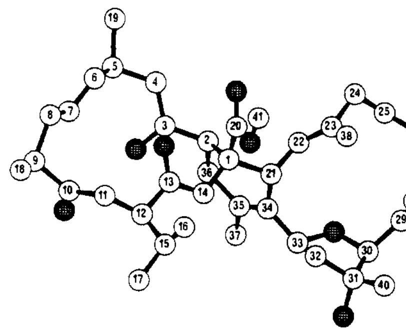

Figure 1. Computer-generated perspective drawing of the X-ray model of methyl isosartortuoate (**1**). Oxygen atoms are crosshatched, hydrogens are omitted for clarity, and no absolute configuration is implied.

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

Methyl isosartortuoate (**1**) is the first tetraterpenoid of this structural type, and its biosynthesis is not known. Since diterpenes of the cembrene[2] 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 isosartortuoate 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 ^{1}H 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^-

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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 reported[3] mass spectrometric dissociation energies. Spectroscopic confirmation of these predictions has not yet been possible, due to the nearly[4] total lack of data for dimers of open d-shell third-row metal atoms.

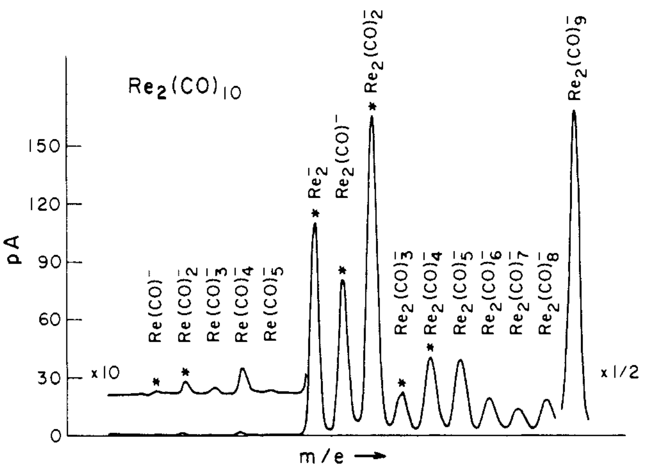

Figure 1. Negative ion mass spectrum following dissociation/ionization of $Re_2(CO)_{10}$ in a flowing afterglow apparatus incorporating a microwave discharge ion source. Anions marked by asterisks photodetached at 488 nm.

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 bonding[6] 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 $Re_2(CO)_n^-$, $n = 0$–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 source[8] by seeding $Re_2(CO)_{10}$ vapor in a 150 STP cm^3 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 $Re_n(CO)_m^-$ 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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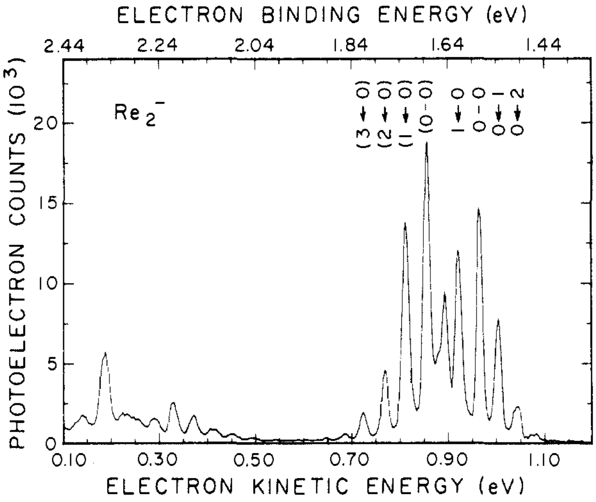

Figure 2. Photoelectron spectrum of Re_2^-. Labels indicate $Re_2 \leftarrow Re_2^-$ vibrational quantum numbers for transitions to the ground and (excited) Re_2 states. The low electron kinetic energy region was obtained at 457.9 nm, but the entire spectrum is displayed as for 488.0-nm (2.540 eV) excitation for clarity. Intensities of the bands below ~0.5 eV are suppressed by up to a factor of 3 by a decreasing instrumental sensitivity in this region.

electrons were energy-analyzed by a hemispherical electrostatic monochromator with multichannel detection. The instrumental resolution was 11 meV (90 cm^{-1}) in the electron kinetic energy region above 0.7 eV and up to ~20 meV at lower energies. A detailed description of the negative ion photoelectron spectrometer has recently appeared.[8]

The photoelectron spectrum of Re_2^-, shown in Figure 2, displays at least four vibronic band systems. The rightmost of these corresponds to the transition between the ground states of the anionic and neutral dimers, and its origin band position yields a Re_2 electron affinity of 1.571 ± 0.008 eV. The observed vibronic structure indicates fundamental vibrational frequencies of 340 ± 20 cm^{-1} for Re_2 and 320 ± 15 cm^{-1} for Re_2^-. The same vibrational frequencies are observed in a second band system 890 ± 30 cm^{-1} higher in energy. Harmonic Franck–Condon analyses of these intensity profiles indicate a change of 0.03 Å in the internuclear separation on electron attachment for both systems and a vibrational temperature of 1200 K. On the basis of this anion temperature and the similar intensities of the two band systems, we assign them to different states of Re_2 rather than Re_2^-. The small shifts in bond lengths and vibrational frequencies on electron attachment suggest that both Re_2 electronic states result from the detachment of a nonbonding or weakly antibonding electron. At least two additional band systems are observed in the low electron kinetic energy region of the spectrum, with intensity maxima approximately 5100 and 6200 cm^{-1} from that of the ground-state band system.

The Re_2 and Re_2^- vibrational frequencies observed here imply unusually large force constants of 6.4 ± 0.8 and 5.6 ± 0.5 mdyn $Å^{-1}$, respectively. Among the homonuclear transition-metal dimers, force constants of this magnitude have been reported[9] only for Mo_2 (6.44 mdyn $Å^{-1}$) and V_2 (4.34 mdyn $Å^{-1}$), which are multiply bonded.[10,11] In contrast, the single 6s–6s bond in Au_2 yields a vibrational force constant[9] only one-third that of Re_2. We conclude that these results provide strong evidence for multiple bonding in both Re_2 and Re_2^-. The bonding in this third row dimer thus differs dramatically from the van der Waals bonding[6] in the isoelectronic first-row molecule, Mn_2.

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Asymmetric Synthesis of Helical Metallocenes[†]

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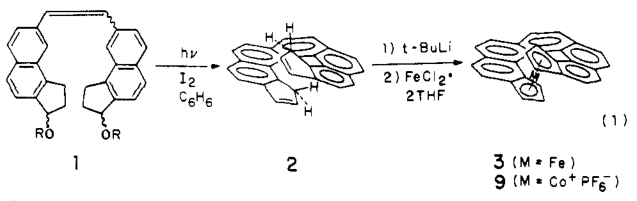
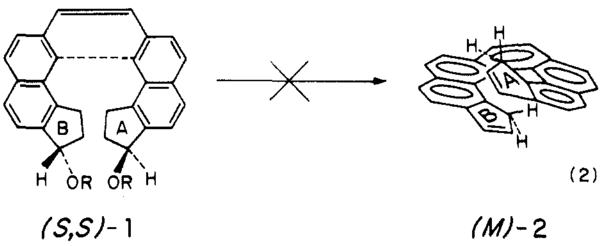
We report that the helical metallocene **3**, prepared previously by the steps summarized in eq 1,[1] can be obtained optically active



by a simple procedure that controls the direction in which the helix winds during photocyclization.[2] Consider the cyclization of diether (*S*,*S*)-**1**. If the steric bulk of the silyloxyls favored their placement outside the helix, ring A would stack above ring B, and the helix would wind to the left (eq 2).[3] In fact, however, when (*S*,*S*)-**1**,



synthesized from (*S*)-**4** (see below), is photocyclized as in eq 1, it gives helical hydrocarbon **2** that is largely racemic.[4] So does the isomer of **1** synthesized[5] from (*R*)-(−)-**5**, giving the isomer of **2** in which both double bonds are shifted one position.[7]

Supposing the scheme's failure to be a consequence of ROH having eliminated from the precursors, **1** and its isomer, *before* they cyclize, experiments were performed to prevent the eliminations. The discovery was that with propylene oxide added to consume HI as it forms,[8] with a full mole of I_2 to effect the

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[†] Dedicated to Professor Harry H. Wasserman on his 65th birthday.

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(4) Synthesized from (*S*)-**4** [40% enantiomeric excess (ee)], it gave (*P*)-(+)-**2** in <3% ee.[5,6]

(5) As in ref 1.

(6) The chiral selectivity is (strangely) opposite to that expected according to eq 2. For absolute configurations see notes 31 and 37 below.

(7) Previously prepared by combining **2** with *t*-BuLi and then aqueous acetic acid;[1] its structure was confirmed by X-ray diffraction analysis of a sample prepared from racemic **5**. We thank Dr. Ian Williams of MIT for the analysis.