the dimeric molecule is coordinated to a triphenyl-phosphine ligand, a π-bonded alkyne group of one bridging phosphinoacetylene molecule, and the phosphorus atom of the second bridging group. The structure of **1** therefore is similar except that the triphenylphosphine group is replaced by another molecule of the phosphinoacetylene. The geometry about the palladium atom is approximately planar. The dihedral angle between the plane defined by P(1)–Pd(1)–P(2) and C(4)–Pd(1)–C(5) is 14.4° and between the planes P(3)–Pd(2)–P(4) and C(1)–Pd(2)–C(2) is only 5.7°. These values are similar to the values of 8.3° in (C$_7$-H$_{10}$)Pt(PPh$_3$)$_2$[13] 14° in (PhC≡CPh)Pt(PPh$_3$)$_2$,[14] and 8° in (NCC≡CNPt(PPh$_3$)$_2$[15] the only zerovalent nickel triad acetylene complexes reported to date. The angles in Ni(0) and Pt(0) olefin complexes range from 1.3 to 12.3°[15] while the only reported angles for a Pd(0)–olefin complex range from 16 to 21°.[16] In general, the trigonal derivatives of zerovalent Ni, Pd, and Pt have the coordinated acetylene or olefin in the molecular plane while, in the +2 state, the olefin is normal to the molecular plane. However, since all the +2 complexes are four-coordinate, this may be simply a steric effect.

The strength of the metal–acetylene interaction is reflected by the C(1)–C(2) and C(4)–C(5) distances of 1.291 (20) and 1.281 (20) Å, respectively, both of which represent a marked increase from the "free" C≡C distance of 1.20 Å.[17] Similarly, the P–C–C–C skeleton shows deviations from linearity in the P(1)–C(1)–C(2) angle of 150 (1)°, P(3)–C(4)–C(5) angle of 156 (1)°, the C(1)–C(2)–C(3) angle of 138 (1)°, and C(4)–C(5)–C(6) angle of 138 (2)°. Although there are few Pd(0) complexes for comparison, the Pd–C distances which range from 1.989 (14) to 2.039 (14) Å are significantly shorter than in the Pd(0)–olefin complex[16,18] which range from 2.19 to 2.28 Å. The Pd(1)–P(1) and Pd(2)–P(3) distances of 2.301 (4) and 2.296 (4) Å are shorter than Pd-(1)–P(2) and Pd(2)–P(4) distances of 2.313 (5) and 2.321 (4) Å, respectively. The difference in the Pd–P bond lengths could reflect a steric effect related to the CF$_3$ groups or an electronic effect related to the difference between a triarylphosphine and a diphenylphosphino-acetylene. Unfortunately, in the absence of additional structural data, an explanation of this difference would be speculation.

In conclusion, we note that the present structural studies suggest that Pd(0)–acetylene interactions are similar to those in the Pt(0) complexes and hence the lack of Pd(0) complexes does not necessarily reflect a weak interaction. Also, the facile synthesis and air stability of complexes **1** make these attractive derivatives for studies of the reactivities of coordinated acetylenes.

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A Simple Total Synthesis of (±)-Dendrobine

Sir:

Dendrobine (**1**), a physiologically active constituent of the Chinese tonic "Chin Shih Hu," is representative of a group of nitrogenous sesquiterpene lactones related to the powerful convulsant picrotoxinin (**2a**).[1] We now report a stereospecific construction of the tricyclic framework of the Dendrobium alkaloids which leads to a simple total synthesis[2] of dendrobine and which has given a tricyclic lactone of interest as a possible precursor to dihydropicrotoxinin (**2b**) itself.

2a, R = C≤CH$_2$ / CH$_3$
b, R = CH(CH$_3$)$_2$
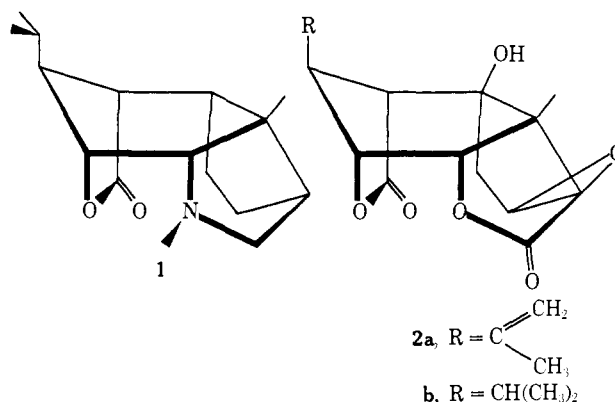
Saponification and ferric chloride oxidation of the known triacetate **3**[3] gives 100% of the quinone **4**, which with butadiene in ethanol (110°, 24 hr) yields 95% of the Diels–Alder adduct **5** (mp 84.5–86°; λ$_{max}$ 293, ε 6050).[4] Its methyl ether **6**[5] (λ$_{max}$ 278, ε 8400) was selectively hydroxylated at the isolated double bond (catalyst OsO$_4$, Ba(ClO$_3$)$_2$, aqueous dioxane)[6] to give 43% of a crystalline diol, mp 164–166°, and 36% of an oily diol, both represented by structure **7**.

Cleavage of crystalline **7** with periodic acid in tetrahydrofuran,[7] followed by aldol cyclization at 50° with pyrrolidine acetate in benzene, gave 65% of a 1:1 mix-

(1) L. A. Porter, *Chem. Rev.*, **67**, 441 (1967).

(2) Longer alternative syntheses of dendrobine have been reported by K. Yamada, M. Suzuki, Y. Hayakawa, K. Aoki, H. Nakamura, H. Nagase, and Y. Hirata, *J. Amer. Chem. Soc.*, **94**, 8278 (1972), and by Y. Inubushi, T. Kikuchi, T. Ibuka, K. Tamaka, I. Saji, and K. Tokane, *J. Chem. Soc., Chem. Commun.*, 1252 (1972).

(3) H. Erdtman, *Proc. Roy. Soc., Ser. A*, **143**, 177 (1934); G. Bargellini, *Gazz. Chim. Ital.*, **53**, 235 (1923).

(4) All new compounds gave satisfactory analytical, spectroscopic, and mass spectrometric data. Nmr, ir, and uv spectra refer to CDCl$_3$, CHCl$_3$, and CH$_3$OH solvents, respectively.

(5) Methylation was quantitatively achieved by methyl iodide and potassium carbonate in acetone at 25°.

(6) *Cf.* L. Plâha, J. Weichet, J. Zvâcek, S. Smolik, and B. Kakâc, *Collect. Czech. Chem., Commun.*, **25**, 237 (1960); I. Ernest, *ibid.*, **29**, 266 (1964).

(7) Use of oily diol **7** gave the same aldehydes in slightly lower yields.

OCOCH₃ / CH₃COO / OCOCH₃

3

4

5, R = H
6, R = OCH₃

7

8, X = O
11, X = ⁺NHCH₃

9
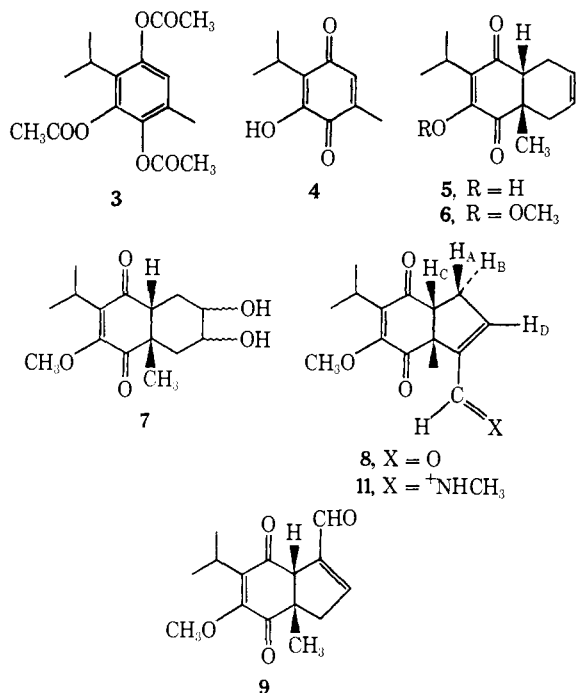
ture of aldehydes **8** and **9** readily separated on Florisil.[8] The more mobile isomer was identified as **8** by its Eu(fod)₃ shifted 100-MHz nmr spectrum which revealed, *inter alia*, the characteristic signal for proton A with first-order couplings $|J_{AB}| = 19$ Hz, $|J_{AC}| = 8$ Hz, and $|J_{AD}| = 2$ Hz.

Reductive amination of **8** (CH₃NH₃Cl, NaCNBH₃, pH 5 in CH₃OH at 20°)[9] gave 30% of alcohol **10**[10] and 35% of a crystalline amine, mp 64–65°, having the structure and stereochemistry of **14** (λ_{max} 257 nm, ϵ 8400). Presumably the protonated imine **11** undergoes conjugate reduction to an enamine which on C-protonation cis to the angular methyl and subsequent reduction yields **12**. Only **12** *and not its 3-epimer* can reach the nearby carbonyl carbon to produce the tricyclic ion **13** which upon exo reduction yields the observed product.

Reduction of the remaining carbonyl in **14** (LiAlH₄, ether, 25°) gave the carbinols **15** which in cold 2 N sulfuric acid produced 80% of the enone **16** (ν_{max} 1670 cm⁻¹; λ_{max} 242 nm, ϵ 6300; nmr δ 6.37, d, 1 H, $J = 7$ Hz). Conjugate addition to **16** (lithium divinylcuprate in ether, −20°) gave 86% of ketone **17** (mp 35–36°; ν_{max} 1695 cm⁻¹).[11] Ruthenium tetroxide in 60% acetic acid[12] at 25° was uniquely effective in cleaving the vinyl group to give, with diazomethane in ether at 20°, a homogeneous keto ester of structure **18** (49% yield; ν_{max} 1700, 1730 cm⁻¹; nmr δ 0.92, d,

(8) Eluting solvent was 20% ether in benzene. The ratio of aldehydes **8** to **9** was insensitive to changes in amine structure, solvent, or reaction temperature.

(9) R. F. Borch, M. Bernstein, and H. D. Dürst, *J. Amer. Chem. Soc.*, **93**, 2897 (1971). Without amine the reduction of **8** with NaCNBH₃ at pH 5 proceeds at sharply lower rate and yields a mixture containing mainly **10**. The rate difference appears to preclude conjugate reduction of **8** prior to imine formation during synthesis of **14**.

(10) Reoxidation of alcohol **10** to aldehyde **8** proceeds in high yield, so that one recycle gives **14** in 45% overall yield from **8**.

(11) Stereochemistry **17** is tentative and is based on analogy to J. A. Marshall and G. M. Cohen, *J. Org. Chem.*, **36**, 877 (1971).

(12) C. Djerassi and R. R. Engle, *J. Amer. Chem. Soc.*, **75**, 3838 (1953); D. M. Piatak, H. B. Bhat, and E. Caspi, *J. Org. Chem.*, **34**, 112 (1969). The reagent, generated from a catalytic amount of RuO₂ in 60% HOAc using excess periodic acid, was mixed with **17** at 25°. Other solvents and oxidants were unsatisfactory.

3 H; 1.02, d, 3 H; 1.10, s, 3 H; 2.12, s, 3 H; 3.68, s, 3 H).

10

12

13

14

15

16

17

18

19
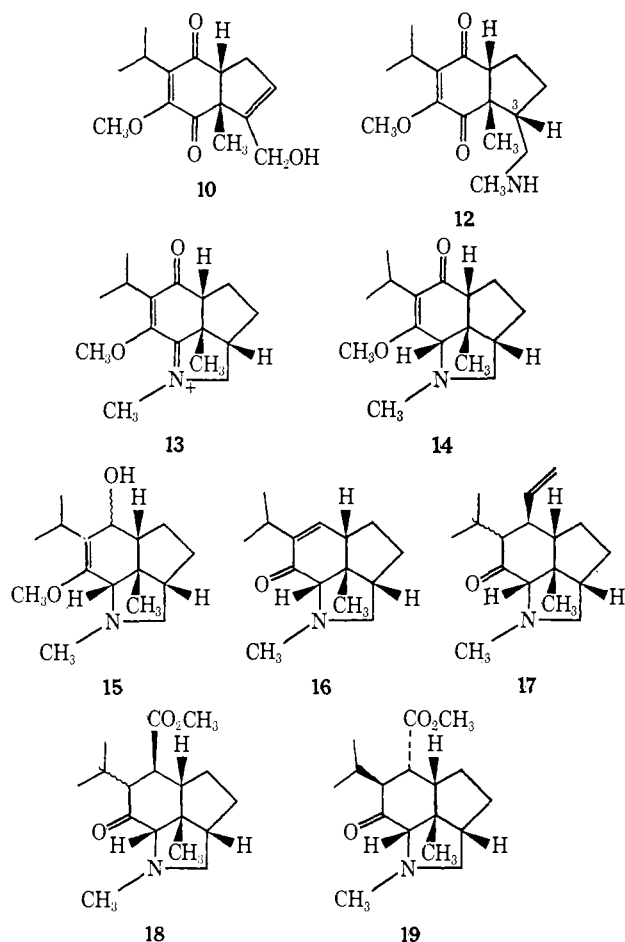
Reflux of **18** for 3 days in anhydrous 0.3 M sodium methoxide in methanol effected partial isomerization[13] to the desired **19** (43% yield based on recovered **18**; nmr δ 0.96, d, 3 H, 1.00 d, 3 H, 1.26 s, 3 H, 2.22, s, 3 H, 3.68, s, 3 H) identical with a sample prepared from authentic methyl dendrobinate (**20**)[14] by Jones oxidation. Sodium borohydride (isopropyl alcohol, 25°, 3 days) reduced **19** to **20** which spontaneously cyclized to yield, after SiO₂ chromatography, 46% of crystalline (±)-dendrobine (**1**), indistinguishable from the natural alkaloid by ir, mass spectral, 100 MHz nmr, and tlc behavior.[15]

20

21

22
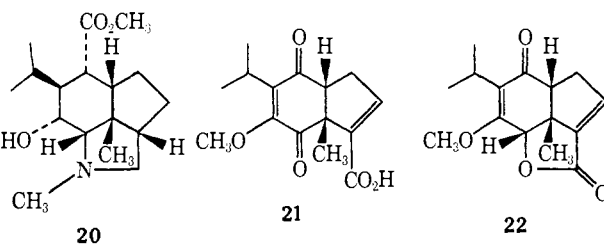
The utility of this sequence for the total synthesis of dihydropicrotoxinin (**2a**) is suggested by the smooth conversion of aldehyde **8** with Jones reagent to acid **21**

(13) *Cf.* Y. Inubushi, E. Katarao, Y. Tsuda, and B. Yasui, *Chem. Ind.* (*London*), 1689 (1964). Equilibration of **18** in our hands gave a mixture of keto esters in which the content of **19** was *ca.* 30% (nmr).

(14) *Cf.* Y. Inubushi, Y. Sasaki, Y. Tsuda, B. Yasiu, T. Konita, J. Matsumoto, E. Katarao, and J. Nakano, *Tetrahedron*, **20**, 2007 (1964).

(15) We are grateful to Professors K. Yamada, Y. Inubushi, and K. Leander for independently supplying generous samples of natural dendrobine.

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(90%, mp 179–180°) which on reduction (NaBH₄, isopropyl alcohol, 25°) and dehydration[16] produced crystalline lactone 22 (mp 150–151°; ν_{max} 1768 cm⁻¹; nmr δ 5.18, s, 1 H, 6.64, t, 1 H). Introduction of the remaining tertiary alcohol and epoxide functions and elaboration of the second lactone ring in dihydropicrotoxinin are under investigation.

(16) Dehydration could be carried out with p-TsCl in pyridine at room temperature or with 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-p-toluenesulfonate in CHCl₃ at room temperature for 2 days.

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Effect of Ligand Substituents on the "d–d" Luminescence of Iridium(III) and Rhodium(III) Complexes of 1,10-Phenanthroline

Sir:

The effects of ligand substituents on the visible charge-transfer emission of several 1,10-phenanthroline complexes of Ru(II) and Ir(III) have recently been reported.[1–3] Certain ligand substituents on 1,10-phenanthroline significantly alter both the radiative and radiationless decay rates of the emitting states of these d⁶ complexes, although only minor effects on the energies of the emitting states are observed. We wish to report that observations of the near-infrared emission from the low-lying d–d states of a series of Ir(III) complexes reveal surprisingly large ligand substituent effects. However, such effects are small in a corresponding series of Rh(III) complexes.

Complexes of the type [H-Xphen][IrCl₄(Xphen)] and (H-Xphen)[RhCl₄(Xphen)], where Xphen represents a substituted 1,10-phenanthroline and H-Xphen the corresponding phenanthrolinium ion, were prepared by the method of Broomhead and Grumley.[4] Studies of the complex [H-phen][IrCl₄(phen)] have shown that this complex displays a blue fluorescence in fluid solution characteristic of the phenanthrolinium ion.[5] A blue-green phosphorescence characteristic of the phenanthrolinium ion is also found to occur from the solids at 77°K. Due to these interfering effects, phenanthrolinium ions are unsatisfactory counterions for studies of the complex emission. The phenanthrolinium salts were converted to the potassium salts by stirring the complexes with 5 M potassium acetate in the dark for 3 hr. The absence of both the blue

fluorescence and the blue-green phosphorescence in the products provided evidence that the metathesis was complete. All emission spectra were measured on solid samples of the potassium salts in liquid nitrogen and were corrected for distortions introduced by the wavelength dependence of the instrumental response. The basic components of the emission apparatus were similar to those described by Demas.[6] For lifetime measurements the potassium salts of the complex ions were excited at 337 nm with an Avco C950 pulsed nitrogen laser. In several instances lifetime measurements on the phenanthrolinium salts were also made with the laser. The emission was detected with an Amperex 56TVP photomultiplier, and decay curves were displayed on a Tektronix type 549 oscilloscope.

The emission spectrum of K[IrCl₄(phen)] has been reported, and both the low energy and the broad, Gaussian shape of the spectrum indicate that the emission is due to a d–d transition.[7] Although no previous measurement of the luminescence lifetime of this complex has been reported, the Avco C950 nitrogen laser provides a 10-nanosec pulse of sufficient intensity to measure a lifetime of 0.63 ± 0.05 μsec for this solid at 77°K. The emission of K[RhCl₄(phen)] also occurs in the near-infrared region and has a broad Gaussian shape. The luminescence lifetime of this complex could not be measured accurately due to its low intensity, but could be estimated to be about 0.1–0.2 μsec. This information, coupled with a previous assignment of the [RhCl₂(phen)₂]Cl emission as a d–d transition,[8–10] leaves little doubt that the K[RhCl₄(phen)] emission is also due to a d–d transition. The energies for the various substituted-phenanthroline complexes of Ir(III) and Rh(III) are reported in Table I. In all cases broad, Gaussian emissions are observed, and like the parent phenanthroline complexes are assigned as d–d transitions.

In view of the relatively small substituent-induced shifts (<1 kK) in the energy of charge-transfer emissions of Ir(III) and Ru(II) complexes of 1,10-phenanthroline,[1] it is surprising to find that the d–d emissions of the Ir(III) complexes in Table I are shifted by as much as 2.6 kK. Equally surprising are the facts that the emissions are blue shifted by electron-withdrawing substituents and red shifted by electron-donating substituents in the case of Ir(III). A similar trend occurs for the Rh(III) analogs, but it is less pronounced.

Simple considerations of the effect of an electron-withdrawing substituent on 1,10-phenanthroline suggest that this should decrease the basicity of the ligand and bring about a decrease in its σ-bonding ability. Studies of various substituted phenanthrolines show, for example, that their pK_a values are decreased by electron-withdrawing substituents.[11,12] Such a decrease would be expected to decrease the value of the crystal field parameter Δ for an octahedral complex.

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