9; R = Me, R′ = Ph, **10**).[13]

Proton NMR spectra of **7** and **8** display only one signal for the two vinylidene substituents at −95 °C (a doublet of doublets for **7** at 3.48 ppm with $^4J_{HP}$ = 4.5 and 3.0 Hz; a singlet for the methyl protons of **8** at 2.04 ppm). The structure of *mer*-$(OC)_3(dppe)W{=}C{=}C(H)CO_2Me$,[8] with the vinylidene ligand nearly in the WP_2 plane, has the two vinylidene substituents in different environments. The ^1H NMR data and the expected ground-state vinylidene orientation indicate that vinylidene rotation is rapid on the NMR time scale, in accord with a calculated barrier of only 5.9 kcal/mol for the model compound *mer*-$(OC)_3(H_2PCH_2CH_2PH_2)W{=}C{=}CH_2$.[14] The orientational preference of the vinylidene ligand is small in **7** and **8** because the dominant π-acceptor orbital of the α-carbon finds a filled $d\pi$ orbital of similar energy and extension in all orientations. Vinylidene[15] and allenylidene[16] ligands rotate rapidly in other systems.

To probe whether the facial to meridional rearrangement accompanying conversion of the acetylide reagent **4** to the vinylidene product **9** involved CO loss, a solution of **4** in THF was protonated under 1 atm of ^{13}CO. The absence of ^{13}CO in the vinylidene product **9** suggests that the isomerization is intramolecular. Facile intramolecular rearrangements of six-coordinate carbonyl derivatives are well documented;[17] the facial to meridional isomerization of $M(CO)_3(dppe)(\eta^2\text{-olefin})$(M=Mo, W) complexes is particularly relevant.[18]

Acknowledgment. We thank the National Science Foundation (CHE8310121) and donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

Registry No. **1**·Li, 98586-58-4; **1**·Na, 98586-59-5; **1**·PPN, 98586-61-9; **1**·Li/HMPA, 98586-62-0; **2**·Li, 98586-63-1; **2**·Na, 98586-64-2; **2**·PPN, 98586-66-4; **3**·Li, 98586-67-5; **4**·Li, 98586-68-6; **5**, 98586-71-1; **6**, 98611-58-6; **7**, 98586-72-2; **8**, 98586-73-3; **9**, 88035-90-9; **10**, 96454-56-7; I (R = Me), 98586-69-7; I (R = *n*-Bu), 98586-70-0; *fac*-$(OC)_3$(dppe)W(acetone), 84411-66-5; *mer*-$(OC)_3(H_2PCH_2CH_2PH_2)W{=}C{=}CH_2$, 98586-74-4; LiCCH, 1111-64-4; LiCCMe, 4529-04-8; LiCCBu, 17689-03-1; LiCCPh, 4440-01-1; NaCCH, 1066-26-8; NaCCMe, 10486-71-2; CO_2, 124-38-9.

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[13] Complex **7**: Addition of 0.1 mL of 0.1 M $HBF_4(aq)$ to a yellow slurry of Na[*fac*-$(OC)_3$dppeW(CCH)] (0.33 g, 0.46 mmol) at 0 °C resulted in an immediate red color. The mixture was kept at 0 °C and dried over $MgSO_4$. The mixture was filtered, and the filtrate was reduced to 5 mL. Addition of hexanes precipitated **7** as a green powder in 53% yield: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2000 m, 1925 s, 1883 vs, $\nu_{C=C}$ 1593 m; ^1H NMR (CD_2Cl_2) δ 7.91–6.84 (m, Ph), 3.48 (dd, $^4J_{HP}$ = 4.5, 3 Hz), 2.72 (m, PCH_2CH_2P); ^{13}C NMR (CD_2Cl_2) δ 332.7 (m, $W{=}C{=}CH_2$), 212.9 (m, CO trans to P), 203.9 (m, 2 trans CO's), 136.1–126.3 (m, Ph), 97.2 (td, $^1J_{CH}$ = 157 Hz, $^3J_{CP}$ = 14 Hz, $W{=}C{=}CH_2$), 30.5 (m, PCH_2CH_2P), 28.0 (m, PCH_2CH_2P). **8**: IR (CH_2Cl_2, cm^{-1}) ν_{CO} 1978 w, 1918 m, 1878 vs, $\nu_{C=C}$ 1667 w. **9**: IR (KBr, cm^{-1}) ν_{CO} 2000 m, 1895 s, 1875 vs, $\nu_{C=C}$ 1612 m, 1578 m. **10** has been previously reported, see: Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474.

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A Reversible Metal Framework Rearrangement Assisted by Coordinated Iodide. X-ray Structure Analysis of $[(Ph_3P)_2N][H_2Os_4(CO)_{12}(I)]$

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Summary: The complex $[(PPh_3)_2N]^+[H_2Os_4(CO)_{12}(I)]^-$, obtained by deprotonation of the butterfly cluster $H_3Os_4(CO)_{12}(\mu\text{-}I)$ with $[(PPh_3)_2N][NO_2]$, is shown by X-ray analysis to consist of a tetrahedral arrangement of metal atoms with the two hydrides bridging adjacent edges and a terminally bonded iodide ligand. Protonation of the anion regenerates the parent neutral complex in a novel reversible structural transformation assisted by the iodide ligand. Crystal data: monoclinic, space group $P2_1/a$, a = 16.841 (2) Å, b = 20.699 (1) Å, c = 29.249 (3) Å, β = 90.91 (2)°, V = 10194.7 Å^3, and Z = 8.

The catalytic potential of coordinatively saturated metal clusters is conditioned by the formation of a vacant coordination site at some stage in the cycle. In the catalytic hydrogenation of ethylene with $HOs_3(CO)_{10}(OSi{\equiv})$, for instance, the formation of the required vacant site has been proposed to involve the reversible opening of the Os–O–Os bridge.[2] Therefore, the presence of ligands with such ability to modify their bonding mode could result in an enhanced reactivity of metal clusters.

Halide ligands on metal clusters can be bound either as doubly bridging, 3e donors, or terminal, 1e donors.[3] Thus,

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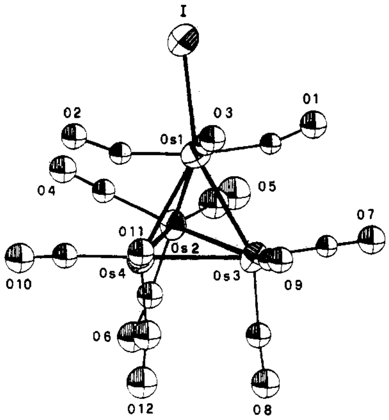


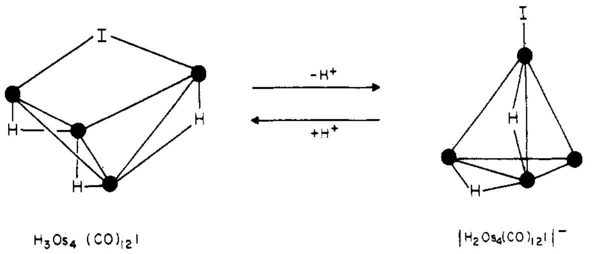
Figure 1. ORTEP diagram of $[H_2Os_4(CO)_{12}(I)]^-$ (2) showing 50% probability thermal ellipsoids. Averaged bond lengths (Å) for the two independent molecules: Os(1)–Os(2) = 2.964 (1), Os(1)–Os(3) = 2.820 (1), Os(1)–Os(4) = 2.799 (1), Os(2)–Os(3) = 2.938 (1), Os(2)–Os(4) = 2.804 (1), Os(3)–Os(4) = 2.774 (1), Os(1)–I = 2.732 (1). Average Os–C and C–O distances are 1.87 (2), and 1.14 (2) Å, respectively.

conversion from a bridging into a terminal mode results in the formation of a vacant coordination site on the polynuclear framework. This type of modification has been invoked to explain mechanistic details in a number of processes;[3a,b] on the other hand, its reversibility would be relevant to catalysis by metal clusters, particularly in reactions promoted by iodide or other halides.[4]

Our previous work[5] on the catalytic potential of several osmium clusters led us to investigate the reactivity of the neutral iodide cluster $H_3Os_4(CO)_{12}(\mu\text{-}I)$ (1), which was shown by X-rays to possess a butterfly arrangement of metal atoms.[3d] We recently reported[6] that the interaction of 1 with $[(Ph_3P)_2N][I]$, $[(Ph_3P)_2N][NO_2]$, or I_2 yields the anionic species $[H_2Os_4(CO)_{12}(\mu\text{-}I)]^-$ (2). On the basis of IR evidence,[7a] together with a high yield regeneration of 1 by protonation of 2,[8] a butterfly metal core configuration similar to that of 1 was proposed for 2. Moreover, since the skeletal electron count remains unchanged during the deprotonation reaction, assuming that no change in the coordination mode of the iodide ligand takes place, a modification of the metal cage geometry was not expected.

However, as previously noted,[6] the ^1H NMR spectrum of 2[7b] shows H–H coupling which is not observed for 1;[3d] furthermore, preliminary results on the catalytic hydrogenation of olefins[9] indicate that the behavior of 2 differs considerably from that of 1 and resembles that of the tetrahedral species $H_4Os_4(CO)_{12}$ and $[H_3Os_4(CO)_{12}]^-$. Also it is known[10] that addition of H^+, or the isolobal fragment $[AuPR_3]^+$, to anionic clusters can induce a metal core rearrangement.

Scheme I



Therefore, in order to unambiguously establish the metal framework geometry and the ligand distribution in 2, an X-ray single-crystal structure determination was undertaken.[11] The anion 2 possesses the structure shown in Figure 1. The four Os atoms define a tetrahedron with four short [mean 2.799 (2) Å] and two long adjacent edges [mean 2.951 (2) Å]. The long Os–Os bonds are bridged by two hydrogen atoms as can be deduced by both the metal–metal bond lengthening and the CO ligand displacements, which usually accompany the presence of bridging hydrides.

The I ligand is terminally bonded to Os(1) which also bears three terminal CO ligands. The remaining nine carbonyls are terminally bonded to the other three Os atoms. Because of the presence of the two bridging hydrides the molecule is completely asymmetric, thus differing from the isoelectronic $[H_2Os_4(CO)_{12}]^{2-}$[12] which shows idealized D_{2d} symmetry having the two H atoms on opposite edges of the metal tetrahedron.

The Os atom bearing the iodide ligand shows a sterically congested situation due to the presence of three CO groups and the involvement in one of the H bridges. Therefore Os(1) is electron rich with respect to the other Os atoms. Such an uneven charge distribution is partially alleviated by pushing two equatorial COs [C(1), C(2)] in close contact with the two contiguous Os atoms (mean Os···C = 2.64 Å) toward semibridging positions. The existence of a weak bonding interaction is also suggested by the slight bending of these two carbonyls [mean Os–C–O = 163°] with respect to the other ones (mean 175°). The structural features exhibited by the "$Os(CO)_3I$" unit in 2 resemble those shown by the same fragment in the pentanuclear cluster $[Os_5(CO)_{15}I]^-$ (3). The anionic species 3 also contains two short Os···C interactions [mean Os···C = 2.70 Å] involving two carbonyls of the $Os(CO)_3I$ moiety.[13] These CO ligands

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(7) (a) IR: ν_{CO} (CH_2Cl_2) 2080 (m), 2048 (s), 2018 (s), 1990 (sh) cm^{-1}. (b) NMR (−20 °C, $CDCl_3$) δ_{Me_4Si} −19.74, −21.66 (J_{H-H} = 1.07 Hz).

(8) Protonation of the anionic species 2 using H_2SO_4 was monitored by IR spectroscopy. The ^1H NMR spectrum obtained in $CDCl_3$ at −20 °C after protonation of 2 has been completed, showed the presence of $H_3Os_4(CO)_{12}(\mu\text{-}I)$ and $H_4Os_4(CO)_{12}$ in ca. 4:1 ratio as the only species present in solution. After TLC the neutral iodide derivative was recovered in ca. 60% yield.

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(11) Crystal data for $C_{48}H_{32}NO_{12}P_2IOs_4$: *Mr* = (1764.4, monoclinic, space group $P2_1/a$ (from systematic absences), a = 16.841 (2) Å, b = 20.699 (1) Å, c = 29.249 (3) Å, β = 90.91 (2)°, U = 10194.7 Å^3, $F(000)$ = 6480, Z = 8, D_{calcd} = 2.30 g cm^{-3}, Mo Kα radiation, λ = 0.710 69 Å, μ (Mo Kα) = 106.7 cm^{-1}. Current R value = 0.0438 (R_w = 0.0345) for 6002 independent reflections [$F_o > 5\sigma(F_o)$] collected in the range 2.5 < θ < 23°. An empirical absorption correction was applied (370 azimuthal reflections measured, transmission range 37%–100%). Two independent molecules were present in the asymmetric unit. Because no significant structural differences were detected, all parameters discussed herein were averaged on corresponding values in the two independent anions.

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have been considered as adopting a semibridging mode.[14] The Os–I bond length of 2.732 (2) Å agrees with other reported values for terminal iodide groups.

The structural parameters for bridged and unbridged bonds [2.951 (2) and 2.799 (2) Å, respectively] ought to be compared with the values reported for other isoelectronic species such as $[H_2Os_4(CO)_{12}]^{2-}$ [12] [2.934 (4), 2.798 (4) Å], $[H_3Os_4(CO)_{12}]^-$ [15] [2.949 (2), 2.798 (2) Å], and $[H_3Os_4(CO)_{11}NO]$[6] [2.925 (2), 2.799 (2) Å] showing substantial agreement. However, a similar comparison with the values reported for 1 [3.010 (3), 2.877 (1) Å, respectively][3d] shows that a general lengthening in the metal–metal bonds is observed on passing from a tetrahedral to a butterfly arrangement of the metal core. Longer bonds were also observed for the butterfly-shaped $[H_3Os_4(CO)_{12}(\mu\text{-}NO)]$ [2.997 (5), 2.853 (5) Å].[16]

It is interesting to speculate about why the actual asymmetric stereogeometry is preferred to a more symmetric C_s configuration. A tentative rationalization could be that one H atom prefers coordination to the more electron-rich Os(1), leaving two nonequivalent sites for the second one. One of the sites [Os(2)–Os(3), Os(2)–Os(4)] is twice as probable as the other [Os(3)–Os(4)]. The statistically favored position could thus be preferred when the molecule is "frozen" in the crystal.

The facile reversible[8] structural transformation herein described (Scheme I) is certainly enhanced by the availability of different bonding modes for the halide ligand; this allows a modification of the iodide from a doubly bridging, 3e donor to a terminal, 1e donor ligand and vice versa.

Three examples of similar metal framework transformations in Fe_4 clusters have been confirmed by structural characterization of the species involved, viz., $[Fe_4(CO)_{13}]^{2-}$ (tetrahedral), which reversibly yields $[HFe_4(CO)_{13}]^-$ (butterfly) on protonation,[10d] and $[Fe_4(CO)_{12}(COCH_3)]^-$ (tetrahedral), which produces $Fe_4X(CO)_{12}(COCH_3)$ (X = H,[10e] $AuPEt_3$[10g]) (butterfly) by reaction with acid and PEt_3 AuCl, respectively. Also, the existence of both tetrahedral and butterfly isomers of $[XFe_4(CO)_{13}]^-$ (X = H,[10f] $AuPEt_3$[10g]) in solution has been proposed on the basis of NMR data. All these rearrangements are accompanied by interconversion of terminal and bridging (or Π) carbonyl ligands.

However, to our knowledge, this is the first report of such a reversible structural transformation assisted by a *halide* ligand. This has important mechanistic implications in a number of reactions of metal clusters, including catalytic processes, which are known to be promoted by halides, and particularly iodide.[4] Preliminary studies on the reactivity of 2 toward the electrophilic reagents $[AuPPh_3]^+$ and NO^+ indicate that its behavior is considerably different from that of the isoelectronic $[H_3Os_4(CO)_{12}]^-$.

Acknowledgment. We gratefully acknowledge CONICIT for financial support. We are also grateful to Professor J. Lewis and Dr. B. F. G. Johnson for their encouragement to develop this work.

Registry No. 1, 67966-16-9; 2, 98331-78-3.

Supplementary Material Available: Crystal data and details of measurement, Figure 2, showing two different orientations of the anion $[H_2Os_4(CO)_{12}(I)]^-$ (2), Table I, fractional atomic coordinates and thermal parameters, Table II, anisotropic thermal parameters, Table III, bond distances, Table IV, bond angles, Table V, contacts, and listings of observed and calculated structure factors for 2 (53 pages). Ordering information is given on any current masthead page.

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Skeletal Reactivity of Metallophosphorus Clusters. *nido*-$Ru_4(CO)_{10}(\mu\text{-}CO)_2[PhPC(Ph)C(Ph)]$ and *closo*-$Ru_4(CO)_9(\mu\text{-}CO)_2(PhP)[C(Ph)C(Ph)]$ via Acetylene Incorporation into the Nido Framework of the Phosphinidene Cluster $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$

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Summary: Reaction of the butterfly phosphinidene complex $Ru_4(CO)_{13}(\mu_3\text{-}PPh)$ with diphenylacetylene affords two metal–carbon–phosphorus clusters, *nido*-$Ru_4(CO)_{10}(\mu\text{-}CO)_2[P(Ph)C(Ph)C(Ph)]$ and closo, pentagonal-bipyramidal $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_3\text{-}PPh)(\mu_4\text{-}\eta^2\text{-}PhC_2Ph)$, characterized by X-ray diffraction and having metal, carbon, and phosphorus atoms in the skeletal framework.

The metallophosphorus clusters,[1] molecules which include both metal and phosphorus atoms in a polyhedral framework are members of a potentially vast class of mixed transition metal–main group compounds.[2] Such molecules are currently of structural and chemical interest because they offer the opportunity to evaluate the validity of current models of bonding for mixed polynuclear systems[3]

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(2) Between the extremes of the homonuclear transition-metal clusters and main-group cages such as the polyhedral boranes lie mixed species such as the metalloboranes and carboranes, carbido, nitrido, phosphido, and sulfido clusters, and numerous metal–hydrocarbon π-complexes in which the carbon atoms can be considered as skeletal. For general surveys of types see: (a) O'Neill, M. E.; Wade, K. In "Metal Interactions with Boron Clusters"; Grimes, R. N. Ed.; Plenum Press: New York, 1982. (b) "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980. (c) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (d) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127.

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