by quenching the reduction product with aqueous ammonium chloride. An 84% yield of 9,10-dibenzylphenanthrene was obtained. Dimethyldichlorosilane quenching gave **4**. The ultimate reduction product of *trans*-**2** is thus $\mathbf{3}^{2-}$. Even at −78° this dianion underwent rapid $Z,E \rightleftarrows E,E$ equilibration, thus invalidating the silane quench as a mechanistic probe.[5] The dramatically different rates of cleavage of *cis*- and *trans*-$2\cdot^-$, nevertheless, form the basis for a relatively secure assignment of reaction stereochemistry, as follows. Despite the greater thermodynamic stability of *trans*- than *cis*-**2**, *trans*-$\mathbf{2}\cdot^-$ cleaves far more rapidly. This phenomenon is familiar in the conrotatory cleavages of neutral 3,4-diphenylcyclobutene derivatives[11-13] and is understood on the basis of strong steric repulsion in the Z,E diene isomer, formed conrotatorily from the *cis*-cyclobutene. The trans > cis rate order may thus be considered diagnostic for conrotation in such systems.

INDO/MO calculations were carried out for the parent cyclobutene-1,3-butadiene anion radical cleavage using as initial and final geometries those of the corresponding neutral substrates.[14] Intermediate state geometrics were calculated assuming a linear relationship between C_3-C_4 bond stretching and rotation. This assumption was validated by more extensive studies on the neutral cyclobutene system. The initial (cyclobutene anion radical) and final (butadiene anion radical) state binding energies thus calculated were −4.0519 and −4.0232 hartrees, respectively. For the conrotatory cleavage, ten intermediate calculations fixed the transition state at $\theta = 45°$, binding energy −3.9901. The smaller activation energy is thus 0.0331 hartree or 20.8 kcal/mol. The disrotatory maximum also occurred at $\theta = 45°$, $E = -3.9233$, the smaller, activation energy being 0.0989 hartree or 62.1 kcal/mol. The *conrotatory* mode is clearly predicted. Incidentally, the perpendicular state corresponding to a "diradical" mechanism has $E = -3.9714$ hartrees, and this mechanism is thus also favored over the dis mode. The parent benzocyclobutene anion radical, the electrocyclic cleavage of which is ideally allowed,[5] was also investigated using INDO. The initial and final state energies are −8.1140 (benzocyclobutene anion radical) and −7.8846 hartrees (*o*-xylylene anion radical). For the conrotatory mode the transition state (again at $\theta \approx 45°$) has energy −7.8838, corresponding to a barrier of only *0.0008 hartree* or *0.5* kcal/mol. In the dis mode, the smaller activation energy is 0.0378 hartree or 23.7 kcal/mol. These results emphatically concur with OCD and with experiment in foreseeing a favored and ideally allowed con mode for this radical. One notes also that the unfavorable interaction between the termini of the *o*-xylylene system in the conrotatory mode envisioned by HOMO is not manifested in the calculation, since virtually no activation barrier exists. Thus not only is the predominance of HOMO's single interaction questioned but even its quantitative importance.

The available facts are consistent with the generalization that ideally allowed electrocyclic reactions of radicals have extremely low barriers and that, in the more numerous instances where neither mode is allowed, both have substantial barriers. In the cyclobutene-butadiene anion radical system the preferred mode is the same as for the neutral cyclobutene system, viz., conrotation.

Acknowledgment. The authors thank the Robert A. Welch Foundation (F-149) for support of this research.

References and Notes

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965).
(2) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).
(3) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).
(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, Germany, 1970, p 44.
(5) N. L. Bauld, C.-S. Chang, and F. R. Farr, *J. Am. Chem. Soc.*, **94**, 7164 (1972).
(6) The naphtho[*b*]cyclobutene and acenaphthylene anion radicals also have allowed electrocyclic modes which are incorrectly treated by HOMO.
(7) M. J. S. Dewar and S. Kirshner, *J. Am. Chem. Soc.*, **93**, 4290 (1971).
(8) M. P. Cava and D. Mangold, *Tetrahedron Lett.*, 1751 (1964).
(9) N. L. Bauld, F. R. Farr, and C. E. Hudson, *J. Am. Chem. Soc.*, **96**, 5634 (1974).
(10) I. B. Goldberg, *Org. Magn. Reson.*, **5**, 29 (1973).
(11) Diphenylbenzocyclobutene: R. Huisgen and H. Seidel, *Tetrahedron Lett.*, 3381 (1964).
(12) Tetraphenylcyclobutene: H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Am. Chem. Soc.*, **87**, 3019 (1965).
(13) 3,4-Diphenylcyclobutene: H. Shechter, W. J. Link, and G. V. D. Tiers, *J. Am. Chem. Soc.*, **85**, 1601 (1963).
(14) Interatomic Distances Supplement, *Chem. Soc., Spec. Publ.*, **No. 18**, M109s (1965).

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Oxidation State Properties of Delocalized, Ligand-Bridged Metal Complexes. $[Ru_3O(CH_3CO_2)_6L_3]^{n+}$ and the Pyrazine-Bridged, Cluster-Cluster Dimer, $[Ru_3O(CH_3CO_2)_6(py)_2]_2pyz^{m+}$

Sir:

Spencer and Wilkinson[1] have investigated the redox properties of the triangular cluster system $[Ru_3O(CH_3CO_2)_6L_3]^{n+}$ (L is a neutral ligand, e.g., H_2O, pyridine) using chemical and electrochemical experiments. They found that the cluster units remain intact for $n = 0$ and +1 (eq 1) but that a two-electron reduction of the neutral cluster gave a compound formulated as $Ru_3(CH_3CO_2)_6L_3$, in which the bridging oxide ion is lost. Cotton and Norman[2] have determined the structure of the mixed-valence cluster $[Ru_3{}^{II,III,III}O(CH_3CO_2)_6(PPh_3)_3]$ by X-ray methods (Figure 1). Since the ruthenium ions are crystallographically equivalent, they have suggested that substantial electron delocalization occurs within the Ru_3O framework and have proposed a qualitative MO scheme to describe the electronic structure of the cluster system.

$$[Ru_3O(CH_3CO_2)_6L_3]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Ru_3O(CH_3CO_2)_6L_3]^0 \qquad (1)$$

Because of our general interest in the chemical and electronic properties of polymetallic systems, including oxo-bridged compounds,[3] we have investigated the redox properties and some aspects of the synthetic chemistry of the triangular ruthenium cluster systems. In Figure 2a is shown a cyclic voltammogram for the system $Ru_3O(CH_3CO_2)_6(py)_2(pyz)$ (py is pyridine, pyz is pyrazine)[4] which demonstrates that the clusters have an extensive oxidation state chemistry.[5] The four electrochemically reversible[6] one-electron waves in the voltammogram indicate that the cluster system remains intact in five discrete molecular oxidation states, $[Ru_3O(CH_3CO_2)_6(py)_2(pyz)]^{+3,+2,+1,0,-1}$.

Ruthenium ESCA[7] experiments have been carried out on a series of the cluster systems including the mixed-valence pyridine cases, $[Ru_3{}^{II,III,III}O(CH_3CO_2)_6(py)_3]$ and $[Ru_3{}^{III,III,IV}O(CH_3CO_2)_6(py)_3]^{2+}$, and $[Ru_3{}^{III,III,III}O(CH_3CO_2)_6(py)_3]^+$ ($PF_6{}^-$ salts). The +2 system was prepared from the +1 system by either chemical (using Cl_2) or electrochemical (at +1.2 V vs. SSCE; $n = 1.2$) oxidation in CH_2Cl_2.[8] The ESCA results reinforce the idea that the clusters are delocalized and that the observed redox properties are carried by valence orbitals delocalized over all three

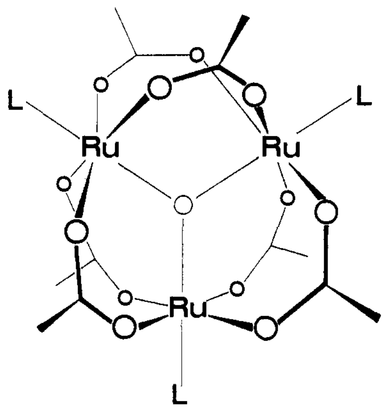


Figure 1. Structure of $Ru_3O(CH_3CO_2)_6L_3$, where L is PPh_3 (ref 2).

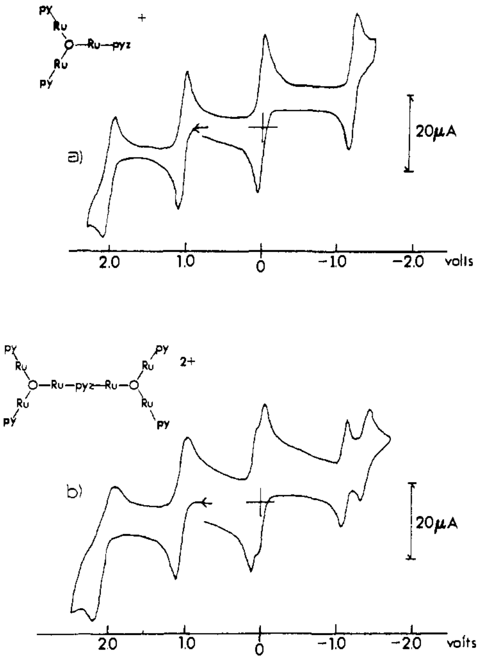
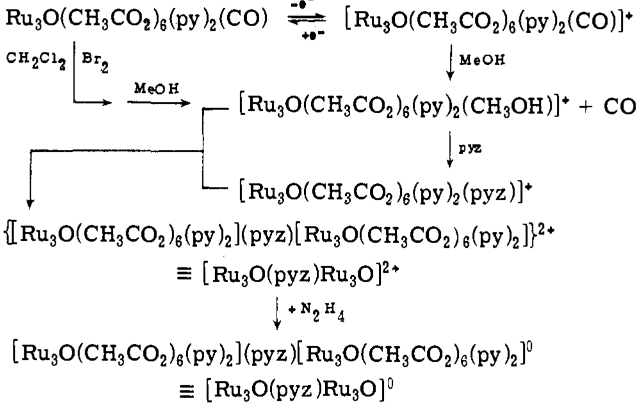


Figure 2. The 50 mV/sec cyclic voltammograms of 1.0×10^{-3} *M* solutions in 0.1 *M* $(n\text{-butyl})_4NPF_6$-CH_3CN (25 ± 2°): (a) $[Ru_3O(CH_3CO_2)_6(py)_2(pyz)]^+$, (b) $[Ru_3O(CH_3CO_2)_6(py)_2](pyz)[Ru_3O(CH_3CO_2)_6(py)_2]^{2+}$.

Scheme I



ruthenium ions. The Ru ($3d_{5/2}$) binding energies for the three systems vs. C (1s) at 284.0 eV are: $[Ru_3O(CH_3CO_2)_6(py)_3]^0$, 279.3 eV; $[Ru_3O(CH_3CO_2)_6(py)_3]^+$, 280.4; $[Ru_3O(CH_3CO_2)_6(py)_3]^{2+}$, ~281.0 eV. Although not definitive, the data are consistent with the idea that for the 0 and +1 systems the ruthenium sites are equivalent or nearly equivalent. The binding energies for the 0 and +1 systems are in a range characteristic of Ru(II) while for the +2 system the binding energy is intermediate between Ru(II) and Ru(III).[3,7] The ruthenium centers remain equivalent in the ESCA experiment if a pyridine group is replaced by pyrazine or other heterocyclic N bases.

We have developed synthetic routes for the preparation of systems in which cluster units are linked by bridging ligands (Scheme I). The preparations utilize the carbonyl cluster system first prepared by Spencer and Wilkinson[9] and are based on the loss of CO from the coordination sphere following a one-electron oxidation.

The pyrazine bridged dimer[10] (shown) has been isolated as its PF_6^- salt and a cyclic voltammogram is shown in Figure 2b. The waves at more anodic potentials, $E_{1/2} = 2.05$ and 1.07 V, are broad with large peak separations ($\Delta E_p = E_{p,a} - E_{p,c} \simeq 85$ mV). The wave shapes can be attributed to two slightly separated one-electron waves and are indicative of, at best, a weak cluster-cluster interaction across the bridging ligand.[11] The two pairs of electrochemically reversible one-electron waves (split by 100 and 270 mV, respectively) at more cathodic potentials indicate that significant cluster-cluster interactions appear as the electron content of the clusters increases. Also, the data show that the pyrazine-bridged, cluster-cluster mixed-valence ions, $[Ru_3O(pyz)Ru_3O]^+$ and $[Ru_3O(pyz)Ru_3O]^-$, are discrete, definable species in solution. The +1 mixed-valence system has been isolated as the PF_6^- salt, $[Ru_3O(pyz)Ru_3O](PF_6)$, by dissolving equimolar amounts of the O and +2 cluster dimers in CH_2Cl_2. The electronic spectrum of solutions of the +1 ion, when corrected for the presence of the +2 and 0 species,[12] has a low energy band at λ_{max} 950 nm (ϵ ~11,000) characteristic of a discrete $[Ru_3O(CH_3CO_2)_6(py)_2(pyz)]^0$ unit and a band at 700 nm (ϵ ~12,000) characteristic of a discrete $[Ru_3O(CH_3CO_2)_6(py)_2(pyz)]^+$ unit.[13] The low-energy electronic spectra show that the valence electron density is not fully delocalized over the two cluster units. This conclusion is reinforced by the Ru ($3d_{5/2}$) ESCA spectrum of the +1 cluster dimer. Two binding energies are observed at 279.4 and 280.3 eV instead of one binding energy at an intermediate energy. The solid state experiment is somewhat ambiguous since in the solid state there could conceivably be an equimolar mixture of the 0 and +2 systems. We have been unable to observe a cluster-cluster intervalence transfer absorption band[14] in low-energy visible or near-infrared spectra, probably because of interference by the intense intracluster electronic transitions.

From our initial work on the synthesis and redox properties of the chemically linked cluster systems, it appears that the preparation of two-dimensional polymeric systems with a controlled number of electron vacancies may prove possible.

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References and Notes

(1) A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1570 (1972).
(2) F. A. Cotton and J. G. Norman, Jr., *Inorg. Chim. Acta*, **6**, 411 (1972).
(3) T. R. Weaver, T. J. Meyer, S. A. Adeyemi, G. M. Brown, R. P. Eckberg, W. E. Hatfield, E. C. Johnson, R. W. Murray, and D. Unterecker, *J. Am. Chem. Soc.*, in press; G. M. Brown, R. W. Callahan, E. C. Johnson, T. J.

Meyer, and T. R. Weaver, in "Extended Interactions between Metal Ions in Transition Metal Complexes", Vol. 5, L. V. Interrante, Ed., ACS Symposium Series, Washington, D.C., 1974.
(4) $[Ru_3O(CH_3CO_2)_6(py)_2(pyz)](PF_6)$ analysis. Calcd for $C_{26}H_{32}N_4O_{13}PF_6Ru_3$: C, 29.55; H, 3.05; N, 5.30. Found: C, 29.41; H, 3.05; N, 4.90.
(5) Potentials were measured by cyclic voltammetry (50–200 mV/sec) and stirred solution voltammetry in CH_3CN solution containing 0.1 *M* $(n\text{-butyl})_4NPF_6$ as supporting electrolyte. A Pt bead electrode was used and potential values are referenced to the saturated sodium chloride calomel electrode at 25 ± 2°. All cationic complexes were prepared as PF_6^- salts.
(6) $\Delta E_p \simeq 60$ mV and $i_{p_a}/i_{p_c} \simeq 1$; see R. W. Murray and C. N. Reilley, "Electroanalytical Principles", Interscience, New York, N.Y., 1963.
(7) (a) W. L. Jolly, *Coord. Chem. Rev.*, **13**, 47 (1974); (b) P. H. Citrin, *J. Am. Chem. Soc.*, **95**, 6472 (1973).
(8) λ_{max} (ϵ) in CH_3CN: 775 nm (4300), 575 (3460), 312 (12,600). Anal. Calcd for $C_{27}H_{33}N_3O_{13}P_2F_{12}Ru_3$: C, 27.01; H, 2.77; N, 3.50. Found: C, 26.89; H, 2.63; N, 3.46.
(9) A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 796 (1974).
(10) $[Ru_3O(pyz)Ru_3O]^{2+}$ has λ_{max} (ϵ) at 703 nm (14,500) and 420 (12,800). Calcd for $C_{46}H_{60}N_6O_{26}P_2F_{12}Ru_6$: C, 28.35; H, 2.97; N, 4.13. Found: C, 28.68; H, 2.96; N, 4.21. $[Ru_3O(pyz)Ru_3O]$ has λ_{max} (ϵ) at 980 nm (20,400), 528 (14,800), 383 (15,400). Calcd for $C_{46}H_{60}N_6O_{26}Ru_3$: C, 33.07; H, 3.47; N, 4.82. Found: C, 32.90; H, 3.64; N, 4.84.
(11) (a) G. M. Brown, Ph.D. Thesis, University of North Carolina, Chapel Hill, N.C., 1974. (b) G. M. Tom, C. Creutz, and H. Taube, *J. Am. Chem. Soc.*, **96**, 7829 (1974).
(12) From cyclic voltammetry in CH_2Cl_2 (0.1 *M* $(n\text{-butyl})_4NPF_6$) the equilibrium constant for the equilibrium $(+2) + (0) \rightleftharpoons 2(+1)$ is 223. Using this value the equilibrium concentrations of the three species were calculated.
(13) In CH_2Cl_2 solution in the region 400–1000 nm the electronic spectrum of $[Ru_3O(CH_3CO_2)_6(py)_2(pyz)]^+$ has λ_{max} (ϵ) 695 (6400) and $[Ru_3O(CH_3CO_2)_6(py)_2(pyz)]$ has λ_{max} (ϵ) 452 (8870), 910 (10,200).
(14) N. S. Hush, *Prog. Inorg. Chem.*, **8**, 391 (1967).

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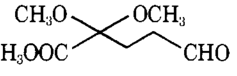
Total Synthesis of (±)-Vermiculine

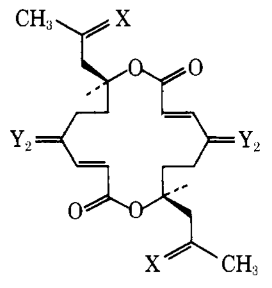
Sir:

The structure of the antibiotic vermiculine has recently been established as I on the basis of X-ray crystallographic analysis.[1,2] The total synthesis of this substance in racemic form, undertaken as part of a program on the synthesis of biologically active macrocycles, is reported herein. The pathway of the synthesis, which involves only ten steps, features several noteworthy functionally selective reactions and the application of the previously described "double activation" method[3,4] to generate *both* ester linkages of the macrocycle in a single operation.

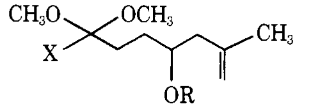
The readily available dimethyl 2,2-dimethoxyglutarate,[5] upon treatment with 1.4 equiv of diisobutylaluminum hydride in methylene chloride at −78° for 1 hr, afforded after workup[6] the pure aldehyde ester II[7] in 50% yield. Reaction of II with 1.5 equiv of dimethallylcadmium[8] in ether at −78° for 1 hr gave the alcohol III which without purification was treated with tribenzylchlorosilane (1.3 equiv) and imidazole (1.3 equiv) in dimethylformamide at 25° for 15 hr to form the corresponding silyl ether IV (70% from II). Reduction of IV with 1.2 equiv of diisobutylaluminum hydride in methylene chloride at −78° for 30 min produced the aldehyde V which was directly condensed with the sodium salt (from NaH) of diethyl ethoxycarbonylmethanephosphonate (1.8 equiv) in tetrahydrofuran at 25° for 1 hr to give the trans α,β-unsaturated ester VI (94% overall from IV). The key intermediate for the synthesis of vermiculine, the hydroxy acid VII, was prepared from VI in 100% yield by hydrolysis with 0.17 *N* lithium hydroxide in methanol-water (2:1) at 25° for 24 hr. The 2-pyridinethiol ester VIII, prepared by reaction of the hydroxy acid VII with 1.5 equiv of 2,2′-dipyridyl disulfide and 1.5 equiv of triphenylphosphine in concentrated solution in xylene at 0° for 20 hr, was obtained in pure form in 77% yield after chromatography on silica gel. Heating of VIII in 0.1 *M* solution in xylene at reflux with 3 equiv of 2,6-lutidine[9] for 24 hr produced in 30% yield a mixture (1:1) of the desired vermiculine derivative IX (methallyl groups cis) and the diastereomer of IX having a trans arrangement of the two methallyl groups.[3,4,10] The mixture was converted without separation to the keto ketal lactone X by reaction with osmium tetroxide (0.1 equiv) and sodium periodate (6 equiv) in 50% aqueous *tert*-butyl alcohol at 25° for 1 hr (70% yield) and thence quantitatively to a mixture of (±)-vermiculine (I) and the trans (meso) diastereomer by exposure to acetic acid-water-tetrahydrofuran (3:1:1) at 45° for 1 hr. Chromatography of the mixture on silica gel using benzene-ethyl acetate (1:1) afforded racemic vermiculine (I), mp 143-144°, and the trans (meso) diastereomer, mp 131-132° (relative R_f values 0.24 and 0.15, respectively). The infrared ($CHCl_3$), ^1H NMR ($CDCl_3$), ultraviolet (EtOH), and mass spectra of synthetic (±)-I were identical with those of an authentic specimen of vermiculine.[11-14]

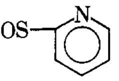


II



IX, X = CH_2; Y = OCH_3
X, X = O; Y = OCH_3
I, X = O; Y_2 = O



III, R = H; X = $COOCH_3$
IV, R = $(C_6H_5CH_2)_3Si$; X = $COOCH_3$
V, R = $(C_6H_5CH_2)_3Si$; X = CHO
VI, R = $(C_6H_5CH_2)_3Si$; X = *trans*-CH=CHCOOC$_2$H
VII, R = H; X = *trans*-CH=CHCOOH
VIII, R = H; X = *trans*-CH=CHCOS– 

References and Notes

(1) R. K. Boeckman, Jr., J. Fayos, and J. Clardy, *J. Am. Chem. Soc.*, **96**, 5954 (1974).
(2) In an earlier paper a different structure had been assigned; see P. Sedmera, J. Vokoun, M. Podojil, Z. Vanek, J. Fuska, P. Nemec, and I. Kuhr, *Tetrahedron Lett.*, 1347 (1973).
(3) E. J. Corey and K. C. Nicolaou, *J. Am. Chem. Soc.*, **96**, 5614 (1974).
(4) E. J. Corey, K. C. Nicolaou, and L. S. Melvin, Jr., *ibid.*, **97**, 653, 654 (1975).
(5) H. Plieninger, L. Arnold, and W. Hoffmann, *Chem. Ber.*, **98**, 1761 (1965).
(6) This involved quenching at −78° with methanol, washing with aqueous sodium potassium tartrate solution, and filtration through silica gel in ether—methylene chloride.
(7) Satisfactory infrared, proton magnetic resonance, and mass spectral data were obtained for all synthetic intermediates.
(8) Prepared from methallyl Grignard reagent and anhydrous cadmium bromide.
(9) Added to the reaction mixture to prevent destruction of the dimethyl ketal unit by neutralization of any acidic material in the reaction mixture.
(10) The formation of this cis-trans mixture is the expected consequence of using racemic hydroxy acid VII. Obviously, application of the cyclization process starting with the proper optically active form of VII would lead only to the vermiculine (cis) series.
(11) We are indebted to Dr. J. Fuska for a sample of vermiculine.
(12) The ^1H NMR spectra recorded by us for *both* authentic and synthetic