clusters $[Cp^*M(CO)_2]_aAs_b$[11] ($a + b = 4$), the π-allyl analogue dimethyltriarsinidene complex $\{Cp^*W(CO)_2[\eta^3\text{-}(MeAsAsAsMe)]\}$[12] (eq 3), and the single-bonded carbonylated metal dimer $[Cp^*M(CO)_3]_2$[13] (eq 4) (see reaction summary, Scheme I).[14]

The structures of **1** and **2** were determined by single-crystal X-ray diffraction.[15] **1** is a neutral organometallic analogue of the well-known hexatungstate $W_6O_{19}{}^{2-}$ structure,[5a] in which two O^{2-} have been replaced (formally) by two Cp^{*-}. Bond distances for **1** reveal extensive distortion of the prototype $W_6O_{19}{}^{2-}$ structure; the W–μ_6O distances occur in three sets: Cp*W–O(3), 2.204 (13) Å; W(3)–O(3), 2.355 (2) Å; and W(2)–O(3), 2.502 (15) Å. This compares to the W–μ_6O bond distances of ca. 2.33 Å in several $W_6O_{19}{}^{2-}$ structures.[16] The variations in the W–μ_6O distances in **1** are comparable to those seen in the heteropolytungstate $[CpTiW_5O_{18}]^{3-}$, in which the bond trans to the substituted metal atom is lengthened.[5b] **1** is sparingly soluble in polar solvents; the Cp* ^{1}H NMR signal (δ 2.611 ppm) is unusually deshielded and in keeping with the abnormally long average W–C_{ring} distance, 2.41 (3) Å.

The octamolybdenum cluster **2** is joined about its inversion center by two d^1 molybdenum(V) atoms which are each capped by three μ_3-O bridges to a trigonal base of equivalent Cp*-coordinated molybdenum atoms. Assignment of oxidation state for Mo(4) was made by comparison of bond distances in **2** to other Mo^V and Mo^{VI} structures.[9,10] The Cp*-coordinated molybdenum atoms are assigned an average formal oxidation state of $4^2/_3$; an absence of charge localization is suggested by the close similarities in the three Cp*Mo coordination spheres. The structure of **2** is unlike the open network of the large anionic polymolybdates that have been studied as either thermal or photolytic oxidation catalysts.[17] A closer structural analogy is that of the oxo-bridged condensed vanadium clusters (e.g., $[Cp_5V_6(\mu_3\text{-}O)_8]_2(\mu\text{-}O)$ and $[Cp_5V_6(\mu_3\text{-}O)_8]_2[(\mu_2\text{-}O_8)V_4Cp_4])$ synthesized by Bottomley and co-workers.[18]

The synthesis of **2** from crystalline $(CH_3AsO)_4$ implicates the arsaoxane as the oxidant in these reactions. Following initial arsaoxane coordination, rapid cleavage of the heterocyclic ring and transfer of oxygen to the metal center occur to form Mo^{VI} and Mo^V–oxo clusters. Evidence for initial arsaoxane coordination comes in reactions of both $Mo(CO)_6$[19] and $Mn_2(CO)_{10}$[20] systems, in which intact, but expanded, arsaoxane systems coordinate as 12- and eight-membered rings, respectively. Reduction of the arsaoxanes to the precursor cycloorganopolyarsines allows for further reaction with either $[Cp^*M(CO)_2]_2$ or $[Cp^*M(CO)_3]_2$ to produce the tetrahedrane-analogue and π-allyl-analogue compounds.

Synthetic routes to, and the structure and bonding modes of, high-oxidation-state metal clusters are generally not well-developed,[21] and further reactions are planned to assess the applicability of this system to other transition metals.

Acknowledgments. The donors of the Petroleum Research Fund, administered by the American Chemical Society, and the donors of the Center for Catalytic Science and Technology (University of Delaware) are thanked for their partial support of this research.

Supplementary Material Available: Details of the structural characterizations of **1** and **2**, including tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (10 pages); tables of observed and calculated structure factors for **1** and **2** (56 pages). Ordering information is given on any current masthead page.

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(8) Preparation of **1**: $[Cp^*W(CO)_2]_2$ (0.30 g, 0.40 mmol) was dissolved in 15 mL of a dry, degassed toluene solution containing 0.217 g (0.48 mmol) of pentamethylcyclopentaarsine (containing 25% arsaoxane) in a sealed tube and heated at 170 °C for 22 h. Yellow-brown, needle-shaped crystals were separated by filtration: 42% yield; mp = 300–305 °C; ^{1}H NMR (CD_3CN) Cp* 2.611 ppm; IR (KBr) ν 984 (s), 853 (m, sh), 816 (vs, br), 785 (vs), 436 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{30}O_{17}W_6$: C, 14.60; H, 1.84. Found: C, 14.99; H, 2.10. Preparation of **2**: $[Cp^*Mo(CO)_2]_2$ (0.50 g, 0.87 mmol) and $(CH_3As)_5$ (0.78 g, 1.74 mmol) were reacted as described above at 150 °C. Dark green insoluble crystals were separated by filtration: 22% yield; mp = 437–440 °C; IR (KBr) ν 1025 (s), 1013 (m, sh), 930 (vs), 911 (sh), 733 (m), 656 (m), 608 (vs, br), 525 (m) cm^{-1}. Alternate preparation of **2**: $[Cp^*Mo(CO)_2]_2$ (0.458 g, 0.797 mmol) and $(CH_3AsO)_4$ (0.065 g, 0.154 mmol) were reacted as described above at 150 °C. Anal. Calcd for $C_{60}H_{90}O_{16}Mo_8$: C, 39.28; H, 4.94. Found: C, 38.20; H, 4.76.

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(15) **1**: $C_{20}H_{30}O_{17}W_6$; monoclinic, $C2/c$, $a = 8.905$ (3) Å, $b = 18.285$ (8) Å, $c = 18.638$ (7) Å, $\beta = 98.97$ (3)°, $V = 2998$ (2) Å^3, $Z = 4$, D(calcd) = 3.65 g cm^{-3}, $T = 23$ °C, $R(F) = 5.95\%$, $R(wF) = 6.21\%$. **2**: $C_{60}H_{90}O_{16}Mo_8$; triclinic, $P\bar{1}$, $a = 11.240$ (2) Å, $b = 11.349$ (3) Å, $c = 15.598$ (3) Å, $\alpha = 70.31$ (2)°, $\beta = 82.19$ (2)°, $\gamma = 60.05$ (1)°, $V = 1622.0$ (6) Å^3, $Z = 1$, D(calcd) = 1.88 g cm^{-3}, $T = 23$ °C, $R(F) = 2.71\%$, $R(wF) = 3.15\%$.

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Unusual C,O-Bridging Coordination of Acetate and Acetylacetonate Ligands in the Platinum Clusters $[Pt^{III}{}_2(\mu\text{-}CH_2COO\text{-}C,O)_2(\mu\text{-}CH_3COO\text{-}O,O')_2Cl_2]^{2-}$ and $Pt^{II}{}_4(\mu\text{-}CH_3COO\text{-}O,O')_4(\mu\text{-}CH_3COCHCOCH_3\text{-}O,C^3)_4$

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While studying the preparation and properties of platinum cluster compounds with acetate as a ligand,[1] we have found two new compounds, given in the title. These Pt–Pt-bonded compounds have acetate or acetylacetonate ligands which bridge between two platinum ions through an oxygen and a carbon atom. Although platinum ions tend to take on a Pt–C-bonded structure, such C,O-bridging modes are to the best of our knowledge unprecedented for these ligands.[2,3]

Platinum(III) dimers with a Pt–Pt single bond are known for various bridging ligands including sulfate and phosphate,[4–6] but

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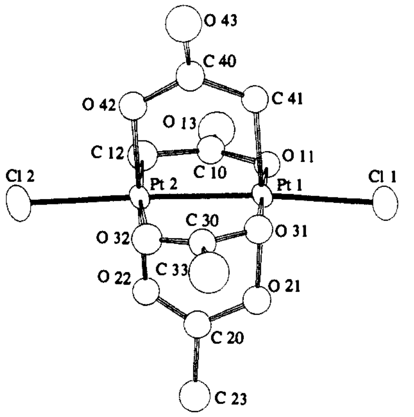

Figure 1. Structures of $[\mathrm{Pt^{III}}_2(\mu\text{-}\mathrm{CH_2COO}\text{-}C,O)_2(\mu\text{-}\mathrm{CH_3COO}\text{-}O,O')_2\mathrm{Cl_2}]^{2-}$ in **1** showing the 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt–Pt = 2.451 (1); Pt–C = 2.01 (2), 2.02 (3); Pt–O (trans to O) = 1.97 (2) – 2.03 (2); Pt–O (trans to C) = 2.18 (2), 2.21 (2); Pt–Cl = 2.46 (1), 2.42 (1); Pt–Pt–Cl = 175.4 (2), 177.5 (2); Pt–C–C (within the chelate ring of C-bonded acetate) = 117.92 (19), 115.83 (19).

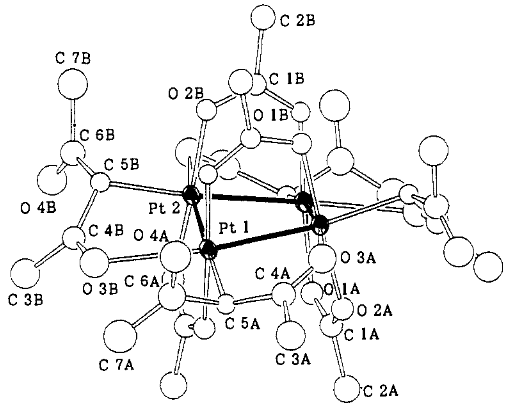

Figure 2. Structures of $\mathrm{Pt^{II}}_4(\mu\text{-}\mathrm{CH_3COO}\text{-}O,O')_4(\mu\text{-}\mathrm{CH_3COCHCOCH_3}\text{-}O,C^3)_4$ (**2**) showing the 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt–Pt = 2.578 (1), 2.595 (1); Pt–O(acetate) = 2.01 (2) – 2.03 (2); Pt–O(acac) = 2.48 (2), 2.57 (2); Pt–C(acac) = 2.09 (2), 2.14 (2); Pt–Pt–Pt = 87.37 (4); Pt–O–C(acac) = 111.9 (16), 117.0 (19); Pt–C–C(within the chelate ring of acac) = 111.1 (15), 119.5 (15).

the most commonly known tetra(μ-acetato) analogue[7] has not been reported previously. The new "tetra(acetato)–diplatinate(III)" complex has been isolated as a cesium salt, $\mathrm{Cs_3[Pt_2(CH_2COO)_2(CH_3COO)_2Cl_2]Cl\cdot 3H_2O}$ (**1**).[8] The ^{13}C NMR spectrum of **1** in $\mathrm{D_2O}$ revealed that the complex contains two types of "acetate" ligands, one of which appears at fairly higher magnetic field with a large $J_{\mathrm{Pt-C}}$ coupling constant.[8] The ^{1}H NMR spectrum shows a sharp $\mathrm{CH_3}$ signal at 2.26 ppm and an AB quartet centered at 3.69 ppm in an approximately 2:3 integrated intensity ratio.[8] The X-ray structure of the complex cation (Figure 1)[9] is superficially similar to those of common tetra(acetato)dimetal complexes. These NMR data strongly suggest, however, that two of the four bridging ligands coordinate with a carbon and an oxygen atom rather than take the O,O′-bridging mode. The X-ray structure is fully consistent with the NMR data by assignment of ligand bonds of ca. 1.5 Å and ca. 1.3 Å to C–C and C–O bonds, respectively. The two "$\mathrm{CH_2COO^{2-}}$" ligands are mutually cis, and each Pt atom is coordinated by one carbon and three oxygen atoms as well as one apical $\mathrm{Cl^-}$ ion. The Pt–Pt distance (2.451 Å) is the shortest ever observed for Pt(III) dimers.[1,4–6,10] A trans influence from the Pt–C bond is apparent, with Pt–O bonds trans to Pt–C longer by ca. 0.2 Å than those cis to Pt–C bonds. Other known Pt–C-bonded Pt(III) dimers are a series of the complexes with Pt–$\mathrm{CH_3}$ bonds ($\mathrm{[Pt_2(CH_3COO)_2(CH_3)_4(py)_2]}$ and its analogues).[10]

The octa(acetato)tetraplatinum(II) complex is unique in that the four platinum(II) ions take on a square-planar arrangement with four Pt–Pt single bonds.[11] We recently reported that in-plane acetates are labile and easily replaced by other carboxylate ligands.[1] Such a facile regioselective substitution of $\mathrm{Pt_4(CH_3COO)_8}$ with acetylacetonate ions ($\mathrm{acac^-}$) gave a new tetrakis(acetylacetonato) complex, $\mathrm{Pt_4}(\mu\text{-}\mathrm{CH_3COO})_4(\mu\text{-acac})_4$ (**2**).[12] X-ray structural analysis disclosed that the acetylacetonate ions bridge between two platinum ions through an oxygen and a central γ carbon (Figure 2).[13] Pt–Pt bond lengths are somewhat longer than those in octa(acetato) (2.50 Å)[11] and tetrakis(acetato)tetrakis(trichloroacetato) complexes (2.49 Å).[1] The Pt–O(acac) bond is fairly long (2.5 Å). Nevertheless, ^{1}H and ^{13}C NMR spectra

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(8) Preparation of complex **1**: $\mathrm{K_2PtCl_4}$ (2 g) and 3.2 g of $\mathrm{CH_3COOAg}$ in 100 cm^3 of $\mathrm{CH_3COOH{-}H_2O}$ (10:1) were refluxed for 3–4 h. Black solid was removed by filtration at room temperature, and the filtrate was evaporated to ca. 5 cm^3. To the concentrate was added 50 cm^3 of concentrated HCl, and the solution was kept at 50 °C for 1 h. After evaporation to dryness, the residue was extracted by 20 cm^3 of water and treated with Dowex 1-X2 column after dilution to 500 cm^3 by water. The yellow eluate in 2 M HCl was evaporated after addition of ca. 500 mg of CsCl, to give a yellow solid of **1**, which was recrystallized from water: yield, ca. 5%. Anal. Calcd: C, 8.11; H, 1.35; Cl, 9.00. Found: C, 8.07; H, 1.04; Cl, 8.73. Electronic absorption maxima in $\mathrm{H_2O}$: 372 nm (ϵ/M^{-1} cm^{-1}, 780), 436 (90). NMR data (JEOL JNM-GSX-270 FT-NMR spectrometer) in $\mathrm{D_2O}$: ^{1}H, 3.69 ppm (q, 2 H, CH_2), 2.26 (s, 3 H, CH_3); ^{13}C{^{1}H}, 190.37, 189.07 (C=O), 22.30 (CH$_3$, $^2J_{\mathrm{Pt-C}}$ = 53 Hz), 6.80 (CH$_2$, $^1J_{\mathrm{Pt-C}}$ = 665 Hz); ^{195}Pt{^{1}H}, 905 ppm vs $\mathrm{[PtCl_4]^{2-}}$ at $\delta = 0$.

(9) X-ray analysis of **1**: Compound **1** crystallizes in the monoclinic space group $P2_1/n$, with a = 13.668 (7) Å, b = 19.319 (8) Å, c = 8.958 (9) Å, β = 101.28 (6)°, V = 2319.7 (28) Å^3, Z = 4. With the use of 4794 unique reflections ($F_o > 3\sigma(F_o)$) collected at room temperature with Mo Kα (λ = 0.71069 A) radiation up to $2\theta = 60°$ on a Rigaku AFC-6A diffractometer, the structure was solved by the heavy-atom method and refined by block-diagonal least squares with anisotropic temperature factors for metal and chlorine atoms to a final R value of 0.078.

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(12) Preparation of complex **2**: $\mathrm{Pt_4(CH_3COO)_8}$ (200 mg) in 20 cm^3 of Hacac–$\mathrm{CH_2Cl_2}$ (2:1) was slowly evaporated at 60 °C. Addition of Hacac–$\mathrm{CH_2Cl_2}$ and evaporation were repeated until all the starting material reacted, to give red oil. This was purified by the use of a silica gel column, and **2** was isolated by evaporating from orange eluate in $\mathrm{CH_3CN}$: yield, ca. 10%. Anal. Calcd: C, 23.27; H, 2.81. Found: C, 23.80; H, 2.83. Electronic absorption maximum in $\mathrm{CH_3CN}$: 288 nm (ϵ/M^{-1} cm^{-1}, 30 500). NMR data (JEOL JNM-GSX-270 FT-NMR spectrometer) in $\mathrm{CDCl_3}$: ^{1}H, 6.13 ppm (s, 1 H, CH), 2.44 (s, 3 H, CH_3(acac)), 2.29 (s, 3 H, CH_3(acac)), 1.89 (s, 3 H, CH_3(acetate)); ^{13}C{^{1}H}, 215.17 (COCH$_3$), 208.34 (COCH$_3$), 191.66 (CH$_3C$OO), 43.86 (CH), 32.61 (CH$_3$CO), 32.25 (CH$_3$CO), 23.70 (CH$_3$COO); ^{195}Pt{^{1}H}, 194 ppm vs $\mathrm{[PtCl_4]^{2-}}$ at $\delta = 0$.

(13) X-ray analysis of **2**: Compound **2** crystallizes in the tetragonal space group $P4_12_12$, with a = 9.644 (1) Å, c = 38.158 (9) Å, V = 3548.7(12) A^3, Z = 4. With the use of 2650 unique reflections ($F_o > 3\sigma(F_o)$) collected at room temperature with Mo Kα (λ = 0.71069 Å) radiation up to $2\theta = 60°$ on a Rigaku AFC-5R diffractometer equipped with a rotating anode (40 kV, 200 mA), the structure was solved similarly as **1**. The final R value is 0.061.

in CD_3CN clearly discriminate between the two types of $COCH_3$ groups within the acac ligand, and the Pt–O bond does not break, even at 70 °C. Lengthening of the Pt-O bond may be caused by the trans influence of the Pt-C bond across the Pt-Pt bond. Such a trans influence has been reported for some Pt(III) dimers.[10b,14]

The present two complexes further indicate that platinum(II) and platinum(III) states prefer to form a Pt–C bond where possible and that platinum complexes will provide further an interesting field even for cluster complexes in the border of classical coordination and organometallic chemistry.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 01612001) on Priority Area of "Dynamic Interactions and Electronic Processes of Macromolecular Complexes" and a Grant-in-Aid for Scientific Research (No. 01430009) from the Ministry of Education, Science and Culture, Japan. We are grateful to Professors Hiroshi Ogino and Mamoru Shimoi and Dr. Chizuko Kabuto for the measurements of the X-ray reflection data.

Supplementary Material Available: Tables of crystallographic data and details of the structural determination, atomic positional and thermal parameters, and interatomic distances and bond angles for **1** and **2** (5 pages); tables of observed and calculated structure factors for **1** and **2** (6 pages). Ordering information is given on any current masthead page.

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Proposal for Blending Classical and Biradical Mechanisms in Antitumor Antibiotics: Dynemicin A

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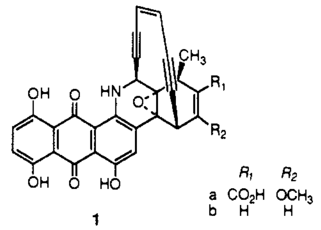
Recently isolated antitumor antibiotics are proving to be extraordinary for their exceptional potency, unusual enediyne bicyclic structures, and remarkable biradical DNA cleaving mechanisms. The glycosylated esperamicin,[1,2] calicheamicin[3,4] and neocarzinostatin[5,6] variations were the first families extracted from widely dispersed soil samples. This year a Bristol-Myers/Cornell team presented another theme with the isolation and structure elucidation of dynemicin A, **1a**.[7] The violet compound combines the enediyne moiety and the classical anthracycline quinone chromophore. Sandwiched between the two funtionalities is a tetra-substituted epoxide.

Several questions beg for resolution. If the compound disables DNA similar to its natural enediyne congeners, which end of the molecule carries the weaponry? Can the two ends act in concert through a common trigger? What mechanistic intermediates are consistent with the actions of other antitumor antibiotics?



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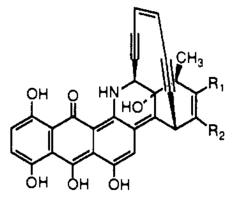
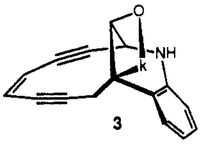


2

Computational methodology offers insights into and projections beyond these issues.

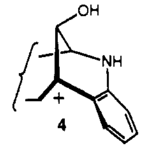
The force field predicted structure of dynemicin A (**1a**) is shown in Figure 1. The calculation assumes hydrogen bonding in the anthraquinone fragment leading to planarity for the extended π-system. Geometric features resemble previous enediyne X-ray structures:[8-13] r(acetylene C---C) = 3.66 Å; $C\equiv C-C$ bonds are bent with predicted angles ranging from 162 to 169 °C. The molecule is an almost perfect right-angled elbow. Perched atop the bicyclic extension of the anthraquinone fragment, the epoxide ring is poised for interaction with the aromatic framework. Nothing has been reported concerning the ability of dynemicin to cleave DNA, but the compound exhibits potent antibacterial activity and extends the life span of mice inoculated with leukemia.[7] If as in neocarzinostatin the epoxide opening is a trigger for biradical formation and subsequent DNA damage,[14-17] two extreme mechanisms for ring opening are suggested: acid-catalyzed ring rupture or base-catalyzed deprotonation of the hydroquinone two-electron-reduction product[18] (**10**, Figure 2) accompanied by simultaneous epoxide cleavage to give **2a**. Both are stereoelectronically favored by the flat architecture of **1** to stabilize a carbocation or a $C{=}C$ double bond, respectively.

The acid-promoted cationic route was evaluated with structures **3–6** by the MM2//PRDDO protocol for calculating ΔE^*(TS–GS) described previously.[13,19]



3

k = (CH2)n, n = 0-3



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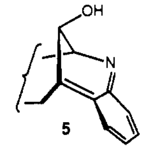

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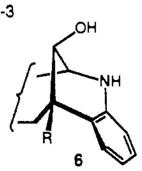
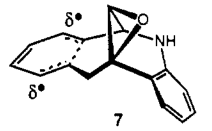


6



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