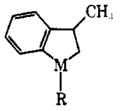
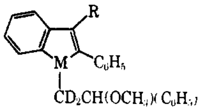
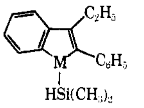
Table I. Selected Substitutent Effects upon Barriers to Pyramidal Inversion at Arsenic and Phosphorus

Compound type[a]	Inversion barrier, $\Delta G^{\ddagger}{}_T$, kcal/mol (T, °C) M = As	Inversion barrier, $\Delta G^{\ddagger}{}_T$, kcal/mol (T, °C) M = P
$(C_6H_5)(CH_3)MR$	43.1 (218)[b]	33.3 (130)[c]
$(C_6H_5)(CH(CH_3)_2)MSi(CH_3)_3$	25.1 (181)[d]	18.9 (62)[e]
	46–48[f]	35.3 (130)[g]
	35.2 (151) (**1**)	23.7 (165)[g]
	24.3 (161) (**2**)	16.6 (18) (**3**)

[a] R in every case refers to an alkyl or aryl group; for specific substitution original references should be consulted. [b] See ref 3. [c] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970). [d] See ref 14. [e] See ref 13. [f] Estimate based on the assumption stated in ref 12. [g] See ref 2.

$^3J_{HH}$ = 7.5 Hz, CH_2CH_3), 1.27 (t, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3), −0.24 (dd, $^3J_{HH}$ = 3.8 Hz, $^3J_{PH}$ = 4.3 Hz, $SiCH_3$). Total line-shape analyses[15] of the temperature-dependent silyl methyl pmr resonances of **2** and **3** provided values for the cited barriers (Table I).

The barriers for **2** and **3** reflect the cooperative nature of silylation and cyclic (p-p)π delocalization, since in both cases the diminution in barrier height is greater than that afforded by either effect alone. However, as in the case for multisilyl substitution at inverting centers,[14] the diminution resulting from the combined effects is less than would be predicted by straightforward application of the proportionality method[14] for estimation of substituent effects.

(15) Based on data obtained on a Varian A-60A spectrometer. Samples of **2** consisted of 10, 20, and 40 vol % solutions in α-bromonaphthalene and a 20 vol % solution in triglyme. A 20 vol % solution of **3** in CF_2Cl_2 was employed. No solvent or concentration dependence was observed.

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Electrogenerated Chemiluminescence. IX. Electrochemistry and Emission from Systems Containing Tris(2,2′-bipyridine)ruthenium(II) Dichloride[1]

Sir:

Previous reports of electrogenerated chemiluminescence (ecl) have demonstrated the formation of excited states by electrogenerated radical ion annihilation reactions of organic aromatic compounds in aprotic media. We report here the first example of ecl derived from electrogenerated species of the tris(2,2′-bipyridine)ruthenium(II) dichloride, [$Ru(bipy)_3Cl_2$], chelate in acetonitrile solutions. Lytle and Hercules[2] previously reported chemiluminescence upon reduction of $Ru(bipy)_3{}^{3+}$ in aqueous media with hydrazine or hydroxyl ion; chemiluminescence with other reductants or in nonaqueous media could not be observed in these studies.

The cyclic voltammetric behavior of $Ru(bipy)_3Cl_2$ in acetonitrile solutions containing 0.2 *M* tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) as supporting electrolyte at a platinum electrode is shown in Figure 1; peak potentials for the different waves are given in Table I. Comparison of peak current values with those of known one-electron processes as well as E_{pa}–E_{pc} values (60 ± 10 mV) show that I involves oxidation to a $Ru(bipy)_3{}^{3+}$ species, and II, III, and IV are stepwise reductions to the +1, 0, and −1 charged species. Wave V occurs at potentials where 2,2′-bipyridine itself reduces and probably arises from liberated free ligand.

Table I. Peak Potentials (E_p) for Oxidation (I) and Reduction (II–V) of $Ru(bipy)_3Cl_2$[a]

	I	II	III	IV	V
E_{pc} (reduction)	+1.63	−1.09	−1.27	−1.53	−2.22
E_{pa} (oxidation)	+1.70	−1.03	−1.22	−1.46	
n[b]	1	1	1	1	∼3

[a] In V *vs.* Ag wire reference electrode. [b] Number of electrons involved in electron-transfer step.

The irreversible oxidation wave at about +1.4 V can be attributed to oxidation of chloride ions, since LiCl shows a similar oxidation wave at that potential. Similar stepwise reduction of bipyridyl complexes of Co(II), Fe(II), Ni(II), and Mn(II) have been observed by Tanaka and Sato.[3]

When the potential of the platinum electrode is cycled at a frequency of 0.2 Hz between E_{pa} of wave I and E_{pc} of wave II, intense orange ecl is observed easily visible to the nondark-adapted eye. The intensity of this emission is at least as intense as the ecl observed with rubrene solutions at similar concentrations. This luminescence occurs with a maximum at 610 nm and is essentially the same as the emission observed upon photoexcitation (Figure 2). Ecl emission is also observed with higher cyclic frequencies and for cycling of the potential between waves I and III or IV. If 10-methylphenothiazine (10-MP), whose cation has previously been employed as an oxidant in ecl,[4] is added to the solution, a new reversible oxidation wave of the 10-MP/10-MP·$^+$ system is observed at +1.1 V *vs.* Ag reference electrode. Cycling between this wave and waves II, III, or IV in this mixed system also results in ecl emission at the same spectral characteristics.

An explanation of the ecl, based on previous spectroscopic studies of $Ru(bipy)_3Cl_2$,[5–9] can be given. The

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(1) This research was supported by the U. S. Army Research Office, Durham, N. C.

(2) F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, **88**, 4745 (1966); *Photochem. Photobiol.*, **13**, 123 (1971).

(3) N. Tanaka and Y. Sato, *Bull. Chem. Soc. Jap.*, **41**, 2059, 2064 (1968); *Inorg. Nucl. Chem. Lett.*, **2**, 359 (1966); **4**, 487 (1968); *Electrochim. Acta*, **13**, 335 (1968).

(4) D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 2097 (1971).

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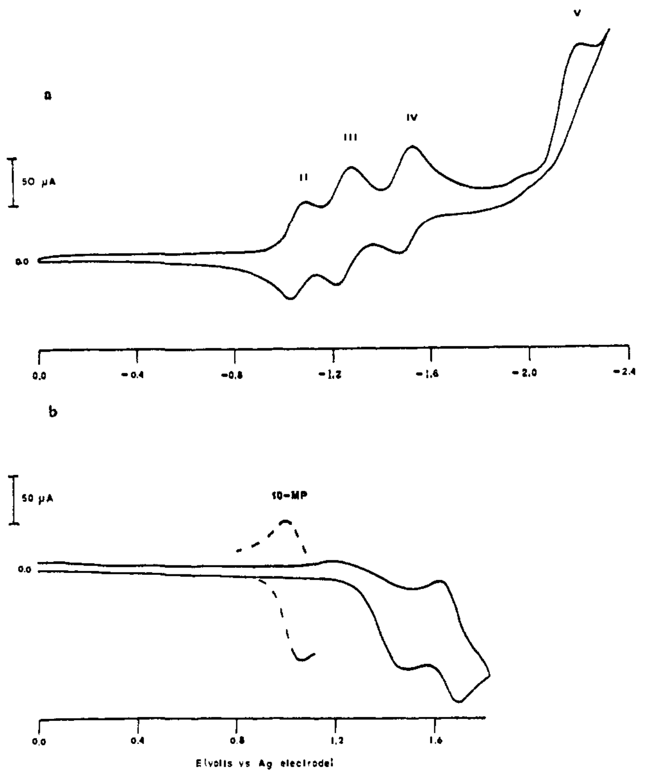

Figure 1. Cyclic voltammogram of 1 m*M* $Ru(bipy)_3Cl_2$ in acetonitrile at a Pt electrode with 0.2 *M* $TBABF_4$ supporting electrolyte. Scan rate = 100 mV/sec: (a) scan from 0.0 to −2.40 V; (b) scan from 0.0 to +1.80 V. The dotted portion marks the 10-methylphenothiazine oxidation wave.

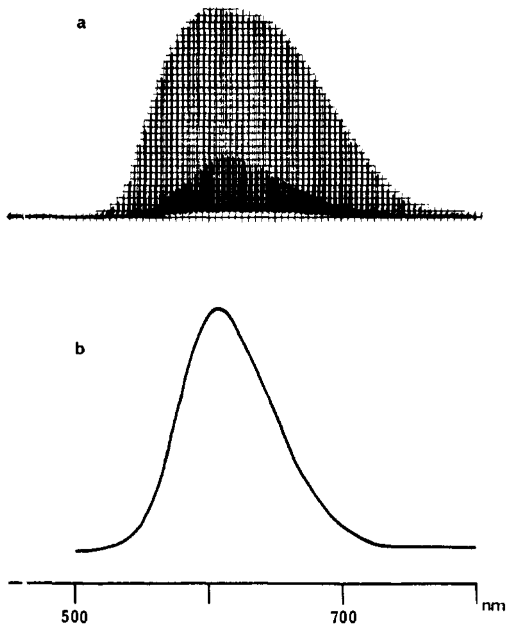

Figure 2. (a) Ecl emission spectrum of $Ru(bipy)_3Cl_2$ from 450 to 800 nm using a cyclic square wave at 0.2 Hz between +1.75 and −1.60 V *vs.* Ag reference electrode. (b) Fluorescence emission spectrum of $Ru(bipy)_3Cl_2$ in acetonitrile with excitation at 500 nm.

longest wavelength absorption peak occurs at about 455 nm (2.7 eV) and has been assigned to a d → π* transition from the singlet ground state to the singlet charge-transfer excited state.[6] Rapid intersystem crossing to the triplet state occurs and the observed emission at 608 nm (2.04 eV) is phosphorescence, greatly enhanced by spin-orbit coupling, from this state.[5,6] This state is also the emitting state in ecl. The reduction step (II) leading to the +1 species probably involves addition of an electron to the a_2 (π*) orbital of the chelate, which shows D_3 symmetry. Similarly, the oxidation (I) to the +3 species probably involves removal of an electron from the a_1 (d) orbital. The reaction

$$Ru(bipy)_3^{+} + Ru(bipy)_3^{3+} \longrightarrow Ru(bipy)_3^{2+*} + Ru(bipy)_3^{2+} \quad (1)$$

occurs. The enthalpy of this reaction, calculated from the peak potentials of waves I and II and corrected for the entropy term,[10] is 2.6 eV and is only marginal for population of the singlet excited state, especially since in this case, unique in ecl annihilation reactions, the redox step involves two positively charged species. The reaction is quite sufficient to populate the emitting triplet state, however. Similarly, when $10\text{-MP}\cdot^{+}$ is the oxidant, the reaction in eq 2 probably produces the

$$10\text{-MP}\cdot^{+} + Ru(bipy)_3^{+} \longrightarrow Ru(bipy)_3^{2+*} + 10\text{-MP} \quad (2)$$

triplet excited state directly, although here the reaction enthalpy is marginal even for this state. This reaction demonstrates that chemiluminescence in this system can be generated by oxidation of the +1 complex, as well as by the reduction of the +3 species previously described.[2] More intense ecl results when the reducing species is either the 0 or −1 complex. Although the reaction enthalpy is larger when these species are the reductants, several electron transfers must occur before the ultimate emitting state is produced, so that the overall ecl process in these cases is more complicated than those described in eq 1 and 2.

Observation of ecl in systems containing metal complexes either alone or with other reactants considerably broadens the scope of possible redox reactions leading to excited state species. These combined electrochemical and spectroscopic studies should also provide information about the spectroscopic states, energy levels, and orbitals in the metal chelates.

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(10) See, for example, L. R. Faulkner, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 691 (1972).

Nature of Photochemically Induced Transannular Hydrogen Abstractions of Taxinines

Sir:

Of the numerous taxanes[1] identified recently, those containing the 11-en-13-one chromophore are characterized by their anomalous uv absorptions[1b] due to the strained and unique cage structures (see **3**). For

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(1) (a) B. Lythgoe, K. Nakanishi, and S. Uyeo, *Proc. Chem. Soc.*, 301 (1964); (b) I. W. Harrison, R. M. Scrowston, and B. Lythgoe, *J. Chem. Soc. C*, 1933 (1966); (c) M. Dukes, D. H. Eyre, J. W. Harrison, and B. Lythgoe, *Tetrahedron Lett.*, 4765 (1965); (d) D. H. Eyre, J. W. Harrison, and B. Lythgoe, *J. Chem. Soc. C*, 452 (1967); (e) H. C. Chiang, M. C. Woods, Y. Nakadaira, and K. Nakanishi, *Chem. Commun.*, 1201 (1967); (f) M. C. Woods, H. C. Chiang, Y. Nakadaira, and K. Nakanishi, *J. Amer. Chem. Soc.*, **90**, 522 (1968); (g) D. P. Della Casa de Marcano and T. G. Halsall, *J. Chem. Soc. D*, 1382 (1970); (h) M. C. Wani, H. L. Taylor, M. E. Wall, P. Coggon, and A. T. McPhail, *J. Amer. Chem. Soc.*, 93, 2325 (1971).