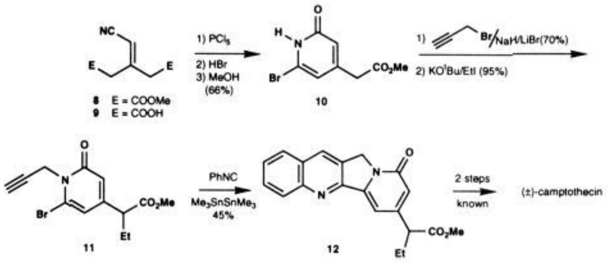
diacid was first treated with PCl_5, and then gaseous HBr (10 equiv) was introduced. After addition of methanol, workup, and purification, we isolated **10** in 66% yield. N-Propargylation (70%) and C-ethylation[15] (95%) then gave the precursor **11** for the 4 + 1 annulation. Reaction of **11** with phenyl isocyanide as described above gave pure **12** in 45% isolated yield. Compound **12** was first prepared by Danishefsky,[16] and it has been a key intermediate in many syntheses of camptothecin.[2] Conversion of **12** to (±)-camptothecin is accomplished in two steps: hydroxymethylation (35%) and oxidation (quantitative).[2,16]



(2)

This synthesis of the key Danishefsky tetracycle **12** requires only six steps starting from dimethyl acetonedicarboxylate, and the overall yield is currently 13%. There is still room for improvement. We plan to use this synthesis as a starting point for further work in the camptothecin area.

Acknowledgment. We thank the National Institutes of Health for funding of this work.

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Tridecavanadate, $[V_{13}O_{34}]^{3-}$, a New High-Potential Isopolyvanadate

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There has been considerable recent research activity on polynuclear high-valent vanadium species in biochemistry,[1,2] sol–gel chemistry,[3] layered or intercalated materials and catalysts,[4,5] and sensor technology.[3,6] Very recently several elegant examples of polyvanadates have been reported by the groups of Klemperer and Day,[7,8] Huan and Jacobsen,[9] and Müller.[10,11] Nearly all of these

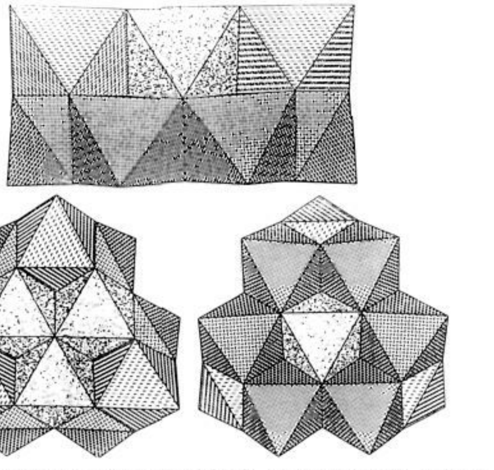

Figure 1. Polyhedral representation of VO_6 components of **1**, oxygens at vertices surrounding the V. Top: side view showing alternating O layers, 2.21 Å between middle and top and bottom parallel planes. Lower left: "top" view showing $V(c)O_6$ and $V(b')O_6$ units with O_{10} plane and three O_9 edges. Lower right: "bottom" view showing $V(a)O_6$ in the center of six $V(b'')O_6$ units with O_{12} plane and three O_6 edge faces.

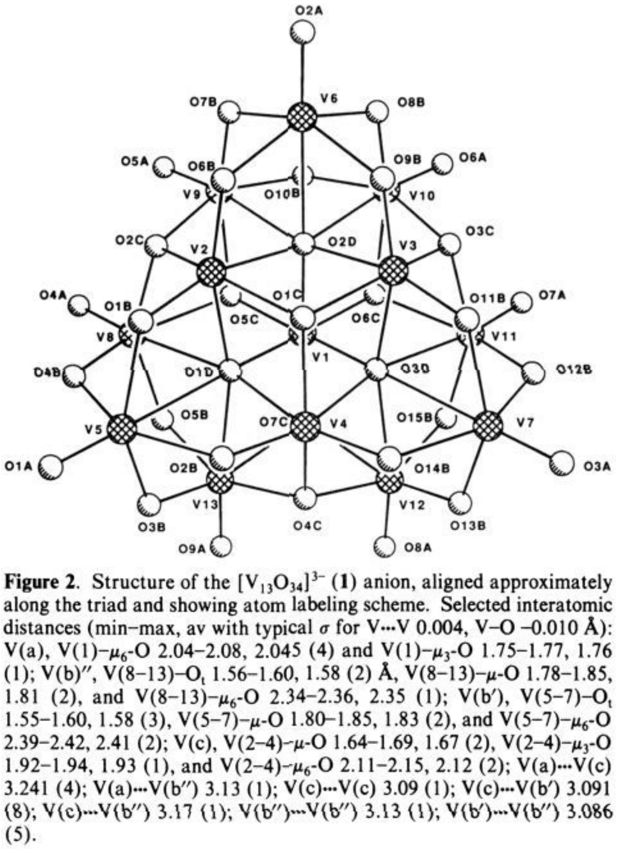

Figure 2. Structure of the $[V_{13}O_{34}]^{3-}$ (**1**) anion, aligned approximately along the triad and showing atom labeling scheme. Selected interatomic distances (min–max, av with typical σ for V···V 0.004, V–O ~0.010 Å): V(a), V(1)–μ_6-O 2.04–2.08, 2.045 (4) and V(1)–μ_3-O 1.75–1.77, 1.76 (1); V(b)″, V(8–13)–O_t 1.56–1.60, 1.58 (2) Å, V(8–13)–μ-O 1.78–1.85, 1.81 (2), and V(8–13)–μ_6-O 2.34–2.36, 2.35 (1); V(b′), V(5–7)–O_t 1.55–1.60, 1.58 (3), V(5–7)–μ-O 1.80–1.85, 1.83 (2), and V(5–7)–μ_6-O 2.39–2.42, 2.41 (2); V(c), V(2–4)–μ-O 1.64–1.69, 1.67 (2), V(2–4)–μ_3-O 1.92–1.94, 1.93 (1), and V(2–4)–μ_6-O 2.11–2.15, 2.12 (2); V(a)···V(c) 3.241 (4); V(a)···V(b″) 3.13 (1); V(c)···V(c) 3.09 (1); V(c)···V(b′) 3.091 (8); V(c)···V(b″) 3.17 (1); V(b″)···V(b″) 3.13 (1); V(b′)···V(b″) 3.086 (5).

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new complexes involve connected VO_5 square pyramids, and their structures, many of which provide inclusion possibilities, can be viewed as derived from partially broken and reassembled V_2O_5 sheets.[8] We have sought new polyvanadates with high potentials and highly condensed and compact structures, principally because they should facilitate the direct thermal oxidation of the greatest range of organic compounds and materials and exhibit a capacity for multielectron reduction, which could form the basis of polyvanadate films with simultaneous photoresist and plasma etching barrier capabilities. We report here the thermal synthesis and properties of the new title complex, $[V_{13}O_{34}]^{3-}$ (**1**), which constitutes the third member of a four-component series of maximally condensed group 5 isopolyanions of increasing nuclearity and decreasing charge, of which only the first two had been reported, the classical hexametalate, $[M_6O_{19}]^{8-}$ (M = Nb, Ta), and decavanadate, $[M_{10}O_{28}]^{6-}$ (M = V, Nb), structures. Successive capping of two adjacent μ_3-O of $[M_{10}O_{28}]^{6-}$ with $((\mu\text{-O})M{=}O)_3$ units affords the final two members of the series, $[M_{13}O_{34}]^{3-}$ (tridecavandate) and the neutral T_d complex, $M_{16}O_{40}$, which has yet to be reported.

Whereas refluxing $(n\text{-}Bu_4N)_4[H_2V_{10}O_{28}]$ in acetonitrile for 1-2 min produces the inclusion complex, $[CH_3CN\cdot(V_{12}O_{32}^{4-})]$,[7a] refluxing $(n\text{-}Bu_4N)_3[H_3V_{10}O_{28}]$ in acetonitrile (26 mM) for ~7 h under dry nitrogen produces the $(n\text{-}Bu_4N)^+$ salt of the new isopolyvanadate, **1**.[12] Single crystals, grown slowly from acetonitrile under diethyl ether atmosphere, were suitable for X-ray crystallography.[13]

Tridecavanadate, **1**, is a highly condensed polyoxoanion exhibiting a layered structural motif with apparent, but not crystallographically imposed, C_{3v} symmetry (Figures 1 and 2).[14] The aggregate is bound by close-packed arrays of six (three edges), nine (three sides), ten (top), and twelve (bottom, Figure 1) oxygens which lie at the vertices of distorted VO_6 octahedra. A central layer of 12 oxygens separates V_7 and V_6 layers. The V_7 layer consists of a new type of coordination for V (type a, V(1)) in which the V is bonded to three μ_3-O (O(5C-7C)) and three μ_6-O (O-(1D-3D)) atoms and surrounded by six V (type b″, V(8)-V(13)) connected to one terminal O (O_t), four μ-O, and one μ_6-O. The V_6 layer consists of a set of three V (type c, V(2)-V(4)) atoms each connected to two μ-O, two μ_3-O, and two μ_6-O and flanked by three V (type b′, V(5)-V(7)) connected to one O_t, four μ-O, and 1 μ_6-O.

Table I. Cyclic Voltammetry and Negative Charge Densities of $[V_{13}O_{34}]^{3-}$ (**1**) and Other Redox-Active Polyoxometalates[a]

complex[b]	E^f, V, ($i_{pc} - i_{pa}$, mv), [n][c]		negative charge density per atom[d]
	Polyvanadates		
1	0.228 (55) [1]	−0.664 (61) [1]	0.064
$[CH_3CN\cdot(V_{12}O_{32}^{4-})]$[e]	−0.52		0.091
$Q_3H_3V_{10}O_{28}$	−0.643 (160)[f]		0.158[g]
	Polymolybdates		
$Q_3PMo_{12}O_{40}$	−0.258 (65) [1]		0.057
$Q_2Mo_6O_{19}$	−0.911 (55) [1]		0.080
	Polytungstates		
$Q_3PW_{12}O_{40}$	−0.769 (65) [1]	−1.289 (75) [1]	0.057
$Q_4W_{10}O_{32}$	−1.369 (65) [1]	−1.929 (65) [1]	0.095

[a] Glassy carbon disk working electrode (BAS), Pt wire counter electrode, and Ag/0.01 M $AgNO_3$ reference electrode in CH_3CN; supporting electrolyte, 0.1 M $(TBA)PF_6$, 1-2 mM solutions of polyoxometalates in CH_3CN at 25 °C, 100 mV/s sweep rate. [b] Q = $n\text{-}Bu_4N^+$. [c] E^f = formal potential = $(i_{pc} + i_{pa})/2$ before parentheses and reported relative to F_c^+/F_c; peak-to-peak separation in millivolts inside parentheses; n = number of electrons, inside brackets. [d] Total negative charge on the molecule/total number of atoms in the polyoxoanion. [e] Value from ref 7a. [f] Irreversible reduction wave. [g] Based on $[V_{10}O_{28}]^{6-}$, not $[H_3V_{10}O_{28}]^{3-}$.

Like the other d^0 isopolyvanadates and most semiconductor metal oxides, **1** has an electronic absorption maximum in the ultraviolet (λ_{max} = 202 nm; ϵ = 20 680 M^{-1} cm^{-1}) with a monotonically decreasing absorbance tailing hundreds of nanometers to lower energy that gives **1** its yellow-brown color (ϵ at 318 nm = 3140 M^{-1} cm^{-1}). The ^{51}V NMR spectrum (131.6 MHz) of **1** (~1.5 mM in CD_3CN, 25 °C, δ relative to external neat $VOCl_3$) indicates that the solid-state structure (Figure 1) is maintained in solution: δ −332 (1 V), −452 (6 V), −497 (3 V), and −501 (3 V). **1** shows reversible or nearly reversible electrochemical and chemical redox behavior, the lowest negative charge density of any polyvanadate, and the highest potential of any monometallic isopolyoxometalate (Table I).[15] The latter point is consistent with two facts: (1) at parity of molecular structure, the d^0/d^1 potentials for the polyoxometalates, in order of the principal polyoxometalate forming elements, are W (most negative potentials) < Mo < V (most positive potentials), and (2) at parity of structure and metal composition, the lower the effective anionic charge density on the complex, which is greatly perturbed by protonation,[16,17] the more positive the potential.

Consistent with the potential, **1** can directly and thermally oxidize a number of organic substrates (S; eq 1). Reduction of **1** by triphenylphosphine (S = Ph_3P) in wet CH_3CN is stoichiometric, rapid at 25 °C, clean to triphenylphosphine oxide, and can be used to generate cleanly the corresponding one-electron-reduced complex, $[V_{13}O_{34}]^{4-}$, **2** (eq 1). The EPR of **2** (X band,

$$\underset{\mathbf{1}}{2V_{13}O_{34}^{3-}} + S + H_2O \rightarrow \underset{\mathbf{2}}{2V_{13}O_{34}^{4-}} + SO + 2H^+ \quad (1)$$

~1.5 mM in frozen CH_3CN, 20 K) shows an octet (g = 1.970; hyperfine coupling constant = 147 G) indicative of minimal electron delocalization among the 13 V atoms under these conditions. Reoxidation of **2** to **1**, eq 2, is facile in CH_3CN (rate (70 °C) = 6.705 × 10^{-4} M s^{-1}), clean with *tert*-butyl hydroperoxide, and slow with O_2 (rate(70 °C) ~1 atm O_2) = 1.429 × 10^{-5} M s^{-1}). The facility of both eqs 1 and 2 indicates that **1** should

$$2V_{13}O_{34}^{4-} + OX \rightarrow 2V_{13}O_{34}^{3-} + RED \quad (2)$$

catalyze the oxidation of organic substrates by O_2 and other oxidants (eq 3, where S = substrate, SO = oxidized product, OX = terminal oxidant, and RED = corresponding reduced form of oxidant). This is indeed the case. One exemplary reaction is

$$S + OX \xrightarrow[\text{(catalyst)}]{V_{13}O_{34}^{3-}} SO + RED \quad (3)$$

the anaerobic thermal oxidation of tetrahydrothiophene (THT)

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(12) Isolated yield = 34%. Infrared (KBr, cm^{-1}): 999 (vs), 989 (vs, sh), 858 (vs), 823 (s), 779 (s), 605 (s), 522 (m), 453 (m), 414 (w). Anal. Calcd for $C_{48}H_{108}N_3O_{34}V_{13}$: C, 29.81; H, 5.59; N, 2.17; V, 34.27. Found: C, 29.89; H, 5.46; N, 2.17; V, 34.39.

(13) Single crystal of $(n\text{-}Bu_4N)_3$**1** crystallized in the monoclinic space group $P2_1/c$ (No. 14) with a = 23.156 (6) Å, b = 11.457 (3) Å, c = 28.936 (7) Å, β = 94.02 (2)°, and Z = 4 formula units [d_{calcd}/d_{obsd} = 1.677/1.687 g cm^{-3}]. A total of 10 958 independent reflections ($2\theta_{max}$ = 45°) were collected at 175 K on a Siemens P4 diffractometer by using Mo Kα (λ = 0.71073 Å) radiation and a graphite monochromator, $\theta/2\theta$ scans. The structure was solved by direct methods, and the resulting structural parameters were refined by full-matrix least-squares refinement of 858 variables (using the Siemens SHELXTL programs) and gave final agreement factors of R = 7.19, R_w = 7.70, and GOF = 1.86 for 4906 reflections with $F > 6.0\sigma(F)$. Hydrogen atoms were fixed in idealized positions (d_{C-H} = 0.96 Å). Azimuthal scans and a small absorption coefficient indicated that the data did not require correction for absorption. One of the $n\text{-}Bu_4N^+$ cations exhibited considerable disorder.

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to the corresponding sulfoxide (THTO) by *tert*-butyl hydroperoxide (TBHP). The catalytic effect in this case (70 °C in CH_3CN): $k_{\text{catalyzed by }1}/k_{\text{uncatalyzed}} = 27$.

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Supplementary Material Available: Tables of crystal data, atom coordinates, temperature factors, and bond lengths and angles for $(n\text{-}Bu_4N)_3V_{13}O_{34}$ (20 pages); table of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Photochemical Generation and Preparative Capture of 1,2,4,5-Tetramethylenebenzene in Fluid Solution. Nanosecond Time-Resolved Spectroscopic Determination of Absolute Rates of Dimerization and Oxygen Trapping of a Disjoint Singlet Hydrocarbon Biradical

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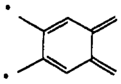
A single species, assigned as 1,2,4,5-tetramethylenebenzene (TMB, **1**), is responsible for both the CP MAS ^{13}C NMR spectrum and the UV–vis (λ_{max} = 490, 570, and 625 nm, $\epsilon \approx 4200$, 600, and 400, respectively) spectrum of matrix-immobilized preparations obtained by irradiation of the ketone **2** at 77 K.[2] The ESR spectrum observed[2,3a] under these conditions is associated with a different carrier.[2] An alternative to **1** as the carrier of the NMR signal, the bicyclic hydrocarbon **3**, was considered to be less satisfactory.[2] These data led to the assignment of a singlet spin state to the biradical **1**.[2] In contrast, the reported[3b,c] "multiplicity-specific" behavior of **1** (O_2 gives peroxides, but alkenes do not react) is interpreted[3b] as consistent with the earlier assignment[3a] of a triplet spin state of **1**.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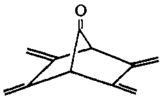
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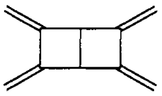
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We now find the capture of **1** not to be multiplicity-specific, since photochemically generated **1**, like other singlet biradicals such as 3,4-dimethylenefuran and 3,4-dimethylenethiophene,[4,5] combines readily in preparative reactions with singlet *or* triplet reagents. For example, photolysis of ketone **2** (0.03 M in $CHCl_3$ solution) in the presence of maleic anhydride (MA, 0.5–1.0 M, Rayonet reactor, 300 nm, 0 °C) leads to the formation of a 2:1 MA:**1** adduct (78% isolated yield). The rate of disappearance of **2** is independent of the concentration of the alkene. Under these conditions, the thermal Diels–Alder reaction of **2**,[2,6] which also could give the same adduct, does not occur. Similar preparative experiments with oxygen-saturated samples of **2** give the bridged monoperoxide and fused diperoxide of **1** in 30% and 55% yields, respectively.

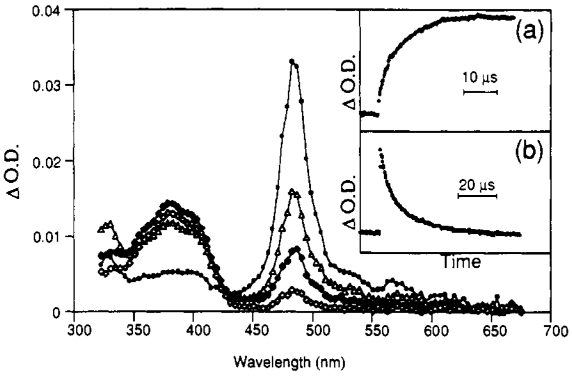

Figure 1. Transient absorption spectra of the biradical 1,2,4,5-tetramethylenebenzene (**1**) generated by 308-nm laser flash photolysis of ketone **2** in $CHCl_3$ at 291 K: 0.3 (●), 7.0 (△), 16.6 (◆), and 33.2 (◇) µs after laser flash. Insets: (a) growth kinetics measured at 380 nm; (b) decay kinetics measured at 490 nm.

Nanosecond laser flash photolysis experiments[7] now have afforded direct measurements of the kinetics of TMB reactions. Deoxygenated samples of **2** in $CHCl_3$, toluene, or CH_3CN in a 7 × 7 mm flow cell (initial optical densities ~0.3 at 308 nm) were subjected to 308-nm laser pulses. Transient spectra (see Figure 1) with maxima corresponding to those observed[2,3a] in the matrix-immobilized experiments were acquired by recording delay traces at various wavelengths. The pulses typically produced initial transient concentrations of $\sim 1 \times 10^{-5}$ M. The decay of the transient absorption as a function of time was monitored by a photomultiplier-transient digitizer system.

The disappearance of the 490-nm absorption could be fitted to second-order (but not first-order) kinetics, with rate constants ($2k_t$ in $M^{-1}\,s^{-1}$, based on $\epsilon_{490} = 4200\ M^{-1}\,cm^{-1}$) for dimerization of 2.1×10^{10} ($CHCl_3$), 1.5×10^{10} (toluene), and 3.0×10^{10} (CH_3CN). The bands at 570 and 625 nm disappeared at the same rate as the 490-nm band, which indicates that all three bands share the same carrier. The probable uncertainty in the rate constants is about 50%, primarily because of the uncertainty of ~25% in the extinction coefficient of the biradical. The dimerization rates, like that of 3,4-dimethylenefuran ($3.3 \times 10^{10}\ M^{-1}\,s^{-1}$ in CH_3CN),[4a,b] are near the encounter-controlled limit calculated for singlet biradicals without spin-statistical correction.

The decay of the 490-nm transient was accompanied by the appearance (Figure 1) of a new species with an absorption maximum at about 380 nm, characteristic[8] of *o*-quinodimethane units. Similar absorption peaks (and emission and excitation spectra) concordant with *o*-quinodimethane were observed in matrix preparations of **2** which had been irradiated, annealed, and refrozen. In the solution-phase flash experiments, the growth at 380 nm initially followed the same kinetic order as the decay at 490 nm, and the absorption profile was similar to that observed for the 380-nm chromophore in the matrix experiments. The subsequent polymerization of the dimer(s) was slow on the nanosecond time scale but was observable as a slight decrease in the 380-nm absorption after several microseconds (33.2-µs curve, Figure 1).

Under the laser flash conditions, the 490-nm transient was quenched by oxygen with pseudo-first-order kinetics in either oxygen-saturated or air-saturated $CHCl_3$, from which we derived

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