apical iron is bound to the three basal borons with a two-center and three-center bond. The total contribution of each $Fe(CO)_3$ group and BH group to the cage bonding is two electrons and three orbitals.[15] An alternate representation of the bonding results if the compound is viewed as being formed by the addition of $B_3H_7^{2-}$ (isoelectronic with the allyl ion, $C_3H_5^-$) to $Fe_2(CO)_6^{2+}$. This formulation is sketched in II where it is suggested that the π system of the pseudo allyl ion donates four electrons to one iron and the two BH bonds donate four electrons to the other iron.[16] With a single bond between the iron atoms, the 18-electron rule is satisfied. In this regard the new compound is related to ferracyclopentadiene complexes.[11b]

A series of compounds containing the B_3H_7 fragment bound to a single metal atom have been described and the structure of one, $[(CH_3)_2C_6H_5P]_2PtB_3H_7$, has been determined.[17,18] There are three striking differences between the B_3H_7 fragment in this compound and in $B_3H_7Fe_2(CO)_6$. In the platinum compound the highest field ^1H resonance occurs at δ −4.9 (assigned to B–H–B bridges) compared with δ −16.6 in the iron compound for which Fe–H–B bridges are established by the static structure. Second, the B–B–B angle is 112.9° in the platinum compound (B(1)–B(3) distance of 3.15 Å), while this angle is 93.8° in the iron compound (B(1)–B(3) distance of 2.59 Å). Finally, the B_3 unit is asymmetrically coordinated to platinum in the solid state, while in the iron compound the coordination is very symmetrical. Thus, $B_3H_7^{2-}$, considered as a ligand, behaves rather differently in these two bonding situations.

The B_3 unit is also of interest in terms of its NMR behavior as triborane compounds are known to display fluxional properties.[19] The ^1H NMR of $B_3H_7Fe_2(CO)_6$ exhibits only three types of hydrogen at temperatures as low as −70 °C. Clearly, the resonance observed at high field is due to the two Fe–H–B bridging hydrogens. The resonance at lowest field is assigned to the terminal hydrogens on B(1) and B(3) based on the magnitude of the chemical shift and on a comparison of the coupled and decoupled spectra. This requires that the resonance in the bridging region (three protons) be assigned to the remaining terminal hydrogen on B(2) and the two B–H–B bridging hydrogens observed in the static structure. The fact that these three hydrogens are magnetically equivalent is most likely the result of some type of rapid (on the NMR time scale) intramolecular exchange. Compounds that exhibit similar behavior have been termed "selectively non-rigid".[20]

Further studies of this diiron and analogue of B_5H_9 are in progress.

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Time-Resolved Resonance Raman Study of the Lowest (dπ*, ³CT) Excited State of Tris(2,2'-bipyridine)ruthenium(II)

Sir:

We report the time-resolved resonance Raman (TR^3) spectrum of tris(2,2'-bipyridine)ruthenium(II) in its lowest electronically excited state, $^*Ru(bpy)_3^{2+}$. This is the first report of the vibrational spectrum of an optically generated excited state in fluid solution. Because of intensive recent investigations of the photophysics[1] and photochemistry[2-5] of $Ru(bpy)_3^{2+}$, the potential of this complex in the conversion of light into chemical energy[2], and the fundamental significance of vibrational spectroscopy of the electronically excited state,[6] our results and their attendant structural information content on $^*Ru(bpy)_3^{2+}$ are of considerable interest.

TR^3 spectroscopy is now established as an important new technique for the study of the structures of transient chemical species with nanosecond,[7a] ultimately picosecond,[7b] time resolution. Quite recently, the first TR^3 studies of excited states, the optically forbidden triplets of β-carotene[6] and *p*-terphenyl[8], have been reported. Because the direct optical yield of these triplets is negligible, in both studies the excited states were produced by pulse radiolysis. The applicability of TR^3 to optically created excited states has not been demonstrated until now. In the present study, we use direct pulsed laser excitation to produce a near-saturation yield of $^*Ru(bpy)_3^{2+}$ and to simultaneously observe the excited-state TR^3 spectrum.

Optical excitation of $Ru(bpy)_3^{2+}$ at 265 nm or longer wavelength produces the emissive and photochemically active state (denoted dπ*, ^{3}CT, or $^*Ru(bpy)_3^{2+}$ by various workers[1-4]), with quantum yields approaching unity, in 10 ps or less.[1] The $^*Ru(bpy)_3^{2+}$ is then relatively long lived (~665 ns) and has a strong ligand-centered $\pi^* \rightarrow \pi^*$ absorption maximum at 360 nm.[3] We therefore used as our excitation source the third harmonic of a Nd:YAG laser (354.5 nm, 5-ns pulse width, ~5 mJ/pulse). The $^*Ru(bpy)_3^{2+}$ is formed sufficiently rapidly, and the ground-state absorbance at 355 nm is sufficiently intense, that we can use a single 355-nm pulse both to excite the $Ru(bpy)_3^{2+}$ and to probe the excited-state TR^3 spectrum. The Raman scattered radiation was detected using a Spex double monochromator, which provided ample rejection

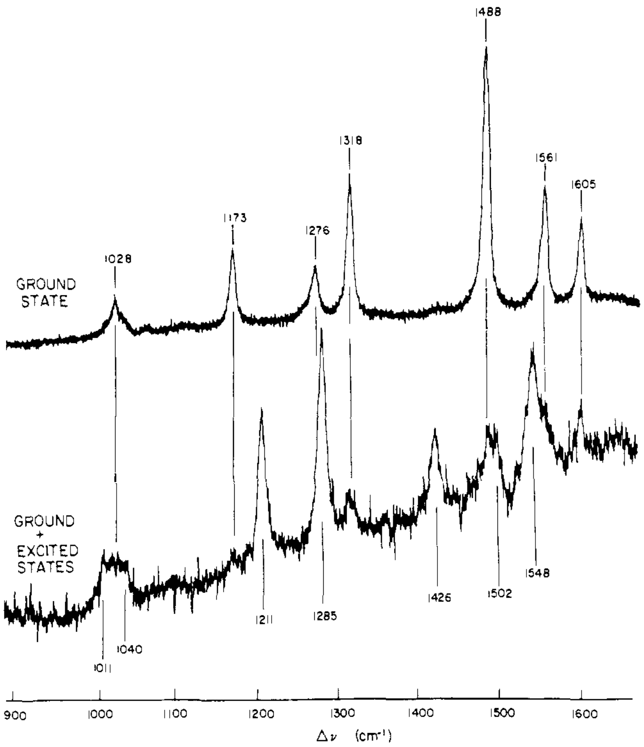

Figure 1. Upper trace, ground-state spectrum of Ru(bpy)$_3^{2+}$ taken with 457.9-nm CW excitation from a Spectra Physics 164 Ar$^+$ laser: ~2.5 × 10^{-4} M solution in H_2O: laser power, 100 mW at the sample; spectral slit width, ~5 cm^{-1}; photon counting interval, 0.5 s; scan speed, 0.5 in./min; no time constant filter. Lower trace, ground- plus excited-state spectrum of Ru(bpy)$_3^{2+}$, taken with 354.5-nm pulsed excitation from a Quanta Ray DCR-1 Nd:YAG laser: ~2.5 × 10^{-4} M solution in H_2O, deoxygenated by bubbling N_2 through the sample; laser operating at 15 Hz, 75 mW average power, ~5 mJ/pulse; electrometer amplifier at 10^{-10} A full scale; time constant, 10 s; scan speed, 0.1 cm^{-1}/s; lock-in amplifier used to minimize stray photomultiplier noise.

of the intense long-wavelength luminescence of *Ru(bpy)$_3^{2+}$. The photomultiplier output was amplified with a conventional electrometer and passed through a lock-in amplifier, tuned to the 15-Hz laser repetition rate, to reject random photomultiplier noise.

The spectral results are shown in Figure 1. The upper trace is the ground-state spectrum of Ru(bpy)$_3^{2+}$ taken with 457.9-nm CW excitation. The bands are ligand-centered bipyridine vibrations; indeed the frequencies are identical within ±3 cm^{-1} with those in the analogous Fe(bpy)$_3^{2+}$ complex.[9] The lower trace is the spectrum acquired with pulsed 354.5-nm Nd:YAG excitation. The ground-state peaks are still detectable, and there are seven new peaks which we attribute to ligand vibration of *Ru(bpy)$_3^{2+}$.[10] The large intensities of these bands relative to the ground-state bands arise from the favorable resonance condition with the excited-state $\pi^* \rightarrow \pi^*$ absorption band (360 nm ($\epsilon \lesssim 27\,000$ M^{-1} cm^{-1}))[3] and also to depletion of the ground state (the dependence of luminescence intensity at 16 000 cm^{-1} upon laser pulse energy indicates near saturation of the excited state at 5 mJ/pulse). The assignment of these new Raman peaks to *Ru(bpy)$_3^{2+}$ vibrations was confirmed by noting that their intensities decreased monotonically compared with those of the ground-state peaks with decreasing energy of the Nd:YAG pulses. At the signal-to-noise ratio that we are currently able to achieve, no excited-state metal-nitrogen stretching vibrations are observable.

The ground- and excited-state frequencies are given in Table I, with the observed frequencies for the bipyridine ligand included for comparison. There are seven symmetric vibrational modes between 900 and 1700 cm^{-1} for both the ground and excited states. Although the correlation of the individual modes is not straightforward, it is reasonable to assume that the seven observed peaks represent essentially the same normal modes in the ground and excited states. Indeed these may be presumed to be the seven C-C and C-N stretching vibrations which exist for chelated bipyridine in either C_{2v} or D_3 symmetry. If this correlation is correct, the frequencies of the observed normal modes are lower in the excited state by an average for all seven peaks of 61 cm^{-1}. The three highest frequency ground-state vibrational modes appear directly correlated in sequence with the three highest frequency excited-state modes, with each shift being ~60 cm^{-1}. The correlation of the ground-state modes in the 1150-1320-cm^{-1} region is more difficult, since direct correlation with either the 1011- or the 1040-cm^{-1} excited-state mode involves a frequency shift of at least 130 cm^{-1}.

Table I. Raman Frequencies for Ground- and dπ(^{3}CT) Excited-State Ru(bpy)$_3^{2+}$

bpy^{a,b}	Ru(bpy)$_3^{2+}$ ground state^b	*Ru(bpy)$_3^{2+}$ excited state^b
997	1028	1011
1046	1173	1040
1236	1276	1211
1302	1318	1285
1448	1488	1426
1485	1561	1502
1575	1605	1548
1594		

^{a} 0.5 M $CHCl_3$ solution. ^{b} Frequencies in reciprocal centimeters.

We note that the frequency shifts which we observe for the bipyridine modes between Ru(bpy)$_3^{2+}$ and *Ru(bpy)$_3^{2+}$ are as great as, or greater than, those observed[12] in the infrared for the *full one-electron reduction* of neutral bipyridine to its radical anion. These large shifts to lower frequency in *Ru(bpy)$_3^{2+}$ are observed despite (a) only partial formal "reduction" of the ligands (maximum one-third electron, if delocalized) upon creation of the dπ^* (MLCT) excited state, and (b) formal "oxidation" of the metal center upon creation of the dπ^* state, which should counteract, not reinforce, shifts to lower frequency owing to formal ligand reduction in the excited state.[12] The significance of these observations is the subject of continuing investigation. However, the present evidence tentatively suggests that the MLCT electron density in the excited state is predominately localized on one of the bipyridine ligands, rather than delocalized over all three, on the vibrational time scale.

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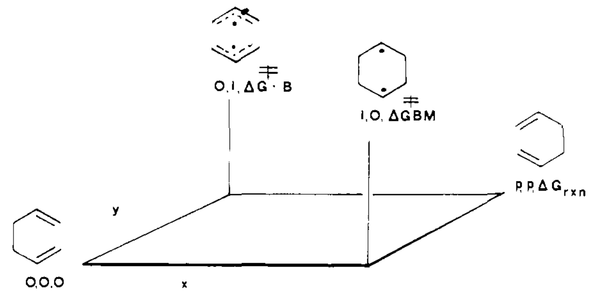
Substituent Effects in Concerted Reactions. A Nonlinear Free-Energy Relationship for the 3,3-Shift and the Diels–Alder Reaction

Sir:

Prediction of absolute rate constants for and substituent effects on concerted pericyclic reactions is useful in synthesis. However, a Hammett LFER approach is inappropriate since transition-state structure can change dramatically with substituents. For instance, the transition-state structure in 3,3 shifts of variously substituted 1,5-hexadienes as deduced from secondary deuterium isotope effects varies substantially between the nonconcerted alternatives resulting from either C_3C_4 bond breaking or C_1C_6 bond making.[1] This relationship can be quantified using the simplest equation for a three-dimensional energy surface with a saddle point, namely, $\Delta G = ax + by + cxy + d$,[2] and the proper boundary conditions. If the reactant is at $x = 0$, $y = 0$, then $\Delta G = 0$ and $d = 0$. If, at $x = 1$, $y = 0$, the pure bond-making transition state is achieved, then $a = \Delta G^{\ddagger}(\mathrm{BM})$. If, at $x = 0$, $y = 1$, the pure bond-breaking transition state is achieved, then $b = \Delta G^{\ddagger}(\mathrm{BB})$. If the product is at an average position $x = p$, $y = p$, then $c = [(\Delta G_{\mathrm{rxn}}/p) - \Delta G^{\ddagger}(\mathrm{BB}) - \Delta G^{\ddagger}(\mathrm{BM})]/p$. Setting the partial derivatives of ΔG with respect to x and to y equal to zero allows determination of the transition-state position which upon substitution in the original equation gives

$$\Delta G^{\ddagger} = [\Delta G^{\ddagger}(\mathrm{BB}) * \Delta G^{\ddagger}(\mathrm{BM}) * p] / [\Delta G^{\ddagger}(\mathrm{BB}) + \Delta G^{\ddagger}(\mathrm{BM}) - (\Delta G_{\mathrm{rxn}}/p)] \quad (1)$$

Scheme I



where p is an empirically determined parameter. Remarkably, for all of the 3,3 shifts, p is a constant and equal to 1.5. The calculated and experimental $\Delta G^{\ddagger}$ values are shown in Table I. The significance of p in eq 1 is that it adjusts the magnitude of $\Delta G^{\ddagger}$ and therefore represents the extent of coupling of the nonconcerted alternatives; it is the non-LFER equivalent of the Hammett ρ.

Highly notable exceptions to the simple formula are the 3,3 shift of *cis*-1,2-divinylcyclopropane[3] and of allyl silyl enol esters[4] (see Table I). A reasonable rationalization for the first is the possible strong coupling of the vinyl groups and the π-like electrons of cyclopropane ring in the ground state. The second may be due to inordinant stabilization of the bond-making alternative by, if not actual rearrangement of, the Me_3Si group. Thus, exceptions to the simple formula may indicate reactions requiring special scrutiny.

While derived from a crude model, eq 1 makes chemically reasonable predictions about the response of $\Delta G^{\ddagger}$ to substituent changes that affect ΔG_{rxn}, $\Delta G^{\ddagger}(\mathrm{BM})$, and $\Delta G^{\ddagger}(\mathrm{BB})$. However, careful scrutiny of eq 1 reveals that it can be applied to neutral or exergonic reactions but not to highly endergonic ones unless certain terms are redefined.[5]

Table I. ΔG Values at 523 K for Various 3,3 Shifts

compd	$\Delta G^{\ddagger}_{\mathrm{xp}}$	$\Delta G^{\ddagger}_{\mathrm{calcd}}$[a]	$\Delta G^{\ddagger}(\mathrm{BB})$	$\Delta G^{\ddagger}(\mathrm{BM})$[c,d]	ΔG
1,5-hexadiene	41[e]	41.2	57[b]	53	0
2-phenyl-	35.5[f]	36.3	57	42	0
2,5-diphenyl-	31[f]	30.1	57	31	0
3,3-dicyano-	32[g]	31.6	37	53	∼−4.5
threo-3,4-dimethyl-	39[h]	38.7	53	53	−4.5
threo-3,4-diphenyl-	31[i]	30.6	35	53	∼−4.5
cis-1,2-divinylcyclobutane	28[j]	28.6	34[k]	60[l]	−19
allyl vinyl ether	33[m]	33.6	47[n]	53[n]	−17
allyl phenyl ether	42[o]	43.2	47[p]	69[n]	+5[h]
allyl acetate	45[f]	43.9	52[n]	67[n]	0
cis-1,2-divinylcyclopropane	21[r]	27.5	35[s]	53	−20
allyl silyl enol acetate	<25[t]	33	47	53	−20
3-oxy anion 1,5-hexadiene	∼26[u]	23.4[v]	26[w]	53	−19[v]

[a] Calculated according to eq 1 with $p = 1.5$. [b] D. M. Golden, N. A. Gac, and S. W. Benson, *J. Am. Chem. Soc.*, **91**, 2136 (1969). [c] See ref 1. [d] Some of the values are calculated using the resonance energies of benzyl radical = 11 kcal/mol, α-CN radical = 9 kcal/mol, and α-Me radicals = 2 kcal/mol. [e] W. von E. Doering, V. G. Toscano, and G. H. Beasley, *Tetrahedron*, **27**, 5299 (1971). [f] M. J. S. Dewar and L. E. Wade, *J. Am. Chem. Soc.*, **99**, 4417 (1977). [g] F. G. Foster, A. C. Cope, and F. Daniels, *ibid.*, **69**, 1893 (1947). [h] W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962) and ref 1. [i] R. P. Lutz and H. A. J. Berg, private communication, 1978. [j] W. von E. Doering, M. Frank-Newman, D. Hasselmann, and R. L. Kaye, *J. Am. Chem. Soc.*, **94**, 3833 (1972). [k] Free energy for cleavage and isomerization of *trans*-1,2-divinylcyclobutane minus 1 kcal/mol for the strain of a *cis*-1,2-divinyl relationship; see *j*. [l] For a boat diyl, −7 kcal/mol destabilization over chair is assumed. [m] F. W. Schuler and G. W. Murphy, *J. Am. Chem. Soc.*, **72**, 3155 (1950). [n] Calculated according to S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976; these values are at 298 K. [o] For a review, see S. J. Rhoads and R. N. Rawlins, *Org. React.*, **22**, 1 (1975). [p] K. W. Egger and A. T. Cocks, *Helv. Chim. Acta*, **56**, 1517 (1973). [q] E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Am. Chem. Soc.*, **90**, 662 (1968). [r] Reference 3. [s] E. Vogel, *Angew. Chem.*, **72**, 4 (1960); E. Vogel et al., *Justus Liebigs Ann. Chem.*, **644**, 172 (1961); R. Sunderman, Ph.D. Dissertation, Köln, 1966, as quoted by M. R. Willcott, R. L. Cargill, and A. B. Sears, *Prog. Phys. Org. Chem.*, **9**, 50 (1972). [t] Reference 4. [u] Potassium salt in THF and 18-crown-6: D. A. Evans and A. Golob, *J. Am. Chem. Soc.*, **97**, 4765 (1975). [v] In the gas phase. [w] ΔG to acrolein and allyl anion, in gas phase at 25 C, not ΔG to acrolein radical anion and allyl radical which is ∼15 kcal/mol higher; see M. L. Steigerwald, W. A. Goddard III, and D. A. Evans, *ibid.*, **101**, 1994 (1979).

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