9, and **10** could not be unambiguously assigned by NMR since the isomers were inseparable by chromatography. Only three of the four possible isomers of **12** were isolated. The major isomer of which bears a cis relationship between the isopropyl and phenyl substituents.

To illustrate the potential synthetic utility of this approach to tetrahydrofuran synthesis, a short total synthesis of the hop ether **16**[9] was carried out as shown in Scheme I. The required α-alkoxystannane **13** was readily prepared from acetone by a condensation reaction with Bu_3SnLi[1a] and subsequent protection of the α-hydroxystannane intermediate with chloromethyl methyl ether. Transmetalation of **13** was accomplished in DME[1i] at −78 °C and cuprate formation[2b,d] proceeded smoothly. The cuprate reagent **14** underwent clean regiospecific addition to cyclopentenone in the presence of trimethylsilyl chloride to afford the silyl enol ether **15** after quenching the reaction mixture with triethylamine. The crude silyl enol ether **15** was obtained in nearly quantitative yield (GC). Without further purification, **15** was treated with titanium tetrachloride in methylene chloride to provide the annelated tetrahydrofuran **11** in 73% overall yield from cyclopentenone. Methenylation, following the procedure of Lombardo,[10] provided the natural product **16** in good yield (91%).

In summary, α-alkoxyorganostannanes, by reaction through the derived α-alkoxyorganocuprate, can be considered as a synthetic equivalent to a carbonyl ylide. Highly substituted tetrahydrofurans are generated in good yields from cyclic and acyclic enones. Further studies are in progress to evaluate the use of other acetal protecting groups (other than MOM) in the final closure step.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Complete spectral and analytical data for compounds **4**–**12** and experimental details (4 pages). Ordering information is given on any current masthead page.

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Bis(μ-acetato)(μ-oxo)bis(tris(pyridine)ruthenium(III)) Ion: A Ruthenium Analogue of the Hemerythrin Active Center

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Received March 9, 1988

Since the discovery of the dimeric core, (μ-oxo)bis(μ-carboxylato)diiron, in the iron-containing protein, methemerythrin,[1,2] considerable efforts have been devoted to prepare simple complexes with this core.[3-7] Iron(III),[3,4] manganese(III),[5,6] and vanadium(III)[7] complexes with the $M_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2$ core have been prepared. Facial-blocking terdentate ligands such as 1,4,7-triazacyclononane (tacn) and hydrotris(1-pyrazolyl)borate have been tactically used for the preparation.[3-7] It is interesting to find out if the dimeric core is also common to tervalent metal ions of the second and third transition series,[8] particularly to ruthenium(III) which is situated just below iron in the periodic table. Ruthenium(III) is known to form the $Ru_2(\mu\text{-OH})_2(\mu\text{-CH}_3COO)$ core rather than an $Ru_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2$ species with the facial-blocking ligand tacn.[9] We wish to report here a new dimeric complex, $[Ru^{III}{}_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2(py)_6]^{2+}$ (py = pyridine).

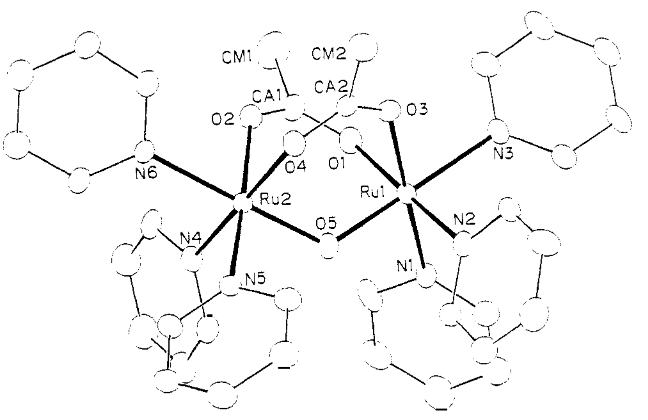

Figure 1. Structure of $[Ru_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2(py)_6]^{2+}$ showing the 20% probability thermal ellipsoids and atomic-labeling scheme. The pyridine ring carbon atoms are not labeled for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Ru1–Ru2 3.251 (2), Ru1–O1 2.087 (9), Ru1–O3 2.085 (9), Ru1–O5 1.869 (9), Ru2–O5 1.845 (10), Ru1–N1 2.091 (11), Ru1–N2 2.072 (10), Ru1–N3 2.208 (11), O1–Ru1–O3 90.4 (4), O1–Ru1–O5 95.0 (4), N1–Ru1–N2 92.3 (4), N1–Ru1–N3 93.1 (4), N2–Ru1–N3 92.9 (4), Ru1–O5–Ru2 122.2 (5).

The dimeric complex was prepared simply by refluxing $RuCl_3 \cdot nH_2O$ in an acetic acid–water–ethanol mixture at 70 °C for 10 min, followed by the addition of pyridine and further refluxing for 30 min. The complex anion was isolated as perchlorate and hexafluorophosphate salts.[10] It should be emphasized that the core is formed by "true" self-assembly without requiring facial-blocking ligands and that the complex formation is much more rapid than the well-known ruthenium acetate complexes, $[Ru_2(CH_3COO)_4]Cl$[11] and $[Ru_3O(CH_3COO)_6(H_2O)_3]^+$.[12] The new dimeric core is likely to be a precursor to these known complexes and has previously been overlooked by prolonged refluxing of the reaction mixture.

The X-ray structure of $[Ru_2(\mu\text{-O})(\mu\text{-CH}_3COO)_2(py)_6]^{2+}$ is shown in Figure 1.[13] The geometry around each ruthenium ion

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(13) X-ray analysis: The compound $[Ru_2O(CH_3COO)_2(py)_6](PF_6)_2$ crystallizes in the monoclinic space group $C2/c$, with a = 42.229 (6) Å, b = 10.726 (1) Å, c = 20.470 (3) Å, β = 112.45 (1)°, V = 8568 (2) Å^3, Z = 8. With the use of 4981 unique reflections ($F_o > 3\sigma(F_o)$) collected at room temperature with Cu Kα (λ = 1.5418 Å) radiation up to 2θ = 126° on a RIGAKU AFC-5R diffractometer equipped with a rotating anode (40 kV, 200 mA), the structure was solved by the heavy-atom method and refined by block-diagonal least squares with anisotropic temperature factors for 63 non-hydrogen atoms to a final R value of 0.077. Atomic positional and thermal parameters are provided as Supplementary Material.

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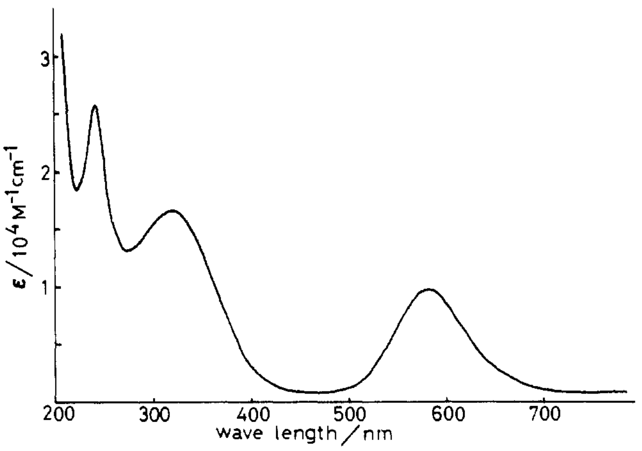

Figure 2. Absorption spectrum of $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6](ClO_4)_2$ in CH_3CN.

deviates only slightly from a regular octahedron. The Ru–Ru distance (3.251 (2) Å) is considerably longer than that (2.572 Å) in $[Ru_2(\mu\text{-}OH)_2(\mu\text{-}CH_3COO)(tacn)_2]^{3+}$ (Ru–Ru single bond is suggested),[9] and a direct Ru–Ru bond is absent. The Ru–O(bridge) and Ru–O(acetate) distances as well as the Ru–Ru one are very close to the corresponding distances of the ruthenium(II,III,III) trimer, $[Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(PPh_3)_3]$,[14] and of the rhodium(III) trimer, $[Rh_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$.[15] Thus the core structure $Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2$ is regarded as a partial structure of the trimeric core $Ru_3(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6$. The two bridging acetates are twisted (torsion angles: O1–Ru1–Ru2–O2, 22.7°; O3–Ru1–Ru2–O4, 21.3°), and in fact the two octahedrons are twisted around the Ru–Ru axis to make the ion asymmetric. The twist could be the result of steric repulsion of coordinated pyridine molecules.

The new dimeric ion has a very strong absorption peak at 581 nm with $\epsilon = 9400\ M^{-1}\ cm^{-1}$ (Figure 2). The absorption should be due to the transitions between molecular orbitals composed of the Ru $d\pi$ and oxygen $p\pi$ orbitals basically similar to those of the $Ru_3(\mu_3\text{-}O)$ complex.[12] ^1H and ^{13}C NMR spectra indicate that the compound is essentially diamagnetic, spectral patterns being fully consistent with the solid-state structure.[16] Cyclic voltammetry in acetonitrile revealed two reversible one-electron oxidation processes at $E_{1/2} = +0.58$ and $+1.72$ V versus Ag/Ag^+, which should correspond to the reversible oxidation to the Ru_2(III,IV) and Ru_2(IV,IV) states, respectively. An irreversible reduction wave was observed at -0.88 V, which is assigned to the reduction to the Ru_2(II,III) state. The potential is more negative than the corresponding quasireversible wave at -0.374 V versus SCE of $[Fe_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(Me_3tacn)_2]^{2+}$.[4] The coordinated pyridines appear to be liberated at least partly in acidic aqueous solution, accompanied by a blue shift of the strong visible absorption band.

Attempts to isolate an aqua derivative of the dimeric core, which is expected to be a precursor to the pyridine complex, have been unsuccessful so far. Nevertheless, the dimeric ion (aqua derivative) can be important as a precursor to various mixed-metal trinuclear complexes of the type, $[Ru_2M(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6L_3]^{n+}$. In fact, the Ru_2Rh complex reported earlier[17] is likely to be formed via the dimeric state.

Acknowledgment. We are grateful to Dr. Akira Nagasawa for the measurement of ^1H and ^{13}C NMR spectra. This work was supported by the Joint Studies Program (1987–1988) of the Institute for Molecular Science.

Note Added in Proof. After the submission of this communication, Professor K. Wieghardt informed us about the preparation of a new complex, $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(Me_3tacn)_2]^{3+}$ (*Angew. Chem.*, in press). We are grateful to Professor K. Wieghardt for providing us with this information.

Supplementary Material Available: Tables of atomic positional and thermal parameters and interatomic distances and bond angles for $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(pyridine)_6](PF_6)_2$ (4 pages); table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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[16] ^1H NMR (270 MHz) data: δ 1.62 (s, 6 H, CH_3COO), 7.34 (t, 8 H, py-*m*-H), 7.58 (t, 4 H, py-*p*-H), 7.87 (d, 8 H, py-*o*-H), 8.33 (t, 4 H, py-*m*-H), 8.43 (t, 2 H, py-*p*-H), 9.41 (d, 4 H, py-*o*-H).

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Boratirane: Preparation and Characterization of *trans*-1,1,2,3-Tetraphenylboratirane

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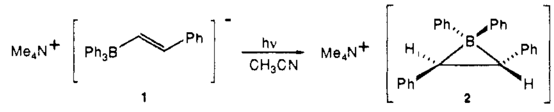
We report herein the preparation, structure, and characterization of the first example[1] of a new class of boron-containing compounds. Irradiation of tetramethylammonium triphenylstyrylborate (**1**) in an acetonitrile solution at 254 nm converts it to *trans*-1,1,2,3-tetraphenylboratirane (**2**), eq 1. Boratirane **2** is a stable, air and water sensitive, colorless crystalline solid.



(1)

The photochemistry of the tetraarylborates (Ar_4B^-) was first studied by Williams and co-workers[5] who concluded that irradiation in protic solvents leads to formation of unobserved bridged-boron intermediates. Later, Eisch and co-workers[6] suggested that photolysis of tetraphenylborate causes its direct fragmentation to biphenyl with concomitant formation of diphenylborate(I)—a hypovalent borene anion. Reinvestigation of this reaction revealed that direct irradiation of tetraphenylborate does not generate a borene anion but promotes intramolecular migration of a phenyl group.[7] We reasoned that this path might provide access to novel boron-containing structures. The photochemistry of **1** supports this hypothesis.

Borate **1** is prepared by reaction of *trans*-β-styryllithium with triphenylborane. As its tetramethylammonium salt, **1** is a colorless solid, unaffected by air or moisture. The ^{11}B NMR spectrum of

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[1] No compounds containing a tetravalent boron atom in a three-membered ring have been reported. There are previous examples of three-membered ring compounds containing trivalent boron atoms.[2-4]

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