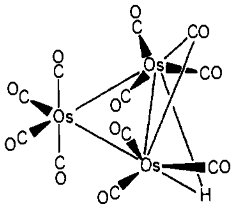
chemical shift region are assigned to the carbonyl ligands[10] and show an approximate intensity ratio of 1:1:1:2:2:2:2 in the fully decoupled spectrum.[11] This resonance pattern is similar to that reported[6] for $[HOs_3(CO)_{11}]^-$ whose structure is sketched in **5**. The structure **6** is thus indicated for $Os_3(CO)_{11}CH_2$. Consistent with the structure **6** is the presence of the weak IR band at 1869 cm^{-1} in the spectrum of $Os_3(CO)_{11}CH_2$ which can be assigned to the bridging carbonyl. The ^1H NMR spectrum of $Os_3(CO)_{11}CH_2$ (Figure 2) shows two equal intensity doublets at δ 6.47 and 7.75 which are due to the two inequivalent hydrogens of the methylene group, with $J_{H_a\text{-}H_b}$ = 7.2 Hz. In the fully coupled ^{13}C NMR spectrum (Figure 1a) an apparent triplet is observed at 62.5 ppm with relative intensity 1 which can be assigned to the methylene carbon. However, the spectra shown in Figure 1b and 1c, in which the two methylene hydrogens are selectively decoupled, indicate that this pseudotriplet is due to a pair of partially overlapping doublets resulting from the coupling of the methylene carbon with the two inequivalent CH_2 protons.



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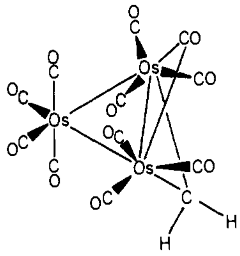

6

Several experiments were conducted in an effort to elucidate the mechanism by which $Os_3(CO)_{11}CH_2$ forms. First, no $Os_3(CO)_{11}CH_2$ was produced when acidification was carried out before $[Os_3(CO)_{11}(CHO)]^-$ formed to a significant extent or after $[Os_3(CO)_{11}(CHO)]^-$ had thermally decomposed. Thus, $[Os_3(CO)_{11}(CHO)]^-$ must be the precursor to the $Os_3(CO)_{11}CH_2$ product. It was also observed that acidification of an $[Os_3(CO)_{11}(CHO)]^-$ solution with CF_3CO_2D gave $Os_3(CO)_{11}CH_2$, but no $Os_3(CO)_{11}CHD$ was detected. Conversely, H_3PO_4 protonation of $[Os_3(CO)_{11}(CDO)]^-$, prepared by reduction of $Os_3(CO)_{12}$ with $Li[BDEt_3]$, gave only $Os_3(CO)_{11}CD_2$. These deuterium labeling experiments clearly indicate that both methylene hydrogens derive from the borohydride reducing agent and that the function of the acid is to remove the carbonyl oxygen, presumably as H_2O. Finally, it was observed that addition of excess $K[BH(O\text{-}i\text{-}Pr)_3]$ did not lead to an increased $Os_3(CO)_{11}CH_2$ yield, implying that this species does not form as a result of a further reaction of $[Os_3(CO)_{11}(CHO)]^-$ with $[BH(O\text{-}i\text{-}Pr)_3]^-$.[12]

The reaction sequence that is most consistent with these various results is shown in Scheme I. Protonation presumably occurs at the formyl oxygen of $[Os_3(CO)_{11}(CHO)]^-$ to yield $Os_3(CO)_{11}(CHOH)$. Analogous formyl oxygen protonation has been shown to occur with $Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CHO)$ to yield $[Re(\eta^5\text{-}C_5H_5)(NO)(PPh_3)(CHOH)]^+$.[13] Hydride transfer to the hydroxymethylene cluster from another $[Os_3(CO)_{11}(CHO)]^-$ would yield $[Os_3(CO)_{11}(CH_2OH)]^-$ and a corresponding amount of $Os_3(CO)_{12}$. An equivalent amount of $Os_3(CO)_{12}$ was isolated after acidification, consistent with this mechanistic proposal. Similar hydride transfer reactions have been observed by Gladysz[13] and Casey[14] and their co-workers. Continued protonation of $[Os_3(CO)_{11}(CH_2OH)]^-$ at the oxygen atom, followed by elimination of H_2O, would yield the observed $Os_3(CO)_{11}CH_2$ cluster. Note that according to this mechanism, both methylene hydrogens derive from the $[BHR_3]^-$ reducing agent, via the intermediacy of $[Os_3(CO)_{11}(CHO)]^-$, in accord with the experimental observations.

When $Os_3(CO)_{11}CH_2$ was heated to 70-80 °C under an H_2 atmosphere, CH_4 was evolved in ~20% yield, as evidenced by mass spectral analysis of the gases above such solutions.[15] Only CH_2D_2 was produced when $Os_3(CO)_{11}CH_2$ was heated under a D_2 atmosphere. The only Os-containing products from these reactions which could be identified were small amounts of $Os_3(CO)_{12}$(<10%) and a trace amount of a material for which mass spectral evidence indicates the formulation $Os_3(CO)_{10}CH_2$. The mass spectrum of this latter compound shows a parent ion at m/e 866 and fragment ions corresponding to loss of 10 carbonyls and 2 hydrogens. This same material was isolated in an 80% yield following 70-80 °C thermolysis of $Os_3(CO)_{11}CH_2$ in benzene solution under N_2; $Os_3(CO)_{12}$ in a 20% yield was the only other product that could be detected from this reaction. When this material was heated to 70-80 °C under an H_2 atmosphere, it did not yield CH_4, and thus this species does not appear to be an intermediate in the CH_4 production. Although we do not know the structure of $Os_3(CO)_{10}CH_2$, the only resonance observed in its ^1H NMR spectrum in benzene-d_6 solution is a sharp singlet at δ -20.1 which implies one or more equivalent hydrides. No resonance which might be assigned to a μ^3-CH group was seen. Experiments directed toward more fully characterizing this latter compound are continuing.[16]

It is interesting that the results reported herein differ from those described by Pruett and co-workers.[7] These workers did acidify $[Os_3(CO)_{11}(CHO)]^-$ solutions with CF_3CO_2H and observed formation of 20-30% methanol, but no mention was made of the cluster products from their reactions or the manner in which the methanol was characterized. In our hands, CH_3OH was not observed by gas chromatographic techniques upon acidifiction with CF_3CO_2H, but $Os_3(CO)_{11}CH_2$ was produced in a yield similar to that obtained upon acidification with H_3PO_4. Also, no CH_3OH was detected when protonation was carried out with H_3PO_4.

In addition to demonstrating the stepwise reduction of CO to CH_4 on a cluster face, the results reported herein also show that reaction sequences similar to those established for monomeric formyl complexes can be carried over to cluster-based systems.[13,14] With regard to the mechanism of the surface-catalyzed reduction of CO, these results show that hydrogenation of surface-bound carbenes is a reasonable path for the production of hydrocarbons. Similar conclusions have been noted by others.[17]

Acknowledgment. We thank the Department of Energy, Office of Basic Energy Sciences, for support of this research and Professor John Shapley for communication of unpublished results from related research being carried out in his laboratories. G.L.C. acknowledges the Alfred P. Sloan Foundation for a research fellowship and the Camille aand Henry Dreyfus Foundation for a Teacher-Scholar award.

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(12) The isolated yield of $Os_3(CO)_{11}CH_2$ actually decreased to 10% when a 6-fold excess of $K[BH(O\text{-}i\text{-}Pr)_3]$ was used compared to the 20% yield when a stoichiometric quantity of the borohydride was employed.

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Improvement of Energy Conversion Efficiency by Specific Chemical Treatments of *n*-MoSe₂ and *n*-WSe₂ Photoanodes

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The apparent stability to photocorrosion reactions exhibited by the semiconducting transition-metal dichalcogenides which crystallize in layered structures has led to an increasing interest

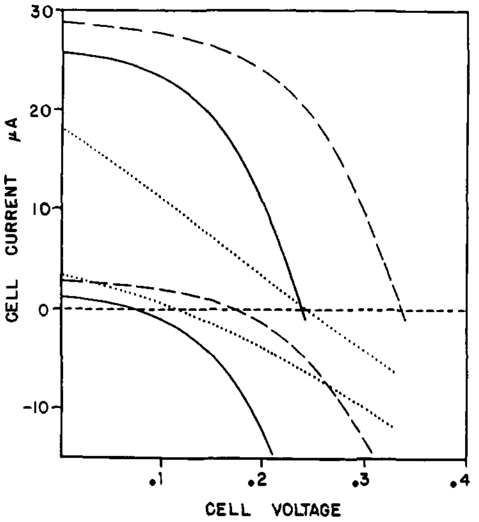

Figure 1. Photoresponse (upper curves) and dark currents (lower curves) for a n-WSe_2 electrode before treatment (solid lines), at maximum improvement after treatment in diphos as described in text (dashed lines), and after 7 h of operation (dotted lines) in 1 M NaI, 0.1 M I_2 electrolyte with 0.1 mW of 632.8-nm light.

in the use of these materials as the photoelectrode in a liquid junction solar cell.[1-16] Respectable light-to-electrical energy conversion efficiencies have been achieved with several of the layered semiconductors provided that only defect-free van der Waals surfaces (planes of selenium atoms) are exposed to the electrolyte.[4-17] The transition-metal atoms, when exposed to the electrolyte, act as potent recombination centers for photogenerated carriers (surface states within the band gap) and severely degrade the energy conversion efficiency of the device.[10,12,16] Dark current processes also occur at the unsaturated transition-metal sites and result in the back reaction of photogenerated redox species, which further degrades the efficiency of light-to-electrical energy conversion.[16,18] We report several novel chemical treatments which reduce the deleterious effect of crystal edge sites on the photoconversion process in several of the layered semiconductors.

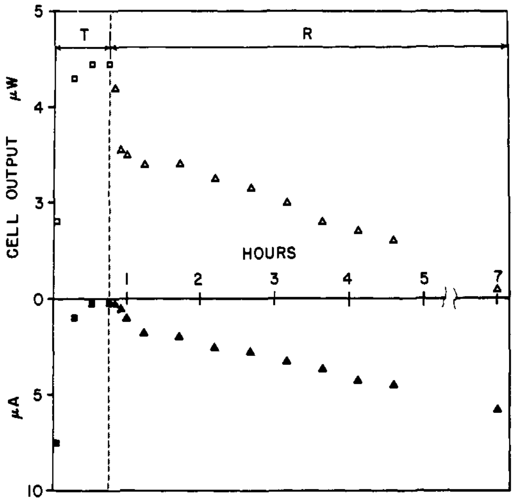

Figure 2. Cell output (above) and dark current measured at 175 mV for a WSe_2 photoanode during treatment with diphos (T) and while running (R) near the maximum power point in a 1 M NaI, 0.1 M I_2 electrolyte with 0.1 mW of 632.8-nm light.

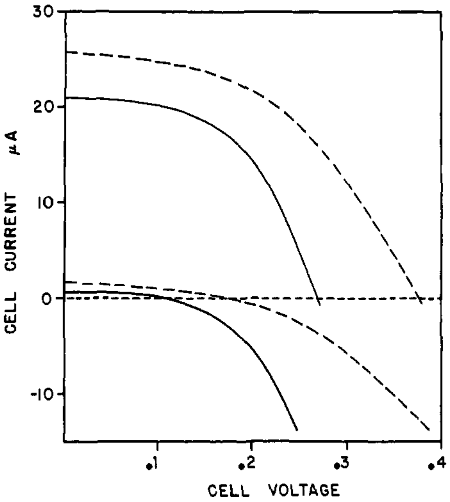

Figure 3. Photoresponse (upper curves) and dark current (lower curves) for a $MoSe_2$ photoanode before treatment (solid lines) and after treatment in neat *tert*-butylpyridine as described in text (dashed lines). Input power was 0.1 mW of 632.8-nm light.

Uncleaved single crystals of the transition-metal dichalcogenide ($MoSe_2$ or WSe_2) with van der Waals surfaces that had visible steps were selected, ohmically contacted with silver paint, and potted in epoxy such that the stepped surface was exposed. The photoresponse in an aqueous 1 M NaI, 0.1 M I_2 solution was then measured and found to be stable at the relatively low output voltages and currents expected for such a sample (solid curve in Figure 1).[10,12,16] The current voltage response in the solar cell region is very sensitive to the occupation and position of surface states within the semiconductor band gap[19] and serves as an indicator of the reactivity of reagents with the surface states.

The samples were then treated in a 0.03 M solution of bis(1,2-diphenylphosphino)ethane (diphos) in 3:1 methanol–chloroform at 60 °C and the photoresponse measured after various treatment intervals. Increased open-circuit voltages and short-circuit currents and decreased dark currents were observed on most samples (dashed curve in Figure 1). After several treatments totalling about 1 h, no further increases in the power output of the cell are realized with additional treatments (Figure 2). No improvements in power output can be observed without phosphine in the treatment solution. However, upon extended illumination,

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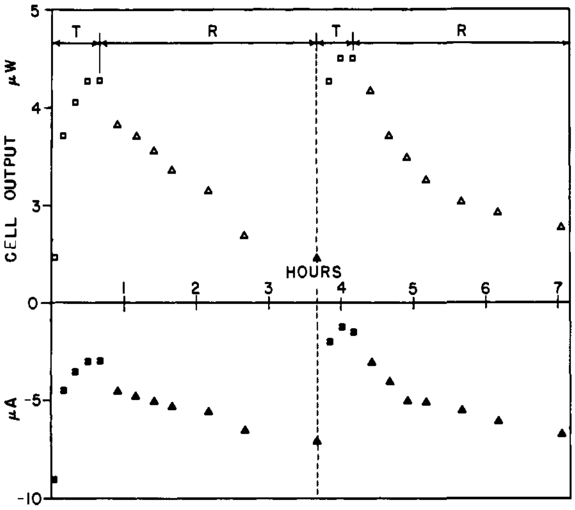

Figure 4. Cell output (above) and dark current measured at 225 mV (below) for a n-MoSe$_2$ photoanode during treatments (T) with *tert*-butylpyridine and while running near the maximum power conversion point (R) in a 1 M NaI, 0.1 M I$_2$ electrolyte with 0.1 mW of 632.8-nm light.

the power output of the cell degrades to a point below its original output (Figure 2 and dotted curve in Figure 1). At this point the crystal does not respond to further treatments in the diphos solution. Auger spectroscopy of the surface of the crystals reveals the presence of phosphorus but the spatial resolution was not sufficient at this writing to determine whether the majority of this phosphorus resides in regions where there is a high density of edge sites.

This behavior is attributed to a specific reaction of the electron-donating phosphine ligand with an unsaturated transition-metal atom at a crystal edge site. Edge selectivity in the chemisorption of O$_2$ on molybdenum disulfide has been observed and used to measure the density of active catalytic sites on hydrodesulfurization catalysts.[20] The strong electronic interaction with the metal atom reduces the ability of the surface state, formed by the metal site, to participate in recombination or dark current processes. However, the diphos is either dissociated or oxidized by photogenerated holes or the iodine in solution which reverses the original beneficial effect. Similar results have also been observed for MoSe$_2$ and WSe$_2$ when several other phosphine ligands are substituted for diphos.

Treatment of electrodes with similar surfaces in neat 4-*tert*-butylpyridine (TBP) at 60 °C also resulted in increased open-circuit voltages and short-circuit currents and decreased dark currents (Figure 3). The improved power output also decays under extended illumination, but unlike the phospine treatments the improvement could be restored, in fact further improved, with additional treatments in TBP (Figure 4). The difference in behavior in this case is attributed to a different mode of binding to the crystal. The pyridine portion of the TBP molecule can insert between the layers of the crystal at an exposed edge. The *tert*-butyl group provides an additional steric anchor to prevent further penetration of the molecule into the lattice so as to localize the electronic interaction at the edge.

The intercalation of metallic transition-metal dichalcogenides by pyridine is well-known[20-23] and attributed to the interaction of partially filled metal d_{z^2} orbitals with electron-donating orbitals on the pyridine molecule. The layered semiconductors have filled d_{z^2} orbitals and are not known to form bulk intercalation compounds; however, the acceptor character of the unsaturated metal atoms at an edge site would allow for the "semiintercalation" of a pyridine functionality. The mechanism of the improvement also involves the donation of the electrons from the pyridine molecules to the surface states created by the termination of the crystal lattice. This is analogous to the reduction of surface and grain boundary recombination rates by chemically binding ruthenium atoms to gallium arsenide photoelectrodes.[19,24] The hydrogen plasma treatments of grain boundaries of polycrystalline silicon is another analogous example of specific chemistry performed on defect sites.[25]

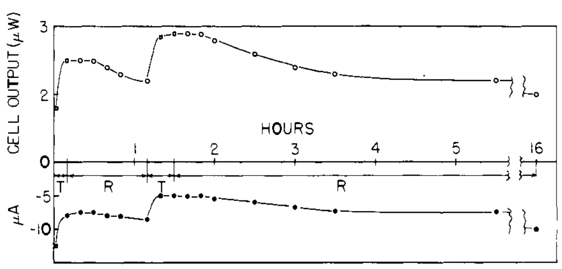

Figure 5. Cell output (above) and dark current (below) for a n-WSe$_2$ photoanode checked after treatments in (polyvinyl)pyridine (T) and while running near the maximum power conversion point (R) in a 1 M NaI, 0.1 M I$_2$ electrolyte with 0.1 mW of 632.8-nm light.

The semiintercalation mechanism is also supported by the fact that after the initial decay the improvement in solar cell response is more easily obtained on subsequent treatments in TBP. This is probably due to the exfoliation of the edge sites by the initial treatment which provides easier access to the sites on the subsequent treatments.

The improvement of the power output of a cell can be sustained for a longer period if a pyridine polymer is used in the treatment. Figure 5 shows the power output and dark current of a WSe$_2$ crystal treated in a 1% solution of 2-poly(vinyl)pyridine in methanol at 60 °C. Presumably the polymer backbone makes it more difficult to dislodge the pyridine from between the crystalline layers when the cell is illuminated. Retreatment after running the cell for about 1 h resulted in an additional improvement in the power output. The initial decay of the cell is much slower than with TBP and does not decay to the original output until more than 16 h of continuous operation. The incorporation of a semiintercalating compound into the electrolyte may provide a way to counteract this gradual decay of the power output.

If a crystal with no visible surface steps (and correspondingly good solar cell response) is treated with either the phosphine or pyridine containing molecules previously described, no improvement in the solar cell response is observed. This is taken as further evidence of the edge specificity of the recombination reducing reagents.

The operation of the surface modified crystals as a photoelectrode in the oxidizing and surface active iodide–triiodide solutions[26] is a stringent test of the ability of the ligation and semiintercalation reagents to compete for edge sites on the layered semiconductors. However, it is clear that the potency and persistence of these edge passivation treatments must be improved to open the way for solar energy conversion devices to be constructed from cheaper and more easily fabricated polycrystalline layered semiconducting materials.

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