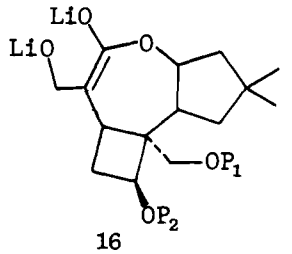
starting material (the hydroxymethyl compound **17**; 40%). The success of the next stage, selenoxide elimination, depends upon the correct order of introduction of the hydroxymethyl group and the phenylselenyl unit, in order to produce the proper configuration at C-2 (as in **11**). From our experience with a related sequence in the synthesis of illudol,[7] it was expected that reaction of the enolate anion at C-2 with electrophiles would occur syn to the hydrogen at C-4 in **10**. Structure **11** is also based on the strong downfield shift (more than 1 ppm) shown by the ^{1}H NMR signal for the proton at C-13, attributed to anisotropic shielding by the phenylselenyl unit. Of course, the successful selenoxide elimination under mild conditions (86% yield, CH_2Cl_2, 20 °C, 20 min) to form **12** is consistent with the syn arrangement of the phenyl–selenyl unit and the hydrogen at C-13.[10] The step of lowest efficiency is the reaction of enolate **16** with phenylselenyl chloride, which proceeds to give **11** in 48% yield under the best conditions, but



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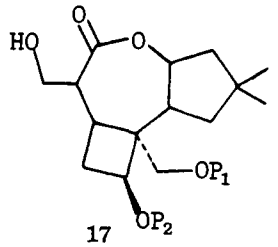

17

a large amount of the reactant (**17**) is recovered (ca. 40%) and can be recycled.

Selective reaction of the primary hydroxyl group in **12** with ethyl vinyl ether at −22 °C by using pyridinium tosylate as catalyst in CH_2Cl_2 was followed by formation of the methanesulfonate ester at C-6, to produce **13**. With aqueous hydrofluoric acid at 20 °C in acetonitrile, cleavage of the silyl ether and spontaneous trans lactonization was observed, to afford **14**. The primary hydroxyl was protected again as the *tert*-butyldimethylsilyl ether in order to allow oxidation (Collins procedure)[11] of the secondary hydroxyl to give **15**. Then tetra-*n*-butylammonium fluoride (1.0 mol equiv, THF, 0 °C for 10 min) brought about cleavage of the silyl ether and induced elimination of methanesulfonic acid which resulted in formation of (±)-fomannosin (**1**). Rapid chromatography on silica gel provided a pure sample which is a rather unstable semisolid. The sample appears to be homogeneous by TLC and ^{13}C NMR spectral data analysis, and to have the correct relative configuration. There is an opportunity for equilibration of configuration via enolization toward C-9, but no evidence for 9-*epi*-fomannosin has been obtained.[12] The ^{1}H NMR spectrum of the synthesized sample was identical with the published spectrum[2] and a spectrum of a sample of natural material. In addition, ^{13}C NMR, TLC, and IR data comparison of synthetic and natural material showed no differences. The overall yield from **4** is 9.2%.

Acknowledgment. We are pleased to acknowledge preliminary work and suggestions from Dr. Kenneth M. Hurst, financial support from the National Institutes of Health, and an important sample of natural fomannosin was supplied by Professor David Cand and Dr. Robert Nachbar (Brown University). A grant from the National Science Foundation to Princeton University contributed to the purchase of the JEOL-FX90Q spectrometer which was used in this work. S. T. thanks the Ministry of Education (Japanese Government) for financial support.

(10) H. J. Reich, F. Chou, and S. K. Shah, *J. Am. Chem. Soc.*, **101**, 6638 (1979), and reference therein.

(11) Professor David Cane (Brown University) has informed us that fomannosin slowly epimerizes during prolonged contact with silica gel, but characterization of 9-*epi*-fomannosin had not been reported.

(12) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

(13) Fellow of the John Simon Guggenheim Foundation, 1978–1979.

(14) On leave from the Department of Chemistry, University of Tokyo, Komaba, Meguro, Tokyo 153, Japan.

Stereochemical Features of the 1,3-Chloropalladation of Bicyclic Methylenecyclopropanes

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The role of transition metals in promoting electrocyclic organic reactions has received renewed scrutiny in the last year. Theoretical analyses, at the extended Hückel level, of the opening of the 2,3-σ bond of a methylenecyclopropane coordinated to either a $[Fe(CO)_3]$[1] or a $[Pt(PPh_3)_2]$[2] fragment, to give a trimethylenemethane ligand, have been reported. These calculations suggest that conrotatory opening should be the most favored mode of ring cleavage; of the two possible disrotatory modes, both of which are formally forbidden by orbital–symmetry considerations, that which involves the breaking bond bending away from the metal (disrotatory away) should be more favored.[1,2]. Experimental data are sparse, but the ring openings of substituted methylenecyclopropanes coordinated to $[Fe(CO)_3]$[3] and $[Mo(CO)_3(\eta\text{-}C_5H_5)]^+$[4] fragments have been shown to occur in the disrotatory away mode, to the exclusion of conrotatory opening. In both cases the final products are η^4-trimethylenemethane complexes. We have described the regiochemistry of a unique 1,3 chloropalladation of alkyl-[5] and aryl methylenecyclopropanes[6] which involves cleavage of the same bond in the three-membered ring to yield η^3-allyl compounds. This communication describes the intimate stereochemistry of this reaction in which the disrotatory away opening is preferred to the exclusion of the conrotatory mode.

Previous attempts to elucidate the stereochemical features of the 1,3 chloropalladation of *cis*- and *trans*-2,3-dimethylmethylenecyclopropane failed because of rapid $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ interconversion of the allyl ligand subsequent to the chloropalladation step; compound **1** was the only product from either of the isomeric methylenecyclopropanes.[5] In contrast *cis*-9-methylenebicyclo[6.1.0]nonane **2**[7a] reacted almost instantaneously with $PdCl_2(PhCN)_2$ ($CDCl_3$ or C_6D_6 solution; 20 °C) to afford a quantitative yield of a single isomer **3**.[8] The acetylacetonato derivative of **3**[9] was subjected to a single-crystal X-ray crystallographic analysis and was shown to have the structure shown in Figure 1.[10] The corresponding chloropalladation of *trans*-9-

†Alfred P. Sloan Research Fellow, 1980–1982.

(1) Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15–17.

(2) Albright, T. A. *J. Organomet. Chem.* **1980**, *198*, 159–168.

(3) Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc. Chem. Commun.* **1980**, 17–19.

(4) Barnes, S. G.; Green, M. *J. Chem. Soc. Chem. Commun.* **1980**, 267–268.

(5) Hughes, R. P.; Hunton, D. E.; Schumann, K. *J. Organomet. Chem.* **1979**, *169*, C37–C41.

(6) Dallas, B. K.; Hughes, R. P. *J. Organomet. Chem.* **1980**, *184*, C67–C69.

(7) (a) Arora, S.; Binger, P. *Synthesis* **1974**, 801–803. (b) Prepared from *trans*-cyclooctene by the method of ref 7a.

(8) Satisfactory microanalytical data were obtained for all compounds described. The ^{1}H NMR spectra of the allylic complexes are sufficient to characterize them structurally. Pertinent ^{1}H NMR data (δ, downfield from Me_4Si, $CDCl_3$, 270 MHz, 25 °C) have been incorporated into structural drawings for clarity. Protons on the unsubstituted allylic terminus appear as singlets while the protons on the substituted allylic carbon and the CHCl carbon appear as doublets of doublets (J = 7, 2) due to coupling with the adjacent CH_2 groups. Compound **3**, **5**, and **6** are all yellow, air-stable, crystalline solids.

(9) Prepared from **3** in 90% yield by treatment with Tl(acac). Corresponding acac derivatives of all compounds reported here have been prepared. The ^{1}H NMR spectra of the organic ligands are identical with those of their chloride precursors except that the three allylic proton resonances are shifted upfield by ~0.2 ppm; the C*H*Cl resonance remains unchanged in each case.

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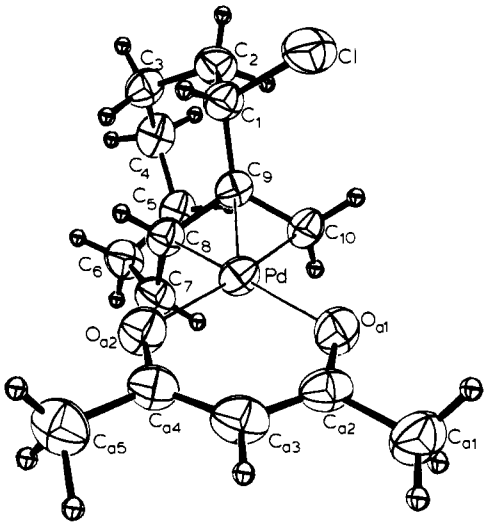
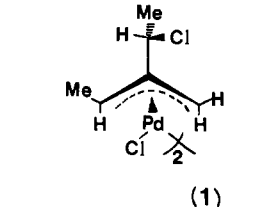
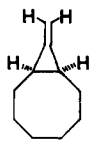


Figure 1. ORTEP drawing of the molecular structure of the acac derivative of compound **3**.[10] All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

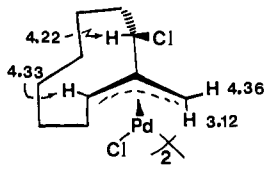
methylenebicyclo[6.1.0]nonane **4**[7b] resulted in quantitative conversion to a 4:1 mixture of palladium complexes **5** and **6**.[8] The chemical shifts of the allylic and C*H*Cl protons in **3**, **5**, and **6** are designated in the structural drawings. Assignment of **5** as the major product of the chloropalladation of **4** rests in the high field chemical shift of the anti proton at the substituted allylic terminus of **5** relative to the corresponding syn protons in **3** and **6**.[8] Compounds **3**, **5**, and **6** show no tendency to interconvert via a $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ reaction, even in refluxing benzene solution containing 5 mol % PPh_3, and must be the products of kinetic control.[11]



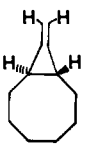
(1)



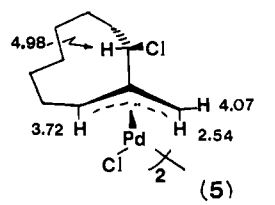
(2)



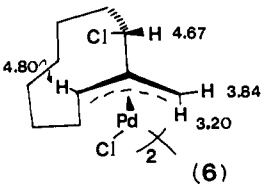
(3)



(4)



(5)



(6)

(10) The structure was solved by Dr. C. S. Day of the Crystalytics Co., Lincoln, NE. Crystals of **3** are monoclinic, $P2_1/c$ (C_{2h}^5), a = 19.314 (5), b = 5.429 (1), c = 15.092 (3) Å; β = 90.79 (2)°; Z = 4. The structure was solved (20 ± 1 °C) by heavy-atom techniques and was refined by full-matrix least-squares procedures to final agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.041$, $R_2 = [\sum_w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} = 0.056$, using 4715 independent reflections, of which 3239 had $I > 3\sigma$. All hydrogen atoms were located by difference Fourier techniques. Selected bond lengths (Å): Pd–C8 = 2.089 (5), Pd–C9 = 2.100 (4), Pd–C10 = 2.119 (5), C8–C9 = 1.436 (6), C9–C10 = 1.404 (7). Full details of this structure will be published separately.

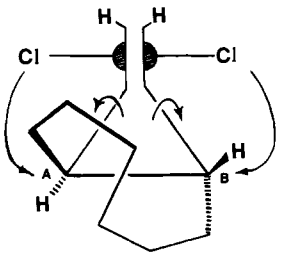


Figure 2. Cis-1,3 chloropalladation of **4**, with disrotatory away opening of the cyclopropane ring; ⊘ = Pd.

The observation of a single product from chloropalladation of **2** and two different products from **4** is consistent with a stereospecific disrotatory opening of the ring during chloropalladation. Molecular models clearly indicate that coordination of a $PdCl_2L$ fragment should occur preferentially to the face of the olefin in **2**, opposite to the eight-membered ring.[12] The observed molecular structure of **3** must arise by migration of Cl directly from Pd (i.e., cis chloropalladation) as the methylene cyclopropane undergoes a *disrotatory away* opening process. Analogous disrotatory away opening of the cyclopropane ring in **4** is depicted in Figure 2; direct transfer of Cl from Pd to the less hindered ring carbon (C_A) affords the major isomer **5**, whereas attack at the more hindered carbon (C_B) yields the minor product **6**. Transfer of Cl from Pd to C must occur very early in the ring-opening process, since neither **2** nor **4** can open very far along a disrotatory pathway.

These results can be rationalized in terms of the dipolar mechanism already proposed for this reaction[5,6] in which the ring opening is governed by the orbital-symmetry requirement for a cyclopropyl cation → allyl cation electrocyclic process.[13,14] This approach to the transition state can be likened to that involved in the solvolysis of cyclopropyl halides, such that a disrotatory away opening mode serves to stabilize better the developing δ+ charge on the cyclopropyl carbon atom.[15]

However, theoretical calculations at the extended Hückel level indicate that disrotatory opening of a η^2-methylenecyclopropane ligand in a *square-planar* d^8 complex is orbital-symmetry *allowed* if the olefin axis lies perpendicular to the coordination plane and that conrotatory opening is allowed if the olefin axis lies in this plane.[16] The former should clearly be the ground state for the intermediate in chloropalladation, and our results appear to support the theoretical analysis.[17]

Notably, in our system conrotatory opening should be more favorable than either of the two disrotatory modes, on the basis of steric and ring strain considerations; its absence speaks of a pronounced destabilization of this pathway. It would be incautious to suggest that our results indicate a preference for disrotatory away rather than disrotatory toward ring opening, since the latter undoubtedly is disfavored by steric effects, particularly in the case of **2**.

(11) This is an initially surprising observation and indicates that the activation barrier to the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ conversion is substantially higher than for the acyclic compound **1**. Interconversion of isomers by this process requires that the Pd atom move from one face of the allyl ligand to the other. This necessitates considerable conformational change within the nine-membered ring and would be expected to increase the overall activation energy.

(12) Similar steric arguments have been used by other authors.[3,4]

(13) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, **1970**.

(14) A similar dipolar mechanism has been proposed in the $Mo(CO)_3(\eta\text{-}C_5H_5)^+$ promoted openings of 2,3-dimethylmethylenecyclopropanes.[4]

(15) Hausser, J. W.; Pinkowski, N. J. *J. Am. Chem. Soc.* **1967**, *89*, 6981–6984. Schleyer, P. v. R.; Dine, G. W. V.; Schöllkopf, V.; Paust, J. *Ibid.* **1966**, *88*, 2868–2869. DePuy, C. H.; Schnack, L. G.; Hausser, J. W. *Ibid.* **1966**, *88*, 3343–3346. Landgrebe, J. A.; Applequist, D. E. *Ibid.* **1964**, *86*, 1536–1542.

(16) Albright, T. A. private communication. This analysis will be the subject of a full paper.

(17) The molecular structure of $Rh(acac)(\eta^2\text{-methylenecyclopropane})_2$ exhibits this geometry: Green, M.; Howard, J. A. K.; Hughes, R. P.; Kellett, S. C.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2005. Futhermore, evidence has been presented for relatively long-lived square-planar Pd(II) complexes containing substituted methylenecyclopropanes: Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1880.

Acknowledgment. We acknowledge generous support of our research efforts by the National Science Foundation (CHE 7717877), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Northeast Regional NSF-NMR Facility at Yale University (supported by Grant CHE 7916210 from the Chemistry Division). We are also grateful to Professor Tom Albright (Houston) and Professor Barry Carpenter (Cornell) for free exchange of information and stimulating discussions.

Supplementary Material Available: Atomic positional and thermal parameters (Tables 1 and 2) (2 pages). Ordering information is given on any current masthead page.

Mixed-Metal Clusters by Metal Hydride Coupling. Crystal Structures of $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$ and $(\mu\text{-H})_5Os_3Re(CO)_{12}$. Direct Conversion of a Metalloligated Cluster to a Closed Polyhedron

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The addition of a metal-containing species to a closed cluster of n metal atoms frequently yields a new closed cluster of $n + 1$ metal atoms.[1-3] This process presumably involves stepwise formation of metal-metal bonds, but only in one case that we are aware of has an open-to-closed metal atom transformation been observed.[4] We previously reported the metalloligated clusters $(\mu\text{-H})_nOs_3(CO)_{12-n}[Re(CO)_5]_n$ (n = 1, 2), prepared by addition of $n[HRe(CO)_5]$ to $Os_3(CO)_{12-n}(NCCH_3)_n$.[5] We have since found $(\mu\text{-H})Os_3Re(CO)_{16}$ and $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ to be related by a third, "lightly stabilized" species $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$, which we now report can be induced to close to $(\mu\text{-H})_5Os_3Re(CO)_{12}$.

The compound $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$[6] is obtained quantitatively by heating $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$ in acetonitrile. After isolation (TLC) and in hydrocarbon solution, treatment of $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$ with $HRe(CO)_5$ causes complete reversion to $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$. Similarly, stirring the solution under a carbon monoxide atmosphere leads exclusively to $(\mu\text{-H})Os_3Re(CO)_{16}$.

We have undertaken an X-ray diffraction study of the complex $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$. This crystallizes in the noncentrosymmetric monoclinic space group $P2_1$ [C_2^2; No. 4] with a = 9.132 (1), b = 16.424 (2), c = 9.457 (1) Å; β = 114.61 (1)°; V = 1289.7 (3) Å^3; ρ_{calcd} = 3.14 g cm^{-3} for M_r = 1219 and Z = 2. Diffraction data were collected on a Syntex $P2_1$ automated four-circle diffractometer (using Mo Kα radiation) as described previously.[7] The structure was solved by a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement, the final discrepancy indices being R_F = 3.1% and R_{wF} = 2.5% for all 3376 data with 4.5° < 2θ < 45°. The molecular geometry is shown in Figure 1. The molecular core consists of a triangular array of osmium atoms, with a rhenium atom bound to one of the *equatorial* sites of an osmium atom. The Os(1)-Re(4) bond length is 2.959 (1)Å and the Os(1)-Os(2) and Os(2)-Os(3) distances are 2.861 (1) and 2.885 (1) Å. The third intratriangular vector, Os(1)-Os(3) = 3.032 (1) Å, is 0.159 Å longer than the average of the two Os-Os distances and [taken in conjunction with the large cis-diequatorial angles adjacent to it—Os(3)-Os(1)-Re(4) = 104.84 (2)° and Os(1)-Os(3)-C(34) = 116.1 (5)°] suggests that the bridging hydride ligand (which was, regretably, not located directly) occupies an equatorial μ_2-bridging site across the Os(1)···Os(3) vector.

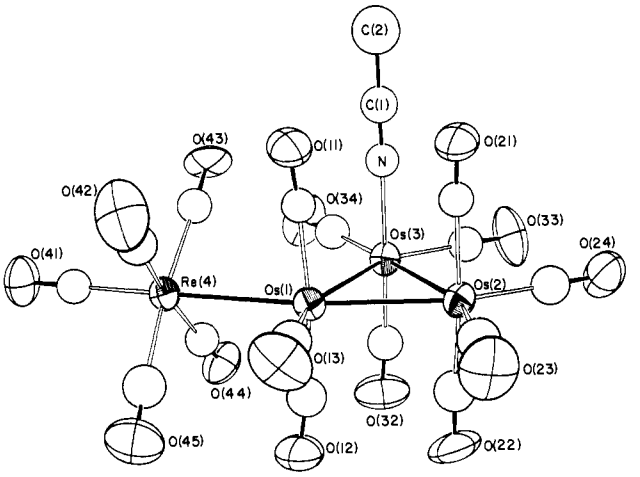

Figure 1. Molecular geometry of $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$, with hydrogen atoms omitted. The bridging hydride ligand lies in a diequatorial site across the Os(1)···Os(3) vector (ORTEP-II diagram).

It is noteworthy that only the $Re(CO)_5$ moiety trans to a bridging hydride is eliminated in forming $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$ from $(\mu\text{-H})_2Os_3Re_2(CO)_{20}$.[8] This may be due to a trans labilizing effect.

Treatment of a refluxing acetonitrile solution of $(\mu\text{-H})Os_3Re(CO)_{15}(NCCH_3)$ under a hydrogen atmosphere with excess (3-4 equiv) trimethylamine *N*-oxide dihydrate leads to a pale yellow solution. Evaporation and preparative TLC yields >70% $(\mu\text{-H})_5Os_3Re(CO)_{12}$ as the only observable product.[9] No stable products are obtained in the absence of the hydrogen atmosphere.

We have also undertaken an X-ray diffraction study of $(\mu\text{-H})_5Os_3Re(CO)_{12}$. This complex crystallizes in the centrosymmetric hexagonal space group $P6_3/m$ [C_{6h}^2; No. 176] with a = 19.087 (5), c = 10.963 (1) Å, V = 3459 (3) Å^3; ρ_{calcd} = 3.16 g cm^{-3} for M_r = 1098 and Z = 6. Data were collected and the structure solved as described above, the resulting discrepancy indices being R_F = 8.0% and R_{wF} = 7.1% for 1425 reflections with $|F| > \sigma(F)$ and 4.5° < 2θ < 45.0° (Mo Kα radiation). We attribute the high discrepancy indices to a combination of (a) the use of an extremely small crystal and (b) disorder, caused by an intrinsically asymmetric molecule lying on (and being disordered about) a crystallographic mirror plane. The gross molecular geometry and intermetallic distances in this molecule are shown in Figure 2. Our interpretation of these results is helped by the observation that the "thermal motion" of Os(1) and Os(1′) [B_{equiv} = 3.21 Å^2] is greater than for Os(2) and Re(4) [B_{equiv} = 2.70 and 2.67 Å^2, respectively]. All $M(CO)_3$ groups are symmetrical, so no *terminal* hydride ligands are present. The five hydride ligands therefore bridge 5 of the 6 edges of the tetrahedron. The observed structure is therefore the composite of the structures I (in which

(1) Churchill, M. R.; Hollander, F. J.; Shapley, J. R.; Foose, D. S. *J. Chem. Soc., Chem. Commun.* **1978**, 534.
(2) Epstein, R. A.; Withers, H. W.; Geoffroy, G. L. *Inorg. Chem.* **1979** *18*, 942-946 and references therein.
(3) Martinengo, S.; Chini, P. *Gazz. Chim. Ital.* **1972**, *102*, 344.
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(5) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064.
(6) This compound was previously[5] reported as $HReOs_3(CO)_{15}$. The present formulation is supported by later observation of a very weak parent ion in the field-desorption mass spectrum, a ^1H NMR signal for coordinated acetonitrile, and elemental analysis.
(7) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J.; *Inorg. Chem.* **1977**, *16*, 265.
(8) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 3546.
(9) MS, m/e 1104 (M^+); IR ν_{CO} ($CHCl_3$) 2078 w, 2040 s, 2014 vs, 2002 sh, 1969 w, 1934 w cm^{-1}; ^1H NMR [25 °C, $(CH_3)_2CO$] τ 29.2 (br s).

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