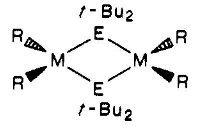
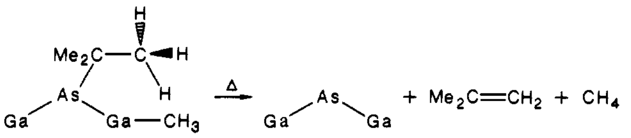
Cr-doped and Si-doped GaAs(100), As-doped Si(100) 3° off (100) toward (011), and quartz have been used as substrates[17] and film composition has been established with XPS. The Ga 3d, As 3d, and C 1s signals at 18.8, 40.9, and 284.6 eV, respectively, reveal the films to be 1:1 Ga:As and void of carbon. (The carbon levels are less than 1000 ppm, which is approximately equal to 2.2 × 10^{19} atoms cm^{-3}.) Growth rates (determined by Dektak) of 0.7 to 1.0 μm/h are found when the source is maintained at 130 °C. X-ray diffraction and SEM results suggest polycrystalline GaAs on quartz and epitaxial GaAs on GaAs(100) and Si(100). Films of indium phosphide have been grown in a similar manner with $[Me_2In(\mu\text{-}t\text{-}Bu_2P)]_2$ as the precursor.[18]



1: R = Me, M = Ga, E = As, M = Al, Ga, In; E = P, As (ref 16)

The use of precursor compounds of type **1** is attractive because they possess the advantages of being much more stable toward air and moisture than either adducts or mixtures of group III and V compounds. They are also sufficiently volatile for OMCVD processes, hydrocarbon soluble, and not appreciably toxic.

A possible mechanism for the deposition of the III/V thin films involves interaction of the group III metal with a C–H bond of a *t*-Bu group followed by elimination of methane. Pyrolysis of **1** under vacuum produces isobutylene and methane as the major hydrocarbons in addition to smaller quantities of isobutane. Further support for the proposed mechanism comes from the solid-state X-ray structure of $[Me_2Ga(\mu\text{-}t\text{-}Bu_2As)]_2$.[16] The H atoms were not located in this study; however, by placing them in idealized positions, we find that there is a "close" Ga···H interaction of 2.62 Å between the Ga atom and a hydrogen atom of a *t*-Bu–As group. Cleavage of the group V–carbon bond would then produce isobutylene. There is precedent for the analogous step in transition-metal chemistry in the formation of arsenidene (AsR^{2-}) complexes from diorganoarsenide (R_2As^-) species.[19]



Other mechanisms are, of course, possible and we are currently carrying out labeling studies and characterization of the volatile products in order to address this point. Further characterization of the grown films by low-temperature photoluminescence, Hall effect, and DLTS (deep level transient spectroscopy) is in progress.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the Texas Advanced Technology Research Program for support and J. A. Cook for XPS analyses. R.A.J. also thanks the Alfred P. Sloan Foundation for a fellowship (1985–1989). We thank Professor B. G. Streetman (U.T. Department of Electrical Engineering) for helpful advice.

---

[17] The GaAs substrates were cleaned by degreasing in tetrachloroethylene, rinsed with methanol and deionized water, and finally etched in a 8:1:1 solution of H_2SO_4, H_2O_2, and H_2O, rinsed with deionized water and dried under a stream of nitrogen at room temperature. GaAs substrates were heated to 580 °C under vacuum prior to deposition to remove any oxides. The silicon substrates were degreased and rinsed in the same manner, dipped in a 25% HF solution rinsed with deionized water, and dried under a stream of nitrogen. The quartz substrates were degreased and dried as for GaAs and Si but not etched.

[18] Professor D. C. Bradley and co-workers have independently synthesized this precursor and described its conversion to InP. For the vapor pressure of $[Me_2In(\mu\text{-}t\text{-}Bu_2P)]_2$, see: Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; Young, K. V. *Chemtronics* **1988**, *3*, 50. For the deposition of InP, see: Bradley, D. C.; Faktor, M. M.; White, E. A. D.; Frigo, D. M. UK patent No. 8703227. Andrews, D.; Davies, G. J.; Bradley, D. C.; Frigo, D. M.; White, E. A. *Appl. Phys. Lett.*, in press.

[19] See, for example: Jones, R. A.; Whittlesey, B. R. *Organometallics* **1984**, *3*, 469. Jones, R. A.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 1078. Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406.

A Novel Synthesis of Tetrahydrofurans via a Synthetic Equivalent to a Carbonyl Ylide

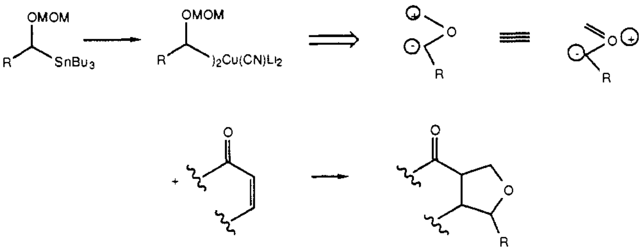
Russell J. Linderman* and Alex Godfrey

Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27695-8204

Received May 13, 1988

α-Alkoxyorganostannanes have enjoyed considerable attention recently as precursors to the corresponding α-alkoxyorganolithium species.[1] Recently the development of α-alkoxyorganocuprates has extended the potential synthetic utility of this class of functionalized carbanions.[2] We would now like to report that α-alkoxyorganostannanes can also function as synthetic equivalents to a carbonyl ylide, providing direct access to highly substituted tetrahydrofurans from enones.

Carbonyl ylides are extremely reactive transient species that have been generated from oxiranes,[3] or by carbene additions to carbonyl compounds.[4] The carbonyl ylides are typically only generated from precursors bearing several stabilizing groups and regiochemical control in subsequent reactions of these 1,3-dipoles is not readily achieved. Due to these constraints, the potential synthetic utility of carbonyl ylides for the construction of oxacyclic compounds has not been realized. We envisioned a potential answer to these problems by the sequential formation of the anionic and cationic components of the carbonyl ylide. This approach required an α-alkoxy anion that would bear the necessary functionality for subsequent formation of an oxonium ion. α-Alkoxystannanes provided ready accessibility to the anionic portion by facile transmetalation. Regiocontrol in additions to electron deficient olefins could then be obtained via the derived organocuprate. The oxonium ion would then be generated by Lewis acid activation of the acetal protecting group present in the initial stannane. In this fashion, the overall reaction would be equivalent to a regiocontrolled tetrahydrofuran synthesis by means of a carbonyl ylide addition reaction.



Carbon–carbon bond-forming reactions for the synthesis of oxacyclic compounds have been rare until recently.[5] In particular,

---

[1] (a) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481. (b) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. (c) Burke, S. D.; Shearouse, S. A.; Burch, D. J.; Sutton, R. W. *Tetrahedron Lett.* **1980**, *21*, 1285. (d) McGarvey, G. J.; Kimura, M. *J. Org. Chem.* **1982**, *47*, 5420. (e) McGarvey, G. J.; Bajwa, J. S. *J. Org. Chem.* **1984**, *49*, 4092. (f) McGarvey, G. J.; Kimura, M.; Kucerovy, A. *Tetrahedron Lett.* **1985**, *26*, 1419. (g) McGarvey, G. J.; Kimura, M. *J. Org. Chem.* **1985**, *50*, 4655. (h) Sawyer, J. S.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 3376. (i) Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842. (j) Lesimple, P.; Beau, J. M.; Sinay, P. *J. Chem. Soc., Chem. Commun.* **1985**, 894. (k) Quintard, J. P.; Elissondo, B.; Pereyre, M. *J. Organomet. Chem.* **1981**, *212*, C31. (l) Quintard, J. P.; Elissondo, B.; Pereyre, M. *J. Org. Chem.* **1983**, *48*, 1559. (m) Dumartin, G.; Pereyre, M.; Quintard, J. P. *Tetrahedron Lett.* **1987**, *28*, 3935.

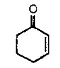
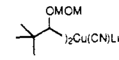
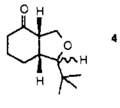
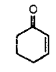
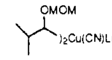
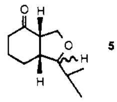
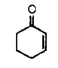
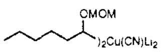
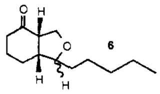
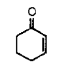
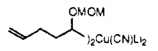
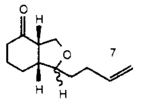
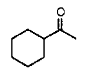
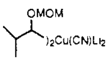
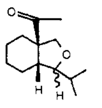
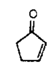
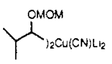
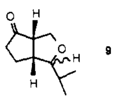
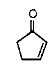
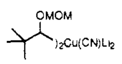
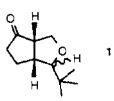
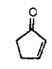
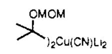
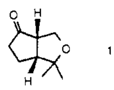
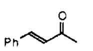
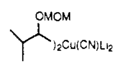
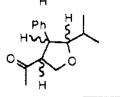
[2] (a) Linderman, R. J.; Godfrey, A. *Tetrahedron Lett.* **1986**, *27*, 4553. (b) Linderman, R. J.; Godfrey, A.; Horne, K. *Tetrahedron Lett.* **1987**, *28*, 3911. (c) Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 4930. (d) Linderman, R. J.; Godfrey, A.; Horne, K. *Tetrahedron*, submitted.

[3] For a theoretical discussion of carbonyl ylides see: Houk, K. N.; Rondan, N. G.; Santiago, C.; Gallo, C. J.; Gandour, R. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 1504. For carbonyl ylide generation by thermolysis of oxadiazolines see: Bekhazi, M.; Warkentin, J. *J. Org. Chem.* **1982**, *47*, 4870.

[4] For preparation of carbonyl ylides via carbene reactions see inter alia: (a) Huisgen, R.; de March, P. *J. Am. Chem. Soc.* **1982**, *104*, 4952. (b) Huisgen, R.; de March, P. *J. Am. Chem. Soc.* **1982**, *104*, 4953. (c) L'Esperance, R. P.; Ford, T. M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 209.

0002-7863/88/1510-6249$01.50/0

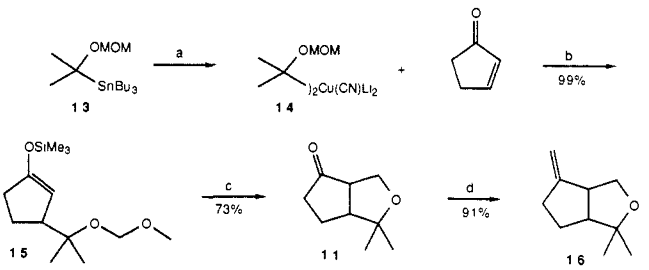
Table I. Trisubstituted Tetrahydrofurans via Carbonyl Ylide Synthon Reaction with Enones

Entry	Enone	Cuprate	Product (No)	Yield, %[a] (Diastereoselectivity)[b]
1			 4	74 (70:30)
2			 5	77 (69:31)
3			 6	68 (65:35)
4			 7	55 (59:41)
5			 8	59 (68:32)
6			 9	82 (50:50)[c]
7			 10	58 (51:49)
8			 11	73 (100:0)
9			 12	88 (68:15:16)

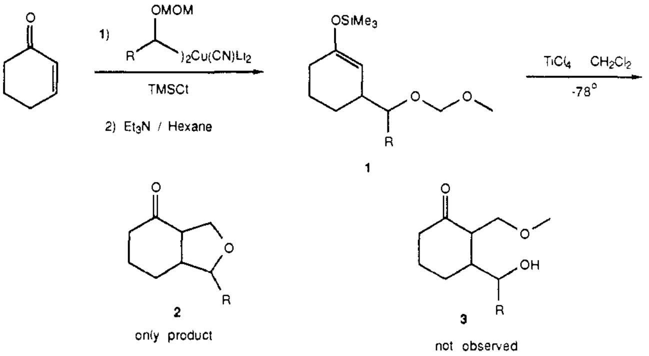
[a] Overall yield of purified material from the enone. All new compounds exhibited correct spectral and analytical data. [b] Diastereoselectivity determined by capillary GC analysis of the crude product mixtures. [c] Diastereoselectivity estimated from ^{1}H NMR. The isomers did not resolve on GC.

several groups have employed C–C bond-forming reactions using oxonium ions generated from acetal protecting groups.[6] To provide complete regiocontrol in the tetrahydrofuran synthesis described, a regiospecific synthesis of an enol silyl ether was also required. Organocuprate conjugate addition reactions are frequently employed to produce a regiospecific silyl enol ether.[7] We had already demonstrated[2b] that a single silyl enol ether regioisomer could be directly obtained from the conjugate addition reaction of α-alkoxyorganocuprates to enones in the presence of trimethylsilyl chloride[8] by employing a nonaqueous workup procedure. Regeneration of the enolate from the γ-substituted ketone derived from the cuprate addition reaction followed by O-silylation led to a mixture of regioisomers. The crude silyl enol ether 1 obtained directly from the cuprate reaction as described was taken up in methylene chloride and treated with titanium tetrachloride at −78 °C. Close examination of the reaction product mixture revealed only the tetrahydrofuran **2** and none of the possible methoxymethyl transfer product **3**. Therefore, each step of the carbonyl ylide synthon procedure had proceeded with complete regioselectivity. This two-step procedure has been examined for the reaction of several α-alkoxyorganocuprates with cyclic and acyclic enones (Table I). The overall yields of the substituted tetrahydrofuran products given in Table I were determined on the basis of the starting enone. The overall yield of 88% (entry 9) corresponds to a 94% yield per C–C bond-forming step.

Scheme I

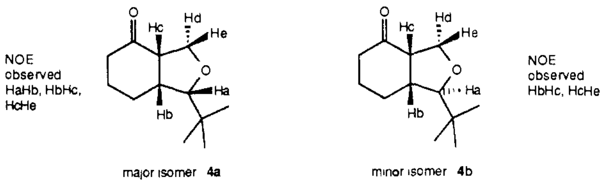


(a) 1. 1.2 *n*-BuLi, DME, −78 °C, 2. CuCN, −78 °C to −65 °C (b) 1. TMSCl (5 equivalents), 2. Et_3N/Hexane (c) $TiCl_4$, CH_2Cl_2, −78 °C (d) Zn, CH_2Br_2, $TiCl_4$



Although the reactions were regiospecific, the diastereoselectivity of the reaction was not as dramatic, ranging from nearly 50:50 for the tetrahydrocyclopenta[*c*]furanones **9** and **10** to 70:30 for the hexahydroisobenzofuranone **4**, see Table I. Compound **11** was obtained as a single isomer, clearly indicating that only the cis-fused annelated tetrahydrofuran product was obtained, and that the diastereomeric ratios reflected the stereochemistry at the exocyclic substituent on the tetrahydrofuran ring. The diastereomeric ratios of the THF products correlate with the ratio obtained in the initial α-alkoxyorganocuprate conjugate addition reaction.[2a] The intermediate silyl enol ether **1** also revealed the same diastereomeric ratio, indicating that the oxonium ion ring closure step occurs without loss of stereochemistry.

The stereochemistry of **4** has been completely assigned. The major **4a** and minor **4b** isomers were separated by radial preparative chromatography. Proton chemical shifts were assigned by COSY and decoupling experiments, allowing for the determination of coupling constants. J_{Hab} for **4a** was 3.6 Hz while in **4b** J_{Hab} was 5.0 Hz. NOESY spectral analysis indicated a NOE for HaHb, HbHc, and HcHe in **4a**, while the NOE for HaHb was absent in **4b**. Compounds **5**, **6**, and **7** exhibited similar spectral characteristics. The stereochemistry of the major isomer of **8**,



---

(5) For a recent review of synthetic routes to oxacyclic compounds see: Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309.

(6) (a) Overman, L. E.; Thompson, A. S. *J. Am. Chem. Soc.* **1988**, *110*, 2248. (b) Overman, L. E.; Blumenkopf, T. A.; Castaneda, A.; Thompson, A. S. *J. Am. Chem. Soc.* **1986**, *108*, 3516. (c) Overman, L. E.; Castenada, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 1303. (d) Mohler, D. L.; Thompson, D. W. *Tetrahedron Lett.* **1987**, *28*, 2567. (e) Melany, M. L.; Lock, G. A.; Thompson, D. W. *J. Org. Chem.* **1985**, *50*, 3925. (f) Nishiyama, H.; Itoh, K. *J. Org. Chem.* **1982**, *47*, 2496. (g) Cockerill, G. S.; Kocienski, P.; Treadgold, R. *J. Chem. Soc., Perkin Trans. I* **1985**, 2093. (h) Cockerill, G. S.; Kocienski, P. *J. Chem. Soc., Chem. Commun.* **1983**, *705*.

(7) Taylor, R. J. K. *Synthesis* **1985**, 364.

(8) (a) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6019. (b) Alexakis, A.; Berlan, J.; Besace, Y. *Tetrahedron Lett.* **1986**, *27*, 1047. (c) Nakamura, E.; Matsuzawa, S.; Horiguchi, Y.; Kuwajima, I. *Tetrahedron Lett.* **1986**, *27*, 4029. (d) Johnson, C. R.; Marren, T. J. *Tetrahedron Lett.* **1987**, *28*, 27.

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.

---

(9) For previous syntheses see: Imagawa, T.; Murai, N.; Akiyama, T.; Kawanisi, M. *Tetrahedron Lett.* **1979**, 1691. Billington, D. C. *Tetrahedron Lett.* **1983**, *24*, 2905.

(10) Lombardo, L. *Org. Synth.* **1986**, *65*, 81.

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

Yoichi Sasaki,* Masakazu Suzuki, Ayako Tokiwa,
Masahiro Ebihara, Tadashi Yamaguchi, Chizuko Kabuto,
and Tasuku Ito*

Department of Chemistry, Faculty of Science
Tohoku University, Aoba, Aramaki
Sendai 980, Japan

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).

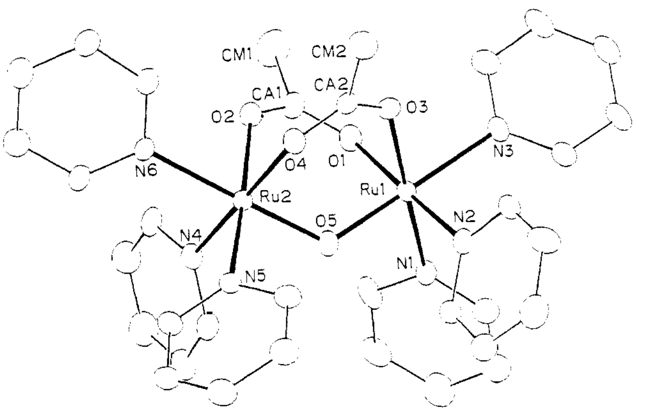


Figure 1. Structure of $[Ru_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2(py)_6]^{2+}$ showing the 20% probability thermal ellipsoids and atomic-labeling scheme. The pyridine ring carbon atoms are not labeled for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Ru1–Ru2 3.251 (2), 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

---

(1) Stenkamp, R. E.; Sieker, L. G.; Jensen, L. H.; Sanders-Loehr, J. *Nature (London)* **1981**, *291*, 263–264.

(2) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 618–622.

(3) Lippard, S. J. *Chem. Br.* **1986**, *22*, 222–229.

(4) Hartman, J. R.; Rardin, R. L.; Chaudhuri, P.; Pohl, K.; Wieghardt, K.; Nuber, B.; Weiss, J.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 7387–7396, and references cited therein.

(5) Wieghardt, K.; Bossek, U.; Ventur, D.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1985**, 347–349.

(6) Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435–1444.

(7) Wieghardt, K.; Koppen, M.; Nuber, B.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1530–1532.

(8) Osmium(IV) complex with this core, $Os^{IV}{}_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2Cl_4(PPh_3)_2$, has been prepared by refluxing *trans*-$Os^{VI}(O)_2Cl_2(PPh_3)_2$ in acetic acid (Armstrong, J. E.; Robinson, W. R.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1301–1306).

(9) Wieghardt, K.; Herrmann, W.; Koppen, M.; Jibril, I.; Huttner, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1335–1343.

(10) Elemental analysis calcd for $[Ru_2(O)(CH_3COO)_2(pyridine)_6](ClO_4)_2\cdot 4H_2O$: C, 37.75; H, 4.10; N, 7.77. Found: C, 37.95; H, 3.93; N, 8.08.

(11) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285–2291. Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388–391.

(12) Baumann, J. A.; Salmon, D. J.; Wilson, S. T.; Meyer, T. J.; Hatfield, W. E. *Inorg. Chem.* **1978**, *17*, 3342–3350.

(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.

0002-7863/88/1510-6251$01.50/0