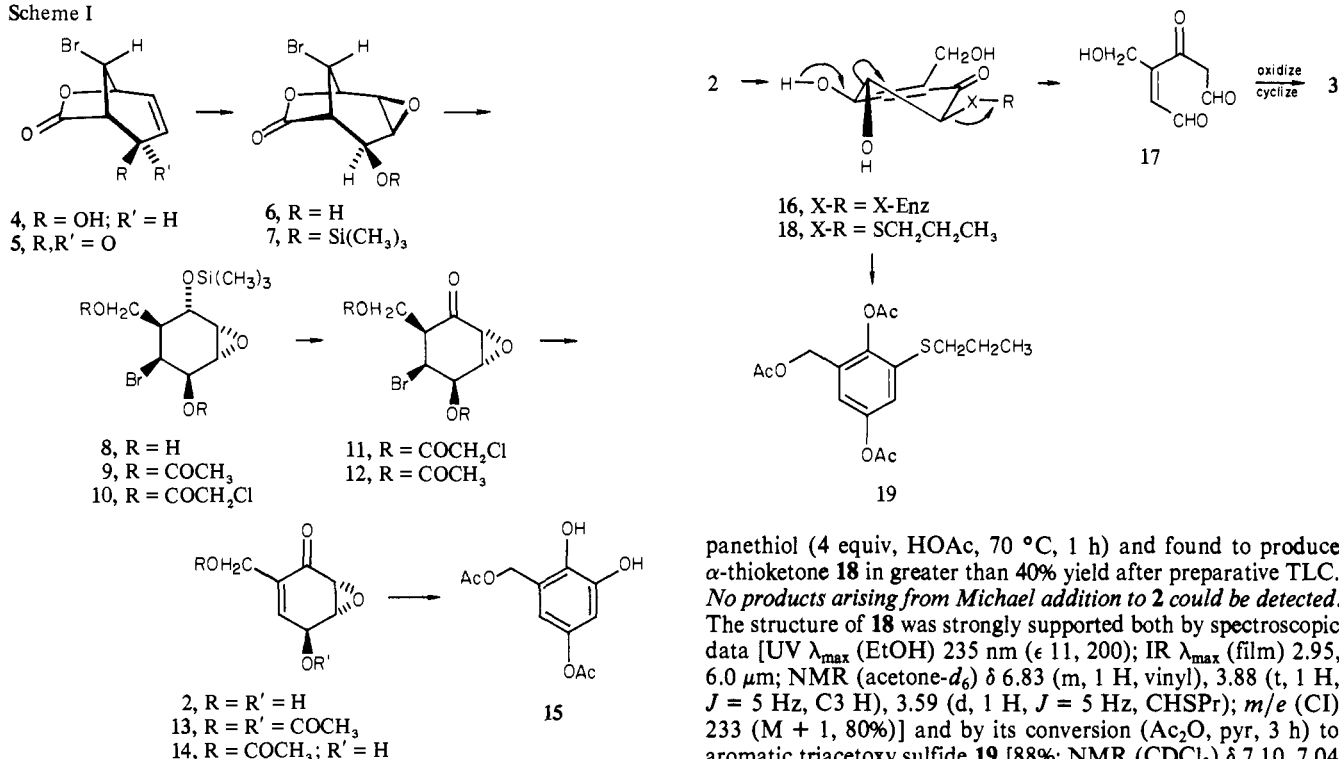


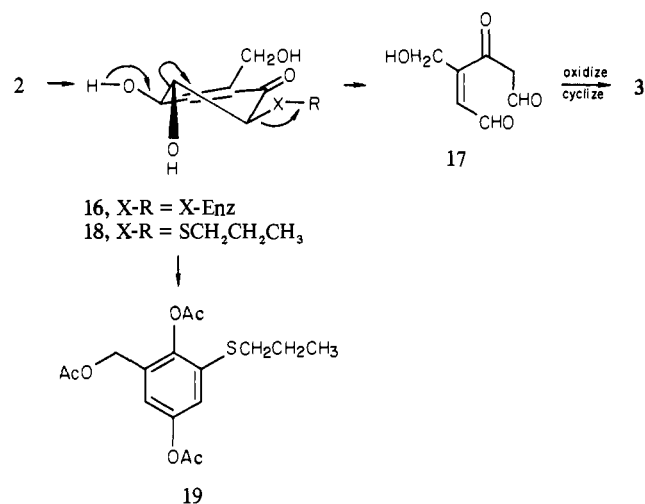
Scheme I



but bis( $\alpha$ -chloroacetyl) derivative **10**, prepared from **8** in 95% yield [(ClCH<sub>2</sub>CO)<sub>2</sub>O, pyr, CH<sub>2</sub>Cl<sub>2</sub>, -20°C], proved to be superior for the completion of the synthesis. Upon exposure to Jones reagent, ether-diester **10** was hydrolyzed and oxidized in one step to keto diester **11** [98%, NMR (CDCl<sub>3</sub>)  $\delta$  5.43 (d, 1 H,  $J$  = 5 Hz, CHBr), 4.28, 4.10 (2 s, 4 H, ClCH<sub>2</sub>); IR  $\lambda_{\max}$  (film) 5.68, 5.75  $\mu\text{m}$ ]. Usually **11** was not isolated; rather the crude oxidation product was immediately dissolved in a mixture of methanol-powdered NaHCO<sub>3</sub> (15 equiv), whereupon alcoholysis of the two protecting groups and elimination of HBr rapidly generated racemic isoeoxydon **2**, mp 79.5–80 °C [(+)-2 lit.<sup>6</sup> mp 53 °C], in 68% yield (six steps and 52% overall yield from **4**). Spectral comparison of synthetic **2** with the natural product showed them to be identical in every respect.<sup>12</sup>

Like its C-4 epimer epoxydon,<sup>13</sup> **2** proved unstable even to weak bases such as aqueous sodium acetate or pyridine. Since direct acetylation was difficult,<sup>6</sup> racemic isoeoxydon diacetate **13** could best be prepared from **9** by a similar oxidation-elimination sequence **9**  $\rightarrow$  **12**  $\rightarrow$  **13** (60% overall). When stirred with base (Et<sub>3</sub>N, room temperature, 20 min, CHCl<sub>3</sub>), **13** was transformed into diacetoxycatechol **15**, whose structure was unequivocally established by its AB pattern of meta aromatic hydrogens [(CDCl<sub>3</sub>)  $\delta$  6.57, 6.77,  $J$  = 3 Hz].<sup>13</sup> Synthetic isoeoxydon was reasonably acid stable, even in glacial HOAc at 70 °C. Added *p*-TsOH had no effect on the epoxide ring and merely catalyzed the formation of primary monoacetate **14** (60%).<sup>11</sup>

The biosynthesis of patulin from isoeoxydon requires an oxidative ring cleavage and is best rationalized by rupture of the C3–C4 bond in **2**. Among possible mechanisms, attack of an enzymic "X-group" nucleophile<sup>14</sup> (RNH<sub>2</sub>, RSH) at the more electropositive oxirane carbon<sup>15</sup> would furnish the necessary antiperiplanar relationship in **16** for a 1,3-fragmentation leading to **17**. As a test of this model, isoeoxydon was warmed with pro-



panethiol (**4** equiv, HOAc, 70 °C, 1 h) and found to produce  $\alpha$ -thioketone **18** in greater than 40% yield after preparative TLC. No products arising from Michael addition to **2** could be detected. The structure of **18** was strongly supported both by spectroscopic data [UV  $\lambda_{\max}$  (EtOH) 235 nm ( $\epsilon$  11, 200); IR  $\lambda_{\max}$  (film) 2.95, 6.0  $\mu\text{m}$ ; NMR (acetone-*d*<sub>6</sub>)  $\delta$  6.83 (m, 1 H, vinyl), 3.88 (t, 1 H,  $J$  = 5 Hz, C3 H), 3.59 (d, 1 H,  $J$  = 5 Hz, CHSP<sub>r</sub>); *m/e* (CI) 233 (*M* + 1, 80%)] and by its conversion (Ac<sub>2</sub>O, pyr, 3 h) to aromatic triacetoxysulfide **19** [88%; NMR (CDCl<sub>3</sub>)  $\delta$  7.10, 7.04 (AB quartet, 2 H,  $J$  = 3 Hz, meta aromatics), 5.06 (s, 2 H), 2.92 (t, 2 H,  $J$  = 7 Hz, CH<sub>2</sub>S), 2.35, 2.30, 2.07 (3 s, 9 H), 1.67 (sextet, 2 H,  $J$  = 7 Hz), 1.01 (t, 3 H,  $J$  = 7 Hz); IR  $\lambda_{\max}$  (film) 5.68, 5.73  $\mu\text{m}$ ; *m/e* (CI) 341 (*M* + 1, 28%)]. Additional experiments to probe this hypothesis further are planned.

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## Taft $\sigma^*$ Values of Alkyl Groups: An Artifact

Sir:

The Taft equation provides a useful quantitative empirical summary of steric effects and polar effects on rates and equilibria of aliphatic compounds.<sup>1-3</sup> Equation 1 is the older form based on the obsolete  $\sigma^*\rho^*$  constants and eq 2 is the more modern form.

$$\log k = a + \rho^*\sigma^* + \delta E_s \quad (1)$$

$$\log k = a + \rho_1\sigma_1 + \rho_s E_s \quad (2)$$

The  $\sigma_1$  constants use  $\sigma_1 = 0$  for H and are now based on a wide range of reactions.<sup>2,4-7</sup> For strongly polar substituents such as

(12) An authentic sample of (+)-isoeoxydon was not available for side-by-side TLC comparisons; however, TLC characteristics in two different solvent systems agreed well with the published data for **2**.

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Table I. Applications of the Taft Equation Based on Alkyl Substituents;  $\log k = a + \rho_s E_s + \rho_I \sigma_I$ 

reaction	$a$	$\rho_s$	$\rho_I$	std dev	DF	ref
1. RCOOEt, 70%; <sup>a-c</sup> acetone, HCl, 25%	-4.3465	0.9945		0.021	5	16
2. same, plus R = Et, CH <sup>a-c</sup>	-4.3976	0.8552		0.11	6	16
	-3.7208	0.7319	12.195 <sup>d</sup>	0.094	5	
3. RCOOEt, NaOH, <sup>a,b,e,f,g</sup> 85% ethanol, 25 °C	-2.2943	1.2267		0.13	6	17
	-1.9040	1.1595	7.003 <sup>h</sup>	0.14	5	
4. RCOOMe, NaOH, <sup>a-c,f</sup> 40% dioxane, 20 °C	0.8277	0.9298		0.045	6	14, 15
	1.2691	0.8181	8.154 <sup>i</sup>	0.031	5	
5. RCOOEt, NaOH, <sup>a-c,e</sup> 70% acetone, 25 °C	-1.5312	1.3205		0.13	6	16
	-0.2934	1.0948	22.306 <sup>j</sup>	0.054	5	
	-0.6064	1.0867	18.809 <sup>k</sup>	0.04	3	

<sup>a</sup> Except for set 4 which used the published  $\log k$  values the other sets are based on  $k$  at 25 °C computed from the least-squares Arrhenius equation. <sup>b</sup> R = Me, Et, *n*-Pr, *n*-Bu, *i*-Pr, *i*-Bu. <sup>c</sup> Plus *t*-Bu. <sup>d</sup> Standard deviation, 7.4. <sup>e</sup> Plus Et, CH. <sup>f</sup> Plus *sec*-Bu. <sup>g</sup> *t*-Bu not included since it appears to be in gross error. <sup>h</sup> Standard deviation, 11; therefore the  $\rho_I \sigma_I$  term is not significant. <sup>i</sup> Standard deviation, 2.9. <sup>j</sup> Standard deviation, 4. <sup>k</sup> Standard deviation, 3.2;  $\rho_I$  is based on  $\sigma_I$  values of ref 7b; all other  $\rho_I$  values are based on  $\sigma_I$  values of ref 7a. *n*-Bu and Et, CH excluded from set 5 because  $\sigma_I$  values were not available.

ClCH<sub>2</sub> or Cl<sub>2</sub>CH the relationship is  $\sigma_I = \sigma^*/6.22$ ,  $\rho_I \sigma_I = \rho^* \sigma^*$ .<sup>1,5,8</sup> Recently  $E_s$  values have been computed theoretically, although the available accuracy, about 0.3, is not capable of probing close distinctions.<sup>9</sup> The general applicability of the Taft equation has been firmly established.

There has, however, been a continuing controversy about polar effects of alkyl groups.<sup>2,3</sup> Some contend that  $\sigma^*$  (or  $\sigma_I$ ) values of alkyl groups are significant and useful in evaluating the sensitivity of reactions to polar influences.<sup>3,6,7,9,10</sup> Others consider that  $\sigma^*$  values are zero for all alkyl groups.<sup>2,11</sup> Our theoretical computations<sup>8,12</sup> of steric effects require reliable experimental data for comparison and for calibration. The question of polar effects of alkyl groups therefore needs to be settled. We have carried out a detailed analysis of acylation reactions and of S<sub>N</sub>2 reactions to be published elsewhere;<sup>13</sup> some important highlights are summarized here.

We present first a brief account of the origin of the  $\sigma^*$  values and show that for alkyl groups  $\sigma^*$  values are unreliable. We then examine the current status of  $\sigma_I$  values for alkyl groups. Finally we consider representative reactions which seem to require a  $\rho_I \sigma_I$  term.

In the original definition<sup>1</sup> the methyl group was selected as the origin for both  $E_s$  and for  $\sigma^*$ , that is  $E_s = 0$  and  $\sigma^* = 0$  for methyl. The range of  $E_s$  was defined by setting  $\delta$  to unity for acid-catalyzed hydrolysis of RCOOEt. On sound experimental grounds  $\rho^* = 0$  for this reaction and then  $E_s = \log(k/k_0)_A$ . The range for the  $\sigma^*$  scale was defined by setting  $\rho^* = 2.48$  for base-catalyzed hydrolysis of RCOOEt. The assumption was made that  $\delta = 1$  to avoid the need to adjust  $\delta$  of eq 1 while  $\sigma^*$  values are computed.

Later work has shown that  $\rho^*$  varies from about 0.5 to greater than 1.7 for various esterifications and hydrolyses.<sup>13</sup> For ethyl esters  $\rho^* \approx 1.25$  and for methyl esters  $\rho^* \approx 0.93$ . This departure from unity is relatively unimportant for polar groups since the polar effect dominates. However, the assumption that  $\delta = 1$  had a serious effect for alkyl groups; it resulted in  $\sigma^*$  values that represent a residual  $E_s$  component plus an error term. Perhaps the most direct demonstration that  $\sigma^*$  of alkyl groups are artifacts can be seen by computing a revised set  $\sigma^*$  from data for

RCOOMe.<sup>13-15</sup> As expected the range of this alternative set is much narrower, and signs of  $\sigma^*$  are reversed for some alkyl groups.

The best of the reported  $\sigma_I$  sets for alkyl groups is based on a detailed analysis of gas phase acidities and basicities.<sup>7b</sup> The polar effect is reported to be a rather small fraction of the polarizability effect. In particular the maximum range of  $\sigma_I$  for C<sub>1</sub>-C<sub>3</sub> alkyl groups is about 0.03, and the range will probably not be increased greatly if larger alkyls are eventually included. Alkaline hydrolysis of esters has  $\rho_I$  about 15, and the maximum range of polar effects is therefore about 0.5 in  $\log(k_i/k_j)$  corresponding to a maximum ratio of 3 in rate constants. The steric effect range for these alkyl groups is about 1.7, corresponding to a maximum ratio of 50 in rate constants. Thus the polar effect is about 5-10% of the steric effect for small groups.<sup>13</sup> For larger alkyl groups the polar fraction would be less, since the polar effect appears to saturate while the steric effect does not.

Other factors contribute to the difficulty of demonstrating a polar effect of alkyl groups for reaction in solution. There is a definite though weak correlation between  $\sigma_I$  and  $E_s$  ( $r^2 = 0.35$ );<sup>1,7</sup> there are the usual uncertainties in the linear-free-energy approximations; there are significant uncertainties in  $E_s$  values. It is therefore instructive to examine representative reactions that seem to require a  $\rho_I \sigma_I$  term for alkyl groups.

The data are summarized in Table I. Reaction 1 is the standard reaction used for defining  $E_s$  values.<sup>1</sup> The value for R = Et, CH appears to be out of line in comparison with other reaction series such as RCOOH + MeOH.<sup>13</sup> If this questionable data value is included, the set then requires a  $\rho_I \sigma_I$  term. This requirement is contrary to conclusions based on data for strongly polar groups which requires  $\rho_I \approx 0$ . The need for the  $\rho_I \sigma_I$  term is clearly an artifact due to the influence of a questionable rate constant.

Results for alkaline ester hydrolysis are variable. There is no clear reason why RCOOEt in 70% acetone (set 5) should have a defined  $\rho_I$  value while the reaction in 85% ethanol (set 3) does not.

The situation with respect to polar effects of alkyl groups may be summarized as follows: A reaction having an especially large  $\rho_I$  value, greater than about 15, and a  $\rho_s$  value not much greater than 1 may provide a marginally detectable  $\rho_I \sigma_I$  term based on alkyl substituents alone. However, the literature shows numerous instances of rate constants that are in gross error (off by factors of 2-3) in what otherwise appear to be particularly careful studies.<sup>13</sup> The rigorous experimental demonstration of a  $\rho_I \sigma_I$  term will therefore be a matter of some difficulty and will necessitate a most careful critical approach.

In a recent study Sjöström and Wold carried out a statistical

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analysis of six reactions, each of which included a set of eight alkyl groups.<sup>18</sup> They used the expression  $\log k = \alpha + \beta_1\theta_1 + \beta_2\theta_2$ , analogous in form to the Taft equation, and evaluated six  $\alpha$ , six  $\beta_1$ , six  $\beta_2$ , eight  $\theta_1$ , and eight  $\theta_2$  values. The  $\theta_1$  terms are correlated strongly with  $E_s$ , while  $\theta_1$  and  $\theta_2$  are themselves uncorrelated. The nonsteric term  $\beta_2\theta_2$  is claimed to be statistically significant.

Closer examination of the data set shows serious deficiencies which invalidate the entire study. For example, reaction 1 is stated to be base-catalyzed hydrolysis of amides, but comparison of rate constants recalculated from the reported  $\beta_1$  and  $\beta_2$  values with the literature shows that the data are instead for an alternative set of acid-catalyzed hydrolysis of amides<sup>19,20</sup> and that reaction 1 therefore duplicates reaction 6. Reaction 5,  $pK_a$  values for RCOOH, shows too narrow a range to provide useful discrimination.

Without these two reaction sets there are too few data to provide a reliable statistical evaluation of the total set of  $\alpha$ 's,  $\beta$ 's, and  $\theta$ 's. But there are yet further problems with the data set. Comparison with other reaction series shows that some of the rate constants for R = *t*-Bu are outliers. The rate constants reported for acid-catalyzed hydrolysis of *t*-BuCONH<sub>2</sub> are too high by a factor of more than 3 (reactions 1 and 6)<sup>13,19,20</sup> while the rate constant reported for base-catalyzed hydrolysis of *t*-BuCOOEt in 85% ethanol is too low by a factor of 2.<sup>13,17</sup> The statistical significance of the  $\beta_2\theta_2$  term is therefore an artifact of these numerous faults in the data set. In statistical terminology the data set analyzed does not properly represent the intended population.

If the purpose of an investigation is to measure steric effects of alkyl groups or of alicyclic structures, there will by little error in assuming that polar effects are constant among all substituents for any reaction having  $\rho_1$  less than about 15. This includes acid-catalyzed and base-catalyzed acyl-transfer reactions (esterification, hydrolysis, ester exchange, etc.) and a wide range of other reaction types. The way is now open for greatly expanding the experimental evaluation of steric effects.

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(21) Note Added in Proof. Communication with Drs. M. Sjöström and S. Wold indicates that the data for reaction 1 of ref 18 came from ref 22. Curiously the rate constants for alkaline hydrolysis of RCONH<sub>2</sub><sup>22</sup> are nearly identical with the reworked rate constants for sulfuric acid catalysis.<sup>19</sup> In fact,  $\alpha_1$ ,  $\beta_{11}$ , and  $\beta_{12}$  correlate either set equally well;<sup>18</sup> the Bruylants' data for alkaline hydrolysis are similar but are not as well correlated by these constants. Reexamination of the Bolton data substantiates his claim that amide hydrolyses do not follow the Taft equation very well. If we use the data at 75 °C for the RCH<sub>2</sub>CONH<sub>2</sub> set<sup>19</sup> to define  $a$  (=1.1157) and  $\rho_2$  (=1.0465) of eq 2, with  $\rho_1 = 0$ , giving a standard deviation of 0.06 in  $\log k$ (calcd), then the observed rates for the several R<sub>1</sub>R<sub>2</sub>COHCONH<sub>2</sub> examples are too fast on average by a factor of 1.8 and *t*-BuCONH<sub>2</sub> is too fast by a factor of 7. The full matrix statistical treatment<sup>18</sup> is a relatively crude technique since it is sensitive to random errors and outliers. Based on extensive data<sup>13</sup> we would expect ester reactions to follow the Taft equation closely with  $\rho_1 = 0$ . Since the  $\theta_1$  values<sup>18</sup> correlate with  $E_s$ , we would thus expect the  $\beta_2\theta_2$  terms to be indistinguishable from zero for ester reactions 2, 3, and 4<sup>18</sup> while the  $\beta_2\theta_2$  term would be significant for the amide reactions 1 and 6. This prediction holds for all reactions except for reaction 4,<sup>18</sup> alkaline hydrolysis in 85% ethanol; this set includes a *t*-Bu outlier value. For the related hydrolysis in 70% acetone<sup>16</sup> where the *t*-Bu value is normal,  $\beta_2 = 0.17 \pm 0.18$ , indistinguishable from zero. The causes of the difference in behavior of amides and esters are not obvious and the situation deserves further exploration.

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## Triangular Triniobium Cluster in Aqueous Solution

Sir:

Recent work on molybdenum and tungsten species in aqueous solutions has revealed the existence of trinuclear, triangular metal clusters in oxidation states between 3+ and 5+.<sup>1-10</sup> The aim of the present work is to explore the possibility that similar triangular clusters may occur in species of other transition elements of the second and third row in aqueous solution.

We report here the first of such species, a triangular niobium cluster prepared by reduction of Nb(V) in aqueous solution.

The aqueous chemistry of niobium in oxidation states lower than 5+ has not been characterized due to the lack of definite structural information.<sup>11</sup> Although the reduction of Nb(V) in mineral acids was used in both qualitative and quantitative determination of this element, the nature of the reduced species remained unknown.<sup>12</sup> One of these species, a red-brown anion, obtained by reduction of pentavalent niobium in aqueous H<sub>2</sub>SO<sub>4</sub>, has been the subject of many studies in this century.<sup>14</sup> Most investigators assigned hexanuclear structures to this species.<sup>14e-g</sup> We now report the results of an X-ray structure analysis<sup>15</sup> of the potassium salt of this species, which was prepared as described previously.<sup>14e</sup> The correct formula derived from the structure is K<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>[Nb<sub>3</sub>O<sub>2</sub>(SO<sub>4</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>2</sub>·5H<sub>2</sub>O. The molecular scheme is shown in Figure 1. It reveals that this much investigated compound is, in fact, a trinuclear, triangular niobium cluster and that previously proposed structures were erroneous.

The overall geometry of the complex is reminiscent of a structural and coordination type found in compounds with the general formula [M<sub>3</sub>X<sub>2</sub>(O<sub>2</sub>CR)<sub>6</sub>L]<sup>n(±)</sup> (M = Mo, W; X = O, CCH<sub>3</sub>; L = H<sub>2</sub>O, OCOCH<sub>3</sub>),<sup>1,3,7</sup> which is depicted schematically in Figure 2. The niobium cluster possesses the same kind of M<sub>3</sub>O<sub>2</sub> core as in [W<sub>3</sub>O<sub>2</sub>(O<sub>2</sub>CR)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>2+</sup><sup>3</sup> but differs from diaqua-hydrogen these structures by its six bridging sulfates which replace the six acetates. Such bridging sulfates have not been observed before in metal clusters. With two molecules in the cell of space group P2<sub>1</sub>, there is no crystallographic symmetry imposed upon the complex, but the deviations from an ideal D<sub>3h</sub> symmetry are small. All the average distances between each of the niobium

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(15) The red-brown compound crystallizes in space group P2<sub>1</sub> with  $a = 9.961$  (2),  $b = 18.088$  (3),  $c = 10.036$  (2) Å,  $\beta = 118.84$  (2)°, and  $Z = 2$ ; 2900 unique reflections with  $I > 3\sigma(I)$  were used in the structure solution and refinement. The structure was solved by direct methods. Least-squares refinement converged to a discrepancy of 0.040. A detailed report will be published later. A table of atomic positional and thermal parameters is available as supplementary material.