

Figure 1. Computer-generated perspective drawing of the X-ray model of methyl isartortuatoate (**1**). Oxygen atoms are crosshatched, hydrogens are omitted for clarity, and no absolute configuration is implied.

stituted double bond. A summary of the significant ^1H NMR data and decoupling experiments is given in the supplementary material.

Methyl isartortuatoate (**1**) is the first tetraterpenoid of this structural type, and its biosynthesis is not known. Since diterpenes of the cembrene² class are commonly found in soft corals, a plausible biogenesis would involve generation of the cyclohexene ring by a Diels-Alder coupling of two cembrenes. This would generate the carbon skeleton of isartortuatoate in an efficient manner. The most obvious precursors suggested by this scheme have not yet been identified as natural products, but examples of the various functionalities can be found in known marine cembrenes.¹ If the proposed Diels-Alder reaction had an endo transition state, the stereochemistries at C1, C2, and C21 would be those observed in **1**.

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Supplementary Material Available: Details of the X-ray structure determination of **1** including tables of fractional coordinates, thermal parameters, interatomic distances, interatomic angles, and ^1H NMR data (6 pages). Ordering information is given on any current masthead page.

Flowing Afterglow Negative Ion Photoelectron Spectroscopy of Dirhenium: Evidence for Multiple Bonding in Re_2 and Re_2^-

Doreen G. Leopold,* Thomas M. Miller,[†] and W. C. Lineberger

Department of Chemistry, University of Colorado and Joint Institute for Laboratory Astrophysics University of Colorado and National Bureau of Standards, Boulder, Colorado 80309

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Although there is now an extensive spectroscopic literature concerning homonuclear diatomics of first-row transition metals, relatively little is known about dimers of the second and third transition series.¹ Theoretical calculations for third-row systems predict more comparable ($n+1$)s and nd orbital sizes and energies than for their lighter congeners, due primarily to relativistic effects.² This trend is expected to yield enhanced d-d bonding in third-row dimers, a prediction consistent with reported³ mass

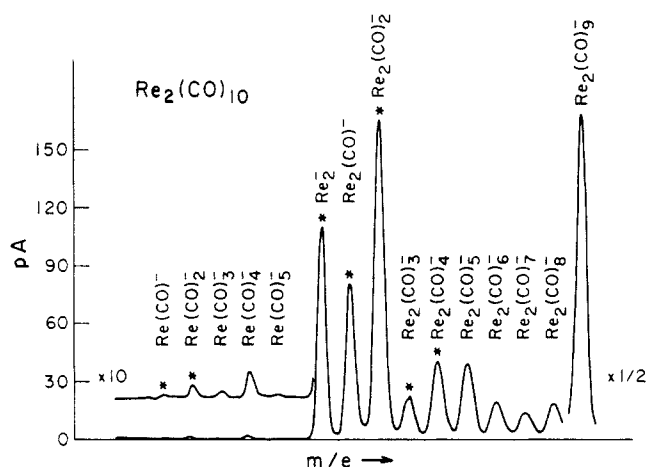


Figure 1. Negative ion mass spectrum following dissociation/ionization of $\text{Re}_2(\text{CO})_{10}$ in a flowing afterglow apparatus incorporating a microwave discharge ion source. Anions marked by asterisks photodetached at 488 nm.

spectrometric dissociation energies. Spectroscopic confirmation of these predictions has not yet been possible, due to the nearly⁴ total lack of data for dimers of open d-shell third-row metal atoms.

In this paper, we report the first spectroscopic observation of Re_2 and Re_2^- , obtained by negative ion photoelectron spectroscopy. This system provides an excellent test of the predicted enhancement of multiple bonding in heavier members of an isoelectronic metal dimer series. Although strong d-d bonding is suggested by the pervasiveness of multiple Re-Re bonding in stable coordination compounds,⁵ a weak bond in the bare Re_2 molecule might be expected in view of the van der Waals bonding⁶ in its first-row congener, Mn_2 . The data reported here provide gas-phase vibrational frequencies for Re_2 and Re_2^- . Their high vibrational force constants indicate that multiple Re-Re bonding does indeed occur in both the neutral and anionic dimers.

These results also illustrate a new synthetic route to metal-metal bonded, coordinatively unsaturated metal carbonyl anions. There has recently been much interest in the synthesis and chemical characterization of mononuclear transition-metal carbonyl anions.⁷ The production of $\text{Re}_n(\text{CO})_m^-$, $n = 0-9$, reported here suggests that the gas-phase chemistries of these dinuclear reactive intermediates are also potentially characterizable by flowing afterglow techniques.

Anions were prepared in our flowing afterglow source⁸ by seeding $\text{Re}_2(\text{CO})_{10}$ vapor in a 150 STP $\text{cm}^3 \text{s}^{-1}$ He flow ~ 10 cm downstream of a 2.45-GHz microwave cavity discharge. The anions were then gently extracted and mass-selected by a Wien filter, yielding the mass spectrum displayed in Figure 1. All possible fragment $\text{Re}_n(\text{CO})_m^-$ metal carbonyl anions were detected. The species marked by asterisks, and only these, were observed to photodetach at 488.0 nm, implying electron affinities below ~ 2.2 eV. The spectra of the ligated anions will be reported in a future publication.

To obtain the photoelectron spectrum reported here, the mass-selected Re_2^- ion beam crossed by the intracavity radiation of a cw argon ion laser. A small fraction of the photodetached

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[†] 1984-1985 JILA Visting Fellow. Permanent address: Department of Physics and Astronomy, University of Oklahoma, Norman, OK 73019.

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