analyses. Especially noteworthy is the efficient conversion of Boc-Tyr-Ala-Thr-OBzl to its phosphonate (entry 1): the threonine residue failed to interfere in either of the transformations.

To demonstrate the applicability of $\mathbf{1} \rightarrow \mathbf{3} \rightarrow \mathbf{4}$ to large (hydrophilic) peptides, we carried out both reactions in hydroxylic solvents containing KHCO$_3$ or K$_2$CO$_3$ as a base. Thus, Z-Ala-Tyr-OEt in 95% aqueous methanol converted to Z-Ala-Tyr(Tf)-OEt in 88% yield, and the triflate in ethanol gave Z-Ala-Phe[4-PO(OEt)$_2$]-OEt in 85% yield.

Phosphonation of simple aryl triflates was general and efficient (Table I, entries 6–15). It was slowed by steric hindrance (entries 8–11) and was fastest with electron-deficient substrates (entries 7, 12–15) and with the electron-rich estrone triflate (entry 6). With *m*-bromophenyl triflate, C–O bond reactivity predominated (entry 14) and we found that it was matched only by that of the aryl C–I bond. In a competition experiment, diethyl phosphite converted ca. 40% of phenyl triflate and 60% of phenyl iodide to the phosphonate. Reactant concentrations, initially equimolar in CD$_3$CN, were estimated by ^{13}C and ^{1}H NMR before and after reaction.

In summary, diethoxyphosphinyl groups replaced tyrosine hydroxyls via sequential trifluoromethanesulfonylation and Pd(0)-catalyzed coupling with diethyl phosphite. The process has wide scope, functionalized several prototypical tyrosyl peptides without detectable racemization, and was compatible with hydroxylic solvents. It is therefore an unusual development in peptide chemistry because processes capable of drastically modifying complex polypeptides to novel, nonproteinogenic derivatives are rare. Moreover, we believe *it is the first formation of an aryl C–P bond in a peptide framework and augurs further modifications of peptides by related Pd-catalyzed processes.* We are currently devising methods to convert tyrosyl polypeptides in aqueous media to the corresponding phosphonic acids and related compounds.

Acknowledgment. We are indebted to Dr. Richard Friary for discussions and decisive assistance with this manuscript. We also thank Drs. B. Pramanik, P. R. Das, and M. Puar for spectra and Professor R. Breslow and Drs. P. P. Trotta and J. G. Berger for discussions.

Discrete Trinuclear Complexes of Niobium Related to the Local Structure in Nb$_3$Cl$_8$

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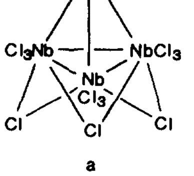
Received January 9, 1987

The three lower halides of niobium, Nb$_3$X$_8$ (X = Cl, Br, I) have been known for a very long time.[1] Their structures consist of close-packed arrays of halide ions with the niobium ions occupying triangular sets of adjacent octahedral interstices; bonding between the neighboring niobium atoms creates triangular metal atom clusters. The structure can be viewed as one in which Nb$_3$(μ_3-X)(μ-X)$_3$X$_9$ units, with the structure a, are fused together by sharing the terminal Cl atoms. A very similar structure exists in compounds of the type Zn$_2$Mo$_3$O$_8$.[2] In 1978 it was first reported that the Mo$_3$(μ_3-O)(μ-O)$_3$L$_9$ type of unit could be obtained as a discrete entity[3a] and the chemistry of such species has since been developed extensively.[3b] We now wish to report a similar development with respect to the haloniobium species, namely, the preparation and characterization of discrete trinuclear complexes containing the Nb$_3$(μ_3-Cl)(μ-Cl)$_3$ core surrounded by nine ligands. The compound, Nb$_3$Cl$_7$(PMe$_2$Ph)$_6$, was prepared[4] by reduction of [NbCl$_2$(THF)]$_2$(μ-Cl)$_2$(μ-THT), where THT is tetrahydrothiophene, with sodium amalgam in THF in the presence of PMe$_2$Ph. The reaction gave a red brown solution from which the brown product was isolated in 45% yield after evaporation to small volume and addition of hexane.



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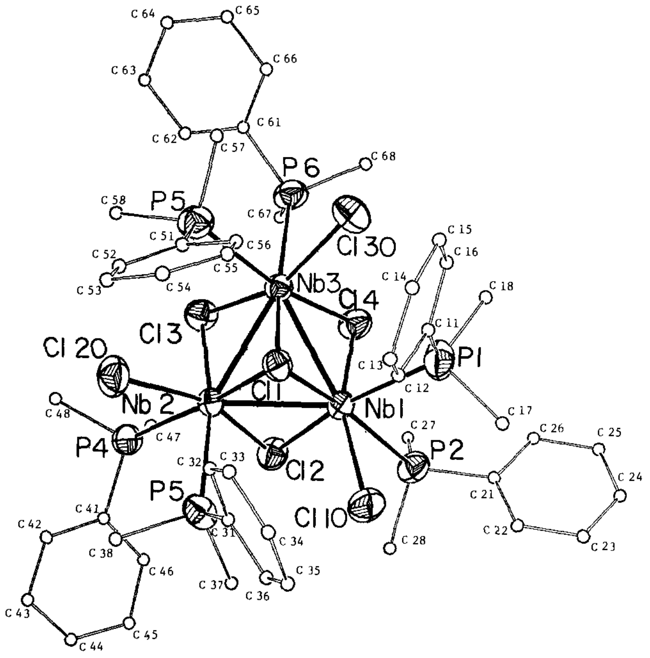

Figure 1. ORTEP drawing of the Nb$_3$Cl$_7$(PMe$_2$Ph)$_6$ molecule. The thermal ellipsoids are drawn at 30% probability level. Carbon atoms have been assigned arbitrarily small thermal parameters for the sake of clarity.

Crystallographic analysis[5,6] has been carried out on the material obtained by recrystallization from toluene/hexane. The asymmetric unit comprises a discrete trinuclear complex, shown in Figure 1, and a molecule of toluene.[7] Each trimer has virtual C_3 symmetry and is chiral; two molecules of each chirality are present in the unit cell. Selected interatomic dimensions averaged according to C_3 symmetry are as follows: Nb–Nb, 2.831 [3] Å;

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(1) (a) v. Schnering, H. G.; Wohrle, H.; Schafer, H. *Naturwissenshaften* **1961**, *48*, 159. (b) Simon, A.; v. Schnering, H. G. *J. Less-Common Met.* **1966**, *11*, 31.

(2) Torardi, C. C.; McCarley, R. E. *Inorg. Chem.*, **1985**, *24*, 476 and references therein.

(3) (a) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252. (b) Birnbaum, A.; Cotton, F. A.; Dori, Z.; Kapon, M.; Marler, D.; Reisner, G. M.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 2405 and references therein.

(4) All operations were performed under inert atmosphere by using standard vacuum line techniques.

(5) Crystal structure determinations were carried out by standard methods, which have been described previously: (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(6) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with the VAX-SDP software package. The crystallographic analysis was carried out at room temperature and Mo Kα (λ = 0.71073 Å) radiation was used.

(7) The compound crystallized in a monoclinic space group $P2_1/n$ with a = 12.339 (2) Å, b = 27.275 (8) Å, c = 19.187 (9) Å, β = 92.76 (2)°, V = 6450 (6) Å^3, Z = 4, and d_{calcd} = 1.491 g/cm^3 for fw = 1447.9. Refinement of 605 parameters using 4805 reflections with $F^2 > 3\sigma(F^2)$ produced residuals R and R_w equal to 0.054 and 0.070, respectively. The tables of atomic positional and thermal parameters, bond distances, and bond angles are provided as supplementary material.

(8) The only comparable structures that we are aware of are those of [Mo$_3$S$_4$Cl$_3$(dmpe)$_3$]$^+$ (Cotton, F. A.; Llusar, R., in press) and the [Ir$_3$H$_7$(dppp)$_3$]$^{2+}$ ion (Wang, H. H.; Pignolet, L. H. *Inorg. Chem.* **1980**, *19*, 1470).

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Nb–Cl_c, 2.468 [4] Å; Nb–Cl_b(trans to P), 2.529 [4] Å; Nb–Cl_b(trans to Cl), 2.474 [4] Å; Nb–Cl_t, 2.483 [7] Å; Nb–P(trans to Cl_b), 2.695 [2] Å; Nb–P(trans to Cl_c), 2.729 [7] Å; where subscripts c, b, and t refer to capping, bridging, and terminal chlorine atoms, respectively. The metal–ligand distances show trans influences: Nb–Cl_b trans to P is longer than Nb–Cl_b trans to Cl_t and Nb–P trans to Cl_c is longer than Nb–P trans to Cl_b.

The cluster has eight electrons in the M_3 core, and based upon the electronic configuration of the M_3X_{13} molecules (vide infra), it is expected to have a singlet ground state and consequently be diamagnetic. This was confirmed by the determination of its magnetic susceptibility[9] which gave a value of χ_M equal $-(560 \pm 60) \times 10^{-6}$ cgs at room temperature. The proton NMR spectrum[10] of the complex was uninformative, with unresolved peaks for both phenyl and methyl protons. Proton-decoupled phosphorus-31 signals were observed[11] only at low temperatures. The spectrum recorded at −90 °C in THF consisted of a sharp peak at −46 ppm due to free phosphine and two broad resonances centered around −10 and −3.5 ppm due to the inequivalent sets of coordinating phosphines. While the width of the signals may to some degree result from partial substitution of the ligands by the solvent (thus giving a number of mixed THF/phosphine species), we believe that the broadening is mainly or entirely due to the quadrupolar moment of ^{93}Nb nuclei. This nuclide has been reported[12] to cause anomalous and unexpected effects in the NMR spectra of some compounds of Nb. Analogous V and Ta species did not exhibit such problems. In general it is not possible to predict in which compounds the interaction with Nb nuclei is going to affect the NMR behavior since the phenomenon is not well understood. Clearly, the preparation and investigation of the Ta trimers would shed some light on this problem.

The compound reported here differs from Nb_3Cl_8 in the number of electrons present in the Nb_3 cluster, but the difference is consistent with a long-established understanding of the electronic structures of compounds with this type of structure.[13] The molecular orbitals that can be assigned primarily metal atom cluster character (in contradistinction to metal–ligand or ligand character) are three: an e and an a_1 orbital which correspond to three M–M σ bonds and another a_1 orbital of somewhat higher energy that is approximately nonbonding in the M–M sense. On this basis, the ideal population of the cluster would be six electrons, which would occupy the e and lower a_1 bonding MO's. However, one or two more more electrons can be accommodated without severely destabilizing the structure.[14] In the case of Nb_3Cl_8 there are seven electrons and in the type of compound described here there are eight.

The reported[1] dimensions of Nb_3Cl_8, which has crystallographically imposed $3m$ symmetry, are Nb–Nb, 2.810 Å; Nb–Cl_c, 2.438 Å; Nb–Cl_b, 2.428 Å; and Nb–Cl_t, 2.634 and 2.522 Å. In this case the metal–metal and metal-capping chlorine distances are somewhat shorter than in the phosphine complex. Such small differences may arise from several sources: the fact that in Nb_3Cl_8 the Cl atoms belong to a continuous array and are shared between clusters; the presence of some phosphine ligands in place of Cl^- ligands; the occurrence of different numbers (seven and eight) of cluster electrons.

Preliminary results obtained with other phosphines indicate the formation of trinucler clusters analogous to the PMe_2Ph complex. In particular the use of PBu_3 followed by reaction of the product with dmpe, bis(dimethylphosphino)ethane, afforded an analogous trinuclear compound with bidentate ligands chelating the Nb atoms.

Acknowledgment. We are grateful to the Robert A. Welch Foundation (Grant 494) for financial support. M.P.D. is a National Science Foundation Fellow and also holds a Texaco/IUCCP Fellowship from this department.

Supplementary Material Available: Tables of positional and isotropic-equivalent thermal parameters, bond distances, and bond angles for $Nb_3Cl_7(PMe_2Ph)_6{\cdot}C_7H_8$ (6 pages). Ordering information is given on any current masthead page.

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[9] A magnetic susceptibility balance manufactured by Johnson Matthey Inc. was used.

[10] Proton NMR spectra were recorded on a Varian XL-200 spectrometer using CD_3CN as solvent.

[11] $^{31}P\{H\}$ spectra were recorded on a Varian XL-200 spectrometer operating at 80.984 MHz with H_3PO_4 as the standard for chemical shifts.

[12] *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1982, vol. 3, pp 707~708.

[13] Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 1217.

[14] Several examples of eight-electron systems containing $Mo_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3$ cores have been reported, namely, $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]ClClO_4$[15] and $(Et_4N)_2[Mo_3OCl_8(O_2CCH_3)_2]$.[16]

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[16] Shang, M.; Huang, J.; Liu, J. *Acta Crystallogr., Sect. C* **1984**, *C40*, 761.

DNA, Light, and Dewar Pyrimidinones: The Structure and Biological Significance of TpT3

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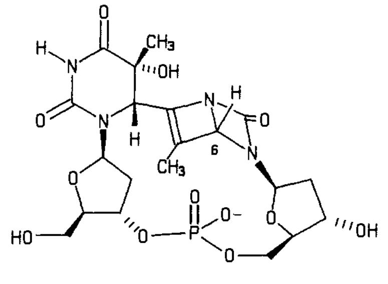
Received December 19, 1986

The cis-syn and (6-4) dipyrimidine photodimers are the major products produced by irradiation of DNA at 254 nm and are considered to be the principal photolesions leading to mutation and cancer by ultraviolet light.[1,2] The existence of perhaps another biologically relevant class of lesions comes from reports in the early 1970s of type III photoreactivation of the lethal effects of 254-nm light on a variety of bacterial strains.[3] Type III photoreactivation was shown to be most efficient at 313 nm and to proceed through an unknown, though nonenzymatic, pathway which was correlated with the disappearance of (6-4) products. Interestingly, in 1964 Johns et al. had reported that the (6-4) product of TpT, known to them only as TpT4, could be converted quantitatively at 313 nm to a new photoproduct, TpT3, and back again at 240 nm (see Scheme I).[4] Such photochemical behavior is quite similar to that observed for simpler pyrimidinones which have been shown to be photoisomerized to their Dewar isomers at wavelengths greater than 300 nm.[5] Herein we report the remarkable structure of TpT3, which we have determined to contain a highly strained Dewar pyrimidinone subunit and which we show can be produced by direct photolysis of TpT with biologically relevant wavelengths of light.



TpT3

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[1] See: (*a*) Friedberg, E. C. *DNA Repair*; Freeman, New York, 1985. (b) Wang, S. Y., Ed. *Photochemistry and Photobiology of Nucleic Acids*; Academic: New York, 1976; Vols. I and II.

[2] For a recent review of the role of (6-4) products in ultraviolet light induced transition mutations, see: Franklin, W. A.; Haseltine, W. A. *Mutat. Res.* **1986**, *165*, 1–7.

[3] (a) Patrick, M. H. *Photochem. Photobiol.* **1970**, *11*, 477–485. (b) Ikenaga, M.; Patrick, M. H.; Jagger, J. *Ibid.* **1970**, *11*, 487–494. (c) Jagger, J.; Takebe, H.; Snow, J. M. *Ibid.* **1970**, *12*, 185–196. (d) Ikenaga, M.; Patrick, M. H.; Jagger, J. *Ibid.* **1971**, *14*, 175–187.

[4] Johns, H. E.; Pearson, M. L.; LeBlanc, J. C.; Helleiner, C. W. *J. Mol. Biol.* **1964**, *9*, 503–524.

[5] (a) Nishio, T.; Katoh, A.; Omote, Y.; Kashima, C. *Tetrahedron Lett.* **1978**, 1543–1544. (b) Nishio, T.; Kato, A.; Kashima, C.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1980**, 607–610.

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