Table II. 60-MHz Pmr Spectral Data[a]

Compd	$M(CH_3)_3$, δ	$CH_{3(a)}$, δ	$CH_{3(b)}$, δ	$\Delta\nu_{ab}$, Hz	$^3J_{HH(a)}$, Hz	$^3J_{HH(b)}$, Hz
2a[b]	0.11	1.21	1.18	1.8	6.8	6.7
3a[b]	0.24	1.20	1.17	1.9	6.8	6.7
4a[b,c]	0.15	1.22	1.20	1.5	6.9	6.7
5a[d]		0.34	0.29	3.2	3.9	3.9
5b[e]		0.34	0.24	6.0	3.7	3.7

[a] All compounds were purified by distillation at 60–80° (0.01–0.1 mm). [b] Data obtained at ambient temperature for *ca.* 30 vol % solutions in toluene-d_8 with tetramethylsilane as internal reference. Cited barriers (Table I) refer to neat samples, in which $\Delta\nu_{ab}$ = 3–4 Hz. [c] Sample decomposition accompanying the coalescence phenomenon was too slow to interfere significantly with the line-shape analysis. [d] Data obtained at −6° for a *ca.* 10 vol % solution in toluene-d_8 with *p*-dioxane as internal reference. [e] Data obtained at −81° for a *ca.* 15 vol % solution in CF_2Cl_2 with dimethyl ether as internal reference; $^3J_{PH(a)}$ = 6.3 Hz, $^3J_{PH(b)}$ = 4.3 Hz.

and **5b** provide satisfactory evidence for the assigned structures. The relevant data are included in Table II. Inversion barriers (Table I) were determined by total line-shape analysis of the temperature-dependent isopropyl methyl pmr resonances in **2a**–**4a** and dimethylsilyl methyl pmr resonances in **5a** and **5b**.

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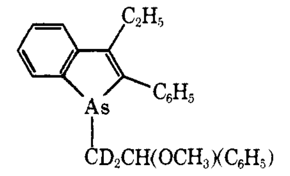
Pyramidal Inversion in Arsindoles. Evidence for Cyclic (4p–2p)π Conjugation[1]

Sir:

Prior work has shown that the barriers to pyramidal inversion in phosphole systems are significantly lowered through cyclic (3p–2p)π delocalization.[2] We now report our finding that the barrier to pyramidal inversion in arsindole **1**, $\Delta G^{\ddagger}_{151}$ = 35.2 kcal/mol, is appreciably



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lower than the barrier in a comparable acyclic arsine, ethylmethylphenylarsine ($\Delta G^{\ddagger}_{218}$ = 43.1 kcal/mol).[3] This result suggests that the electron pair on arsenic is involved in cyclic (4p–2p)π delocalization. The effect is maximal in the planar transition state, and in this sense the planar arsole system may be regarded as aromatic.[4]

The synthesis of **1** was achieved by the reaction of *d,l*-2-phenyl-2-methoxyethyl-*1*-d_2 bromide[5] with 1-lithio-2-phenyl-3-ethylarsindole[6] to yield a mixture of diastereomers (kugelrohr distilled, bp 160–175° (0.02 mm)) whose pmr spectrum featured absorptions at δ 6.9–7.8 (m, aromatic *H*), 4.16 (broadened s, C*H*(a)), 4.10 (broadened s, C*H*(b)), 2.93 (s, OCH_3(b)), 2.89 (s, OCH_3(a)), 2.62 (broadened q, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3), 1.12 (broadened t, $^3J_{HH}$ = 7.5 Hz, CH_2CH_3). The diastereomers (*ca.* 50:50 mixture) were oxidized (H_2O_2 in acetone) to the respective arsindole 1-oxides. Diastereomeric enrichment by column chromatography (95:5 v/v benzene–ethanol on silica gel) afforded a 72:28 mixture of the oxides.[8] Stereospecific reduction (phenylsilane in benzene) yielded a 72:28 diastereomeric mixture of **1**.[8] Equilibration of this mixture at 151.1 ± 0.1° in a 20 vol% toluene-d_8 solution[9] yielded first-order rate constants[10] ($k_1 = 6.1 \times 10^{-6}$ sec^{-1}, $k_{-1} = 5.9 \times 10^{-6}$ sec^{-1}), whence an average $\Delta G^{\ddagger}$ was obtained by substitution into the Eyring equation.

An estimate for the barrier lowering effect in phosphindoles due to increased cyclic (3p–2p)π delocalization in the planar transition state relative to the pyramidal ground state has been placed at 11 kcal/mol.[2] Comparison of the barrier of **1** with that of ethylmethylphenylarsine[11] sets a lower limit[12] for the barrier lowering effect due to cyclic (4p–2p)π delocalization at 8 kcal/mol.

Substitution of silicon on phosphorus[13] and arsenic[14] markedly lowers barriers to pyramidal inversion at these centers. The silylarsindole **2** and its phosphorus analog **3** (Table I) provide the first examples of systems in which this effect and the effect due to cyclic (p–p)π delocalization are simultaneously operative.

The silylarsindole (**2**) (bp 115–120° (0.04 mm)) was obtained by reaction of 1-lithio-2-phenyl-3-ethylarsindole[6] with dimethylchlorosilane. The pmr spectrum featured absorptions at δ 6.7–7.9 (m, aromatic H), 4.18 (septet, $^3J_{HH}$ = 3.8 Hz, Si*H*), 2.75 (broadened q, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3), 1.20 (t, $^3J_{HH}$ = 7.0 Hz, CH_2CH_3), −0.11 (d, $^3J_{HH}$ = 3.8 Hz, $SiCH_3$(a)), −0.18 (d, $^3J_{HH}$ = 3.8 Hz, $SiCH_3$(b)). Silylphosphindole (**3**) (bp 110–115° (0.05 mm)) was synthesized in a manner strictly analogous to that of **2**, and featured pmr absorptions at δ 7.05–7.75 (m, aromatic *H*), 3.95 (d septet, $^2J_{PH}$ = 25.0 Hz, $^3J_{HH}$ = 3.8 Hz, Si*H*), 2.84 (broadened q,

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(1) This work was supported by the National Science Foundation (GP-30257).

(2) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 6205 (1971).

(3) Based on $\Delta G^{\ddagger}$ of racemization (42.4 kcal/mol) reported by G. H. Senkler, Jr., and K. Mislow, *ibid.*, **94**, 291 (1972).

(4) (a) D. A. Brown (*J. Chem. Soc.*, 929 (1962)) has previously suggested, on the basis of HMO calculations, that arsole in the planar conformation gains considerable conjugation energy through involvement of the 4p orbital of arsenic. (b) Cyclic (4p–2p)π conjugation has also been invoked for arsabenzene (arsenin) by A. J. Ashe, III, *J. Amer. Chem. Soc.*, **93**, 3293 (1971).

(5) R. A. Lewis and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 7009 (1969).

(6) Synthesized by lithium cleavage of 1,2-diphenyl-3-ethylarsindole, which in turn was prepared by an extension of the cyclization reaction reported by Rausch and Klemann.[7]

(7) M. D. Rausch and L. P. Klemann, *J. Amer. Chem. Soc.*, **89**, 5732 (1967).

(8) The diastereomeric ratios were determined from the methoxy proton nmr signals. For the oxides of **1** these signals appeared at δ 3.25 and 2.70.

(9) The sample was degassed and sealed in an nmr tube, placed in a constant temperature bath, and removed at periodic intervals. No decomposition was observed.

(10) Obtained from a least-squares treatment (correlation coefficient = 0.998) of ln $((R - K)/(1 + R))$ *vs.* *t* using 11 data points collected over *ca.* 2 half-lives. *R* is the ratio of the diastereomers at time *t*, and *K* is the equilibrium constant (K = 1.03).

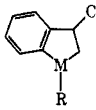
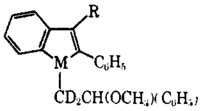
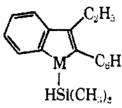
(11) $\Delta G^{\ddagger}$ values are assumed to be temperature independent throughout since $\Delta S^{\ddagger}$ is typically near zero for simple inversion processes.

(12) By analogy with similar phosphorus compounds,[2] incorporation of arsenic into a five-membered ring may be assumed to raise the inversion barrier by 4–6 kcal/mol due to increased angle strain in the planar transition state.

(13) R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 4758 (1970); R. D. Baechler and K. Mislow, *ibid.*, **93**, 773 (1971).

(14) R. D. Baechler, J. P. Casey, R. J. Cook, G. H. Senkler, Jr., and K. Mislow, *ibid.*, **94**, 2859 (1972).

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	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)$_3$Cl$_2$], 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)$_3$Cl$_2$ 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)$_3$Cl$_2$[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)$_3$Cl$_2$,[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).

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