caution, because the intensities are extremely sensitive to small changes in the geometry, the position of the jet stream, etc. As a preliminary interpretation, the lack of a major intensity change under the two polarizations suggests that the excited-state Raman peak belongs to a nontotally symmetric normal mode. If this assignment is valid, the change in the stretching frequency between the ground and excited state is a maximum of only -6 cm^{-1}. If the excited state peak is the totally symmetric stretch, the shift would be a maximum of -14 cm^{-1}. In both cases, the shift is small.

The small shift is consistent both with the observed photochemical reactions[12] of the nitroprusside ion and with the molecular orbital interpretations of the bonding.[8] The primary photochemical reaction is loss of nitric oxide and aquation, yielding $Fe(CN)_5H_2O^{2-}$.[12] The metal–cyanide bonds are not broken. The excited-state Raman spectrum suggests that the metal–cyanide bonding is not strongly perturbed. The molecular orbital calculations show that the major cyanide component in the depopulated orbital is C–N *bonding* in character.[8] Thus depopulating this orbital should lead to C–N bond weakening and a Raman shift to lower frequencies. However, the populated orbital is mainly nitrosyl antibonding in character. Populating this orbital does not directly affect the C–N bond, but it indirectly changes the bonding by increasing the formal positive charge on the metal, decreasing the back-bonding to the cyanide, and thus strengthening the C–N bond leading to a Raman shift to higher frequency. The two effects occurring as a result of the electronic transition are thus in opposite directions and partially cancel, leading to only a small change in the C–N stretching frequency in the excited state.

Acknowledgment. We thank the National Science Foundation for financial support and Professor M. A. El-Sayed, J. Hsieh, and M. Nagumo for helpful discussions.

---

(11) The dependence of the Raman signal intensity on the degree of focus provides a qualitative test of the origin of the signal. As expected, the intensity of the 2148-cm^{-1} peak increases as the focus is tightened. The peaks in the metal–ligand stretching region also exhibited this dependence on the focus, suggesting that they could also be excited-state Raman peaks. The qualitative nature of these observations prevents us from drawing quantitative conclusions.

(12) Wolfe, S. K.; Swinehart, J. H. *Inorg. Chem.* **1975**, *14*, 1049.

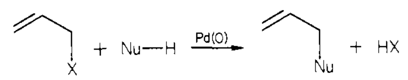
Neutral Alkylations via Palladium(0) Catalysis

Barry M. Trost* and Gary A. Molander

McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received May 27, 1981

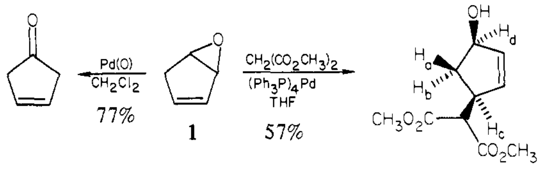
Alkylation reactions almost invariably involve either base or acid catalysis. Preclusion of such catalysts would generate one of the mildest ways to form C–C bonds. Palladium-catalyzed allylic alkylation[1] offers such an approach provided the leaving group X (eq 1) is sufficiently basic to remove a proton from Nu–H.



(1)

Unfortunately, an X^- which would be of sufficient basicity is normally too poor a leaving group in this reaction.[1b] In this paper, we wish to report that vinyl epoxides surprisingly offer a very nice solution to this problem and involve an unusual regioselectivity. Furthermore, the characteristics of the reaction indicate a fundamentally different reaction type than other reactions of vinyl epoxides.

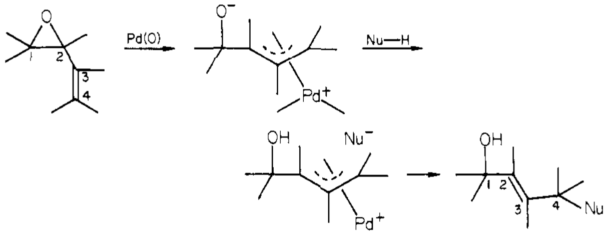
The recently reported palladium-catalyzed isomerization of vinyl epoxides to α,β-unsaturated ketones and/or dienols, which invoked an insertion of the palladium in the C–O bond, would appear to preclude their being substrates in allylic alkylation.[2] Nevertheless, while epoxide **1** is reported to isomerize to 3-cyclopenten-1-one with a Pd(0) catalyst, treatment of **1** with $(Ph_3P)_4Pd$ (**2**) in the presence of 1.2 equiv of malonic ester leads only to a single alkylation product **3**[3] (eq 2). Its regio- and stereochemistry is clearly assigned on the basis of the 270-MHz proton NMR spectrum where H_a (δ 1.58) couples with both H_c (δ 3.27) and H_d (δ 4.79) with similar couplings of J = 5.0 and 3.3 Hz, respectively, indicative of a trans orientation, and H_b (δ 2.56) couples with the same two hydrogens with appreciably larger couplings of J = 8.7 and 7.5 Hz, respectively, indicative of a cis relationship.[4]



(2)

3

Table I establishes the generality of the observation according to eq 3. While ~5 mol % of **2** generally serves as the catalytic system, with more sterically hindered substrates $(dppe)_2Pd$ proves superior.[5] Cyclic and acyclic vinyl epoxides participate equally



(3)

---

(1) (a) For reviews, see: Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. *Tetrahedron* **1977**, *33*, 2615. (b) See: Tsuji, J.; Kobayashi, Y.; Kataoka, H.; Takahashi, T. *Tetrahedron Lett.* **1980**, 3393.

(2) Suzuki, M.; Oda, Y.; Noyori, R. *J. Am. Chem. Soc.* **1979**, *101*, 1623. Also see: Suzuki, M.; Watanabe, A.; Noyori, R. *Ibid.* **1980**, *102*, 2095.

(3) This compound has been fully characterized by spectral data and its elemental composition established by high-resolution mass spectroscopy and/or combustion analysis.

(4) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(5) Trost, B. M.; Runge, T. A.; Jungheim, L. N. *J. Am. Chem. Soc.* **1980**, *102*, 2840.

0002-7863/81/1503-5969$01.25/0 © 1981 American Chemical Society