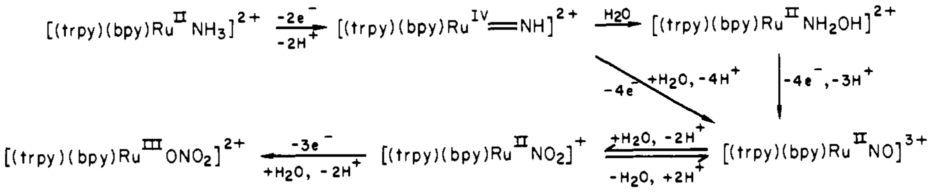

in the visible region because of the loss of bands arising from $d\pi(\mathrm{Ru(II)}) \rightarrow \pi^*(\mathrm{bpy})$ transitions. For the rapid reaction observed by the stopped-flow technique, the observed absorbance changes are consistent with the reappearance of ~50% of the stoichiometric amount of $[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{III}NH_3}]^{2+}$. The rapid reaction is followed by a slower reaction that follows first-order kinetics ($k = 5 \times 10^{-3}\ \mathrm{s^{-1}}$ at 25 °C) independent of pH over the range 2–10. At the end of the slow reaction nearly the total absorbance of the initial solution before oxidation is recovered but with slight changes in spectral detail. Oxidation of the solution at 0.8 V at the end of the slow reaction occurs with $n = 5$ to give $[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{II}NO_2}]^+$ quantitatively.

Although complete details are lacking, our surmise is that following oxidation to Ru(III) a disproportionation occurs to give $[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{II}NH_3}]^{2+}$ and the Ru(IV) imido complex $[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{IV}{=}NH}]^{2+}$. The reaction is entirely analogous to the disproportionation in eq 4[3] and the proposed imido complex

$$2[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{III}{-}OH}]^{2+} \underset{K = 5 \times 10^{-3}}{\rightleftharpoons} [(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{IV}{=}O}]^{2+} + [(\mathrm{trpy})(\mathrm{bpy})\mathrm{RuOH_2}]^{2+} \quad (4)$$

is isoelectronic with the oxo complex $[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{IV}{=}O}]^{2+}$. There is precedence for the suggested disproportionation from the work of Taube and Rudd[4] who suggested that disproportionation occurs following the addition of base to solutions containing $[\mathrm{Ru(NH_3)_5py}]^{3+}$. Following the rapid disproportionation, the slow step appears to involve the pH independent attack of H_2O on the coordinated imide to give the related hydroxylamine complex (eq 5). This conclusion is supported by the observed spectral changes;

$$[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{IV}{=}NH}]^{2+} + \mathrm{H_2O} \xrightarrow{k} [(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{II}NH_2OH}]^{2+} \quad (5)$$

$[(\mathrm{trpy})(\mathrm{bpy})\mathrm{RuNH_2OH}]^{2+}$ is expected to be closely related spectrally to $[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{II}NH_3}]^{2+}$.

The results described above appear to establish, at least in preliminary detail, the initial two-electron stage of the ammonia to nitrate oxidation. We have no mechanistic details for the second stage, which is a four-electron oxidation, except for the nature of the initial product of oxidation. If the ammine complex is oxidized at pH 4.9 rather than pH 6.8, the initial product is the nitrosyl complex, $[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{II}NO}]^{3+}$, rather than the nitro complex. An acid–base equilibrium exists between the nitrosyl and nitro complexes (eq 6),[1] and although the nitro complex is

$$[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{II}NO_2}]^+ + 2\mathrm{H^+} \overset{K}{\rightleftharpoons} [(\mathrm{trpy})(\mathrm{bpy})\mathrm{Ru^{II}NO}]^{3+} + \mathrm{H_2O} \quad (6)$$

the thermodynamically favored form at pH 4.9, conversion of the nitrosyl to the nitro is slow at this pH.

As previously mentioned, the final stage of the ammonia to nitrate conversion is the two-electron oxidation of bound nitrite to nitrate which has been studied in some detail.[1] A set of reactions describing oxidative conversion of ammonia to nitrate suggested by the results described both here and earlier are shown in the scheme below. The evidence for direct oxidation of the Ru(IV) imido intermediate comes from cyclic voltammetry where the irreversible oxidation leading to the $\mathrm{RuNO_2}$ product occurs rapidly on the time scale for attack by water.

It seems clear that our results and results reported earlier on the oxidation of amines coordinated to ruthenium[3] or osmium[5] both presage an extensive chemistry. One benefit of this chemistry may be the insight that it brings to the design of catalytic reagents for multiple electron-transfer reactions.

Acknowledgment is made to the National Science Foundation (Grant CHE8008922) and the National Institutes of Health (Grant 5-R01-GM15238-14) for support of this research.

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[3] Thompson, M. S.; Meyer, T. J., manuscript in preparation. Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436.

[4] Rudd, De F. P.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1543.

[5] Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208.

Synthesis Applications of Aza-Cope Rearrangements.[1a] A Stereoselective Synthesis of *cis*-3a-Aryloctahydroindoles and a New Short Entry to *Amaryllidaceae* Alkaloids

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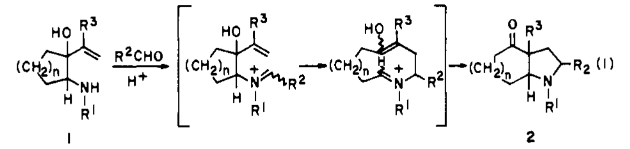
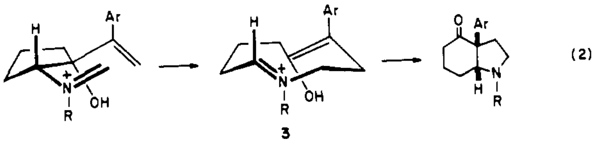
The use of "directed" cationic aza-Cope rearrangements (2-azonia[3,3]sigmatropic rearrangements) for the synthesis of a variety of heterocyclic systems, under mild conditions, has been described in recent reports from this laboratory.[1a,2] An unusual annulation sequence which exploits this chemistry is illustrated in eq 1. This sequence, which would accomplish a "ring-enlarging pyrrolidine annulation", would be of particular importance in synthesis if the widely occurring[3,4] *cis*-3a-aryloctahydroindole ring system (*cis*-**2**, $n = 1$, $R^3 = \mathrm{Ar}$) could be prepared in this fashion. If the amine and vinyl groups are oriented trans in the cyclopentyl precursor **1** ($n = 1$), this sequence should *stereorationally* lead to the formation of *only* the *cis*-octahydroindole ring system, since pericyclic rearrangement *via* only a single "chair-type" transition state is possible for systems of this type (eq 2).[5-8] A *cis*-octa-





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[1] (a) Part 5 in the series. For part 4, see: Overman, L. E.; Yokomatsu, T. *J. Org. Chem.* **1980**, *45*, 5229. (b) Camille and Henry Dreyfus Teacher–Scholar, 1976–1981.

[2] (a) Overman, L. E.; Kakimoto, M. *J. Am. Chem. Soc.* **1979**, *101*, 1310. (b) Overman, L. E.; Kakimoto, M.; Okawara, M. *Tetrahedron Lett.* **1979**, 4041. (c) Overman, L. E.; Fukaya, C. *J. Am. Chem. Soc.* **1980**, *102*, 1454.

[3] This ring system is found, for example, in alkaloids of the mesembrine, *Amaryllidaceae*, *Aspidosperma*, and *Strychnos* familes.

[4] Cf.: Dalton, D. R. "The Alkaloids. The Fundamental Chemistry"; Marcel Dekker: New York, 1979.

[5] This prediction assumes that intramolecular Mannich ring closure of the presumed azacyclononadiene intermediate **3** would be more rapid than any loss of stereochemical integrity of this intermediate.

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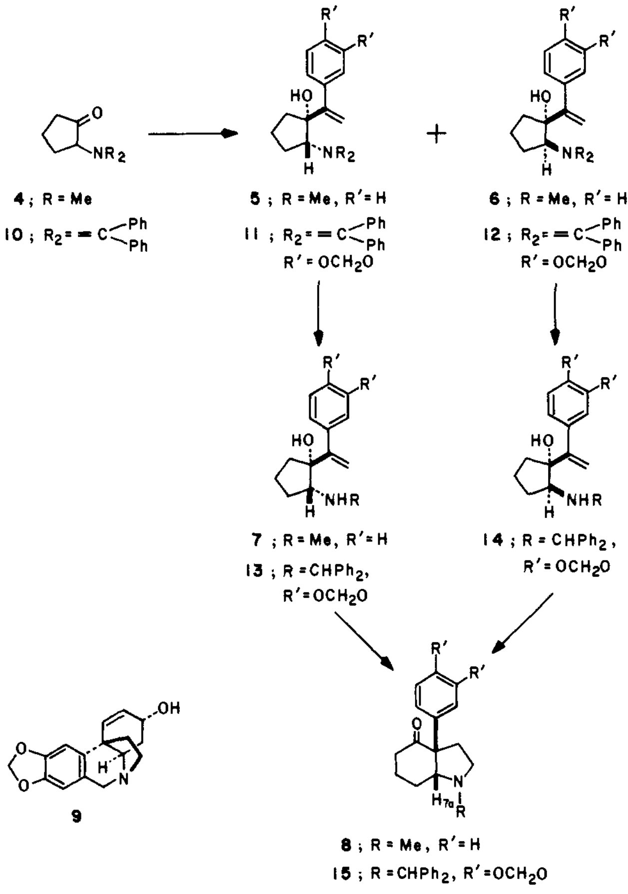
Scheme I



hydroindolone could also result from the rearrangement of the precursor **1** ($n = 1$) with cis-oriented amine and vinyl groups, although the stereochemical prediction is much less secure, since four (two "chair" and two "boat") pericyclic transition states are possible in this case.[9,10] Herein we describe the efficient use of the ring enlarging pyrrolidine annulation reaction for the preparation of *cis*-3a-aryl-4-octahydroindolones and the formal total synthesis of the Amaryllidaceae alkaloid *dl*-crinine.

The new annulation reaction was first examined with amino alcohol **7**, which was prepared as summarized in Scheme I. Addition of (1-phenylvinyl)lithium[11] to aminocyclopentanone (**4**)[13,14] occurred primarily from the side opposite the dimethylamino group to give alcohol **5**[13] in 54% yield after chromatographic purification. Less than 10% of the diastereomeric alcohol **6**[13] was formed. Dilution infrared studies allowed the stereochemistry of these alcohols to be assigned with certainty.[17] Thus, the major alcohol **5** showed a weak absorption at 3604 cm^{-1} (CCl$_4$, free OH) and a strong intramolecular hydrogen-bonded OH absorption at 3340 cm^{-1} (relative intensity did not change with concentration, 0.1–0.006 M), while **6** showed absorptions at 3600 and 3430 cm^{-1} whose relative intensities depended upon concentration. Conversion of **5** to the secondary amine **7**[13] was accomplished in 86% yield by sequential treatment with phenyl chloroformate and 20% ethanolic KOH.[18] When **7** was heated in refluxing ethanol for 20 h with 1 equiv of paraformaldehyde,[19] the crystalline *cis*-octahydroindolone **8**,[13,20] mp 84–85 °C, was obtained in 78% yield. Desulfurization of the ethylene dithioketal of **8** gave the known[21] *cis*-1-methyl-3a-phenyloctahydroindole.[22] The ring enlarging pyrrolidine annulation reaction afforded *only* the *cis*-octahydroindolone **8**, since no isomers of **8** could be detected by GC, TLC, or ^{13}C NMR analysis of the crude reaction product.

For a demonstration of the utility of this chemistry for alkaloid total syntheses, a formal total synthesis of the *Amaryllidaceae* alkaloid *dl*-crinine (**9**)[23] was accomplished as follows. Reaction of [1-[3,4-(methylenedioxy)phenyl]vinyl]lithium[11] with imino

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(6) It is interesting to note that the carbocyclic analogue of intermediate **3**, *trans,trans*-1,5-cyclononadiene, is not known, although it should be more stable than the known cis,trans isomer.[7] The *trans,trans*-1,5-cyclononadiene ring system (in parallel, rather than the crossed conformation) is known[8] in bicyclic systems.

(7) This is apparent from an examination of molecular models. See also: Zuccarello, F.; Buemi, G.; Favina, G. *J. Mol. Struct.* **1971**, *8*, 459. White, D. N. J.; Bovill, M. J. *J. Chem. Soc., Perkin Trans 2* **1977**, 1610.

(8) Rastetter, W. H.; Richard, T. J.; Bordner, J.; Hennessee, G. L. A. *J. Org. Chem.* **1979**, *44*, 999.

(9) At 220 °C, *cis*-1,2-divinylcyclopentane and *cis,cis*-1,5-cyclononadiene thermally equilibrate.[10] Rearrangement of *cis*-1-(azavinyl)-2-vinylcyclopentane **1** via the same "boat" transition state would eventually lead[5] to the formation of a cis-fused octahydroindolone. This prediction is not terribly secure, since an iminium ion derived from **1** differs significantly from a divinylcyclopentane.

(10) Vogel, E.; Grimme, W.; Dinne, E. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 739.

(11) Prepared from the corresponding bromide[12] and 1.0 equiv of *tert*-butyllithium at –60 °C in ether. The use of 2.0 equiv of *tert*-butyllithium was unsatisfactory.

(12) Newman, M. S.; Dhawan, B.; Hashem, M. M.; Khanna, V. K.; Springer, J. M. *J. Org. Chem.* **1976**, *41*, 3925.

(13) All compounds reported were homogeneous by TLC analysis and showed ^{1}H NMR, ^{13}C NMR, IR, and mass spectra consistent with the assigned structures; the molecular composition of all key intermediates was determined by high-resolution mass spectrometry or combustion analysis. Partial characterization data for selected intermediates are as follows. **5**: ^{1}H NMR (60 MHz, CDCl$_3$) δ 5.64 (d, $J = 2$ Hz, =C*H*H), 5.09 (d, $J = 2$ Hz, =CH*H*). **6**: ^{1}H NMR (60 MHz, CDCl$_3$) δ 5.52 (d, $J = 1$ Hz, =C*H*H), 5.19 (d, $J = 1$ Hz, =CH*H*). **7**: ^{1}H NMR (60 MHz, CDCl$_3$) δ 7.34 (apparent s, Ph*H*), 5.60 (d, $J = 2$ Hz, =C*H*H), 5.06 (d, $J = 2$ Hz, =CH*H*), 2.9–3.3 (m, CHN), 2.46 (s, NCH$_3$). **8**: IR (CCl$_4$) 1711 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) 7.33 (apparent s, Ph*H*), 2.95–3.3 (m, CHN and CH$_2$N); ^{13}C NMR (CDCl$_3$) 209.8, 140.9, 128.8, 126.7, 126.4, 69.6, 63.2, 53.0, 39.4, 39.3, 33.4, 22.9, 21.8. **13**: ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.1–7.4 (m, PhH), 6.5–6.7 (m, ArH), 5.92 (s, OCH$_2$O), 5.52 (d, $J = 1.8$ Hz, =C*H*H), 5.07 (d, $J = 1.8$ Hz, =CH*H*), 4.85 (s, C*H*Ph$_2$), 3.03 (apparent t, $J = 8.8$ Hz, CHN); MS (isobutane CI), *m/e* (relative intensity) 414 (63), 246 (25), 167 (100). **14**: ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.1–7.3 (m, PhH), 6.6–7.0 (m, ArH), 5.96 (AB q, $J = 1.2$ Hz, $\Delta\nu = 3.5$ Hz, OCH$_2$O), 5.36 (d, $J = 1.0$ Hz, =C*H*H), 5.29 (d, $J = 1.0$ Hz, =CH*H*), 4.73 (s, C*H*Ph$_2$), 2.94 (apparent d, J = 5 Hz, CHN); MS (isobutane CI), *m/e* (relative intensity) 414 (35), 396 (12), 246 (15), 215 (32), 167 (100). **15**: IR (CCl$_4$) 1710 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.15–7.4 (m, PhH) 6.6–6.8 (m, ArH), 5.92 (ABq, $J = 1.2$ Hz, $\Delta\nu = 2$ Hz, OCH$_2$O), 5.18 (s, C*H*Ph$_2$), 3.51 (br s, half-height width = 5 Hz, C$_{7a}$–H), 2.8–3.0 (m, NCH$_2$); MS (isobutane CI), *m/e* (relative intensity) 426 (26), 260 (71), 167 (100), 91 (36). **16**: IR (CCl$_4$) 1710 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$) δ 6.6–6.8 (m, ArH; appears as single line at 60 MHz[23b]), 5.94 (br s, OCH$_2$O), 3.95 (br s, C$_{7a}$-H), 2.9–3.1 (m, C$_{3\alpha}$-H and CH$_2$N).

(14) Prepared in 83% yield by oxidation of *trans*-2-(dimethylamino)-cyclopentanol[15a] by the method of Swern.[16]

(15) Prepared from the reaction of commercially available cyclopentene oxide with the corresponding amine: (a) Mousseron, M.; Granger, R.; Combes, G.; Pertzoff, V. A. *Bull. Soc. Chim. Fr.* **1947**, 850. (b) Bannard, R. A. B.; Gibson, N. C. C.; Parkkari, J. H. *Can. J. Chem.* **1971**, *49*, 2064.

(16) Mancuso, A. J.; Huang, S.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

(17) Golfier, M. In "Stereochemistry: Fundamentals and Methods"; Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977; Vol. I, pp 29–34.

(18) The direct preparation of **7** by the reaction of salts of 2-(methylamino)cyclopentanone with 2–4 equiv of (1-phenylvinyl)lithium could not be accomplished in good yield. The use of acyl nitrogen protecting groups (COCF$_3$ and COOMe) was also not successful, since enolization predominated when ketones of this type were treated with (1-phenylvinyl)lithium.

(19) This reaction was faster and proceeded in similar yield, when carried out in the presence of 0.9 equiv of *d*-10-camphorsulfonic acid.

(20) The cis stereochemistry of **8** was apparent from the 250-Mz ^{1}H NMR spectrum which showed the angular hydrogen H$_{7a}$ as a narrow multiplet (half-height width = 7 Hz), which is consistent only with H$_{7a}$ being equatorial in the cyclohexane ring. Cf: Stevens, R. V.; Dupree, L. E., Jr.; Lowenstien, R. L. *J. Org. Chem.* **1972**, *37*, 977.

(21) Langlois, M.; Guillonneau, C.; Meingan, J.; Maillard, J. *Tetrahedron* **1971**, *27*, 5641.

(22) This correlation is not unambiguous, since epimerization during the Ra-Ni desulfurization is possible. The ^{1}H NMR data[20] for **8**, however, leave little doubt that this material is cis.

(23) For previous total syntheses of *dl*-crinine, see: (a) Muxfeldt, H.; Schneider, R. S.; Mooberry, J. B. *J. Am. Chem. Soc.* **1966**, *88*, 3670. (b) Whitlock, H. W., Jr.; Smith, G. L. *Ibid.* **1967**, *89*, 3600. For a recent review of the synthesis of other closely related 5,10b-ethanophenathridine alkaloids, see: Tsuda, Y. *Heterocycles* **1978**, *10*, 555.

ketone **10**[13,24] occurred, somewhat to our surprise, mainly from the side of the imine substituent. Chromatographic purification allowed the crystalline amino alcohol **12**,[13,25] mp 91–91.5 °C, to be isolated in 62% yield, together with 10% of recovered ketone **10** and 20% of a mixture of amino alcohol **11**, the corresponding oxazolidine, and a small amount of an unknown material. The formation of both amino alcohol isomers in reasonable amounts provided an opportunity to examine the stereoselectivity of the hydroindolone synthesis with both cyclopentane stereoisomers. Reduction of **11** with $NaCNBH_3$ in acidic ethanol gave, after chromatographic purification, pure **13**[13] in 77% yield. Amino alcohol **13** showed a characteristic intramolecular hydrogen-bonded OH absorption at 3460 cm^{-1} (CCl_4) in the infrared spectrum. Treatment of secondary amine **13** at 70 °C in Me_2SO[26] with 1 equiv of paraformaldehyde and 0.9 equiv of *d*-10-camphorsulfonic acid, afforded *cis*-octahydroindolone **15**,[13,27] mp 157.5–158.5 °C, in 91% yield. In a similar fashion, imine **12** was reduced with $NaCNBH_3$ to give the crystalline secondary amine **14**,[13] mp 98.5–99 °C, in 88% yield. The reaction of **14** with 1 equiv of paraformaldehyde and a sulfonic acid catalyst in benzene or ethanol was less clean than that of stereoisomer **13** and gave **15** together with varying amounts of the corresponding *trans*-octahydroindolone.[27,28] However, when Me_2SO was used as the solvent,[28] the cis isomer was formed with high stereoselectivity (cis/trans > 30:1, 250-MHz ^1H NMR analysis)[27] and pure *cis*-octahydroindolone **15** could be isolated in 65% yield. The diphenylmethyl group of **15** was easily removed by transfer hydrogenation[29] (Pd/C, cyclohexene, ethanol, 1 N HCl) to give *cis*-octahydroindolone **16**,[13] in 95% yield after chromatographic purification. The *N*-acetyl derivative of **16** melted at 126–127 °C (lit.[23b] 126.5–127.5 °C), and **16** showed spectroscopic properties identical with those reported[23b] for an authentic sample, thereby completing a formal total synthesis of *dl*-crinine (**9**). This efficient four-step sequence afforded *cis*-octahydroindolone **16** in 47% overall yield from protected amino ketone **10** and 24% overall yield from *trans*-2-aminocyclopentanol.

The results described here provide a further illustration of the use of "directed" aza-Cope rearrangements in organic synthesis. The ring-enlarging pyrrolidine annulation reaction proceeds in excellent yield under mild conditions and allows *cis*-3a-aryl-octahydroindolones to be assembled in a stereoselective fashion in 3–4 steps from a 2-aminocyclopentanone precursor. It is significant that cyclopentanols **7** and **13** which have the amine and vinyl groups oriented trans were converted with *complete stereoselectivity* to *cis*-octahydroindolone products (see eq 2). Also important for future applications of this chemistry is the demonstration that cyclopentanols with the opposite orientation of vinyl and amine groups may also be transformed with high stereoselectivity to *cis*-octahydroindolones. Further extensions of this chemistry, for example, for the preparation of *Aspidosperma* alkaloids,[30] will be described in future publications from this laboratory.

Acknowledgment. The support of the National Institutes of Health (NS-12389) and the Camille and Henry Dreyfus Foundation is gratefully acknowledged. NMR and mass spectra were determined with spectrometers purchased with the assistance of NSF departmental instrumentation grants.

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(24) Prepared in 52% yield from *trans*-2-aminocyclopentanol[15b] by reaction with benzophenone followed by oxidation.[16]

(25) The structure of this amino alcohol was confirmed by single-crystal X-ray analysis. Details will be published in a subsequent full account.

(26) This conversion occurs similarly in other solvents such as benzene.

(27) The 250-MHz ^1H NMR spectrum of **15** showed a characteristic narrow multiplet (half-height width = 5 Hz) for the angular H_{7a} hydrogen at δ 3.51 and a singlet at δ 5.18 for the diphenylmethyl hydrogen. No trace of the trans isomer (δ 4.76, s, C*H*Ph_2; δ 3.0–3.2, m, C_{7a}-H) was seen in the 250-MHz ^1H NMR spectrum of the crude reaction product.

(28) Although **15** was always the major product, the stereoisomer ratios varied considerably with solvent and other reaction details. This aspect of the reaction will be treated in detail when a full account of the work is published.

(29) Cf.: Jackson, A. E.; Johnstone, R. A. W. *Synthesis* **1976**, 685.

(30) Overman, L. E.; Sworin, M. *Tetrahedron*, in press.

Synthesis and Structure of the Distorted Tetrahedral Cluster (η^5-C_5H_5)$_4Cr_4O_4$, the Third Member of the [(η^5-C_5H_5)$_m$$M_m$$O_n$] Series Where *m* and *n* Satisfy Euler's Theorem

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We recently described the synthesis and properties of $Cp_5V_5O_6$ (Cp = η^5-C_5H_5), a trigonal-bipyramidal cluster of five vanadium atoms with an oxygen above each of the six faces of the trigonal bipyramid and a Cp ring capping each vanadium atom.[1] Previously Caulton and co-workers described $Cp_6Ti_6O_8$, a cluster with an oxygen atom above each of the eight faces formed by an octahedron of titanium atoms capped by Cp rings.[2] Geometrical considerations (Euler's theorem) alone suggest that $Cp_4Cr_4O_4$, $Cp_3Mn_3O_2$ and $Cp_7Sc_7O_{10}$, each with O atoms above triangular faces of metal atoms, should exist. We have begun a synthetic search for these clusters, using dinitrogen oxide to oxidize Cp_2M derivatives,[1,3-5] and describe here the synthesis, structure, and some properties of the distorted tetrahedral cluster $Cp_4Cr_4O_4$. A compound of this formula was in fact described over 20 years ago by Fischer, Ulm, and Fritz.[6] They considered various structures, including a tetrahedron of chromium atoms, but concluded that a planar eight-membered –Cr–O–Cr– ring was most probable on the basis of infrared spectroscopy.

Treatment of a toluene solution of Cp_2Cr with 1 equiv of N_2O followed by sublimation at 275–300 °C and recrystallization of the sublimate from hexane gave deep blue, very air- and water-sensitive crystals of $Cp_4Cr_4O_4$ in 8% yield. These have the remarkable structure shown in Figure 1.[7] The chromium atoms form an approximate tetrahedron, capped by the Cp rings and with the oxygen atoms above each face, as predicted. All except 1 of the 12 Cr–O distances lie within 2 standard deviations of the average distance of 1.937 (4) Å.[8] The heights of the four oxygen atoms above the triangular faces are essentially identical (average 1.055, range 1.043–1.063 Å), and the four Cr–Cp (ring center) distances are also identical (average 1.920, range 1.912–1.925 Å). However, the Cr–Cr distances are markedly unequal, there being three pairs of similar distances: 2.900 (6) and 2.897 (5), 2.841 (6) and 2.811 (6), and 2.712 (2) and 2.702 (6) Å (see Figure 2). The $Cp_4Cr_4O_4$ molecule therefore has D_2 symmetry within experimental error.

If it is assumed that each oxygen atom donates four of the possible six electrons to the cluster, then $Cp_6Ti_6O_8$ has a total of 86 electrons with which Ti–Cp, Ti–O, and Ti–Ti bonds can be formed; $Cp_5V_5O_6$ has 74, and $Cp_4Cr_4O_4$ 60; $Cp_7Sc_7O_{10}$ would have 96 and $Cp_3Mn_3O_2$ 44. It is clear from the structures of $Cp_6Ti_6O_8$, $Cp_5V_5O_6$, and $Cp_4Cr_4O_4$ that the M–O distances are those of a single bond. The average distances are Ti–O 1.973 (3);[2] V–O, 1.861 (6) (axial) and 1.992 (6) (equatorial);[1] Cr–O, 1.937 (4) Å. From the literature Ti^{IV}–O bond distances average close to 1.89[9] and Ti^{III}–O close to 2.13 Å;[10] V^{IV}–O close to 1.93[11] and

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(1) Bottomley, F.; White, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 28–29.

(2) Huffman, J. C.; Stone, J. G.; Krussell, W. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829–5831.

(3) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Am. Chem. Soc.* **1981**, *103*, 703.

(4) Bottomley, F.; Lin, I. J. B.; Mukaida, M. *J. Am. Chem. Soc.* **1980**, *102*, 5238–5242.

(5) Bottomley, F.; Brintzinger, H. H. *J. Chem. Soc., Chem. Commun.* **1978**, 234–235.

(6) Fischer, E. O.; Ulm, K.; Fritz, H. P. *Chem. Ber.* **1960**, *93*, 2167–2173.

(7) Determined by X-ray crystallography. Crystal data: $C_{20}H_{20}Cr_4O_4$, $M = 532.4$; monoclinic, $P2_1/c$; $a = 10.442$ (3), $b = 20.958$ (8), $c = 11.022$ (3) Å; $\beta = 124.24$ (2)°; $R = 0.030$, $R_w = 0.046$ for 334 variables and 2162 observed reflections out of 2616 measured. Full details will be published elsewhere.

(8) Cr–O = 1.944 (4), 1.929 (3), 1.936 (3), 1.944 (6), 1.939 (3), 1.932 (4), 1.934 (3), 1.936 (3), 1.949 (6), 1.935 (5), 1.944 (4), 1.918 (3) Å.

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