gives[4] exclusively the quinone corresponding to IV, whereas MTA gave IV free from the quinone. In order to achieve this result, it is necessary to exclude oxygen and to work in a neutral aprotic solvent; thus, in a recent paper[5] Shono and his collaborators have shown that MTA in a mixture of pyridine and chloroform oxidizes III to polyphenylene oxides, whereas in chloroform alone the quinone corresponding to N was formed.

Further preliminary studies suggest that MTA in carbon disulfide or acetonitrite acts very generally as a coupling agent for phenols and other related compounds; full details will be reported in due course.

Acknowledgment. This work was supported by a grant from the Robert A. Welch Foundation.

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[6] Robert A. Welch Postdoctoral Fellow; on leave of absence from Osaka City University, Osaka, Japan.

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The Characterization of an Anionic Rhenium Carbonyl Hydride, $[H_2Re_3(CO)_{12}^-]$[1]

Sir:

We wish to report the isolation and crystal structure of $[(C_6H_5)_4As^+][H_2Re_3(CO)_{12}^-]$ (I), the anion of which is obtained in the treatment of $H_3Re_3(CO)_{12}$[2] with base The structure of the anion thus provides some insights into the nature of its conjugate acid, $H_3Re_3(CO)_{12}$, a compound which has thus far proved not to be susceptible to a detailed crystallographic analysis.[3]

To a colorless slurry of 0.5 g of $H_3Re_3(CO)_{12}$[2] in 25 ml of C_2H_5OH an ethanolic solution of 0.1 *M* KOH in slight molar excess is added at room temperature. The solid dissolves to give a bright yellow solution; a precipitate of I is obtained[4] upon addition of $(C_6H_5)_4AsCl$ in ethanol and cooling to −5°.

Conductivity measurements in CH_3CN show that I is a 1:1 electrolyte. The compound is soluble in acetone, tetrahydrofuran, CH_2Cl_2, and CH_3CN and slightly soluble in diethyl ether and ethanol, giving yellow solutions. An H^1 nmr spectrum in acetone shows sharp singlets at τ 2.05 and 27.2 (relative intensity 20.0:2.0 ± 0.1) due, respectively, to $[(C_6H_5)_4As^+]$ protons and hydrogen on rhenium.

Compound I crystallizes from acetone solution as yellow needles in the noncentrosymmetric orthorhombic space group $Pna2_1$ (C_{2v}^9; no. 33) with a = 16.097 Å, b = 28.725 Å, c = 8.145 Å, and V = 3766 Å^3. The observed density (ρ_{obsd} = 2.255 g cm^{-3}) is in excellent agreement with the value calculated for M = 1280 and Z = 4 (ρ_{calcd} = 2.257 g cm^{-3}). A set of X-ray diffraction data complete to $\sin\theta = 0.42$ (Mo Kα radiation) was collected with a Supper-Pace "Buerger" automated diffractometer using a stationary-background, ω-scan, stationary-background counting sequence. All data were corrected for absorption (μ = 118.8 cm^{-1}), and the structure was solved by a combination of Patterson and difference-Fourier techniques. All 52 nonhydrogen atoms have been located. Four cycles of least-squares refinement (in which thermal parameters for rhenium and arsenic atoms were allowed to refine anisotropically) have resulted in a discrepancy index of R_F = 9.6% for the 2393 independent nonzero reflections. Refinement is continuing.

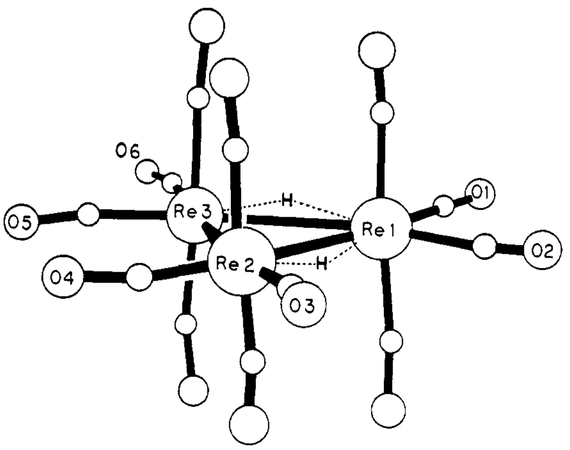

Figure 1. The $[H_2Re_3(CO)_{12}^-]$ ion. Note that the hydride ligands were not located and are drawn in the most sensible chemical positions (see text).

As may be seen in Figure 1, the $[H_2Re_3(CO)_{12}^-]$ anion has approximate C_{2v} symmetry, with the three rhenium atoms defining an isosceles triangle in which Re(1)–Re(2) = 3.173 Å, Re(1)–Re(3) = 3.181 Å, and Re(2)–Re(3) = 3.035 Å, esd 0.007 Å.[5] Four terminal carbonyl groups are bonded to each rhenium atom; two occupy *axial* sites and two occupy *equatorial* sites. Although hydrogen atoms have not been detected directly in the crystallographic investigation, some information on the positions of the hydride ligands may be obtained by a consideration of the Re–Re bond lengths and the angular disposition of carbonyl ligands about each of the rhenium centers. The *axial* carbonyls are more-or-less regularly arranged, but (as may clearly be seen in Figure 2) the *equatorial* carbonyls possess a much less regular arrangement. The *equatorial* OC–Re–CO angles are all in the range 91–93°, and the Re–Re–$(CO)_{eq}$ angles involving the short side of the triangle [*i.e.*, Re(2)–Re(3)–C(5)O(5) and Re(3)–Re(2)–C(4)O(4)] are 91 and 95°. The Re(2)–Re(1)–C(2)O(2) and Re(3)–Re(1)–C(1)O(1) angles are significantly larger (106 and 107°) and the Re(1)–Re(2)–C(3)O(3) and Re(1)–Re(3)–C(6)O(6) angles (112 and 118°) are the largest of all the *cis* angles. This general pattern of bond angles suggests that C(1)O(1)/C(6)-O(6) and C(2)O(2)/C(3)O(3) are each being forced apart, most probably because of the presence of hydrogen atoms somewhere along the two sides Re(1)–Re(3) and Re(1)–Re(2) of the triangle. The only classical valence-bond structure compatible with the structural data and the diamagnetism of the compound is A; however,

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[1] Work supported by NSF Grants GP-8077 (M. R. C.) and GP-6720 (H. D. K.) and ARPA Contract SD-88 (M. R. C.).

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[3] H. D. Kaesz, R. Bau, and M. R. Churchill, *ibid.*, **89**, 2775 (1967).

[4] Satisfactory C and H analyses were obtained by Miss Heather King of the UCLA Laboratories. A good oxygen but no satisfactory rhenium analyses could be obtained on this compound by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

[5] Esd includes errors in measurement of the unit cell.

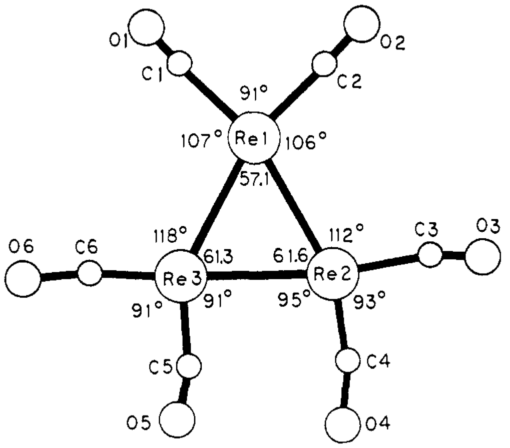
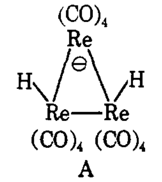
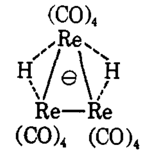


Figure 2. Angles around the equatorial carbonyl ligands in the $[H_2Re_3(CO)_{12}^-]$ ion.

the spectroscopic data (*vide infra*) are clearly not in agreement with this.



A



B

In acetone solution four principal absorptions were observed in the carbonyl stretching region of the infrared: 2053 m, 2008 vs, 1949 m, and 1897 m cm^{-1} (Beckman IR-4, LiF prism). A fifth very weak absorption was observed at 2105 cm^{-1} which corresponds to the most intense carbonyl band in the Raman spectrum (Cary Model 81, Laser Raman). With appropriate shift to lower energy on account of the negative charge, the pattern of four principal infrared bands largely resembles that of the parent compound $H_3Re_3(CO)_{12}$[2] (2093 m, 2030 vs, 2008 s, 1983 m cm^{-1}). It would appear that only a small perturbation from D_{3h} symmetry of the neutral species has occurred in the anion; structure A of C_{2v} symmetry would require up to ten CO absorptions in the infrared. The apparent high symmetry inferred from the infrared bands denotes extensive delocalization of the negative charge and corresponding shift of hydrogen atoms, structure B.

A sample of $[(C_6H_5)_4As^+]$ $[D_2Re_3(CO)_{12}^-]$ was prepared from $D_3Re_3(CO)_{12}$,[6] and its infrared and Raman spectra were compared with those of I. No bands characteristic of a terminal Re–H (*ca.* 1800–2200 cm^{-1}) or a terminal Re–D (*ca.* 1250–1550 cm^{-1}) were observed. On the other hand, we did observe absorptions near 1100 cm^{-1} in the Raman spectrum of the Re–H derivative which changed or disappeared in the spectrum of the Re–D derivative while new bands appeared near 800 cm^{-1}. From work on other metal hydride complexes,[7] we have come to associate such features with metal–hydrogen in the bridging environment shown in structure B and Figure 1.

If one assumes that the hydride ligands are approximately *trans* to C(1)O(1) and C(4)O(4), and to C(2)O(2) and C(5)O(5), the Re–H distance may be estimated as ~1.7 Å, in good agreement with the value predicted from the Re–H–Re distance of 3.392 Å in $HRe_2Mn(CO)_{14}$.[3]

The yellow anion $H_2Re_3(CO)_{12}^-$ is also obtained by acidification of the red dianion $HRe_3(CO)_{12}^{2-}$ which has recently been isolated as the $(C_6H_5)_4As^+$ salt from the carbonyl metalate solutions derived from $Re_2(CO)_{10}$ and $NaBH_4$ and whose characterization and structure is presently also under investigation.

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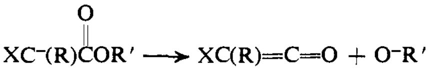
The Establishment of a Carbanion Mechanism for Ester Hydrolysis and the Unimportance of Electrostatic Effects of α Substituents on the Rates of Hydroxide Ion Attack at the Ester Carbonyl Group[1]

Sir:

Ionization of an α-H from esters of type XCH(R)-COOR′ to produce a carbanion has been suggested: (a) to *impede* alkaline hydrolysis of *p*-nitrophenyl acetate carbanion *via* electrostatic repulsion of the attacking hydroxyl ion,[2] and (b) to *enhance* ester hydrolysis[3] (or alcoholysis[4]) *via* an elimination reaction which would yield a highly reactive ketene intermediate (eq 1).[3] In addition it has been stated[5] that a negative charge on X decreases the rates of alkaline hydrolysis due to electrostatic shielding.



$$XC^-(R)\overset{O}{\overset{\|}{C}}OR' \longrightarrow XC(R){=}C{=}O + O^-R' \qquad (1)$$

Results obtained in this laboratory when OR′ = *o*- or *p*-nitrophenolate (*o*-NP and *p*-NP, respectively) establish: (a) the first really compelling evidence for mechanism 1; (b) the experimental basis for the suggestion that electrostatic shielding by the carbanion of *p*-nitrophenyl acetate inhibits HO^- attack is fallacious; and (c) electrostatic shielding or acceleration of HO^- attack by negative or positive charges on X is kinetically unimportant.

The second-order rate constant for HO^--catalyzed hydrolysis of *p*-nitrophenyl acetate (*p*-NPA) is invariant (882 l. mol^{-1} min^{-1}) in the range $[HO^-] = 10^{-6}$ to 0.5 *M* (with KOH at 30 ± 0.1° in H_2O; $\mu = 1.0$ with KCl). Thus, there is no evidence for an anionic species of *p*-NPA and the suggested[2] shielding of HO^- attack by this species.

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(1) This work was supported by a grant from the National Institutes of Health.

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