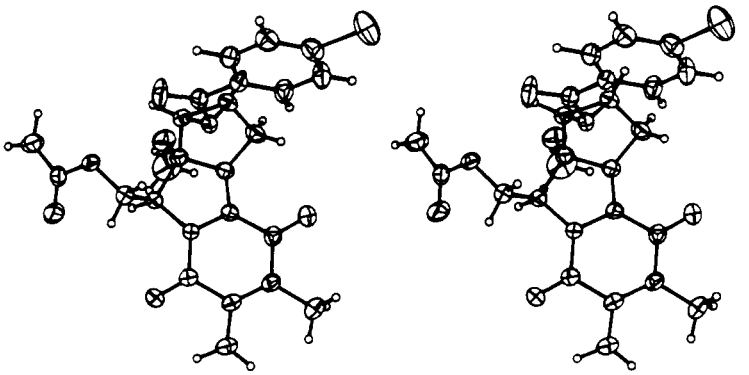

Figure 3. Stereoview of the molecule.

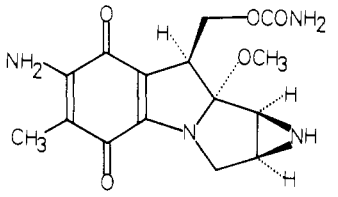

Figure 4. Revised absolute configuration of mitomycin C.

cleavage of C–C and C–N bonds of the amino sugar during biosynthesis.[5] On the other hand, feeding experiments with L-glucosamine and D-mannosamine, both have the configuration at C2 corresponding to the reported mitomycin structures, showed evidently that they can not be incorporated as a precursor of the C6 unit (Figure 2).[6] These results raised serious doubt on the reported stereochemistry, and we have tried reinvestigation of the problem. In this communication we report the determination of the absolute configuration of 1-*N*-(*p*-bromobenzoyl)mitomycin C by X-ray analysis.

The title compound was recrystallized from water–ethanol. Large hexagonal prismatic crystals of the compound belong to the hexagonal space group $P6_5$, with $a = 13.534$ (1) Å, $c = 21.146$ (2) Å, $V = 3355$ Å^3, and $Z = 6$. Intensities of 2356 reflections with $2\theta < 150°$ were measured on a Nonius CAD-4 automatic diffractometer, using graphite-monochromated Cu Kα radiation and employing ω–2θ scan technique. Out of the total, 2097 reflections were considered observed on the basis that $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization factors.

The structure was solved by direct methods using MULTAN 11/82.[7] The phases of 255 reflections with $|E_o| > 1.56$ were assigned. The best set of phases was used to calculate an E map, which gave the location of Br atom and six aromatic carbon atoms of the *p*-bromobenzoyl group. The 26 other nonhydrogen atoms were located from the successive difference Fourier synthesis. The structural parameters were refined by full-matrix least squares with the CAD-4 structure determination package.[8] The position of H atoms were calculated geometrically. They were included in the calculation of structure factors, but not refined. The final refinement converged to an R factor of 0.0361 for 2097 observed reflections.

The absolute configuration was determined by the Bijvoet difference method. The structure was independently refined with the atoms in both enantiomorphic configurations, the f' and f'' values for C, N, O, and Br were taken from "International Tables for X-ray Crystallography".[9] Twenty-one reflections with F_{calcd} differing significantly at the end of the two refinements were remeasured with great care. The signs of ΔF_{calcd} and ΔF_{obsd} are the same for 20 reflections. The final R factors, 0.0361 and 0.0401, also justified the configuration on a basis of Hamilton's R factor test.[10] Figure 3 shows a stereoscopic drawing of the molecule.

Our result corresponds to the enantiomer of the stereochemistry reported previously, and the configurations at C1, C2, C9a, and C9 are *S*, *S*, *R*, and *S*, respectively. Thus the absolute configuration of mitomycin C, at least, must be revised as shown in Figure 4. Although we can not clearly trace out the reasons that led to the wrong absolute configurations in the analyses by Tulinsky et al.[1] and Yahashi et al.,[2] the high R values of both analyses seem to be responsible for them. We are now undertaking the redetermination of the absolute configuration of mitomycin A by X-ray analysis. The result and the details of the present work will be published in the near future.

Acknowledgment. We thank Kazuo Yamaguchi, Tokyo Research Laboratories, Kyowa Hakko Kogyo Co., Ltd., for providing the crystals.

Registry No. 1-*N*-6-Bromobenzoyl)mitomycin C, 87729-17-7; mitomycin C, 50-07-7.

Supplementary Material Available: Listings of structural parameters and structure factors (25 pages). Ordering information is given on any current masthead page.

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Carbon–Carbon Bond Formation by Light-Assisted B_{12} Catalysis. Nucleophilic Acylation of Michael Olefins[1]

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1,4-Dioxo compounds are valuable precursors for the synthesis of cyclopentanoids and furanoids.[2] 1,4-Dioxo compounds may

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Table I. Synthesis of 4-Oxo Aldehydes, Ketones, Esters, and Nitriles (1) by Vitamin B_{12} Catalyzed Reductive Acylation of Activated Olefins (3) with Anhydrides (2)[a-e]

entry	anhydride (2) R^1	activated olefin (3) R^2	R^3	R^4	Z	product 1[f]	molar ratio 2:3:catalyst	yield[g]
1	CH_3	H	H		CHO	$CH_3COCH_2CH_2CHO$	1.2:1:0.02	47
2	n-C_7H_{15}	H	H			n-$C_7H_{15}COCH_2CH_2CHO$	1:10:0.02	71
3	CH_3	H	(E) CH_3			$CH_3COCH(CH_3)CH_2CHO$	1.3:1:0.02	50
4	n-C_7H_{15}	H	(E) CH_3			n-$C_7H_{15}COCH(CH_3)CH_2CHO$	1.4:1:0.1	80
5	CH_3	CH_3	H			$CH_3COCH_2CH(CH_3)CHO$	1.4:1:0.03	34
6	CH_3	CH_3	(E) CH_3			$CH_3COCH(CH_3)CH(CH_3)CHO$[h]	2.3:1:0.05	30
7	CH_3	H	H	CH_3	CR^4O	$CH_3COCH_2CH_2COCH_3$	1:4:0.04	63
8	n-C_6H_{13}	H	H	CH_3		n-$C_6H_{13}COCH_2CH_2COCH_3$	2:1:0.10	55
9	CH_3	H	$-(CH_2)_2-$			3-acetylcyclopentanone	1:2:0.04	42
10	CH_3	H	$-(CH_2)_3-$			3-acetylcyclohexanone	1:2:0.04	40
11	CH_3	H	H		$COOCH_3$	$CH_3COCH_2CH_2COOCH_3$	1.5:1:0.05	70, 55[b]
12	CH_3	H	(E) CH_3		$COOC_2H_5$	$CH_3COCH(CH_3)CH_2COOC_2H_5$	2:1:0.07	80, 50[b]
13	C_6H_5	H	H		CN	$C_6H_5COCH_2CH_2CN$	1:1:0.10	55, 50[b]
14	CH_3	H	H			$CH_3COCH_2CH_2CN$	1:2:0.04	60, 30[b] 50,[c] 60,[d] 30[e]

[a] Solutions of vitamin B_{12a} (0.2 mmol), anhydride (2), and olefin (3) (in the indicated molar ratio) in 20 mL of electrolyte (0.3 N $LiClO_4$ in DMF) were electrolyzed at a constant potential of −0.95 V (vs. SCE) in a divided (H-type) cell at a stirred Hg-pool cathode under Ar at room temperature upon irradiation with two 500-W unfocused incandescent bulbs at 30-cm distance for 10–15 h. Products 1 were isolated by extraction with ether or pentane, followed by column chromatography on silica gel. [b] See *a* but controlled-potential electrolysis at −1.5 V (vs. SCE) in the dark. [c] See *a* but Br_2[1-HO-8H-HDP]Co^{III}[8] (0.2 mmol) as catalyst. [d] See *a* but carbon felt (Sigratherm KFA) as cathode material. [e] A suspension of vitamin B_{12a} (0.4 mmol), acetic anhydride (50 mmol), acrylonitrile (75 mmol), and zinc dust (80 mmol, activated by subsequent washing with 1 N HCl, water, DMF) was stirred in the dark under Ar at room temperature over night and worked up as usual. [f] Constitution confirmed by spectral and elemental analysis. The optical rotation of products (entries 3, 4, 5, 6, 9, 10, and 12) have been determined to be zero. [g] Yield of isolated pure product, calculated with respect to starting material 2 or 3 not in excess. Where not indicated the yields refer to method *a*. [h] Mixture of diastereomers.

be obtained by Michael addition of acyl anion equivalents to activated olefins.[3] Although several methods have been reported for the synthesis of 1,4-diketones, there is still demand for a general and mild procedure for the preparation of the more sensitive 4-oxo aldehydes.[4]

Here we report a novel one-step synthesis of 4-oxo aldehydes, ketones, esters, and nitriles (**1**) from the corresponding carboxylic anhydrides (**2**) and activated olefins (**3**). The procedure consists in the electrochemical or chemical reduction of a mixture of **2** and **3** in dimethylformamide under irradiation with visible light in the presence of catalytic amounts of vitamin B_{12a}[5] or related cobalt complexes[6] (eq 1).

$$\underset{\mathbf{2}}{(R^1CO)_2O} + \underset{\mathbf{3}}{R^3HC{=}CR^2Z} \xrightarrow[\text{DMF, } B_{12}]{e^-,\ h\nu} \underset{\mathbf{1}}{(R^1CO)R^3HC{-}CHR^2Z} + R^1COO^- \quad (1)$$

Z = electron-withdrawing group: CHO, CR^4O, $COOR^5$, CN

The Co catalyst allows reductive coupling to take place at a reduction potential at which neither compound **2** or **3** nor a mixture of both undergoes a reaction.[7] The reduction potential of the electron source has to be −0.95 to −1.0 V (vs. SCE) on irradiation of the solution with visible light[8] or −1.5 to −2.0 V (vs. SCE) when working in the dark. The electron source might consist of the cathode (mercury pool or carbon) in controlled potential electrolysis or a chemical reducing agent such as activated zinc dust. Aromatic and aliphatic short- and long-chain carboxylic anhydrides (**2**) are suitable acyl derivatives; acid chlorides gave poor yields of **1**. Activated olefins (**3**) containing at least one hydrogen in the β-position[9] react regiospecifically by conjugate addition. Examples of the nucleophilic acylation of activated olefins catalyzed by vitamin B_{12} or Br_2[1-HO-8H-HDP]Co^{III}[10] are listed in Table I.

The action of the catalyst involves the formation and cleavage of a Co–C bond.[11] Macrocyclic Co(I) complexes (easily obtained by reduction of the corresponding Co(II) or Co(III) complexes at −0.8 to −1.0 V (vs. SCE)[12] are known to react with carboxylic anhydrides and other acyl derivatives to form Co(III) acyl compounds.[13] The Co–C bond of these intermediates is cleaved as a consequence of photochemical excitation by visible light or one-electron reduction at −1.4 to −1.6 V (vs. SCE) in the dark.[14] Under both conditions the acyl fragment[15] is liberated and adds to the activated olefin.[16] The reaction sequence is terminated by the transfer of a hydrogen or proton from the solvent[17] to the

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(8) Light with wavelengths λ = 400–550 nm is efficient, maximum at 470 nm.

(9) 3,3-Dimethylacrylonitrile as well as 4-cholesten-3-one have found not to be acylated at the given conditions.

(10) Full name: dibromo[1-hydroxy-2,2,3,3,7,7,8,8,12,12,13,13,17,17,-18,18-hexadecamethyl-10,20-diazaoctahydroporphinato]cobalt(III).[6]

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(15) In absence of activated olefins but in presence of protons (H_2O, CH_3COOH, or NH_4Cl) carboxylic anhydrides **2** are reduced to the corresponding aldehydes R_1CHO. In presence of activated olefins and absence of protons, conjugate addition is observed with a charge consumption corresponding to one electron per molecule **1** formed. These facts suggest that the acyl fragment might behave as potential carbanion or radical depending on the reaction conditions.

(16) Kinetic studies show that the light-induced reaction in presence of activated olefins follows second-order kinetics (fist order in acylcobalt(III) and first order in olefin). See full paper in *Helv. Chim. Acta* **1984**.

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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}.

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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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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]

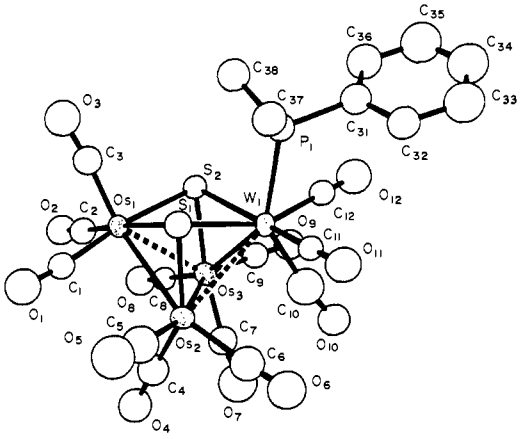

Figure 1. ORTEP diagram of $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3\text{-}S)_2$ (II) showing 50% probability thermal ellipsoids.

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, α = 87.02 (8)°, β = 83.82 (5)°, γ = 66.82 (5)°, V = 2838 (2) Å^3, Z = 4, ρ_{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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