organic intermediate and by reductive regeneration of the catalytically active Co(I) species.

The ready accessibility of starting materials, mild reductive neutral reaction conditions, and simple manipulation make this regiospecific nucleophilic acylation of activated olefins a further useful C–C bond-forming reaction[18] catalyzed by vitamin B_{12}.

Acknowledgment. This work was supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung.

Registry No. 1 ($R^1 = CH_3$; $R^2 = R^3 = H$; Z = CHO), 626-96-0; **1** ($R^1 = n\text{-}C_7H_{15}$; $R^2 = R^3 = H$; Z = CHO), 71525-51-4; **1** ($R^1 = R^3 = CH_3$; $R^2 = H$; Z = CHO), 83440-17-9; **1** ($R^1 = n\text{-}C_7H_{15}$; $R^2 = H$; $R^3 = CH_3$; Z = CHO), 87682-79-9; **1** ($R^1 = R^2 = CH_3$; $R^3 = H$; Z = CHO), 23260-39-1; **1** ($R^1 = R^2 = R^3 = CH_3$; Z = CHO) (isomer 1), 87682-80-2; **1** ($R^1 = R^2 = R^3 = CH_3$; Z = CHO) (isomer 2), 87682-81-3; **1** ($R^1 = CH_3$; $R^2 = R^3 = H$; Z = $COCH_3$), 110-13-4; **1** ($R^1 = n\text{-}C_6H_{13}$; $R^2 = R^3 = H$; Z = $COCH_3$), 7018-92-0; **1** ($R^1 = CH_3$; $R^2 = H$; $R^3 = R^4 = -(CH_2)_2-$; Z = CR^4O), 84602-27-7; **1** ($R^1 = CH_3$; $R^2 = H$; $R^3 = R^4 = -(CH_2)_3-$; Z = CR^4O), 1504-97-8; **1** ($R^1 = CH_3$; $R^2 = R^3 = H$; Z = $COOCH_3$), 624-45-3; **1** ($R^1 = R^3 = CH_3$; $R^2 = H$; Z = $COOC_2H_5$), 55424-74-3; **1** ($R^1 = C_6H_5$; $R^2 = R^3 = H$; Z = CN), 5343-98-6; **1** ($R^1 = CH_3$; $R^2 = R^3 = H$; Z = CN), 927-56-0; **2** ($R^1 = CH_3$), 108-24-7; **2** ($R^1 = n\text{-}C_7H_{15}$), 623-66-5; **2** ($R^1 = n\text{-}C_6H_{13}$), 626-27-7; **2** ($R^1 = C_6H_5$), 93-97-0; **3** ($R^2 = R^3 = H$; Z = CHO), 107-02-8; (*E*)-**3** ($R^2 = H$; $R^3 = CH_3$; Z = CHO), 123-73-9; **3** ($R^2 = CH_3$; $R^3 = H$; Z = CHO), 78-85-3; (*E*)-**3** ($R^2 = R^3 = CH_3$; Z = CHO), 497-03-0; **3** ($R^2 = R^3 = H$; Z = $COCH_3$), 78-94-4; **3** ($R^2 = H$; $R^3 = R^4 = -(CH_2)_2-$; Z = CR^4O), 930-30-3; **3** ($R^2 = H$; $R^3 = R^4 = -(CH_2)_3-$; Z = CR^4O), 930-68-7; **3** ($R^2 = R^3 = H$; Z = $COOCH_3$), 96-33-3; (*E*)-**3** ($R^2 = H$; $R^3 = CH_3$; Z = $COOC_2H_5$), 623-70-1; **3** ($R^2 = R^3 = H$; Z = CN), 107-13-1; vitamin B_{12a}, 13422-51-0.

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Cluster Compounds with Unusual Reactivity. The Syntheses and Crystal and Molecular Structures of the Electron-Rich Cluster $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ and Its Dimethylphenylphosphine Adduct

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Received July 29, 1983

Much interest has been focused on transition-metal cluster compounds for their potential as a new class of reaction catalysts.[1,2] A key step in the achievement of this goal will be the preparation and identification of compounds that can readily add and eliminate selected ligands under mild conditions. In mononuclear metal complexes this frequently occurs by ligand addition or substitution processes that involve coordinatively unsaturated species.[3,4] While such processes may also occur in cluster compounds, clusters have other mechanisms, one being the cleavage of metal–metal bonds, that may permit the facile addition of more ligands.[5]

We have recently described the cluster compound $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ (I), which reversibly adds 1 mol of carbon monoxide under mild conditions. In the course of the addition, two of the metal–metal bonds in I are cleaved. The unusual reactivity of I was attributed to its electronic structure in which the metal atoms formally violate the requirements of the 18-electron rule.[6]

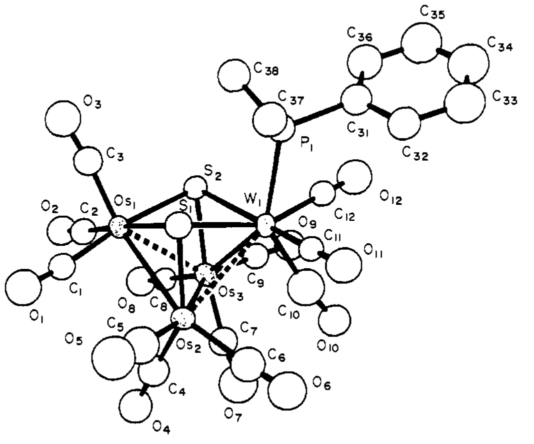

Figure 1. ORTEP diagram of $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (II) showing 50% probability thermal ellipsoids.

We have now synthesized the mixed-metal cluster $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (II), which adopts a structure analogous to I, exhibits similar anomalies in its metal–metal bonding, and readily adds donors via a process that leads to the cleavage of two of the metal–metal bonds in the cluster. Compound II, one of several products, was obtained in 28% yield by UV photolysis of mixture of $W(CO)_5(PMe_2Ph)$ and $Os_3(CO)_9(\mu_3\text{-}S)_2$ in hexane solvent for 2 h.[7] The dark green product was isolated by TLC on silica gel by using hexane solvent for elution.

The molecular structure of II was established by a single-crystal X-ray diffraction analysis.[8,9] There are two structurally analogous molecules in the asymmetric crystal unit. An ORTEP diagram of one of these molecules is shown in Figure 1. The molecule consists of a butterfly tetrahedron of three osmium atoms and one tungsten atom. The two open triangular faces contain triply bridging sulfido ligands. In both molecules the metal–metal bonding is irregular. One tungsten–osmium bond is significantly longer than the other, W(1)–Os(2) = 3.031 (1) Å [3.068 (1) Å], vs. W(1)–Os(3) = 2.969 (1) Å [2.976 (1) Å].[10,11] The osmium–osmium bonds range from the long Os(1)–Os(3) bond of 3.060 (1) Å [3.047 (1) Å], which is diametrically opposite the long tungsten–osmium bond, to the short Os(1)–Os(2) bond, 2.908 (1) Å [2.899 (1) Å]. The hinge bond Os(2)–Os(3) is roughly midway between the two extremes, 2.980 (1) Å [2.946 (1) Å]. All Os–Os bonds are longer than those found in $Os_3(CO)_{12}$, 2.877 (3) Å.[12] The unusual lengthening of two of the bonds may be a consequence of the molecule's unusual electronic structure. With five metal–metal bonds the metal atoms in this 64-electron cluster violate the requirements of the 18-electron rule since there are two too many electrons.[13–15] Similar irregularities were also observed in the metal–metal bonding of I.[6] Each metal atom contains three linear

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(7) For II: IR (ν CO) in hexane; 2093 m, 2062 s, 2055 s, 2042 sh, 2012 s, 2000 m, 1994 m, 1982 m, 1927 br, 1908 br; ^1H NMR ($CDCl_3$) δ 7.61 m C_6H_5, 2.69 d CH_3, $^2J_{PH} = 9.5$ Hz.

(8) For II: space group $P\bar{1}$, No. 2, $a = 9.229$ (4) Å, $b = 11.785$ (3) Å, $c = 28.559$ (9) Å, $\alpha = 87.02$ (8)°, $\beta = 83.82$ (5)°, $\gamma = 66.82$ (5)°, $V = 2838$ (2) Å^3, $Z = 4$, $\rho_{calcd} = 3.03$ g/cm^3. The structure was solved by direct methods (MULTAN, 444 reflections, $E_{min} = 1.80$) and after correction for absorption was refined by the method of full-matrix least squares (6034 reflections, $F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals $R = 0.033$ and $R_w = 0.034$.

(9) Intensity data were collected on an Enraf-Nonius CAD-4 automatic diffractometer by using Mo Kα radiation and the ω-scan technique. All calculations were performed on a Digital Equipment Corp. PDP 11/45 computer by using the Enraf-Nonius SDP program library, version 18.

(10) Selected interatomic distances (Å) for II:[11] Os(1)–Os(2) = 2.908 (1) [2.899 (1)], Os(1)–Os(3) = 3.060 (1) [3.047 (1)], Os(2)–Os(3) = 2.980 (1) [2.946 (1)], Os(2)–W(1) = 3.031 (1) [3.068 (1)], Os(3)–W(1) = 2.969 (1) [2.976 (1)].

(11) The values in brackets are the corresponding distances for the second crystallographically independent molecule in the asymmetric crystal unit.

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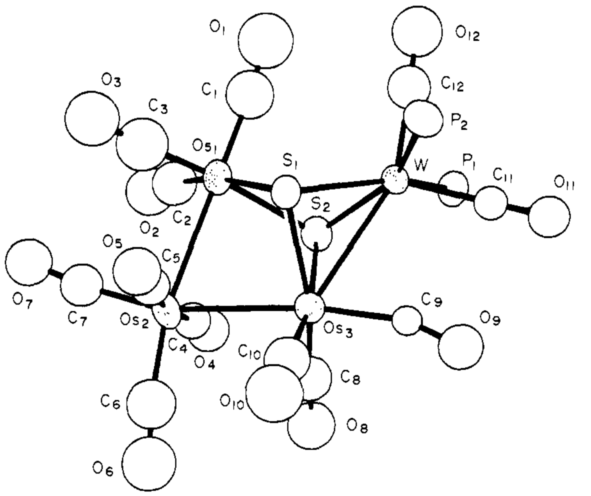

Figure 2. ORTEP diagram of $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (III) showing 50% probability thermal ellipsoids.

terminal carbonyl ligands. The tungsten atom, in addition, contains one dimethylphenylphosphine ligand.

Compound II adds 1 mol of PMe_2Ph, 7 h/room temperature in CH_2Cl_2 solvent, to give 69% yield of $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3\text{-}S)_2$ (III).[16] The molecular structure of III was determined by a single-crystal X-ray diffraction analysis, and an ORTEP drawing of its structure is shown in Figure 2.[9,17] The cluster is structurally similar to that of the compound $Os_4(CO)_{13}(\mu_3\text{-}S)_2$, which is formed by the addition of CO to I.[6] It consists of a planar cluster of four metal atoms containing three metal–metal bonds.[18] The two Os–Os bonds, Os(1)–Os(2) = 2.895 (1) Å and Os(2)–Os(3) = 2.887 (1) Å, are similar to those found in $Os_3(CO)_{12}$, 2.877 (3) Å.[12] The tungsten–osmium bond, W–Os(3) = 3.044 (1) Å, is similar to those found in II. Two triply bridging sulfido ligands bonded to the Os(1), Os(3), and W atoms are symmetrically disposed about the M_4 plane. Metal atom Os(1) contains three linear terminal carbonyl ligands and Os(2) contains four. Os(3) contains two linear carbonyl ligands and one semibridge (C(9)–O(9)) leading toward the tungsten atom. The tungsten atom contains two linear terminal carbonyl ligands and the two dimethylphenylphosphine ligands.

The formation of III from II has occurred apparently via phosphine addition to the tungsten atom, one of the "wing-tip" atoms of the cluster. This is accompanied by a CO ligand shift, a cleavage of the two elongated metal–metal bonds, and a shift of one of the sulfido ligands from one "hinge" metal atom to the other (e.g., from Os(2) to Os(3)).

The principal results gleaned from this study are (1) sulfido ligands by virtue of their ability to serve as bridging ligands can play an important role in the *synthesis* of new metal cluster compounds, especially mixed-metal clusters, (2) there may be a series of mixed-metal clusters analogous to I that exhibit the same unusual reactivity of I, and (3) mechanistically the point of ligand entry into II is a "wing-tip" metal atom and not the "hinge" atom which ultimate acquires one additional ligand. Whether or not this latter result is a feature of a greater affinity of the tungsten atom than an osmium atom for the phosphine ligand or due to the intrinsic reactivity of the cluster remains to be established. Studies focusing on the synthesis of mixed-metal analogues of I, the addition of other ligands to I and II, and the nature of ligand loss from III are currently in progress.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE-8019041. NMR studies were supported by Grant CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. We thank Engelhard Industries for a loan of osmium tetraoxide.

Supplementary Material Available: Tables of structure factor amplitudes, fractional atomic coordinates, bond distances, and bond angles are available for both structures (54 pages). Ordering information is given on any current masthead page.

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[14] We have assumed that the sulfido ligands serve as four-electron donors. The structure of this cluster does, however, conform with the requirements of the polyhedral skeletal electron-pair theory, if the cluster is viewed as a *nido*-pentagonal bipyramid containing eight skeletal electron pairs.[15]

[15] Wade, K. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: Chichester, England, 1980; Chapter 3, p 193.

[16] Compound III is also a minor product in the reaction that yields compound II. Compound III was isolated by TLC on silica gel. IR ν(CO) (hexane) 2092 s, 2050 s, 2037 m, 2014 s, 2007 sh, 1982 m, 1978 m, 1970 m, 1942 m, 1912 w, 1895 w, 1837 s, 1833 sh. ^1H NMR ($CDCl_3$ at 28 °C) δ 7.41 m C_6H_5, 2.16 d CH_3, $^2J_{PH} = 9.2$ Hz.

[17] For III: space group $P2_1/n$, No. 14, $a = 19.917$ (9) Å, $b = 9.560$ (3) Å, $c = 21.392$ (8) Å, $\beta = 113.74$ (3)°, $V = 3728$ (5) Å^3, $Z = 4$, $\rho_{calcd} = 2.55$ g/cm^3. The structure was solved by direct methods (MULTAN, 264 reflections, $E_{min} = 1.78$) and after correction for absorption was refined by the method of full-matrix least squares (3135 reflections, $F^2 \geq 3.0\sigma(F^2)$) to the final values of the residuals $R = 0.046$ and $R_w = 0.051$.

[18] Selected interatomic distances (Å) and angles (deg) for III: Os(1)–Os(2) = 2.895 (1), Os(2)–Os(3) = 2.887 (1), Os(3)–W = 3.044 (1), Os(1)–S(1) = 2.440 (4), Os(1)–S(2), = 2.482 (5), Os(3)–S(1) = 2.447 (4), Os(3)–S(2) = 2.461 (4), W–S(1) = 2.470 (4), W–S(2) = 2.497 (4), Os(1)–Os(2)–Os(3) = 70.90 (2), Os(2)–Os(3)–W = 123.20 (3).

Chemistry of the Dianions of 3-Heteroatom-Substituted Cyclopent-2-en-1-ones: An Expedient Route to *dl*-Coriolin

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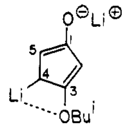
The 3-heteroatom-substituted cyclopent-2-en-1-ones smoothly generate dianions upon treatment with 2 equiv of a strong base, and the resulting dianions (e.g., **1**) undergo efficient dialkylations at both C-4 and C-5.[1] The most synthetically attractive example of such a reaction is the one-step synthesis of the *cis*-4-alkoxybicyclo[3.3.0]oct-3-en-2-one system from reaction with 1,3-diiodopropane.[1] We have further explored this versatile reaction in conjunction with the synthesis of polycyclopentanoid natural products.[2] In this communication, we wish to delineate a highly expedient route to the antitumor agent coriolin (**2**).[3,4] The



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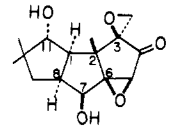

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