

that a wide range of new devices is possible. In particular, we are intrigued with the prospect of designing gas sensors using conventional redox polymers having chemically dependent $E^{0'}$ values. Since $E^{0'}$ corresponds to the value of V_G where I_D is a maximum,¹⁰ chemically sensitive microelectrochemical transistors responsive to gases are possible. Further, small dimensions of microelectrochemical devices allow their use in very resistive media.¹¹ Finally, it is worth noting that the solid-state microelectrochemical device reported here is a molecule-based device having all of its components (reference, source, drain, counter electrode, switching material, and "solvent"/electrolyte) on a chip, representing the demonstration of a complete system on the chip.

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Isolation and Structure of $\text{Os}_2\text{Cl}_4(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4)_2$. An M_2L_8 Compound with an Unprecedented Geometry and a Short Os-Os Bond

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Multiple-bond chemistry of the early-transition elements, especially Cr, Mo, W, and Re, has been the focus of intensive research efforts for the past 20 years.¹ Until quite recently, the analogous chemistry of later transition metals such as Ru and Os has been somewhat neglected. Rapid advances are being made in these areas,²⁻⁵ but our knowledge of the bonding properties and reactivity patterns of multiply bonded diruthenium and diosmium compounds is still in a rudimentary stage.

Current efforts in this research group are aimed at expanding diosmium chemistry through the synthesis of new classes of Os_2^{6+} complexes that contain tertiary phosphine ligands. Our recent investigation⁶ into the reaction between PPh_3 and $\text{Os}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2$ led to the discovery of $\text{Os}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_2$, an unusual compound with bridging *o*-(Ph_2P) C_6H_4 groups. It is worth noting that $\text{Rh}_2(\mu\text{-O}_2\text{CCH}_3)_4$ reacts similarly with PPh_3 to give $\text{Rh}_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{L}_2$.⁷ The X-ray structures of these products have appeared in the literature, but at the time the results were published, we had not yet investigated their reaction chemistry. We

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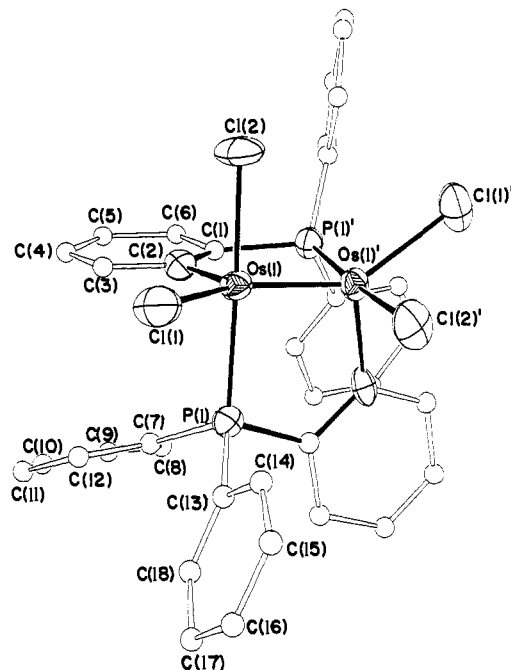
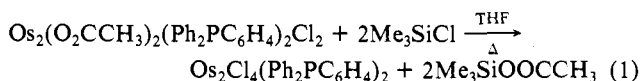


Figure 1. ORTEP drawing of the $\text{Os}_2\text{Cl}_4(\text{Ph}_2\text{PC}_6\text{H}_4)_2$ molecule with the unique atom-labeling scheme. All phenyl-group carbon atoms not in the coordination sphere are represented as small circles, for clarity. All other atoms are represented by their 50% probability ellipsoids. Some important distances (Å) and angles (deg): Os(1)-Os(1'), 2.231 (1); Os(1)-Cl(1), 2.320 (3); Os(1)-Cl(2), 2.366 (3); Os(1)-P(1), 2.385 (3); Os(1)-C(2), 2.003 (11); P(1)-C(1), 1.812 (11); Os(1)'-Os(1)-Cl(1), 143.02; Os(1)'-Os(1)-Cl(2), 92.28 (8); Os(1)'-Os(1)-P(1), 90.78 (6); Os(1)'-Os(1)-C(2), 102.2 (3); Cl(1)-Os(1)-Cl(2), 89.0 (1); Cl(1)-Os(1)-P(1), 87.0 (1); Cl(2)-Os(1)-P(1), 176.0 (1); Cl(1)-Os(1)-C(2), 114.8 (3); Cl(2)-Os(1)-C(2), 90.6 (3); P(1)-Os(1)-C(2), 91.2 (3).

now wish to report some preliminary results from reactions of $\text{Os}_2(\text{O}_2\text{CCH}_3)_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_2$ in which the acetate ligands are removed by using Me_3SiCl . This approach has also been used successfully in the preparation of unusual dirhodium compounds from $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{L}_2$ ⁸ and $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$.⁹

Treatment of $\text{Os}_2(\text{O}_2\text{CCH}_3)_2(\text{Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_2$ with 2 equiv of Me_3SiCl in refluxing THF for 0.5 h leads to the formation of a yellow-brown solution and the deposition of the product as a brown microcrystalline material (eq 1).¹⁰ Additional compound crys-



tallizes from the filtrate upon reduction of the volume; combined yield 88%. The product is air-stable and is soluble in a variety of organic solvents.

Single crystals of $\text{Os}_2\text{Cl}_4(\text{Ph}_2\text{PC}_6\text{H}_4)_2$ were grown by slow diffusion of hexane into a solution of the compound dissolved in THF. An IR spectrum of the crystals (Nujol mull) shows bands arising from vibrations of the *o*-(Ph_2P) C_6H_4 ligands but none that can be attributed to acetate groups.¹¹ In addition, the far-infrared region of the spectrum (200-300 cm^{-1}) displays several $\nu(\text{Os}-\text{Cl})$ modes. A cyclic voltammogram of the sample in 0.2 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$ reveals the presence of an accessible one-electron reduction process at $E_{1/2} = +0.106$ V vs. Ag/AgCl .¹² This redox behavior is very similar to that reported for a variety

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(11) Selected infrared absorption frequencies (cm^{-1}) for a Nujol mull: 1560 m, 1545 m, 1485 m, 1420 m, 1340 w, 1315 w, 1240 m, 1190 m, 1165 m, 1140 m, 1108 s, 1095 s, 1070 m, 1040 m, 1030 m, 1000 m, 910 w, 745 s, 730 s, 720 s, 695 s, 540 s, 530 s, 525 s, 480 m, 370 m, 355 m, 330 s, 315 s.

(12) $\Delta E_p = |E_{p,c} - E_{p,a}| = 63$ mV; $i_c/i_a = 1$ at 200 mV/s sweep rate at a Pt-disk electrode.

of triply bonded Os_2^{6+} complexes, for which one-electron reductions occur at potentials in the range -0.20 to $+0.60$ V.^{4c,13}

An analysis of the X-ray data for $\text{Os}_2\text{Cl}_4(\text{Ph}_2\text{PC}_6\text{H}_4)_2$ established the identity of the compound and revealed that the molecule has a unique geometry with C_2 symmetry.¹⁴ The compound crystallizes in the chiral space group $C222_1$ with 4 molecules/unit cell, each of which resides on a crystallographic C_2 axis.¹⁵ The 2-fold axis is aligned perpendicular to the Os–Os bond vector, and it bisects the two cis-bridging $o\text{-(Ph}_2\text{P)C}_6\text{H}_4^-$ groups.

As can be clearly seen in the ORTEP drawing of the molecule in Figure 1, there are two types of chloride ligands on each Os atom; Cl(2) is in an apical position defined by the nearly linear (176.0 (1)°) chain Cl(2)–Os(1)–P(1), and Cl(1) resides in the equatorial plane containing Os(1), Os(1)', and C(2). This arrangement defines a distorted trigonal bipyramid (tbp) (see angles in Figure 1 caption), which is not an uncommon geometry for metal centers in a binuclear complex. However, the orientations of the two separate tbp units about each Os atom in this case are not parallel to one another in the usual way (a) but instead are perpendicular as in (b).



We know of no precedent for this arrangement of ligands for an M_2L_8 compound. The reasons that the molecule prefers to adopt this unusual geometry are presumed to be steric in nature, due to the constraints imposed upon the structure by the cis ortho-metalated PPh_3 groups. Although it is feasible from an electronic point of view, the molecule cannot alleviate steric repulsions across the Os–Os bond by a rotation about the Os≡Os bond axis because the C–P bridging groups are much too rigid. As a consequence, the chloride ligands stagger themselves in another way that involves Cl(1) becoming “swept back” from the center of the molecule toward the axial site (Os(1)–Os(1)–Cl(1) = 143.02°). This leaves Cl(2) to occupy an apical position for an overall stable arrangement of ligands that minimizes unfavorable steric interactions.

The Os–Os bond length of 2.231 (1) Å in $\text{Os}_2\text{Cl}_4(\text{Ph}_2\text{PC}_6\text{H}_4)_2$ is very short, the shortest one reported for an Os≡Os complex other than those in the $[\text{Os}_2\text{X}_8]^{2-}$ anions (X = Cl or Br).^{4d} The magnetic properties of the new compound have not been investigated yet, but it is expected to possess a diamagnetic ground state, by analogy to the parent compound $\text{Os}_2(\text{O}_2\text{CCH}_3)_2\text{-(Ph}_2\text{PC}_6\text{H}_4)_2\text{Cl}_2$, which also has an unusually short Os–Os distance.

This study was undertaken in order to explore the possibility of preparing new classes of binuclear osmium compounds containing a metal-to-metal triple bond. Our isolation of $\text{Os}_2\text{Cl}_4\text{-(Ph}_2\text{PC}_6\text{H}_4)_2$ represents a significant contribution to Os≡Os chemistry. It is the first example of a neutral Os_2L_8 compound, and it possesses a hitherto unknown M_2L_8 geometry. Furthermore,

it constitutes another example of a multiply bonded complex with ortho-metalated ligands, of which there are only a few examples in the literature.^{6,16} We are continuing to work toward a better understanding of the syntheses and reactivities of these elusive classes of M_2 compounds. A more detailed account of these results will be submitted.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Tables of crystallographic parameters, atomic positional parameters and equivalent isotropic displacement parameters, bond distances and angles, and anisotropic thermal parameters (5 pages); a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Intramolecular Formal Iron-Catalyzed Ene Reactions: New and Highly Stereoselective Iron-Catalyzed Carbocyclizations of Triene Ethers

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New catalytic transition-metal-mediated carbon-carbon bond-forming reactions have found exceptional utility in organic synthesis.^{1,2} Of particular note are the applications of organo-transition-metal chemistry to the problem of constructing carbocyclic rings.³ We have recently reported the *intermolecular* L·Fe(0)-catalyzed formal ene reactions of 1,3-dienes with allylic ethers.⁴ These reactions complement the known thermal, Lewis acid catalyzed, and magnesium ene reactions and expand the utility of 1,3-dienes as enophilic substrates in the ene reaction.⁵ We now wish to report that acyclic triene ethers will undergo new iron-catalyzed carbocyclization reactions at ambient temperature with high cis or trans simple diastereoselectivity and with high

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(15) The complex crystallizes in the orthorhombic space group $C222_1$ with $a = 16.083$ (1) Å, $b = 17.280$ (7) Å, $c = 12.173$ (2) Å, $V = 3383$ (3) Å³, $Z = 4$, $d_{\text{calc}} = 2.051$ g/cm³, and $\mu(\text{Mo K}\alpha) = 79.53$ cm⁻¹. An Enraf-Nonius CAD-4 diffractometer was used to gather 1571 unique data at 22 °C using the ω -scan technique. The data were corrected for Lorentz and polarization effects, and azimuthal scans (ψ -scans) of nine reflections having an Eulerian angle χ near 90° were used as a basis for an empirical absorption correction. The position of the unique Os atom was derived from a three-dimensional Patterson map, and all other atoms were located in subsequent difference maps. Refinement of 199 parameters using 1414 reflections with $F_o^2 > 3\sigma(F_o^2)$ produced residuals of $R = 0.024$ and $R_w = 0.032$. The quality-of-fit index is 0.948, and the largest shift/esd = 0.15.