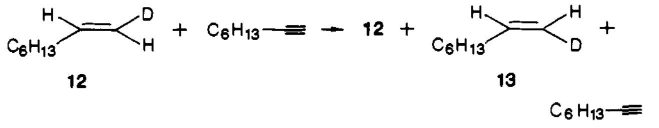
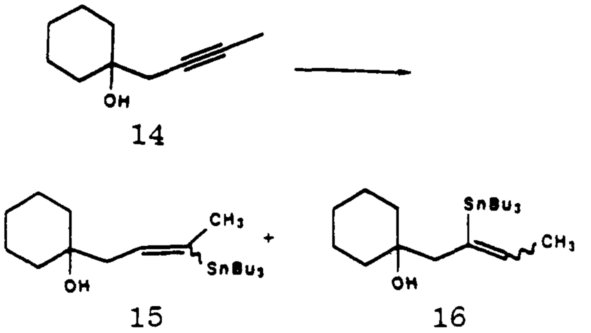
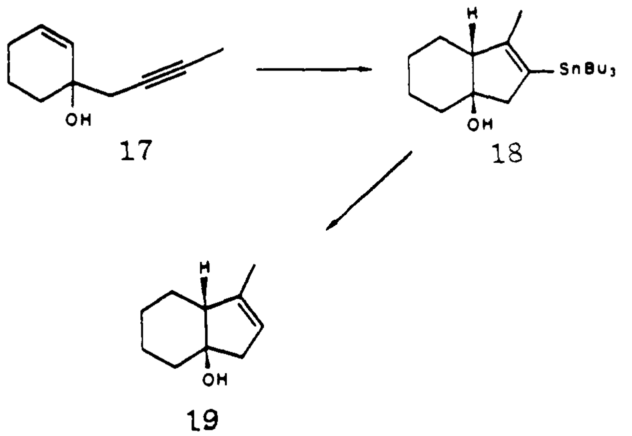
show that these results are the consequence of the reversibility of the addition of stannyl radicals not only to double bonds[12] but *to triple bonds as well*. The operational selectivity for addition of a trialkylstannyl radical to an alkyne in the presence of a double bond suitable for cyclization was not anticipated since radical additions to isolated alkenes and alkynes either show no great selectivity or are faster with the former.[13]

The following experiment shows that the enyne cyclizations are successful because cyclization is faster, and reversal slower, for vinyl radicals than for their alkyl counterparts, so that the whole cyclization pathway is via the adduct of the stannyl radical to the acetylene rather than to the olefin: A 1:1 mixture of *trans*-1-deuterio-1-octene (**12**)[12a] and 1-octyne was heated under argon for 1 h at 80 °C, with 0.85 equiv of tributylstannane and 1 mol % of AIBN. The products consisted, in addition to a considerable recovery of 1-octyne, of a mixture of (*E*)- and (*Z*)-deuterio-1-octene. This was deduced by the presence in the infrared spectrum of the reaction products of an absorption band at 2250 cm$^{-1}$ due to the *Z* isomer **13**,[12a] in addition to that at 2270 cm$^{-1}$ corresponding to the *E* isomer **12**.



The surprising regioselectivity toward one end of the triple bond in the cyclization of **9** to **10** implies that the addition of stannyl radicals to the *triple bond* of an olefinic acetylene is *also reversible* under the reaction conditions. This is demonstrated by the following two experiments. (1) No addition of tributylstannane to the ethynyl carbinol **14** took place under the usual 0.02 M conditions in benzene with AIBN, but increasing the stannane concentration to 0.77 M now gave a 1.2 to 1 mixture of the two possible vinylstannanes **15** and **16**, in addition to some recovered **14**. (2) When **17**, the cyclohexenyl analogue of **14**, was submitted to the 0.02 M cyclization conditions which left **14** unchanged, it was cyclized to give **18**, which was destannylated to **19**[14] with silica gel, in an overall yield of 76% from **17**. It, thus, is the reversibility of the addition of stannyl radicals to the triple bonds of **9** and **17**, which leads to selection of the more rapidly formed ring (in the case of **9** to **10** and of **17** to **18**, to a five-membered rather than a four-membered ring).





**Acknowledgment.** We wish to thank the National Science Foundation and the National Institutes of Health for their support of this work.

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(12) (a) Sommer, R.; Kuivila, H. G.; *J. Org. Chem.* **1968**, *33*, 802. (b) Neumann, W. P.; Albert, H. J.; Kaiser, W. *Tetrahedron Lett.* **1967**, 2041. (c) Kuivila, H. G., Sommer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5616. (d) Albert, H. G.; Neumann, W. P.; Kaiser, W.; Ritter, H. P. *Chem. Ber.* **1970**, *103*, 1372. (e) Mitchell, T.; Amamrin, A. *J. Organomet. Chem.* **1980**, *199*, 49. (f) Podesta, J. C.; Chopa, a. B.; Ayala, A. D. *J. Organomet. Chem.* **1981**, *212*, 163.

(13) (a) Kharasch, M. S.; Jerome, J. J.; Urry, W. H. *J. Org. Chem.* **1950**, *15*, 966. (b) Gazith, M.; Szwarc, M. *J. Am. Chem. Soc.* **1957**, *79*, 3339. (c) Abell, P. I. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tripper, C. F. H., Eds.; Elsevier: Amsterdam, 1976; Vol. 18. (d) Giese, B.; Lachein, S. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 768. Giese, B.; Meixner, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 965. Giese, B.; Lachein, S.; Meixner, J. *Tetrahedron Lett.* **1980**, *21*, 2505. (e) Heiba, E. I.; Dessau, R. M.; *J. org. Chem.* **1967**, *32*, 3837. (f) Ito, O.; Matsuda, M. *J. Org. Chem.* **1984**, *49*, 17 and references therein.

(14) The stannylindene **18** was purified by flash chromatography on silica gel with 7% ethyl acetate–petroleum ether ($R_f$ 0.65; starting hydroxyenyne **17**, $R_f$ 0.35). Destannylation was effected by stirring overnight with silica gel to give **19** in 76% yield after chromatography. $^1$H NMR δ 5.27 (br s, 1 H), 2.48 (br d, *J* = 16 Hz, 1 H), 2.16 (d, *J* = 16 Hz) 2.16 (m), 1.71 (br s, 3 H); MS (EI), *m/z* 152 ($M^+$), 137 ($M^+ - CH_3$), 135 ($M^+$ − OH).

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# Palladium-Catalyzed Substitutions of Triflates Derived from Tyrosine-Containing Peptides and Simpler Hydroxyarenes Forming 4-(Diethoxyphosphinyl)phenylalanines and Diethyl Arylphosphonates[†]

Konstantinos S. Petrakis* and Tattanahalli L. Nagabhushan

*Schering Corporation, Bloomfield, New Jersey 07003*

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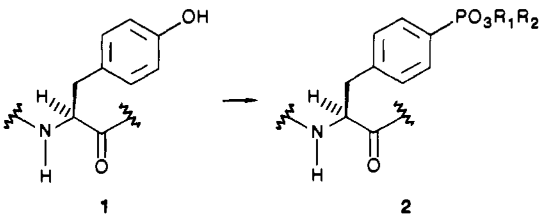
*Inhibitors of tyrosine protein kinases which oncogenes or retroviruses encode may lead to* avant garde, *mechanism-based anticancer and antiviral drugs*. These kinases are of central importance in retroviral or oncogenic cell transformation, and their cellular homologues with the associated phosphatases regulate normal cell growth.[1] Together the kinases and phosphatases catalyze reversible transfer of phosphate to tyrosyl residues of proteins and enzymes. Thus, to design inhibitors of enzymes catalyzing phosphate transfer, we sought to change tyrosyl peptides to 4-phosphonophenylalanyl derivatives (**1** → **2**). Here we report that tyrosine-containing peptides and certain functionalized hydroxyarenes formed 4-(diethoxyphosphinyl)phenylalanines and diethyl arylphosphonates in a novel, two-step sequence.[2]



Direct replacement of an aryl C–O bond by a C–P bond is, to our knowledge, unprecedented. This is in sharp contrast to analogous processes involving the aryl carbon–metal,[3] –halogen,[4]

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[†] In memoriam Stylianos K. Petrakis.

(1) Krebs, E. G. *Biochem. Soc. Trans.* **1985**, *13*, 813. Hunter, T.; Cooper, J. A. *Annu. Rev. Biochem.* **1985**, 897. Weinberg, R. A. *Science* (*Washington, D.C.*) **1985**, *230*, 770.

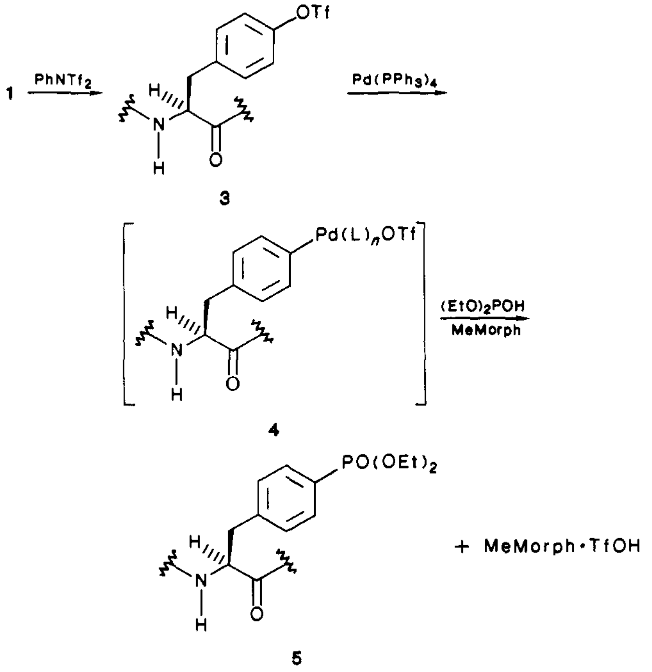
(2) Tf = (trifluoromethyl)sulfonyl; TfO = [(trifluoromethyl)sulfonyl]oxy; MeMorph = *N*-methylmorpholine; Boc = *tert*-butyloxycarbonyl; Bzl = benzyl; Z = benzyloxycarbonyl; MeO = methyl ester.

**Table I.** Palladium-Catalyzed Conversion of Aryl Triflates to Diethyl Arylphosphonates[a]

| entry | triflate | product(s) | yield, %[b] | time, h |
|---|---|---|---|---|
| 1 | Boc-Tyr(Tf)-Ala-Thr-OBzl | Boc-Phe[4-PO(OEt)$_2$]-Ala-Thr-OBzl | 82 | 12 |
| 2 | Boc-Tyr(Tf)-Ala-Phe-OMe | Boc-Phe[4-PO(OEt)$_2$]-Ala-Phe-OMe | 87 | 12 |
| 3 | Z-Ala-Tyr(Tf)-OEt | Z-Ala-Phe[4-PO(OEt)$_2$]-OEt | 88 | 12 |
| 4 | MeOCO-Tyr(Tf)-Ala-OMe | MeOCO-Phe[4-PO(OEt)$_2$]-Ala-OMe | 81 | 15 |
| 5 | Ac-Tyr(Tf)-OMe | Ac-Phe[4-PO(OEt)$_2$]-OMe | 85 | 15 |
| 6 | 3-(TfO)-estra-1,3,5(10)-trien-17-one | 3-[(EtO)$_2$OP]-estra-1,3,5(10)-trien-17-one | 88 | 4 |
| 7 | 3-TfOC$_5$H$_4$N | 3-(EtO)$_2$OPC$_5$H$_4$N | 83 | 4 |
| 8 | 2-MeC$_6$H$_4$OTf | 2-MeC$_6$H$_4$PO(OEt)$_2$ | 87 | 34 |
| 9 | 2-MeOC$_6$H$_4$OTf | 2-MeOC$_6$H$_4$PO(OEt)$_2$ | 92 | 40 |
| 10 | 2-ClC$_6$H$_4$OTf | 2-ClC$_6$H$_4$PO(OEt)$_2$ | 92 | 32 |
| 11 | 2-TfOC$_6$H$_4$OTf[c] | 2-TfOC$_6$H$_4$PO(OEt)$_2$[d] | 65 | 40 |
| 12 | 2-MeOCOC$_6$H$_4$OTf | 2-MeOCOC$_6$H$_4$PO(OEt)$_2$ | 83 | 9 |
| 13 | 3-MeOCOC$_6$H$_4$OTf | 3-MeOCOC$_6$H$_4$PO(OEt)$_2$ | 95 | 6 |
| 14 | 3-BrC$_6$H$_4$OTf[c] | 3-BrC$_6$H$_4$PO(OEt)$_2$, 3-TfOC$_6$H$_4$PO(OEt)$_2$[e] | 75 | 6 |
| 15 | 4-NO$_2$C$_6$H$_4$OTf | 4-NO$_2$C$_6$H$_4$PO(OEt)$_2$ | 89 | 5 |

[a] General procedure: A mixture of aryl triflate (10 mmol), (EtO)$_2$POH (12 mmol), and MeMorph (13 mmol) or, for nonpeptide triflates, (*i*-Pr)$_2$EtN (13 mmol), Pd(PPh$_3$)$_4$ (0.3 mmol), and CH$_3$CN (10 mL) in a sealed tube was stirred at 70 °C under N$_2$ until TLC analysis indicated complete conversion. [b] Yield of isolated product. All compounds were fully characterized by 400-MHz $^1$H NMR and IR spectroscopy and MS. New compounds gave satisfactory elemental analyses; in exact mass measurements using FAB high-resolution MS, the products in entries 1–3 gave the expected molecular ions. [c] Reactions run with equimolar amounts of aryl triflate and (EtO)$_2$POH. [d] Product mixture contained 2-TfOC$_6$H$_4$OTf (15%). No 2-(EtO)$_2$OPC$_6$H$_4$PO(OEt)$_2$ was isolated. [e] 3-BrC$_6$H$_4$PO(OEt)$_2$:3-TfOC$_6$H$_4$PO(OEt)$_2$ = 3:1 as determined by $^1$H NMR. No 3-(EtO)$_2$OPC$_6$H$_4$PO(OEt)$_2$ was isolated.

–nitrogen,[5] or –hydrogen[6] bond, which have been used extensively for the synthesis of *simple* aryl phosphonates. We discovered that trifluoromethanesulfonates (triflates) **3**, which were prepared from tyrosyl peptides **1** in excellent yield with *N*-phenyltriflimide,[7] underwent efficient substitution producing diethyl arylphosphonates **5**. The reaction occurred in hot acetonitrile con-



taining diethyl phosphite, *N*-methylmorpholine (MeMorph), and tetrakis(triphenylphosphine)palladium(0) catalyst. No reaction took place in the absence of Pd(0), which we postulate to mediate the reaction via structure **4**. Established[8,9] oxidative addition of vinyl triflates to Pd(0) is analogous.

The conversion of MeOCO-Tyr-Ala-OMe (**6**) via MeOCO-Tyr(Tf)-Ala-OMe (**7**) to MeOCO-Phe[4-PO(OEt)$_2$]-Ala-OMe (**8**) illustrates the experimental procedure. To a stirred mixture of **6** (0.47 g, 1.45 mmol), (*i*-Pr)$_2$EtN (0.187 g, 1.45 mmol), and CH$_2$Cl$_2$ or MeCN (4 mL), at 0 °C, was added *N*-phenyltriflimide (0.646 g, 1.81 mmol). The reaction mixture was stirred at room temperature for 13 h, concentrated, and partitioned between EtOAc and H$_2$O; the organic phase was dried (Na$_2$SO$_4$) and concentrated to an oil, which was purified by flash chromatography (silica gel, EtOAc/hexanes) to give 0.60 g (91%) of **7**, mp 144–145 °C (EtOAc/hexanes), $[\alpha]^{26}_{D}$ –3.1° (*c* 0.0045, MeOH). A suspension of triflate **7** (0.25 g, 0.55 mmol), MeMorph (0.073 g, 0.72 mmol), (EtO)$_2$POH (0.091 g, 0.66 mmol), and Pd(PPh$_3$)$_4$ (0.019 g, 0.016 mmol) in dry MeCN (1.5 mL) was stirred at 70 °C in a sealed tube under N$_2$ for 15 h. The acetonitrile-free reaction mixture in EtOAc was washed with 5% citric acid and aqueous NaHCO$_3$, dried (Na$_2$SO$_4$), concentrated, and purified by flash chromatography (silica gel, EtOAc/hexanes) furnishing 0.20 g (82%) of the phosphonate **8**, mp 106–107 °C (MeOH/H$_2$O), $[\alpha]^{26}_{D}$ +1.6° (*c* 0.0053, MeOH), shown by 400-MHz $^1$H and $^{13}$C NMR to be diastereomerically homogeneous.[10]

Tyrosyl peptides containing common protective groups formed the corresponding diethyl arylphosphonates via triflates (Table I, entries 1–4). Both processes took place efficiently and without detectable racemization, as shown by TLC and spectroscopic

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(3) Koszuk, J. F.; Czech, B. P.; Walkowiak, W.; Babb, D. A.; Bartsch, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1504.

(4) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3612. Obrycki, R.; Griffin, C. E. *J. Org. Chem.* **1968**, *33*, 632. Tavs, P.; Korte, F. *Tetrahedron* **1967**, *23*, 4677. Tavs, P. *Chem. Ber.* **1970**, *103*, 2428. For a palladium-promoted synthesis of diethyl arylphosphonates from aryl iodides or bromides, see: Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *Synthesis* **1981**, 56.

(5) Doak, G. O.; Freedman, L. D. *J. Am. Chem. Soc.* **1951**, *73*, 5658. Freedman, L. D.; Doak, G. O. *Chem. Rev.* **1957**, *57*, 479.

(6) Kosolapoff, G. M.; Huber, W. F. *J. Am. Chem. Soc.* **1947**, *69*, 2020.

(7) Synthesis of peptide aryl triflates appears to be unreported. *N*-Phenyltriflimide reacts rapidly with phenoxide and very slowly with amines, alcohols, or carboxylates: Hendrickson, J. B.; Bergeron, R. *Tetrahedron Lett.* **1973**, *146*, 4607.

(8) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7600. Scott, W. J.; Pena, M. R.; Sward, K.; Stoessel, G. J.; Stille, J. K. *J. Org. Chem.* **1985**, *50*, 2302. Baillargeon, V. P.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 452. Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271.

(9) During the preparation of this manuscript, palladium-catalyzed couplings between naphthyl triflate and hexamethyldistannane and between aryl triflates and alkenes or alkynes were reported: Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277. Chen, Q.; Yang, Z. *Tetrahedron Lett.* **1986**, *27*, 1171. After submission of the manuscript, carbonylation and hydrogenolysis of certain aryl triflates were reported: Cacchi, S.; Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1986**, *27*, 3931, 5541.

(10) 3-(Diethoxyphosphinyl)estra-1,3,5(10)-trien-17-one, mp 109–111 °C, $[\alpha]^{26}_{D}$ +108.8° (*c* 0.00535, dioxane); Boc-Tyr(Tf)-Ala-Thr-OBzl, mp 149–151.5 °C, $[\alpha]^{26}_{D}$ –22.5° (*c* 0.0121, MeOH); Boc-Phe[4-PO(OEt)$_2$]-Ala-Thr-OBz, foam, $[\alpha]^{26}_{D}$ –10.2° (*c* 0.0098, MeOH); Boc-Tyr-(Tf)-Ala-Phe-OMe, mp 137–137.5 °C, $[\alpha]^{26}_{D}$ –16.0° (*c* 0.0203, MeOH); Boc-Phe[4-PO(OEt)$_2$]-Ala-Phe-OMe, foam, $[\alpha]^{26}_{D}$ –8.4° (*c* 0.0098, MeOH); Z-Ala-Tyr(Tf)-OEt, mp 114–115 °C, $[\alpha]^{26}_{D}$ –10.6° (*c* 0.0088, MeOH); Z-Ala-Phe[4-PO(OEt)$_2$]-OEt, oil, $[\alpha]^{26}_{D}$ –23.9° (*c* 0.0097, MeOH); Ac-Tyr(Tf)-OMe, mp 79–80 °C, $[\alpha]^{26}_{D}$ +14.7° (*c* 0.0053, MeOH); AcPhe[4-PO-(OEt)$_2$]-OMe, mp 71–72 °C, $[\alpha]^{26}_{D}$ +19.4° (*c* 0.0053, MeOH). The optical purity of the last two compounds has not been determined as yet.

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 **1** → **3** → **4** to large (hydrophilic) peptides, we carried out both reactions in hydroxylic solvents containing $KHCO_3$ or $K_2CO_3$ 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 $CD_3CN$, 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.

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## Discrete Trinuclear Complexes of Niobium Related to the Local Structure in $Nb_3Cl_8$

F. Albert Cotton,* Michael P. Diebold, and Wieslaw J. Roth

*Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University College Station, Texas 77843*

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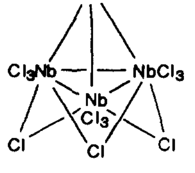
The three lower halides of niobium, $Nb_3X_8$ (X = Cl, Br, I) have been known for a very long time.[1] Their structures consist of close-packed arrays of halide ions with the niobium ions occupying triangular sets of adjacent octahedral interstices; bonding between the neighboring niobium atoms creates triangular metal atom clusters. The structure can be viewed as one in which $Nb_3(\mu_3\text{-}X)(\mu\text{-}X)_3X_9$ units, with the structure a, are fused together by sharing the terminal Cl atoms. A very similar structure exists in compounds of the type $Zn_2Mo_3O_8$.[2] In 1978 it was first reported that the $Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3L_9$ 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 $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}Cl)_3$ core surrounded by nine ligands. The compound, $Nb_3Cl_7(PMe_2Ph)_6$, was prepared[4] by reduction of $[NbCl_2(THF)]_2(\mu\text{-}Cl)_2(\mu\text{-}THT)$, where THT is tetrahydrothiophene, with sodium amalgam in THF in the presence of $PMe_2Ph$. 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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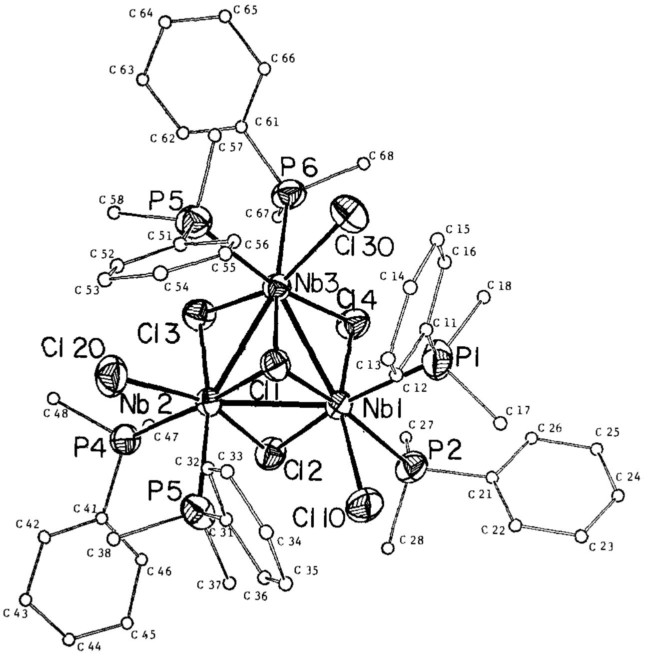

**Figure 1.** ORTEP drawing of the $Nb_3Cl_7(PMe_2Ph)_6$ molecule. The thermal ellipsoids are drawn at 30% probability level. Carbon atoms have been assigned arbitrarily small thermal parameters for the sake of clarity.

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 K$\alpha$ ($\lambda$ = 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, $\beta$ = 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 $[Mo_3S_4Cl_3(dmpe)_3]^+$ (Cotton, F. A.; Llusar, R., in press) and the $[Ir_3H_7(dppp)_3]^{2+}$ ion (Wang, H. H.; Pignolet, L. H. *Inorg. Chem.* **1980**, *19*, 1470).

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